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To Gwenola, Elisabeth, Anne-Melaine,
in memory of my parents.

Acknowledgments

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Preliminary Information

It is pertinent to give some advice regarding the use of some terms in this book:

- The word particle is used as a generic term. It can mean molecule, atom, or ion. In this book, it does not signify an elementary particle with the meaning given to them by the physicists, although such may be (and are) the subject of studies through statistical thermodynamics. Likewise, the author indiscriminately uses the words compounds and species to refer to the chemical species that constitute a thermodynamic system or are a part of a thermodynamic system, without trying to attribute a specific meaning to them.
- The author has tried to ensure that the logarithm is a dimensionless number. When it was not the case in this book, it was for an economy of writing. From a general standpoint, it is sufficient to introduce into the denominator of the argument the quantity 1, unity, which is the same as in the numerator. The author recalls that the argument of a logarithm being dimensionless or not has been the matter of a considerable number of discussions.
- First of all, the author indicates that the pressure unity most often found in this book is the atmosphere, although it is no longer recommended by IUPAC. The reason for this discrepancy is practical. A great deal of data is expressed with it in the thermodynamic literature.
- The term "concentration" written in quotes in this book is endowed with its largest meaning as it may designate either a molality, a molarity, a molar fraction, or a density number. In no case does it only designate a molarity. However, written without any quotes, it exclusively means molarity.
- Concerning the part of the book which requires the use of statistical thermodynamics, two points must be stressed.
  - In order to introduce this part of thermodynamics, we follow the development of T.L. Hill (see the general bibliography). It is rather brief. Several strategies exist to delve into it. Hill's treatment of the subject is one of the clearest.

  - The introduction and the reasoning based on molecular functions have been done by writing and handling them with the symbolism used by A. Ben-Naim in his books and publications.
- Finally, the word thermodynamics used alone signifies classical thermodynamics exclusively.

Glossary

A	Absorbance
A	Coefficient of Debye–Hückel's relations
A	Helmholtz energy
$A(N, V, T)$	Characteristic function of the canonical ensemble
A	Ion size parameter (extended Debye–Hückel's relation)
a, a', a_i or ()	General symbols of an activity
B	Coefficient of the extended Debye–Hückel's relation
$\mathbf{B}$	Matrix of B^{ij} (Kirkwood–Buff's theory)
B or $B(\mathbf{R}_0,\ldots,\mathbf{R}_N)$	Sum of the interaction energies between the added particle and the other particles of the solute
$B(\mathbf{R}',\mathbf{R}'')$	Coefficient of the series expansion of g $(\mathbf{R}',\mathbf{R}'')$ in the density ρ
$B_n(T)$ or B_k	Successive terms of the series expansion of the virial in ρ
B_{ij} (T)	Successive terms of the expansion of the virial in ρ (binary mixture)
$B_j^*(T, \lambda_1)$	Virial terms of the osmotic pressure (McMillan–Mayer's theory)
b_{02}, b_{03}, b_{20}, b_{30}, b_{11}, b_{ij} …	Expansion in series terms in z of p/kT (binary mixture)
C_p	Heat capacity at constant pressure
$(C_\mathrm{p})_\mathrm{l}$, $(C_\mathrm{p})_\mathrm{s}$	Molar heat capacities at constant pressure in the liquid and solid states
$C(\mathbf{R}', \mathbf{R}'')$	Expansion in series terms of g $(\mathbf{R}', \mathbf{R}'')$ in ρ
C	General symbol of a "concentration" whichever it is (molar fractions, molalities, molarities, density numbers)
c_i or [ ]	Molarity (molar concentration of i)
E	Electromotive force of an electrochemical cell
E°	Standard electromotive force of an electrochemical cell

E_j	Junction potential
$E_1, E_2, \ldots, E_j$	Stationary quanto-energetic states of a system belonging to an ensemble
$E_i(N, V)$	Allowed energy of a great ensemble system possessing N particles
E_i	Total energy of the particle i
E_k	Kinetic energy of a particle
E_t	Total energy of an ensemble
E	Internal energy of a system
E	Total energy of a system
E_p (or U)	Potential energy of a particle
$\overline{E}$	Mean energy of a system in an ensemble
e_0	Elementary electric charge
e	Base of natural logarithms
$F(\mathbf{R}^N)$	Every function depending on the configuration $\mathbf{R}^N$
$\langle F(\mathbf{R}^N)\rangle$ or $\langle F\rangle$	Mean value of a function F depending on the configuration $\mathbf{R}^N$
F	Faraday
f	General symbol of the fugacity
$f_\mathrm{s}, f_\mathrm{l}, f_\mathrm{g}$	Fugacities in the solid, liquid, and gaseous states
f_i°	Fugacity of i in the standard state
f_i^*	Fugacity of i in the pure state
f^*	Fugacity in the reference state (at very low pressure)
$f\,(\mathbf{X}_i, \mathbf{X}_j)$ or $f(\mathbf{R}', \mathbf{R}'')$ or $f_\mathrm{AA}, f_\mathrm{AB} \cdots f_{\alpha\beta}$	Potential energy functions in pairs into which a more complex energy function can be divided
$f\,(r_{12})$ and so $f\ldots$	….Mayer's f-function
$G(T, P, N)$ or G	Characteristic function of the isothermal–isobaric ensemble
G, $G_{\alpha\beta}$, G_{11}, G_{12}, G_{22}, G_{12}, or G_AA, G_AB, G_BB	Kirkwood–Buff's integral
$G_\mathrm{AA}{}^\circ$, $G_\mathrm{AB}{}^\circ$, $G_\mathrm{BB}{}^\circ$	First terms of the expansions in ρ_A of the Kirkwood–Buff's integrals
$\overline{G_{12}}$ or $\overline{G_{\alpha\beta}}$	Kirkwood–Buff's integral between the species 1, 2 or α, β (grand ensemble)
G	General symbol of the Gibbs energy function
$G_{\mathrm{m}\,i}$ or G_i	Molar Gibbs energy
G_m^*	Molar Gibbs energy in the reference state
$\overline{G_{i\,\mathrm{m}}}$	Partial molar Gibbs energy of i
G_i°	Gibbs energy of i in the standard state
G^E	Excess Gibbs energy of a mixture
G_m^E	Molar excess Gibbs energy of a mixture
G	Conductance of a solution
$g(R)$ or $g(R, T, \rho)$ or g_{21}	Radial distribution function (R scalar)

$g_{\alpha\beta}\,(\mathbf{R}', \mathbf{R}'')$ or $g\,(\mathbf{R}', \mathbf{R}'')$ or $g(r)_{ik}$	Pair correlation function (between the particles α and β or j and k or those located in $\mathbf{R}'$ and $\mathbf{R}''$)
$\overline{g_{\alpha\beta}\,(\mathbf{R}', \mathbf{R}'')}$ or $\overline{g\,(\mathbf{R}', \mathbf{R}'')}$ or $\overline{g_{12}\,(R)}$, $g(r)_{\alpha\beta}$	Pair correlation function between the particles α and β in the grand ensemble
$g^{(2)}{}_{++}$, $g^{(2)}{}_{+-}$, $g^{(2)}{}_{--}$, $g^{(2)}{}_{+\mathrm{solv}}$, $g^{(2)}{}_{\mathrm{solv-solv}}$ $g^{(3)}(r_{12}, r_{13}, r_{23})$, $g^{(4)}$, $g^{(5)}$, $g^{(6)}$,. . .,$g^{(n)}$	Radial distribution functions between two or several species
H	Hamilton's function
H	General symbol of enthalpy
$\overline{H_{\mathrm{m}i}}$	Partial molar enthalpy of i
$H_{\mathrm{m}i}$	Molar enthalpy of i
$H_{\mathrm{m}}{}^{\circ}$	Molar enthalpy in the standard state
H_{m}^{*}	Molar enthalpy in the reference state
h	Planck's constant
I	Ionic strength of the solution
K	General symbol of an equilibrium constant
K° or $K^{\circ}(T)$	Thermodynamic equilibrium constant or standard equilibrium constant
$K(T)$ or $K'(T)$ or K', K''	Formal or conditional equilibrium constants
K_{f}	Equilibrium constant related to fugacities
K_{p}	Equilibrium constant related to partial pressures
K_{m}	Equilibrium constant related to molalities
K_{c}	Equilibrium constant related to molarities
$K_{\mathrm{a}}{}^{\circ}$	Thermodynamic acid dissociation constant of an acid
K_{a}	Acid dissociation constant (general symbol)
$K_{\mathrm{w}}{}^{\circ}$	Thermodynamic ionic product of water
K_{w}	Ionic product of water
K_{s}	Solubility product
$\langle K \rangle$	Mean kinetic energy of a system
k	Boltzmann's constant
k_{H}	Henry's law constant
$\mathbf{M}$	Matrix of partial derivatives at constant volume (Kirkwood–Buff's theory)
M	Molar mass
m	General symbol of the molality
N	Composition of a system
N_1, N_2,. . .	Number of particles of a system
n_i or n	Number of moles in the solution
$n_j(N_1, N_2)$	Number of systems possessing N_1 and N_2 particles (grand ensemble)
$\overline{N_i}$	Mean number of particles i in the canonical ensemble
N_t	Number of moles of a species in the ensemble

$\langle N_i \rangle$ or $\overline{N}$ (V, T, μ)	Mean number of particles of the species i in one system of the grand ensemble
$n_i(j)$	Number of systems of the grand ensemble possessing j particles
n_j^*	How many times appears the quanto-energetic state E_j in the most probable distribution (canonical ensemble)
$n_j^*(N)$	How many times appears the quanto-energetic state E_j in the most probable distribution for a number N of particles (grand ensemble)
n	Number of exchanged electrons during an electrochemical reaction
p	Pressure of a system
p_i	Partial pressure of i
p_i°	Partial pressure of i in the standard state
P_i^*	Pressure of i in the pure state
p^*	Pressure in the reference state
$\overline{p}$	Average pressure of the systems in an ensemble
p_j	Pressure of the system j in the energetic state E_j
$P(\mathbf{R}^N)$	Basic density function or probability density function of the occurrence of the configuration $\mathbf{R}^N$
$P(\mathbf{R}^N)d\mathbf{R}^N$	Probability of the occurrence of the configuration $\mathbf{R}^N$, i.e., probability to find the particle 1 in $d\mathbf{R}_1$ at $\mathbf{R}_1$, 2 in $d\mathbf{R}_2$ at $\mathbf{R}_2,\ldots,N$ in $d\mathbf{R}_N$ at $\mathbf{R}_N$
$P^{(n)}\ (\mathbf{R}_1, \mathbf{R}_2,\ldots,\mathbf{R}_n)$	Specific function of order (n) or density probability for the particle 1 to be in $\mathbf{R}_1,\ldots$ the particle n in $\mathbf{R}_n$, whichever the configuration of the (N–n) remaining particles
$P^{(2)}(\mathbf{R}', \mathbf{R}'')$	Specific pair distribution function (probability density)
$P^{(\mathrm{n})}\ (\mathbf{R}_1, \mathbf{R}_2,\ldots,\mathbf{R}_n)$ $d\mathbf{R}_1, d\mathbf{R}_2,\ldots,d\mathbf{R}_n$	Specific probability of order (n) for a well-specified particle be in the volume element $d\mathbf{R}_1$, another well-specified one in $d\mathbf{R}_2,\ldots$ a last well-specified one in $d\mathbf{R}_\mathrm{n}$, whichever are the configurations of the remaining N–n particles
$P(N)$	Probability to find a system in the grand ensemble with exactly N particles of a species
P_j or $P_j(N, V, T)$	Probability for the system to be in the energy state E_j (canonical ensemble)
$P_j(N)$	Probability for a system of the grand ensemble to be in the energetic state $E_j(N, V)$
$P_j(N, V, T, \mu)$	Probability for a system of the grand ensemble to be in the energetic state $E_j(N, V, \mu)$
pV	Characteristic function of the grand ensemble
P_v	Probability for a system to exhibit the volume V (ensemble isothermal–isobaric)
$\mathbf{p}$	Momentum of a particle (vector)

$\mathbf{p}^N$	Symbol of the dependence of Hamilton's function on the momenta of the N particles of the system
Q, Q_N or $Q_N\ (V, T)$ or $Q(N, V, T)$	General symbol of the partition function of the canonical ensemble
Q_1	Canonical partition function corresponding to the occurrence of only one molecule in the system
$Q_{N_1N_2}$, Q_{10}, Q_{01}, Q_{20}, Q_{02}, Q_{ij}	Canonical partition function for a mixture of two particles
q	Generalized coordinate
q_{cloud}	Total charge excess around the central ion (Debye–Hückel's theory)
q	Electrical charge
q, q_i,. . ., or $q_i(V, T)$	Molecular partition function
q^{int}	Internal molecular partition function
q^{rot}	Rotation molecular partition function
q^{tr}	Translation molecular partition function
q^{v}	Vibrational molecular partition function
q^{elect}	Electronic molecular partition function
q	Heat exchanged with the surroundings
R	Perfect gases constant
R, r, r_{o}, r_{12}	Scalar distance between two particles (R: scalar)
$\mathbf{R}$	Vector defining the location of a species
$\mathbf{R}^N$	Configuration taking only into account the location of the N particles
$\mathbf{R}^{N_{\mathrm{A}}+N_{\mathrm{B}}}$	Configuration of the N_{A} and N_{B} particles of A and B of the system
S	Entropy
$\overline{S_{i\,\mathrm{m}}}$	Partial molar entropy of i
T	Absolute temperature of the system
U	Internal energy (IUPAC)
U	General symbol of the potential energy of a species
$\langle U_N \rangle$	Mean energy of interaction between particles
$U_N(\mathbf{X}^N)$	Total potential energy of interaction between the particles in the configuration $\mathbf{X}^N$
$U_N(\mathbf{R}^N)$, U_{N+1} $(\mathbf{R}^{N+1})$ or U_N, U_{N+1}	Total potential energies in the configurations $\mathbf{R}^N$ and $\mathbf{R}^{N+1}$
$U(R)$ or $U(\mathbf{R}', \mathbf{R}'')$ or U_{ij} or $U(\mathbf{R}_o, \mathbf{R}_j)$ or U_{AB} or $U(\mathbf{r}_1, \mathbf{r}_2)$	Interaction energy between two particles as a function of the distance R (between them)
V	Volume of the system
V_{m_i} or v_i	Molar volume of i
$\overline{V_{\mathrm{m}_i}}$	Partial molar volume of i
$W(A \vert A)$	Coupling work of A with its surroundings consisting solely in particles A

$W(A \mid A+B)$	Coupling work of A with its surroundings consisting in a mixture of A and B
$W(A \mid B+B)$	Coupling work of A with its surroundings consisting solely in particles B
$W(B \mid B+A)$	Coupling work of B with its surroundings consisting in a mixture of particles B and A
$w_{ik}(r)$ or w_{ik}	Potential of average force between the ions i and k (Debye–Hückel's theory)
w	Exchanged work between a system and its surroundings
$\overline{X}$	General symbol of a partial molal quantity
X	Every thermodynamic quantity
X_{m}	Molar quantity
$\overline{X_{i\,\mathrm{m}}}$	Molar partial quantity
$\mathbf{X}^N$	Configuration of an ensemble of N rigid and nonlinear particles
$\mathbf{X}_i$	Configuration of a rigid and nonlinear particle
x_i	Molar fraction of i in solution
y_i	Molar fraction of i in gaseous phase
z_i or z	Statistical analogue of activity i
z_i	Electrical charge of ion i
Z_N, Z'_N, Z_1, Z_2, etc..	Configurational partition function (configuration integral)
Z_{01}, Z_{02}, Z_{10}, $Z_{11}, \ldots, Z_{N_1N_2}$	Configuration integrals (mixture of two or several types of particles)
α	Lagrange multiplier
β	$=1/kT$
β	Lagrange multiplier
δ_{ij}	Kronecker's function
δ_2	Solute activity coefficient (McMillan–Mayer's theory)
ε	Absolute permittivity of the medium
ε_{o}	Vacuum permittivity
ε_r	Relative permittivity (dielectric constant)
$\varepsilon^{\mathrm{int}}$, $\varepsilon^{\mathrm{tr}}$, ε^{v}, $\varepsilon^{\mathrm{rot}}$, $\varepsilon^{\mathrm{elec}}$	Internal, translational, vibrational, rotational, and electronic energies of a molecule
μ	General symbol of the chemical potential
μ_i	Chemical potential of the species i
$\mu_{i\ \mathrm{eq}}$	Chemical potential of species i at equilibrium
μ_i°	Standard chemical potential of i $\mu_i^{\circ\alpha}$, $\mu_i^{\circ\beta}$ standard chemical potentials of i in the phases α and β
μ_i^* or μ^*	Chemical potential in the reference state
$\mu_i^{\circ\ \mathrm{g}}$ $\mu_i^{\circ\ \mathrm{l}}$ $\mu_i^{\circ\ \mathrm{s}}$	Standard chemical potentials of i in the gaseous, liquid, and solid states
$\mu_i^*(T, p)$	Integration constant of the differential equation defining an ideal solution (molar fractions scale, liquid phase)

$\mu_{i\ y}{}^{*}(T, p)$	Integration constant of the differential equation defining an ideal solution (molar fractions scale in gaseous phase)
μ	Obsolete symbol of the ionic strength
ρ_r	Charges density at the distance r of the central ion i (Debye–Hückel's theory)
ρ_i	Density number of i
ρ	Total density number of a binary solution ($\rho = \rho_A + \rho_B$)
ρ	Mass density of the solution
$\rho^{(n)}\ (\mathbf{R}^N)$	Generic molecular function of density of probability of distribution of order (n) in the configuration $\mathbf{R}^N$
$\rho^{(n)}\ (\mathbf{R}^N)\ d\mathbf{R}^N$	Probability for a molecule (not necessary molecule 1) to be in $d\mathbf{R}_1$,...... and a n^{nd} molecule to be in $d\mathbf{R}_n$
$\rho^{(2)}(\mathbf{R}', \mathbf{R}'')$ or $\rho^{(2)}{}_{\alpha\beta}(\mathbf{R}', \mathbf{R}'')$	Generic molecular function of distribution by pairs $\rho^{(n)}$ $\overline{\left(\mathbf{R}^N\right)}$ mean molecular distribution function of the n^{nd} order in the grand ensemble
ρ_r	Charges density at the point located at the distance r of the central ion
$\rho_{AB}(\mathbf{R}'/\mathbf{R}'')$, $\rho(\mathbf{R}'/\mathbf{R}'')$	Conditional probability density of finding the particle A in $d\mathbf{R}'$ at the configuration $\mathbf{R}'$ when another B is in $\mathbf{R}''$
$\rho(\mathbf{R}'/\mathbf{R}'')\ d\mathbf{R}''$	Conditional probability to find a particle in $d\mathbf{R}''$ at $\mathbf{R}''$ whereas another one is located in $d\mathbf{R}'$ at $\mathbf{R}'$
$\rho_A{}^{(1)}(\mathbf{R}')$, $\rho_B{}^{(1)}(\mathbf{R}')$ or $\rho^{(1)}(\mathbf{R}')$, $\rho^{(1)}(\mathbf{R}')$	Probability densities to find a particle A or B in $\mathbf{R}'$ and $\mathbf{R}''$
γ	General symbol of an activity coefficient
γ_r	Rational activity coefficient
$\gamma_{x\ i}$	Activity coefficient of i, molar fractions scale (reference, dilute solution)
$\gamma_{\mathrm{m}\ i}$	Activity coefficient of i, molalities scale (reference, dilute solution)
$\gamma_{\mathrm{c}\ i}$	Activity coefficient of i, molarities scale (reference, dilute solution)
γ_i^S	Activity coefficient (reference state, pure compound)
γ_2, $\gamma_2{}'$	Solute activity coefficient (McMillan–Mayer's theory)
$\gamma_2{}^{\circ}$	Limit value of γ_2 (McMillan–Mayer's theory)
γ	Lagrange multiplier
θ	Spherical coordinate
λ	Solvent molar cryoscopic constant
λ_i	Absolute activity of i
ξ	Extent degree of a reaction
ξ	Coupling parameter
ϕ_i	Fugacity coefficient of a gas
ϕ	Spherical coordinate
ϕ	Thermodynamic potential

ϕ_{m}	Practical osmotic coefficient "scale of molalities"
ϕ_x	Rational osmotic coefficient "scale of molar fractions"
ϕ	Flux
ψ	Spherical coordinate (nonrigid molecule)
ψ	Wave function (Schrödinger's equation)
ψ	Electrostatic potential
ψ_{r}	Mean electrostatic potential at the distance r of the central ion (Debye–Hückel's theory)
ψ_{cloud}	Electrostatic potential due to the ions distribution around the central ion (Debye–Hückel's theory)
ψ_{ion}	Electrostatic potential due to the central ion itself (Debye–Hückel's theory)
ψ_{o}	Semi-grand partition function (McMillan–Mayer's theory)
ψ_1	Semi-grand partition functions (McMillan–Mayer's theory)
Ψ_{N_2}	Canonical partition function of a mixture of N_1 molecules 1 and of N_2 molecules 2. N_1 is a changing value, N_2 is a constant
ν_i	Stoichiometric coefficient of species i
ν	Total number of a given ion given by an electrolyte $\nu = \nu_+ + \nu-$
ν_t	Total number of particles in the grand ensemble
ΔG	Gibbs energy change
ΔG°	Standard Gibbs energy change accompanying a process
$\Delta_{\mathrm{r}}G$	Gibbs energy change accompanying a chemical reaction
$\Delta_{\mathrm{r}}G^\circ$	Standard Gibbs energy change accompanying a chemical reaction
$\Delta\mu(i{-}I)$	Chemical potential change due to the interactions between the ion i and the other ions j
ΔH	Enthalpy change
ΔH°	Standard enthalpy change
$\Delta H_{\mathrm{fusion}}$	Enthalpy change accompanying the fusion of a solid
ΔH_{vap}	Molar latent heat of vaporization
$\Delta_{\mathrm{mix}}H$	Mixing enthalpy
Δ_{12} or $\Delta_{\mathrm{AB}} = G_{\mathrm{AA}} + G_{\mathrm{BB}} - 2G_{\mathrm{AB}}$	Parameter originating in the Kirkwood–Buff's theory permitting to introduce different concepts of the ideality
$\Delta S_{\mathrm{isol\ syst}}$ or $\Delta S_{U,V}$	Entropy change in an isolated system
Δ or $\Delta\ (T, P, N)$	Partition function of the isothermal–isobaric ensemble
Λ	de Broglie's thermal wavelength
Λ	Equivalent conductance of an electrolyte
Λ_{e}	Effective conductance of an ion
Λ_O	Limit equivalent conductance
Ξ or $\Xi\ (T, V, \mu)$	Grand canonical partition function

κ_T or κ	Isothermal compressibility coefficient
τ	Volume
π, π'	Osmotic pressure
Γ	Function semi-grand partition depending on the variables N_1, P, T, μ_2 (Mc-Millan's theory)
$\boldsymbol{\Omega}_i$	Vector specifying the orientation of a nonspherical molecule i
Ω	Number of possibilities to group a total of $n_1+n_2+n_3$ ...objects in groups of n_1, n_2, n_3 ones
Ω_t	Number of possible quantic states of the grand ensemble
Ω_t	Degenerescence of a quanto-energetic state
χ	Constant (Debye–Hückel's equation)
$\chi-1$	Thickness of the ionic cloud (Debye–Hückel's theory)
ℵ	Number of systems in an ensemble
ω_i, ω_j	Degenerescence of the energetic levels ε_i, ε_i

Introduction

This book is, before all, an attempt to demystify the notion of activity. Activity is interesting and intriguing for chemists, physicists, and others and has been for more than a century. Outside of the physical sciences, it remains often ignored, even unknown.

The notion of activity originates from the application of the basic principles and methods of thermodynamics to chemical processes. It proves to be particularly useful when this application encounters some difficulties. Its introduction permitted the study of the thermodynamic behavior of imperfect gases and nonideal solutions. The particular behavior of systems in both cases is related to the occurrence of mutual non-negligible interactions between molecules of gases or of solutes. It is now well established that handling the intimately linked concepts of activity and fugacity permits one to neatly take into account these interactions. With their introduction, the chemical potentials of imperfect gases and those of the components of nonideal solutions can be expressed in a useful manner in order to study different processes, despite the already mentioned difficulties. This is an important point. Change of the chemical potential of a substance during a physical or a chemical process, indeed, determines its result and its term, which is not a kinetic one. This is the reason why chemical potentials must be expressed in the most realistic way possible.

The chemical potentials of perfect gases or of components of ideal solutions are simply expressed with respect to their partial pressures or concentrations. This is no longer possible with imperfect gases or with the components of nonideal solutions. This is the origin of the introduction of the fugacity and activity concepts by G. N. Lewis in 1907. Lewis' thought process in order to overcome the problem may be summarized by the following comment:

> ... partial pressures and concentrations do not permit the satisfactory thermodynamic behavior of imperfect gases and of non-ideal solutions? No problem! Let us introduce new physical quantities, even if they are virtual, in such a way that they allow the right description of chemical potentials, with the same formalism as that used in cases of ideal behaviors ...

Miraculously, this approach proved to be successful! It works well, at least under well-defined experimental conditions.

But the purely arbitrary introduction of the fugacity and activity concepts immediately calls for the following central recurrent question: what is the physical meaning of these two quantities? It is the goal of this book to provide the reader with an answer to this question.

A second question is also frequently asked: why introduce these quantities? Its answer has already been given above by recalling the part played by the chemical potential.

Finally, a somewhat neophyte practitioner of the activity quantity (e.g., one engaged in their calculations) cannot fail to be troubled by the arbitrariness of the definitions of the activities and by its repercussion upon the validity of the results obtained by using them. This is also a very legitimate question.

Let us recall, at this point, that the concept of activity is also of utmost importance from a practical standpoint. It is sufficient to take the two following examples to be convinced. They are the study of equilibria between gases and the definition of pH. It is an experimental fact that satisfactory conditions of synthesis of some gaseous compounds are frequently extreme. Under such conditions, the behaviors of the reactants and products are no longer ideal. As a result, if we calculate the equilibrium constants by taking into account only the partial pressures, the obtained values are inconsistent. In brief, equilibrium constants obtained in such a way are no longer constant! Using fugacities and activities rectifies this failure. Concerning the case of pH, let us recall that it is formally defined as being the decadic cologarithm of the activity of the solvated proton in the medium. Thus, in principle, pH meters respond to the activity of the proton and not to its concentration.

Finally, the fact that the notion of activity is in common use in laboratories in which the study of solutions is practiced must not be forgotten. The relative silence which the concept of activity seems to be surrounded with is due certainly to its mysterious character. But, it is also due to the constant success of its utilization. This is the case of all great scientific theories.

It seems to us that all that we have recalled before may be classified as being some good reasons to revisit the concept of activity.

This book is, before all, a book of chemical thermodynamics necessitated by the concept to which it is devoted. Of course, it must be of interest for chemists and physicists. However, the author thinks that it can also be of interest for all the scientists engaged in the study of experimental sciences. They may be, for example, biologists, who consider the evolution of biological systems, given the part played by the changes in the Gibbs energy during these transformations. Let us recall, for this purpose, that many biological systems evolve at constant temperature and pressure. Hence, here stands the relevance of the notion of activity which permits the obtaining of the changes in the chemical potentials in these conditions, which are often far from being ideal.

Nevertheless, it is essentially centered on the chemistry of solutions. This must not be a surprise because of the fact that it is in this area that the concept is the most used. However, the case of gases will be also considered for the sake of continuity with that of liquids.

The book is divided into two main parts, each of them supplemented by some appendices developing some particular points of physical or mathematical nature.

The first one is devoted to the concept of activity in classical thermodynamics. At its beginning, there are some reviews of elementary thermodynamics directly related to our purpose. They are followed by definitions of fugacity and activities since there are several possible kinds of activities which may be adopted, which is another troublesome point. The link between the fugacity and the activity of a species is then established. It is at this point that the influence of the arbitrary character of the definition is investigated. Some examples of determinations of activities of electrolytes and nonelectrolytes are also given. The description of a strategy of calculation of activities of electrolytes by a so-called simulation process with the help of informatics concludes the first part.

The second one concerns activities from the point of view of statistical thermodynamics. It begins by some review of generalities about statistical thermodynamics. Developments from these fundamentals complete those given at the beginning of the first volume, as could be expected, at the molecular level. It is in this part that quantitative relations between activities and concentrations are set up. They are set up with the help of the introduction of new functions such as molecular distribution functions and, in particular, the radial distribution function. It is these quantitative relations which give some physical meaning to the activity quantity. The two theories leading to them are mentioned. They are that of Mc-Millan on one hand and that of Kirkwood–Buff on the other hand.

The author has done his best to express the subject as concretely as possible. This is not an easy task because statistical thermodynamics necessarily involves elaborate and frequently cumbersome mathematical developments. This is the reason he has deliberately mentioned some results without any demonstration, as if they were postulates. This is not very satisfactory, but in the mind of the author, the book is a first level approach to the subject.

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Part I
The Activity in Classical Thermodynamics

Chapter 1
Thermodynamic Systems

Abstract Definitions and properties of some thermodynamic systems and of some quantities in relation with the notion of activity are recalled in this chapter. The properties of thermodynamic systems and of their states, and the notions of extensive and intensive properties, of transformations, equilibria, state functions, and reversible or irreversible processes are also mentioned. Especially, emphasis is given on the different expressions of the composition of a solution and on the pathways between them.

Keywords Composition (expressions) • Density number • Number of moles • Molality • Molar fraction • System (state) • State (functions) • Properties (extensive and intensive) • Process (reversible, quasi-static, irreversible) • System (thermodynamic) • Transformation • Equilibrium (thermodynamic)

Here, we recall the definitions and the properties of some thermodynamic systems and of some quantities in relation with our purpose.

1.1 Thermodynamic Systems

A system is a part of the space and its contents, delimited by a real or a fictitious closed surface. Figure 1.1 shows an example of system composed by a solution and its vapor and its container closed by a fictitious surface.

The surroundings of the system are all but the system. Said with some emphasis, surroundings are the remaining of the universe. According to the choice of the operator, the container may or may not be a part of the system. The essential point for the following operations is not going against the initial arbitrary definition of the system.

One distinguishes several kinds of systems:

- The closed system which can only exchange energy (heat and work) and not matter with the surroundings.
- The open system which exchanges energy (heat and work) and matter with the surroundings.

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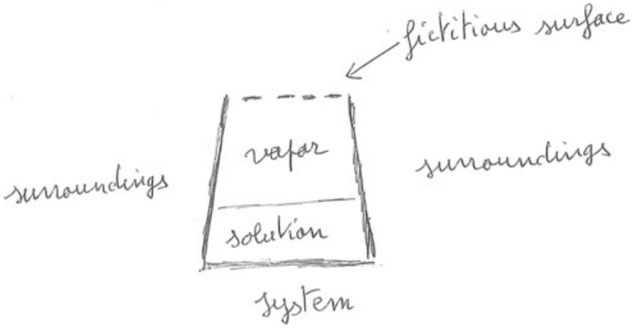

Fig. 1.1 An example of a thermodynamic system with its surroundings

- The isolated system which exchanges nothing with the surroundings, neither energy nor matter. The definition of the isolated system inevitably rises the metaphysical question: Is the universe an isolated system?

As already said, **p** in order to specify that is a "p in minuscules" to indicate that it is a pressure in question and not a probability which must be written in majuscules.

1.2 State of a System

We are speaking here of thermodynamic state. The state of a thermodynamic system is defined by the values of some parameters. Most often in chemistry, but not obligatorily, the thermodynamic state of a system is defined by the values of four measurable properties, called "state variables" which are:

- The composition
- The pressure **p**
- The volume V
- The temperature T

of the system. When the system is homogeneous, that is to say when it is constituted by only one phase and when, moreover, the latter itself is composed by only one species, its composition is fixed quite evidently. Then, its state only depends on its volume, its pressure, and its temperature. Actually, the experience shows that only two of these three variables V, **p**, and T are sufficient in order to fix the state of the system since they are related to each other by a mathematical equation called *equation of state*.

In unusual conditions of chemistry such as those resulting from the occurrence of intense electric, magnetic, and gravitational fields to which the system is submitted during a process, supplementary variables are necessary to define its state.

When the state variables are known, all the other physical properties of the system such as its mass, density, viscosity, refraction index, and dielectric constant are fixed.

1.3 Extensive and Intensive Properties

A property is said extensive when it is additive. This means that its value for the whole system is equal to the sum of the values of the different parts constituting it. In other words, the values of the extensive quantities are proportional to the quantity of matter under consideration. As examples, let us mention the volume and the mass.

An intensive property is not additive. It is not necessary to specify the quantity of sample under study to which the property is referring. As examples, let us mention the density, pressure, molar quantities, temperature, and "concentrations."

1.4 Transformation

We call transformation any process which expresses itself by one or several changes in, at least, one of the state variables of the system. This definition encompasses the cycles at the end of which the system is returned to its initial state.

1.5 Thermodynamic Equilibrium

One considers that a system is at the thermodynamic equilibrium when the observable values which characterize it do not change with time. The thermodynamic equilibrium entails that mechanical, thermal, and chemical equilibria are simultaneously reached. That means that the temperature, pressure, and concentrations must be identical in all the parts of the system.

1.6 State Functions

Let us consider a process taking place from an initial state up to a final state. It entails changes in one or several thermodynamic quantities. The changes may follow several pathways (Fig. 1.2).

When the change is independent of the pathway, the measured quantity is called *a thermodynamic state function.* Several thermodynamic functions are state functions. For example, let us mention the temperature, volume, etc. State functions

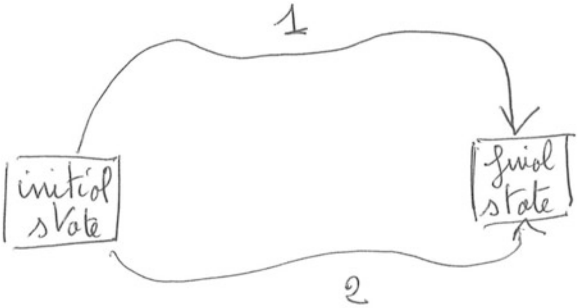

Fig. 1.2 Different pathways of a change in a thermodynamic quantity

exhibit very interesting mathematical properties, the consequences of which are very important in thermodynamics (viz. total exact differential in Appendix A).

1.7 Reversible or Quasi-Static Processes and Irreversible Processes

A process is said reversible or quasi-static when, at every moment of its course, the system is at equilibrium. Said in other words, the process is reversible when it takes place through a succession of equilibrium states. If it is not the case, the process is said *irreversible*. A consequence of the reversibility is the fact that at every stage of the process, the state equation of the system applies.

One may conceive that one transformation carried out very slowly is reversible. Actually, the least infinitesimal departure from equilibrium, carried out reversibly, gives sufficient time to the system to recover the (further) equilibrium state, before the next departure occurs and so forth.

The concept of reversible process is extremely fruitful.

1.8 Different Expressions of the Composition of a Solution

The composition of a liquid solution expresses the relative proportions of the solute and of the solvent in the solution. Here, we only mention the expressions which are the most usual.

- The total number of particles of species i: N_i. It is a huge dimensionless number. This is the reason why one rather uses the notion of number of moles or that of quantity of molecules (viz. immediately under).
- The number of moles n_i. The unity is the mole, symbol mol. It is the total number of the species N_i related to the Avogadro number (N_A or L). The latter is expressed in mol^{-1}:

$$n_i = N_i/N_\mathrm{A}$$

- The density number C_i or ρ_i is the number of molecules per unit volume:

$$C_i = N_i/V$$

  It is expressed in m^{-3}. Actually, this expression of the composition is mainly used in statistical thermodynamics. ρ_i is the symbol most often used.
- Molarity, also called amount concentration (IUPAC), is expressed by symbol c_i. It is the number of moles of molecules related to the volume V of solution:

$$c_i = n_i/V$$

In SI units, it is expressed in mol m^{-3}. For practical reasons, one rather uses the number of moles per dm^3 or equivalently per liter. A solution 1 mol L^{-1} is often called a molar solution and it is often written: solution 1 M. The symbol [i] is very often encountered instead of c_i. This unit is the most used in analytical chemistry.

- The molality is the number of moles of solute i per kilogram of pure solvent. Its symbol is m_i. In the SI system, it is expressed in mol kg^{-1}. Let n_i be the number of moles of solute i dissolved in the mass m_o of pure solvent. The molality m_i is

$$m_i = n_i/m_\mathrm{o} \quad \text{mass of pure solvent (in kg)}$$

It is easy to show that, in a binary solution (where the index 1 points out the solvent and index 2 the solute), the number of moles n_2 of solute in the solution is given by the expression

$$n_2 = (n_1 M_1/1000) m_2$$

where M_1 is the molar mass of the solvent and n_1 its number of moles, m_2 being the molality of the solute.

The molality is overall used in physical chemistry. The great advantage it exhibits with respect to the molarity lies in the fact that it is independent of the temperature. For dilute aqueous solutions, the solute molality value differs very little from that of its molarity, and the more diluted the solution is, the truer this assertion is (viz. under).

- The molar fraction

  The molar fraction is the ratio of the number of moles of the solute and of the total number of moles in the solution. Its symbol is x. If, in a binary solution, the number of moles of the solute is n_i and that of solvent is n_o, the molar fractions of the solute and of the solvent are, respectively,

$$x_i = n_i/(n_o + n_i) \quad \text{and} \quad x_o = n_o\,/(n_o + n_i)$$

Molar fractions are dimensionless quantities. They are very often used in thermodynamics.

- Pathway from molar fractions to the molalities and molarities

  The pathway from a scale of "concentration" to another one is not obvious. It entails using the density of the solution.

Let us consider a solution composed of n_o moles of solvent, n_A, n_B, ... moles of solutes A, B,.... By definition the molar fraction of A is

$$x_A = n_A/\sum n_i \quad \text{with} \quad \sum n_i = n_o + n_A + n_B + \cdots$$

- The molar concentration of A is by definition

$$c_A = n_A/V$$

where V is the total volume of the solution. Let us seek to express c_A as a function of x_A. The mass of the solution $\sum n_i M_i$ (grams) is

$$\sum n_i M_i = n_o M_o + n_A M_A + n_B M_B + \cdots$$

where M_o, M_A, M_B, ... are the molar masses (g mol^{-1}) of the solvent and of the solutes. The volume V of the solution is

$$V = \sum n_i M_i/\rho 1000$$

where ρ is the volumic mass (g cm^{-3}) of the solution. The factor 1000 permits to express the volume V in liters. Then, from the previous relations, one can immediately deduce the following ones:

$$c_A = 1000\rho n_A/\sum n_i M_i$$

and

$$c_A = \left(1000\rho \sum n_\mathrm{i}/\sum n_i M_i\right) x_A$$

We notice that there is no proportionality between c_A and x_A since $\sum n$ and $\sum nM$ do change with x_A. However, proportionality appears when the solution is sufficiently dilute. Under this condition, indeed

$$\sum n_i \approx n_{\mathrm{o}}$$
$$\sum n_i M_i \approx n_{\mathrm{o}} M_{\mathrm{o}}$$

whence

$$c_{\mathrm{A}} = (1000\rho/M_{\mathrm{o}})x_{\mathrm{A}}$$

where ρ[1] is the volumic mass of the pure solvent since the solution is diluted. In particular, for water at usual temperature,

$$\rho \approx 1$$

and

$$c_{\mathrm{A}} = (1000/M_{\mathrm{o}})x_{\mathrm{A}} \quad \text{(water—usual temperature)}$$

- The molality of A is by definition

  $$m_{\mathrm{A}} = 1000 n_{\mathrm{A}}/n_{\mathrm{o}} M_{\mathrm{o}}$$

  The factor 1000 is introduced since M_{o} is expressed in grams and since m_{A} is expressed in moles number per kilogram of solvent. By introducing the expression defining x_{A} in the latter, we obtain

  $$m_{\mathrm{A}} = \left(\sum n_i 1000/n_{\mathrm{o}} M_{\mathrm{o}}\right) x_{\mathrm{A}}$$

  Again, there is no proportionality between m_{A} and x_{A}. However, it appears in diluted solution, since then

  $$\sum n_i \approx n_{\mathrm{o}}$$

  whence

  $$m_{\mathrm{A}} = (1000/M_{\mathrm{o}})x_{\mathrm{A}}$$

  The latest relation clearly shows that in diluted aqueous solutions

  $$\rho \to 1 \quad \text{and} \quad \sum n_i M_i \to n_{\mathrm{o}} M_{\mathrm{o}}$$
  $$m_{\mathrm{A}} \approx c_{\mathrm{A}}$$

---

[1] Do not confuse ρ (volumic mass here) with the density number.

In brief, it is only in sufficiently dilute aqueous solutions that the numerical values of the molality and of the molarity of a solute can be considered as being equal and that they are proportional to the molar fraction.

Generally, for the same kind of solution in different conditions as those of high dilution, just previously discussed above, the numerical values of the molar fractions differ considerably from those of their molality or molarity. However, numerical values of both latter ones remain close to each other.

In a gaseous mixture, the molar fraction is the most used unity. Its symbol is then y. In a gas mixture in which n_i and n_j are the mole numbers of gases i and j, the respective molar fractions are

$$y_i = n_i \,/\left(n_i + n_j\right) \quad \text{and} \quad y_j = n_j/\left(n_i + n_j\right)$$

Chapter 2
Gibbs and Helmholtz Energies

Abstract Some properties of the *Gibbs and Helmholtz energies*, two thermodynamic functions of utmost importance in chemistry especially for the study of the notion of activity, are recalled. The chemical potential of a species in a system, which is the pivotal notion of the chemical reactivity (most of the time entailing the notion of activity), is, indeed, a particular Gibbs energy. Hence, for example, the changes in Gibbs and Helmholtz energies accompanying a process provide us with an equilibrium criterion, at least in some experimental conditions.

In a first time, a brief recall of some properties of the entropy function is mentioned in order to grasp the significance of these two functions. Later in the chapter, for additional information, some notions concerning potential functions are also given.

Keywords Chemical potential • Entropy enthalpy • Electrochemical cell • Gibbs–Helmholtz relation • Gibbs energy • Helmholtz energy • Isolated system • Potential functions • Surroundings

In this chapter, we recall some properties of two thermodynamic functions of utmost importance in chemistry, especially for our purpose. They are the *Gibbs and Helmholtz energies*. The chemical potential of a species in a system, which is the pivotal notion of the chemical reactivity (most of the time entailing the notion of activity), is, indeed, a particular Gibbs energy (viz. Chap. 5). Hence, for example, the changes in Gibbs and Helmholtz energies accompanying a process provide us with an equilibrium criterion, at least in some experimental conditions.

Grasping the significance of these two functions requires, in a first time, to briefly recall some properties of the entropy function and, later, to summarize some notions concerning the potential functions.

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2.1 Brief Recalls About the Second Principle and Entropy

2.1.1 General Points

It is a well-known fact that the knowledge of the changes in internal energy or enthalpy accompanying a process does not permit to forecast their direction nor their maximum possible extent (their "quantitativity"). The introduction of a new function turned out to be necessary to answer these questions.

The study of cyclic processes (that is to say that kind of processes according to which a system is brought back in its initial state after having been submitted to varied transformations) shows that another thermodynamic function answers the previous questions. It is the entropy function (symbol S, unity J K^{-1}) (in Greek: evolution). It is endowed with remarkable properties. It is a state function and it is extensive.

The second principle of thermodynamics is based on the existence of this function. It states that the entropy of an *isolated* system cannot do anything else than to increase during a spontaneous transformation. This is quantified by the expression

$$\Delta S_{\text{isolated syst}} > 0 \quad \text{(spontaneous process)}$$

or equivalently

$$\Delta S_{U,V} > 0$$

(It is evident, indeed, that, according to the definition of an isolated system, the internal energy remains constant since heat, mechanical work, and matter exchanges with the surroundings cannot exist. The nonexistence of work exchange requires that the volume V of the system is constant.)

For a reversible process, the second principle states that in an isolated state the change in entropy is null, i.e.,

$$\Delta S_{\text{isolated syst}} = 0 \quad \text{(reversible process)}$$

or

$$\Delta S_{U,V} = 0$$

The following relation

$$\Delta S_{\text{isolated syst}} \geq 0$$

is the mathematical counterpart of the most general statement of the second principle of thermodynamics. The increase of the entropy of the studied system plus the increase of entropy of its surroundings is called entropy creation.

2.1.2 Studied System, Surroundings, and Isolated System

One of the difficulties of the understanding of the entropy concept comes from the mix-up of the entropy of the studied system and of the entropy of the isolated system containing the studied one.

In a general manner in thermodynamics, in order to study a process, one may consider both the studied system and its surroundings with which it can, at first sight, exchange work, heat, and matter. The studied system plus the surroundings constitute an isolated system, *but the studied system*, *solely*, *may not be isolated.*

The important point is the following one: when a spontaneous process is occurring in the studied system, the entropy of the isolated system (studied system plus its surroundings) does obligatorily increase (except the case in which the process is reversible) according to the second principle, whereas it is not at all obligatory in case when it is not an isolated one. Hence, the studied system may exhibit an *increase or even a decrease* of its entropy during this spontaneous process.

Let us *already* mention that there exist other criteria of spontaneity than that of entropy, in particular in the case of a process at constant temperature and pressure. It is the point which will occupy us up to the end of this chapter.

2.2 Gibbs Energy

This function has been introduced by Gibbs.

The symbol of Gibbs energy is G. Its significance and use are related to an isothermal and isobaric process. More precisely, the Gibbs energy is related to a process in which the temperature and the pressure of the studied system remain equal to the temperature and pressure of its surroundings (at least at the beginning and at the end of the process provided, in this case, that during it, the surroundings remain at the constant temperature T_{ext} and pressure $\mathbf{p}_{\text{ext}}$):

$$\mathbf{p} = \mathbf{p}_{\text{ext}} \quad \text{and} \quad T = T_{\text{ext}}$$

The Gibbs energy is defined by the expression

$$G = U + \mathbf{p}V - TS$$

where U, $\mathbf{p}$, V, T, and S are, respectively, the internal energy, pressure, volume, temperature, and entropy of the system. Its unity is the Joule J. Owing to its definition, the Gibbs energy is a state function.

The interest of the introduction of this function is the following one: it turns out that the Gibbs function may constitute a criterion of equilibrium and also of evolution specially convenient for any process at constant pressure and temperature.

Let us, for example, study the process with the aid of which we want to recover useful work (every work other than that stemming from the change in the volume of the system), starting from the system. (A good example is that of an electrochemical cell producing electrical energy which is connected to an electrical motor. The cell has the property to transform the chemical energy—coming from the two electrochemical reactions which simultaneously take place at each of both electrodes—to electrical work.) It is demonstrated in an absolute general manner that the work given to the surroundings is always weaker than the change in internal energy of the system. In other words, the Gibbs energy of the system cannot do anything else than to decrease when it supplies work to the surroundings, in any case when the process is spontaneous. Hence, we can deduce that

$$\Delta G \leq 0$$

or in differential writing

$$dG \leq 0$$

At equilibrium

$$dG = 0$$

For a system at equilibrium at given pressure and temperature, the Gibbs energy is at its minimum value.

Hence, with the introduction of the function of Gibbs energy, the criterion of spontaneous evolution of a system, that is to say that of the change in the total entropy (that of the system plus that of its surroundings—both forming an isolated system), is transformed into another one which is the criterion of the decrease of the Gibbs energy of the *studied system alone*. The latter criterion is evidently less heavy than the former and is easier to handle because it does not require the knowledge of the thermodynamic parameters defining the state of the surroundings. However, the criterion of the Gibbs energy is by far less general than that of entropy because, for its handling, it implies that the process evolves at constant temperature and pressure.

In this sense, we shall see that the Gibbs energy plays the part of a potential function (viz. paragraph 5).

The Gibbs energy function can be defined in another way. Of course, all its definitions are equivalent. For example, taking into account the fact that the enthalpy of a system is defined by the expression

$$H = U + \mathbf{p}V$$

the Gibbs energy can also be written

$$G = H - TS$$

or

$$dG = dH - TdS - SdT \tag{2.1}$$

2.3 Some Properties of the Gibbs Energy Function

2.3.1 Changes in the Gibbs Energy with the Pressure and the Temperature

Let us consider the relation which expresses the enthalpy:

$$H = q + w + \mathbf{p}V$$

where q and w are the heat and the work exchanged with the surroundings during the process. For an infinitesimal transformation,

$$dH = dq + dW + \mathbf{p}dV + Vd\mathbf{p} \tag{2.2}$$

If this one is reversible and isothermal

$$dq = dq_{\text{rev}}$$

and after the second principle

$$dq = TdS$$

If, finally, the sole work done by the system is that of expansion as it is usually the case in chemistry

$$dw = -\mathbf{p}dV$$

the infinitesimal change in the enthalpy of the system becomes

$$dH = TdS - \mathbf{p}dV + \mathbf{p}dV + Vd\mathbf{p}$$

or

$$dH = TdS + Vd\mathbf{p}$$

By comparison with relation (2.1) which is a definition of the Gibbs energy

$$dG = dH - TdS - SdT$$

we find

$$dG = Vd\mathbf{p} - SdT \tag{2.3}$$

Now, let us write the total differential of G, which is a state function (viz. Appendix A):

$$dG = (\partial G/\partial T)_P dT + (\partial G/\partial \mathbf{p})_T d\mathbf{p}$$

We immediately deduce that

$$(\partial G/\partial T)_P = -S \quad \text{and} \tag{2.4}$$

$$(\partial G/\partial \mathbf{p})_T = V \tag{2.5}$$

These two equations give the variations of the Gibbs energy with the temperature and pressure.

In general, the Gibbs energy depends not only on the temperature and the pressure but also on the quantities of substance (viz. Chap. 4).

2.3.2 Gibbs–Helmholtz Equation

The Gibbs–Helmholtz equation permits, as we shall see, to know the change in an activity value with the temperature. It is obtained from the general definition of the Gibbs energy function:

$$G = H - TS$$

Substituting the entropy by its expression (2.4) into it, we obtain

$$G = H + T(\partial G/\partial T)_P \tag{2.6}$$

It can be modified into another one. We obtain an expression of the variation of G with the temperature T by the division of (2.6) by the factor T^2. The relation found is

$$G/T^2 = H/T^2 + 1/T(\partial G/\partial T)_P$$

It is easy to check the following relation by a simple calculation of derivatives:

$$[\partial(G/T)/\partial T]_P = [T(\partial G/\partial T) - G]/T^2$$

Finally,

$$[\partial(G/T)/\partial T]_P \ = -H/T^2 \tag{2.7}$$

It is interesting to notice that relation (2.3) is valid, whatever the reversibility of the process is, since all the quantities which are in it are state quantities. It is the same for those which follow it. The sole existing constraint in order that all these considerations are valid is that the system must be closed.

2.4 Helmholtz Energy

It has been introduced by Helmholtz.

It is slightly less interesting in the realm of chemistry than the Gibbs energy is. The developments to which it leads are analogous to those stemming from the Gibbs energy.

It applies to a process in which the temperature T of the system is equal to that of the surroundings $T_{\text{ext.}}$ and during which its volume is constant. The Helmholtz energy A is defined by the relation

$$A = U - TS$$

It is a state function. It is extensive. It is expressed in joules.

The Helmholtz energy A is related to the Gibbs energy G by the expression

$$G = A \ + \mathbf{p}V$$

Following the same kind of reasoning as that developed in the case of Gibbs energy, it is found that the physical significance of the Helmholtz energy is the following one. The value of its change is the maximal work that can produce the system in reversible and monothermal conditions. At equilibrium and at constant temperature, the Helmholtz energy function is minimal.

The difference between the Helmholtz and Gibbs energies lies in the fact that in the first case, the maximal work is equal to the sum of the useful work and of that of expansion whereas in the case of the Gibbs energy its decrease is only equal, in reversible conditions, to the useful work.

2.5 Gibbs and Helmholtz Energies, Potential Functions: Thermodynamic Potentials

We have seen that the Gibbs and Helmholtz functions give important indications on the possibilities of transformations of a system, respectively, at constant temperature and pressure and at constant temperature and volume. One knows that during a spontaneous process, these functions evolve in such a manner that their values tend toward a minimal value. By such a property, their behavior is that of potential functions, called thermodynamic potentials.

2.5.1 Potential Energy and Evolution of a Mechanical System

In order to make explicit this notion of potential function, let us recall the relation linking the potential energy and the evolution of a mechanical system.

Let us consider a material point M which moves freely in a force field deriving from a potential energy $E(x)$. A representative example is that of the gravitational field. One knows that if we initially abandon M at the point I (initial) of vertical coordinate $h(\mathrm{I})$ with a null speed, then it spontaneously tends to go to the F point (F: final) of minimal potential (viz. Fig. 2.1).

During its evolution, the body is getting a kinetic energy $1/2mv^2$. The constancy of the mechanical energy is written for each intermediate point of the path:

$$Mgh(\mathrm{I}) = Mgh\ + 1/2\, mv^2$$

where h is the coordinate of the intermediate point. The kinetic energy being obligatorily positive, we immediately can deduce that during this spontaneous evolution, the term potential energy can only decrease. Its minimum $Mgh(\mathrm{F})$ corresponds to the state of stable equilibrium. In I, the state of equilibrium was unstable.

Fig. 2.1 Potential energy $E = Mgh$ and the evolution of a mechanical system

2.5.2 Entropy and Thermodynamic Potential

Let us consider an isolated thermodynamic system evolving toward a final state (F) starting from the initial one (I). According to the second principle of thermodynamics, the system evolves in such a manner that its entropy is increasing:

$$S(\mathrm{F}) \geq S(\mathrm{I})$$

When the entropy is already maximal in the initial state, it cannot increase and, moreover, since it cannot, in any case, decrease, it remains constant. Then, the system is at equilibrium. Let us, now, consider the function—S. One immediately conceives that, during the same process, it cannot do anything else than to decrease in order, finally, to get its minimal value at equilibrium. The function—S plays the same part as that played by the potential energy in the mechanical system above. It is a potential function called, since we are considering a thermodynamic system, a *thermodynamic potential*. The function—S, called negentropy, is not easy to handle for several reasons. The first one is probably due to the fact that there exist very few true isolated systems; this is the reason why other thermodynamic potentials have been conceived.

2.5.3 Generalization: Definition of a Thermodynamic Potential

One calls thermodynamic potential of a system submitted to some constraints a function Φ depending on the state parameters of the system and, possibly, on the external constraints such as, during the evolution of the system, it tends to take an extremal value (minimal or maximal) at equilibrium. The nature of the thermodynamic potential functions depends on the constraints imposed to the system, prevailing on the thermodynamic quantities extensive or intensive.

It is evident that, according to these considerations, the Gibbs and Helmholtz energy functions are thermodynamic potentials, at least for the conditions for which they have been established. The constraints imposed to the system are these conditions. We will again briefly evoke this notion of potential function when we shall mention the genesis of the notion of activity.

Chapter 3
Escaping Tendency

Abstract The “escaping tendency,” notion due to the American scientist G.N. Lewis, is the tendency of a substance to leave its thermodynamic state by either a physical or a chemical process. Firstly, the content of the chapter shows the analogy of the equilibrium distribution of the matter with the thermal one which may exist between two bodies. Secondly, it also shows that the escaping tendency is closely related to the decrease of the Gibbs energy of the studied system which commands the spontaneous process at constant pressure and temperature.

Actually, in order to study the course of a chemical reaction from the thermodynamic standpoint, it is convenient to relate the criterion of the decrease of the Gibbs energy (and of its cancelling at equilibrium) to the chemical properties of the reactants and products of the studied reaction. In the case of ideal gases, it is shown that it is their molal Gibbs energy which is the essential property in the domain. The part played by the molal Gibbs energy in the case of ideal gases induces the introduction of the chemical potential in order to play this part in every kind of system. In addition, the chemical potential is nothing but a particular molal Gibbs energy. Actually, it will be further mentioned in the book that, in turn, the chemical potential induces the introduction of the notions of the auxiliary functions that are the fugacity and the activity for the study of nonideal systems.

Keywords Standard Gibbs energy • Escaping tendency • Fugacity • Ideal gas • Molal Gibbs energy • Chemical potential

The expression “escaping tendency” is due to G.N. Lewis. It is the tendency of a substance to leave its thermodynamic state by either a physical or a chemical process. Quite evidently, it must be closely related to the decrease of the Gibbs energy of the studied system which, as we have seen, commands the spontaneous process at constant pressure and temperature.

Actually, in order to study the course of a chemical reaction from the thermodynamic standpoint, it is convenient to relate the criterion of the decrease of the Gibbs energy (and of its cancelling at equilibrium) to the chemical properties of the reactants and products of the studied reaction. In the case of ideal gases, we shall see that their molal Gibbs energy is the essential property in the domain. The part played by the molal Gibbs energy in the case of ideal gases induces the introduction of the chemical potential in order to play this part in every kind of system. In

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addition, it will be seen later that the chemical potential is nothing but a particular molal Gibbs energy. Later on, we shall see that, in turn, the chemical potential induces the introduction of the notions of the auxiliary functions that are the fugacity and the activity for the study of nonideal systems.

3.1 Analogy of the Equilibrium Distribution of the Matter with the Thermal One Between Two Bodies

We know that to make sure that a system is in thermal equilibrium, its temperature must be the same in every point. We also know that every body with a temperature higher than that of another tends to leave its heat. This is not the case of the second body. The tendency to leave heat of the first body is higher than that of the second one.

By analogy with this case, one may conceive that a substance of a system may exhibit some tendency to modify its thermodynamic state by changing its moles number. Lewis has introduced and also kept the name "escaping tendency" to this tendency.

The material equilibrium condition for this substance, that is to say the equilibrium of the distribution of its number of moles, is such that its escaping tendency might be the same at every point of the system.

Hence, as a first example, we must consider the system of water and ice. The escaping tendency at the fusion point of both phases is the same. At lower temperature, we may consider that the escaping tendency of water is larger than that of ice, since it tends to disappear. It, actually, spontaneously transforms into ice. The inverse is true for the temperatures which are higher than that of the fusion point.

A second example is provided by the system made up by a solute in a solvent, as for example a solution of sodium chloride in water. The escaping tendency of sodium chloride may be either higher or lower than that of solid sodium chloride (or equal) depending on whether the solution is saturated or not. In the first case, the sodium chloride spontaneously crystallizes. Just at the saturation point, there exists the equilibrium. In the last case, the solid sodium chloride is endowed with a larger escaping tendency than that it possesses in solution. Hence, it disappears by solubilization.

3.2 The Molal Gibbs Energy of a Substance as a Measure of Its Escaping Tendency

Let us again consider the example consisting of water and ice at 0 °C and under 1 atm. Owing to the fact that the system is maintained at constant pressure and temperature, it is judicious to reason by considering the Gibbs energies of both phases. The status of thermodynamic potential conferred to this function permits to rationalize the evolution of the process.

Hence, let us consider the transformation

$$\mathrm{H_2O}_{(\text{solid, 1 atm.})} \rightarrow \mathrm{H_2O}_{(\text{liq, 1 atm.})}$$

or its inverse. Let ΔG be the change in Gibbs energy accompanying it:

$$\Delta G = G_{\text{liq}} - G_{\text{solid}}$$

At equilibrium, at the melting point, under the pressure of 1 atm

$$G_{\text{liq}} = G_{\text{solid}}$$

At a temperature higher than the previous one, the transformation follows the direction already indicated since $G_{\text{ice}} > G_{\text{liq}}$. At a lower temperature, it is the inverse $\left(G_{\text{liq}} > G_{\text{ice}}\right)$.

Hence, the molal Gibbs energy may be used to quantify the escaping tendency of a substance. We must remark that the molal Gibbs energy function is an intensive quantity since it is related to one mole of substance. As a result, it is independent of the number of moles of substance. Of course, this example is particularly simple since the system only contains one substance. Only the temperature, pressure, and number of moles of the substance play a part as variables permitting to reach the equilibrium.

It remains to relate the molal Gibbs energy of a substance to the thermodynamic parameters of the system. This is done through the introduction of auxiliary functions such as the fugacity and the activity. Later, in turn, relating these last functions to some molecular parameters will be considered. The link will be obtained through application of statistical thermodynamics.

3.3 Change of Molal Gibbs Energy of a Perfect Gas with Pressure

In this paragraph, we give a relation expressing the Gibbs energy of a perfect gas as a function of the pressure. As we shall see later (viz. Chaps. 7 and 9) this relation is particularly important since it can be considered as a limit of the expression relating the chemical potential of a substance in a given thermodynamic state to its activity or to its fugacity.

Let us recall that a perfect gas can be defined by the fact that it obeys an equation called state equation which is

$$\mathbf{p}V = nRT$$

where $\mathbf{p}$ and T are the pressure and the temperature of the gas, n its number of moles, and V the volume of the container into which it is. R is the (molar) gas constant. (Some complements concerning perfect gases are given in Chaps. 26 and 27.) By definition, the state equation of a system is the relation which occurs between the different state variables thermodynamically defining the system at equilibrium.

Let us study the infinitesimal isothermal expansion of a pure perfect gas. We know that (viz. Chap. 2)

$$dG = Vd\mathbf{p} - SdT$$

At constant temperature

$$dG = Vd\mathbf{p}$$

whence from the state equation

$$dG = nRT\,d\mathbf{p}/\mathbf{p}$$

From the change in pressure from $\mathbf{p}_{\mathrm{A}}$ to $\mathbf{p}_{\mathrm{B}}$, the change in the Gibbs energy ΔG accompanying the process is

$$\Delta G = G_{\mathrm{B}} - G_{\mathrm{A}}$$

$$\Delta G = nRT\int_{\mathrm{PA}}^{\mathrm{PB}} d\mathbf{p}/\mathbf{p}$$

$$\Delta G = nRT\ln(\mathbf{p}_{\mathrm{B}}/\mathbf{p}_{\mathrm{A}})$$

We notice that the Gibbs energy of a perfect gas depends on the pressure. (In passing, let us recall that this is not the case of its internal energy nor of its enthalpy.)

Usually, the Gibbs energy of a gas is related to that G° it possesses in a state called the "standard state" which is arbitrarily chosen and in which its pressure is $\mathbf{p}^\circ$ and also in which its temperature is arbitrarily chosen to be T. (The imposition of a given temperature does not intervene in the definition of a standard state.) Its molal Gibbs energy G is then given by the relation

$$G = G^\circ + RT\ln \boldsymbol{p}/\boldsymbol{p}^\circ \tag{3.1}$$

When the pressure chosen for the standard state is $\mathbf{p}^\circ = 1$ atm, its molal Gibbs energy is then given by

$$G = G^\circ + RT\ln(\mathbf{p}_{\mathrm{atm}}/1_{\mathrm{atm}})$$

The index atm is used here to recall that $\mathbf{p}$ and 1 are physical quantities endowed with a dimension. The writing often encountered in the literature when $\mathbf{p}^\circ = 1$ atm, i.e.,

$$G = G^\circ + RT \ln \mathbf{p}$$

is fallacious. It appears, indeed at first sight, owing to the properties of the function logarithm, that the pressure is a dimensionless quantity!

3.4 Gibbs Energy Change Accompanying a Reaction Between Perfect Gases

Let us consider the following chemical reaction going to completion:

$$\nu_M M + \nu_L L \ \rightarrow \nu_N N + \nu_P P$$

where ν_L, ν_M, ν_N, and ν_P are the stoichiometric coefficients. Our goal is to calculate the maximal work which can be done by this system at constant temperature and pressure. This calculation may be carried out by taking into account the properties of the Gibbs energy function (viz. Chap. 2). The important point, in the occurrence, is that the maximal work available is equal (in absolute values) to the change in the Gibbs energy. Let us define the system as being constituted by the four gases. The change in the Gibbs energy $\Delta_r G_{syst}$ accompanying the above total transformation is

$$\Delta_r G_{syst} = \nu_N G_N + \nu_P G_P - \nu_L G_L - \nu_M G_M \tag{3.2}$$

where G_L and G_M are the molal Gibbs energies of L and M in the initial state and G_N and G_P those of N and P in the final state. *It is very important to notice at this point of the reasoning that relation (3.2) taking into account the molal Gibbs energies can be used,* here*, because the process concerns perfect gases which in mixtures exhibit the same behavior as that they have when they are alone. It is this property which authorizes the handling, in the present case, of the molar Gibbs energies and expression of them by relation (3.1).*

By replacing G_i by their expressions (3.1), one obtains

$$\Delta_r G_{syst} = \Delta G^\circ - RT \ln \left(\mathbf{p}_N{}^{\circ \nu N} \mathbf{p}_P{}^{\circ \nu P} / \mathbf{p}_L{}^{\circ \nu L} \mathbf{p}_M{}^{\circ \nu M} \right) + RT \ln \left(\mathbf{p}_N{}^{\nu N} \mathbf{p}_P{}^{\nu P} / \mathbf{p}_M{}^{\nu M} \mathbf{p}_L{}^{\nu L} \right) \tag{3.3}$$

or

$$\Delta_r G^\circ = \nu_N G_N{}^\circ + \nu_P G_P{}^\circ - \nu_L G_L{}^\circ - \nu_M G_M{}^\circ$$

$\Delta_r G^\circ$ is evidently a constant at a given temperature.

Hence the change in Gibbs energy accompanying the reaction (3.2) where the perfect gases L and M, initially at pressures $\mathbf{p}_\mathrm{M}$ and $\mathbf{p}_\mathrm{L}$, are transformed at constant temperature and pressure into the perfect gases N and P at pressures $\mathbf{p}_\mathrm{N}$ and $\mathbf{p}_\mathrm{P}$, is given by the expression (3.3). We shall see (viz. Chap. 7) that the pressures $\mathbf{p}_\mathrm{M}$, $\mathbf{p}_\mathrm{L}$ and $\mathbf{p}_\mathrm{N}$, $\mathbf{p}_\mathrm{P}$ are, in the occurrence, called partial pressures. In these conditions, $\Delta_\mathrm{r}G_\mathrm{syst}$ is the maximal work available from the chemical energy supplied by the gases L and M. This process may be actually realized with a convenient galvanic cell working in the conditions of reversibility.

Unfortunately, in the case of reactions between non-perfect gases and also in the case of reactions between components in solutions, the problem of the calculation of the Gibbs energy changes accompanying the chemical reaction is not so simple to solve, as we shall see in the following chapters.

Chapter 4
Partial Molar Quantities

Abstract This chapter is concerned with the very essential notion of partial molar quantities in chemical thermodynamics. During the determination of changes in thermodynamic quantities accompanying a chemical reaction, especially the Gibbs energy one, the question of the physical interpretation of the measured change is frequently asked. Actually, it is not the case when the studied reaction is one between perfect gases or when each of the reactants or products constitutes an independent phase. But, it is set up as soon as intervene species in solutions as reactants or products. The problem is overcome through the handling of partial molar quantities among which the chemical potential stands. This is exemplified by considering the reaction of dihydrogen gas with solid silver chloride to give hydrochloric acid and solid silver. Definitions, properties, and handling of the partial molar quantities are given. The chapter begins by the consideration of closed and open systems.

Keywords Molal quantities • Partial molal quantities • Natural thermodynamic variables • Systems (closed and open) • Electrochemical cell

During the determination of changes in thermodynamic quantities accompanying a chemical reaction, especially the Gibbs energy one, the question of the physical interpretation of the measured change is frequently asked. Actually, it is not the case when the studied reaction is one between perfect gases or when each of the reactants or products constitutes an independent phase. But, it is set up as soon as intervene species in solutions as reactants or products. The problem is overcome through the handling of partial molar quantities among which the chemical potential stands (viz. Chap. 5).

4.1 Closed and Open Systems

Closed systems are those the composition of which is fixed, i.e., those of which the substance quantities are constant. There exists no increase or decrease of matter in the system nor the system can exchange it with the surroundings. In these

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conditions, all the relations previously recalled can be applied without any exception. For example, it is the case of the relation

$$dG = -SdT + Vd\mathbf{p}$$

which entails a mechanical work as the only one which is developed (viz. Chap. 2).

Open systems are systems into which matter can enter or go out. That is to say, they are systems in which the matter quantity may vary during the course of the transformation. Then, the previous formula is no longer convenient. For example, it is the case of the relation above. That which must be used in the same occurrence is

$$dG = -SdT + Vd\mathbf{p} + \sum_i (\partial G/\partial n_i)_{T,P,\,nj}\, dn_i \tag{4.1}$$

The new last terms on the right-hand side take into account the exchanges of matter with the surroundings through the differentials dn_i which express the changes in the number of moles of the components i. The partial derivatives which appear are examples of partial molar quantities that are studied now.

Let us note in passing that when two phases are in contact, each one constitutes an open system whereas, when both are maintained in the same container which precludes any matter exchange with the surroundings, the whole system (constituted by both phases) is closed.

4.2 On the Necessity to Introduce the Partial Molar Quantities When the Species Are in Solution

In order to set up the problem, let us consider the chemical reaction

$$\mathrm{Ag(s)} + 1/2\,\mathrm{Cl_2(g)} \rightarrow \mathrm{AgCl(s)}$$

where (s) and (g) mean solid and gaseous states. Let us focalize on the volume change accompanying the reaction. Let us define the system as being constituted by the chemical substances and the container. The whole volume is given by the relation

$$V = V_{\mathrm{Ag}} + V_{\mathrm{Cl_2}} + V_{\mathrm{AgCl}} + \mathrm{Cte}$$

where Cte is the volume of the container. Let us consider the volume change $\partial V/\partial n$ of the system per mole of consumed silver, n being the number of moles of silver. We can write

$$\partial V/\partial n = \partial V_{\mathrm{Ag}}/\partial n + \partial V_{\mathrm{Cl_2}}/\partial n + \partial V_{\mathrm{AgCl}}/\partial n$$

Among the partial derivatives of the right-hand member, none exhibits any difficulty of interpretation. Each represents the molar volume of the substance, that is to say its molal volume when it is pure. This is the case, here, because each component constitutes a pure phase. For each phase, indeed, one can write

$$V = nv^{\bullet}$$

where $v^{\bullet}$ is the molal volume of the pure compound. It is evident that

$$\partial V/\partial n = v^{\bullet}$$

As a result, for that system

$$\partial V/\partial n = v^{\bullet}{}_{\mathrm{AgCl}} - v^{\bullet}{}_{\mathrm{Ag}} - 1/2\,v^{\bullet}{}_{\mathrm{Cl_2}}$$
$$\partial V/\partial n = \Delta v$$

with

$$\Delta v = v^{\bullet}{}_{\mathrm{AgCl}} - v^{\bullet}{}_{\mathrm{Ag}} - ½\,v^{\bullet}{}_{\mathrm{Cl_2}}$$

Hence, there is no problem of meaning for this example.

- Now, let us consider the following reaction:

  $$1/2\,\mathrm{H_2(g)} + \mathrm{AgCl(s)} \rightarrow \mathrm{HCl(m)} + \mathrm{Ag(s)}$$

  where m is the molality of the hydrochloric acid being in solution. Actually, this reaction is the global relation of the following electrochemical cell:

  $$\mathrm{H_2}\big|\mathrm{HCl}(m)\big|\mathrm{AgCl}\big|\mathrm{Ag}$$

- As a concrete example of such a study, it may be interesting to know the effect of the pressure on the electromotive force of this cell, that is to say actually, on the change in Gibbs energy accompanying the reaction cell. In order to determine it, we use the general expression (viz. Chap. 2)

  $$(\partial G/\partial \mathbf{p})_T = V$$

  i.e., for the reaction cell

  $$(\partial \Delta G/\partial \mathbf{p})_{\mathrm{T}} = \Delta V$$

  The solution of the problem imposes to know the volume V of the system and its change. It is given by the relation

$$V = V_{H_2} + V_{AgCl} + V_{HCl\ soln} + V_{Ag} + \text{Cte}$$

The volume change per mole of consumed silver $\partial V/\partial n$ is

$$\partial V/\partial n = \partial V_{H_2}/\partial n + \partial V_{AgCl}/\partial n + \partial V_{HClsoln}/\partial n + \partial V_{Ag}/\partial n$$

The true meaning of the term $\partial V_{HClsoln}/\partial n$ remains to be clarified. Here, is the problem.

Let us symbolize it by $\overline{v_{HCl}}$:

$$\overline{v_{HCl}} \equiv \partial V_{HClsoln}/\partial n$$

As we shall see it in the next paragraph, it is the partial molal volume $\overline{v_{HCl}}$ of hydrochloric acid at the molality m. The change $\overline{\Delta v}$ in the volume of the system when one mole of silver has disappeared is given by the relation

$$\overline{\Delta v} = v_{Ag} + \overline{v_{HCl}} - 1/2\, v_{H_2} - v_{AgCl}$$

(The symbol v, in this last relation, appears in place of V in order to notice the reader of the fact that the volumes which are in question are the molar ones, partial or not.)

4.3 Definition of Partial Molar Quantities

According to what is previously mentioned, it is evident that we must express the relations between the thermodynamic functions X and the variables playing a part in their values in a closed system (such as the temperature, pressure, volume) by using a supplementary type of variable, i.e., the number of moles of every component.

Numerous thermodynamic experiments show that the “great” thermodynamic functions U, G, H, and A do possess the variables given immediately under, as *natural* ones. Formally, we can, hence, formulate the following relations:

$$\begin{aligned} U &= U(S, V, n_1, n_2, \ldots n_k) \\ G &= G(T, \mathbf{p}, n_1, n_2, \ldots n_k) \\ H &= H(S, \mathbf{p}, n_1, n_2, \ldots n_k) \\ A &= A(T, V, n_1, n_2, \ldots n_k) \quad \text{relations} \end{aligned} \tag{4.2}$$

in which n_1, $n_2, \ldots n_k$ are the number of moles of the components $1, 2, \ldots k$. n_1, $n_2, \ldots n_k$ are the supplementary variables evoked.

From the mathematical standpoint, the partial molal quantity corresponding to $\overline{X}$ is defined as being its partial derivative with respect to the number of moles n_i of the compound i, that is to say

$$\overline{X} = (\partial X/\partial n_i)_{\text{other variables}} \tag{4.3}$$

The partial molal quantities are symbolized by the same symbols as usually but they are highlighted. Their unity, of course, is that of the considered quantity. The introduction of the partial molar quantities permits to write thermodynamic quantities as being function of the different variables which command their values, in particular in the case of open systems.

Hence, for example, the total differential of the Gibbs energy of an open system is written as

$$\begin{aligned} dG = {} & (\partial G/\partial T)_{P,n} dT + (\partial G/\partial \mathbf{p})_{T,n} d\mathbf{p} + (\partial G/\partial n_1)_{P,T,n2,\ldots} dn_1 \\ & + (\partial G/\partial n_2)_{P,T,n1,\ldots} dn_2 + \cdots \end{aligned} \tag{4.4}$$

An important point is that the variables—see relations (4.2)—*S*, *V* and others, …; characterizing *U*, the variables *T*, **p** and so f., characterizing *G* a.s.f…are not associated with them, randomly. They are said to be natural. Hence, *T* and *V* are the natural variables of the Helmholtz energy *A*. From theoretical and practical viewpoints, this means that when *A* is known either experimentally or even theoretically through the partition functions (viz. Chaps. 22 and 24) as a function of *T* and *V*, all the other thermodynamic quantities are accessible (entropy, pressure, chemical potentials—see the following chapter). It is the same with the other functions *U*, *G*, and *H* mentioned in relations (4.2).

Some authors consider the relations (4.2) as being postulates.

4.4 Physical Meaning of the Partial Molal Quantities

The physical meaning of a partial molal quantity may be grasped by considering the example of the volume of a solution.

Let us consider a binary solution in order to simplify the reasoning and let the components 1 and 2 be the solvent and the solute. (However, it must be noticed that for the following theory the fact that one of the components is the solvent and the other the solute does not confer them any particular part to play.) Their initial numbers of moles are, respectively, n_1 and n_2. The initial total volume of the solution is V_o. Let us successively add some quantities of solute to the solution. The total volume V changes. Let us draw the diagram V as a function of n_2 (Fig. 4.1).

The partial molar volume $\overline{v_2}$ is defined by

$$\overline{v_2} = (\partial V/\partial n_2)_{n_1, n'_2}$$

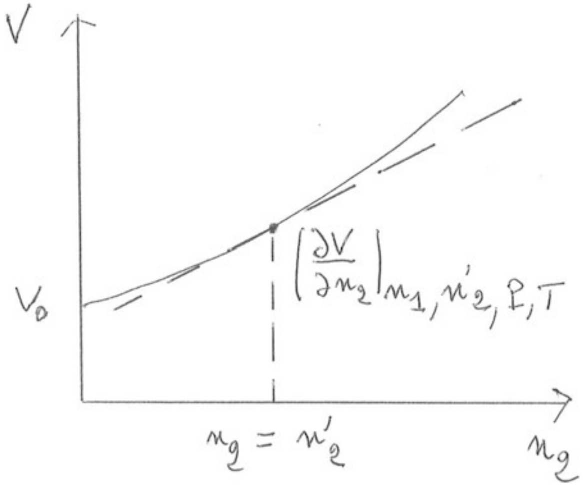

Fig. 4.1 Total volume of the solution V as a function of the number n_2 of moles of solute added

It is nothing different than the slope of the curve V/n_2, for the values n_1 and n'_2 considered. The immediate conclusion which can be drawn from this fact is that the partial molecular volume $\overline{v_2}$ (as all the other partial quantities intervening in the system, in this case $\overline{v_1}$) does vary with the "instantaneous" composition of the solution. The above diagram, indeed, clearly shows that the slope varies for each composition. However, in rare cases, the slope does not change with the composition (viz. below: molar quantities).

The same considerations can be addressed to any other quantity. In brief, one can conclude that a partial molal quantity is equal to its increase or its decrease for the whole solution when one mole of solute is added to a very large volume of solution in order that the different concentrations do not noticeably change during the addition.

4.5 Molal Quantities and Partial Molal Quantities

It may happen that the measured thermodynamic quantity is in linear relation with the number of moles of a component. Hence, for example, it may occur that it is the case for the volume of a binary solution, that is to say, the total volume V of the solution linearly varies with the number n_2 of moles of solute (Fig. 4.1). The definition of the partial molal volume $\overline{v_2}$, of course, immediately shows that it is the molal volume $v_m(2)$ of the pure solute 2:

$$\overline{v_2} = v_m(2)$$

Remark: Concerning, now, the chemical potential (see the following chapter), this term is generally used when a mixture is under consideration. When it is the case of a pure substance to be under consideration, it is the term molal Gibbs energy which is used.

4.6 Fundamental Equation of the Molal Partial Quantities

Let X be an extensive property of a system constituted by a solution (for example, it can be its volume, its calorific capacity, its internal energy). By definition of an extensive property, it is a function of the number of moles of each component. Let us suppose (for the sake of simplification) that the natural variables are maintained constant (for example, in the case of the Gibbs energy, the temperature and pressure are maintained constant). As a consequence, the relation (4.4) applied to X by taking into account the properties of total differentials (viz. Appendix A) becomes

$$dX = (\partial X/\partial n_1)dn_1 + (\partial X/\partial n_2)\,dn_2 + \cdots$$

(the indexes being missed in order to lighten the writing). The total differential may also be written as

$$dX = \overline{X}_1 dn_1 + \overline{X}_2 dn_2 + \cdots$$

The partial molal quantities $\overline{X}_1, \overline{X}_2, \ldots$ are intensive ones since they are related to a well-defined quantity of matter (one mole). Because of this fact, they do not depend on the total quantity of each component but only on the relative composition of each one. As a result, if to a solution containing several components with a given relative composition is added an identical solution of the same composition, the partial molal quantities $\overline{X}_i$ do not change whereas the numbers of moles $n_1, n_2, \ldots$ vary. The consequence is that the total differential dX can be immediately integrated and we can write

$$X = n_1\overline{X}_1 + n_2\overline{X}_2 + \cdots \tag{4.5}$$

(From the strict mathematical viewpoint, obtaining the equation (4.5) is possible because the function X is homogeneous of order 1—see Appendix A.) This relation is very important.

It is sufficient to consider the case in which an extensive property of a solution is in linear relation with the number of moles of each of the components to be convinced by its interest. In these conditions, we have seen above that the partial molal quantities are constant and, moreover, are equal to the molal properties of pure components, that is to say

$$X = n_1 X_m(1) + n_2 X_m(2) + \cdots \tag{4.6}$$

The comparison of relations (4.5) and (4.6) shows that partial molal quantities play the part of the molal quantities of pure compounds and that they can be handled as the latest. However, there exists a double difference between both kinds of quantities:

- On the one hand, the partial molal quantities are not constant whereas the molal ones are.
- On the other, the partial molal quantities may be positive or negative. This property is inconceivable with the molal ones.

4.7 Thermodynamic Relations Between Partial Molar Quantities

The relations between the thermodynamic molal partial quantities are the same as those which exist between molal quantities. For example, the validity of the following relation can be demonstrated:

$$\overline{G} = \overline{H} - \overline{TS}$$

We limit ourselves to mention that the demonstration is carried out by application of the Schwartz's theorem (viz. Appendix A). A particularly interesting example is the obtaining of the relation which expresses the influence of the temperature on the chemical potential (viz. Chap. 5).

4.8 Experimental Determination of Partial Molal Quantities

The partial molal quantities are experimentally accessible:

- Either through graphical methods based on the study of the curves' extensive quantity/number of moles of the component (or its logarithm)
- Or analytically by starting from apparent molal quantities

In some cases, it is the absolute value of the partial molal quantity which is accessible. Let us mention that this is the case of partial molal volumes for example. In other cases, it is not possible. Only their relative values are accessible. It is the case, for examples, of the partial molal enthalpy and partial molal Gibbs energy. The reason lies simply in the fact that the molal quantities of pure compounds cannot, themselves, be known in absolute values.

Chapter 5
Chemical Potential or Partial Molal Gibbs Energy

Abstract The chapter concerns the definition of the chemical potential as being a partial molar Gibbs energy. It also mentions its physical meaning, some of its properties with, especially, its change accompanying a chemical transformation. The chemical potential is, by far for our purpose, the most important partial molal quantity. As we shall see it later, the value of the chemical potential of a species is, indeed, very often expressed in terms of the auxiliary functions that are the fugacity and the activity. The notion of chemical potential, notably, permits the study of the change in the Gibbs energy accompanying a chemical process and is the thermodynamic basis of the so-called mass action law.

Keywords Gibbs' relation • Mass action law • Partial molal Gibbs energy • Electromotive force

The chemical potential is by far, for our purpose, the most important partial molal quantity. As we shall see it later, the value of the chemical potential of a species is, indeed, very often expressed in terms of the auxiliary functions that are the fugacity and the activity. Actually, the chemical potential appears to be of utmost importance as soon as one takes into account the fact that it has the significance of a Gibbs energy and as soon as one remembers that a Gibbs energy change may be a very interesting criterion of spontaneity of a process.

The notion of chemical potential, notably, permits the study of the change in the Gibbs energy accompanying a chemical process and is the thermodynamic basis of the so-called mass action law. From the general standpoint, let us anticipate what is following by saying that the mass action law must be expressed in terms of activities.

5.1 Definitions of the Chemical Potential

- The chemical potential μ_k of a compound k in a given state (temperature T, pressure $\mathbf{p}$, numbers of moles of the different species making up the system n_i) is expressed by the following mathematical relation:

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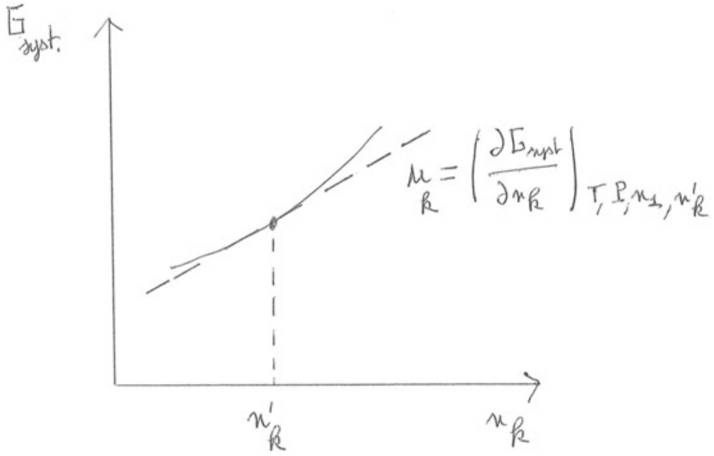

Fig. 5.1 Chemical potential μ_k or partial molal gibbs energy $\overline{G_k}$ in the case of a solute k in the solvent 1

$$\mu_k = (\partial G/\partial n_k)_{T,P,ni \neq nk} \tag{5.1}$$

Quite evidently, it is the partial molal Gibbs energy $\overline{G_k}$ defined by (viz. Chap. 4)

$$\overline{G_k} = (\partial G/\partial n_k)_{T,P,ni \neq nk} \tag{5.2}$$

In this case, G is the Gibbs energy of the whole solution considered as being the system (Fig. 5.1). According to what was mentioned before (viz. Chap. 4), one can write

$$G = n_1\overline{G_1} + n_k\overline{G_k}$$

Hence, both terms are synonymous and the unity of the chemical potential in use is J mol^{-1}.

- Let us also recall other definitions of the chemical potential based on the following relations:

$$\mu_k = (\partial U/\partial n_k)_{S,V,\, ni \neq nk} \quad \mu_k = (\partial H/\partial n_k)_{S,P,\, ni \neq nk} \quad \mu_k = (\partial A/\partial n_k)_{T,V,\, ni \neq nk}$$

Hence, the chemical potential turns to be, also, either a molal partial internal energy, a molal partial enthalpy, or a partial molal Helmholtz energy. But, it must be noticed that the variables maintained constant in the partial derivatives are not the same. However, it is demonstrated that all these definitions are equivalent such as they are written above.

5.2 Physical Meaning of the Chemical Potential: Equilibrium Condition

The chemical potential of a substance can be considered as being a quantity which represents its escaping tendency as does the molal Gibbs energy (viz. Chap. 3). It is by no means surprising since as we have seen it, it is also a molal Gibbs energy, but a partial one. With this point in mind, it appears that the chemical potential extends the notion of molal Gibbs energy to complex media.

Actually, the notion of molal Gibbs energy can be only applied to pure compounds. This is the reason why the chemical potential of a pure compound is also its molal Gibbs energy:

$$\mu_i = G_{\mathrm{m}}(i) \quad \text{(pure } i \text{ compound)}$$

Hence, at this point of the reasoning, we can say that the chemical potential of a compound is a quantity which is liable to quantify its tendency to leave its current thermodynamic state by every sort of process, physical, chemical, or biochemical one.

In the realm of physical processes, a simple example is given by the partition of a solute i between two immiscible phases α and β. Let us suppose that at the beginning of the process the whole solute is only present in the phase α. Its chemical potential is then $\mu_{i\alpha}$ whereas $\mu_{i\beta} = 0$, that is to say

$$\mu_{i\alpha} > \mu_{i\beta} \quad \text{(initial state)}$$

By stirring both phases (this has the only effect to increase the speed of matter exchanges between the phases but does not change anything to the thermodynamic aspect of the process) a part of the solute spontaneously goes into the phase β. There exists a moment at which the transfer process ceases. Then, the concentrations in both phases no longer vary. The partition equilibrium is reached. The equilibrium condition (concerning, of course, the exchange of i) is the equality of its chemical potential in both phases, that is to say

$$\mu_{i\alpha} = \mu_{i\beta} \quad \text{(equilibrium)}$$

The partition spontaneously occurred because, initially, there existed an inequality of the chemical potentials. We also may notice that the matter exchange process follows the direction of a decreasing chemical potential. A difference of chemical potentials plays an analogous part as that played by an electrical potential difference. Electrons flow between two points of an electrical circuitry because there exists a difference of electrical potentials between them. It is also analogous to the differences in temperature and pressure which, respectively, command a heat transfer and a mechanical motion. Some authors assimilate the chemical potential to a kind of "chemical pressure."

Likewise, a spontaneous chemical reaction occurs when a well-defined linear combination of the chemical potentials of reactants and products of the reaction differs from 0 (viz. paragraph 4 below).

An equilibrium state related to a species is a state in which its escaping tendency is null. It is clear that the constancy of the chemical potential of a component is an equilibrium criterion. This result is general. Hence, the chemical potential values, as a rule, constitute a general criterion of evolution and equilibrium. It remains to quantify a chemical potential. It is at this point that the notions of fugacity and activity take all their importance (viz. Chaps. 7, 9, and 10).

5.3 Some Properties of the Chemical Potential

- The chemical potential is an intensive property, since it is a molal quantity,
- Since the chemical potential of a compound *i* is its partial molal Gibbs energy, it provides a way to quantify the infinitesimal change in the Gibbs energy of the whole system when the number of moles of species *i* varies under the influence of a physical or chemical process change of an infinitesimal quantity, other variables defining the state of the system (temperature, pressure, numbers of moles of other species) being maintained constant,
- The chemical potential is expressed in J mol^{-1},
- The chemical potential of a perfect gas tends toward $-\infty$ when its pressure tends toward zero. This property is endowed with important practical consequences.
- As all the other partial molal quantities, the chemical potentials very often vary with the composition of the system. In some scarce cases, it may be independent of it,
- The chemical potential of a pure compound is simply its molal Gibbs energy G_{m}:

$$\mu_i = G_{\mathrm{m}}(i) \quad \text{(pure } i \text{ compound)}$$

- The absolute value of the chemical potential cannot be known since it is a Gibbs energy and since the absolute values of the Gibbs energies are not accessible. Only changes in chemical potentials can be measured. This property is an essential one. As we shall see it, it is one of the reasons of the introduction of the concept of activity (viz. Chap. 9),
- The influence of the temperature on the chemical potential is given by the expression

$$(\partial\mu_i/\partial T)_{P,nj} = -\,\overline{S_i}$$

$\overline{S_i}$ being the partial molal entropy of *i*. The demonstration of the obtaining of this result is as follows.

For an open system, the chemical potential of *i* is defined by relation (5.1). As a result

$$\begin{aligned}(\partial\mu_i/\partial T)_{P,nj} &= \left[\partial/\partial T(\partial G/\partial n_i)_{T,P,nj\neq ni}\right]_{P,ni}\\ &= \left[\partial/\partial n_i(\partial G/\partial T)_{P,ni}\right]_{T,P,nj\neq ni}\end{aligned}$$

equality which results from the crossing of the derivatives (viz. Appendix A: Schwartz's theorem). Since the occurrence of the relation (viz. Chap. 2)

$$(\partial G/dT)_P = -S$$

we find

$$\begin{aligned}&= -(\partial S/\partial n_i)_{T,P,nj\neq ni}\\ &= \ -\ \overline{S_i}\end{aligned}$$

Another interesting expression relating the temperature and the chemical potential is

$$[\partial(\mu_i/T)/\partial T]_{P,nj} = -\overline{H_i}/T^2$$

It results from the following expression, set up by a general reasoning starting from the Gibbs–Helmholtz relation (viz. Chap. 2):

$$\partial[(G/T)/\partial T]_{P,x} = -H/T^2$$

This last relation results itself from the Gibbs–Helmholtz equation (viz. Chap. 2).

- The influence of the pressure on the chemical potential is given by the expression

$$(\partial\mu_i/\partial\mathbf{p})_{T,nj} = \overline{V_{mi}}$$

The demonstration is analogous to the previous one. It results from the relation (viz. Chap. 2)

$$(\partial G/\partial\mathbf{p})_T = V_m$$

- A very important relation for the thermodynamic study of solutions and, hence, for our purpose is that of Gibbs–Duhem. It expresses the fact that the simultaneous changes in the temperature, pressure, and chemical potentials (all intensive quantities) are not independent from each other. They are "interrelated" by the Gibbs–Duhem's relation, which is

$$-SdT + Vd\mathbf{p} - \sum_i n_i d\mu_i = 0$$

S and V are the total entropy and the total volume of the phase. n_i is the number of moles of every component, and μ_i is its chemical potential. At constant temperature and pressure, it becomes

$$\sum_i n_i \, d\mu_i = 0$$

In these conditions, when the phase contains n components, only $(n-1)$ chemical potentials can vary independently. In the case of a binary solution, the Gibbs–Duhem's relation may be written in a different manner. It becomes

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

Dividing this relation by the total number of moles, it becomes

$$\begin{gathered}[n_1/(n_1 + n_2)]d\mu_1 + [n_2/(n_1 + n_2)]d\mu_2 = 0 \\ x_1 d\mu_1 + x_2 d\mu_2 = 0 \qquad (5.3)\end{gathered}$$

where x_1 and x_2 are the molar fractions of both components. The Gibbs–Duhem's relation may still be written in a different manner, at, as before, constant temperature and pressure (for a binary solution). In these conditions, the chemical potential of each component only depends on its molar fraction. Then, we can write

$$d\mu_i = (\partial \mu_i / \partial x_i)_{T,P} \, dx_i$$

Hence, (5.3) can be rewritten:

$$x_1 (\partial \mu_1 / \partial x_1)_{\mathrm{T,P}} dx_1 + x_2 (\partial \mu_2 / \partial x_2)_{\mathrm{T,P}} dx_2 = 0$$

or

$$(\partial \mu_1 / \partial \ln x_1)_{\mathrm{T,P}} \, dx_1 + (\partial \mu_2 / \partial \ln x_2)_{\mathrm{T,P}} \, dx_2 = 0$$

Since, in this reasoning, we only consider binary solutions

$$\begin{gathered} x_1 + x_2 = 1 \\ dx_1 = -dx_2 \end{gathered}$$

and finally

$$(\partial \mu_1 / \partial \ln x_1)_{\mathrm{T,P}} = (\partial \mu_2 / \partial \ln x_2)_{\mathrm{T,P}} \qquad (5.4)$$

It is clear that the great interest of the Gibbs–Duhem's relation lies in the fact that it provides information concerning the changes in the chemical potentials of the components of a solution.

- For a solution containing n components, the Gibbs energy of the whole chemical system (defined as being constituted by the solvent and all the solutes) G_{syst} is given by the relation

$$G_{\text{syst}} = n_1\mu_1 + n_2\mu_2 + \cdots n_n\mu_n$$

where n_i are the numbers of moles of the components. This relation results from the fact that the function of Gibbs energy is extensive and that its mathematical counterpart is a homogeneous one (viz. Appendix A).

5.4 Change in the Gibbs Energy Accompanying a Chemical Transformation

When a system is constituted by the compounds $1, 2\ldots$ before the transformation (initial state), the numbers of moles of which being n_1, $n_2, \ldots$, and after transformation (final state) by n'_1, $n'_2\ldots$ the change in Gibbs energy of the system accompanying the chemical transformation is given by the expression

$$\Delta_r G_{\text{syst}} = \left(n'_1\mu'_1 + n'_2\mu'_2 + \cdots\right) - (n_1\mu_1 + n_2\mu_2 + \cdots) \tag{5.5}$$

where μ_1, $\mu_2, \ldots \mu'_1$, μ'_2 are the chemical potentials in the initial and final states.

This expression is absolutely general. As an example, let us consider the following chemical reaction:

$$n_{\text{A}}\text{A} + n_{\text{B}}\text{B} \rightarrow n_{\text{M}}\text{M} + n_{\text{N}}\text{N}$$

and suppose that the reaction is total. The change in the Gibbs energy accompanying the reaction is given by the expression

$$\Delta_{\text{r}} G = (\nu_{\text{M}}\mu_{\text{M}} + \nu_{\text{N}}\mu_{\text{N}}) - (\nu_{\text{A}}\mu_{\text{A}} + \nu_{\text{B}}\mu_{\text{B}}) \tag{5.6}$$

This relation can be generalized to the case of a more complex reaction. When the linear combination of the kind of the type (5.6) just above is null, there is equilibrium (viz. Chap. 3).

5.5 Electromotive Force of a Reversible Electrochemical Cell and Change in the Gibbs Energy Accompanying the Reaction Cell

Let us recall that the electric potential difference E that occurs at the terminals of an electrochemical cell is a function of the temperature, pressure of the system, and, also, the activities of the species taking part in the electrochemical reactions which are developing onto the electrodes (viz. Chaps. 13 and 14). There exists a mathematical relationship between the decrease of the Gibbs energy (of the chemical system) accompanying a *reversible* process occurring in the cell and the electric potential difference until the obtaining of the equilibrium. This is true at constant pressure and temperature and, also, at *null current*. This relation is

$$\Delta G = -\, nFE$$

E is called the electromotive force of the cell, n is the number of exchanged electrons, and F is the faraday. This relation is of utmost important. It is the base of the Nernst's relation.

The use of electrochemical cells may permit, in some cases, to determine the activities of nonelectrolytes and those of electrolytes (viz. Chaps. 13 and 14).

Chapter 6

The Notion of Activity: An Overview

Abstract The chapter is a brief overview of the concept of activity. It can be considered as a general scientific introduction of the book. It mentions:

– Some properties of the quantity activity in relation to the chemical equilibria governed by the mass action law.
– Its relation with the corresponding concentration and the chemical potential of the substance, with its standard state and the arbitrary character of the choice of the latter.
– The link between a fugacity and an activity.
– The ideal character of a system and interactions between the particles constituting it and the intermolecular forces which may exist between them.

The possibility of their determination is also tackled. Finally, a recall of the genesis of the notion of activity is given.

Keywords Constant conditional (or formal) • Determination of activities (general) • Thermodynamic equilibrium constant • Intermolecular forces

It seems interesting for us, as a general scientific introduction of the book, to give a brief overview of the concept of activity before, of course, delving later into its more thorough study.

6.1 Some Properties of the Quantity Activity: Activities and Chemical Equilibria

A patent example of the interest in chemistry of the use of activities is the following.

Let us, for example, consider the following chemical reaction:

$$\nu_A A + \nu_B B \rightleftharpoons \nu_M M + \nu_N N$$

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We shall see (viz. Chap. 17) that, *at equilibrium*, the activities a_A, $a_B, \ldots$ of the different species A, B, M, and N (participating in it through the relation above) are related to each other by the expression

$$K^\circ = a_M{}^{\nu M} a_N{}^{\nu N} / a_A{}^{\nu A} a_B{}^{\nu B} \tag{6.1}$$

This result is quite general.

Let us stress the fact that the activities taken into account in relation (6.1) are those and only those occurring once the equilibrium is reached. K° is a constant at a given temperature. It is called *the standard equilibrium constant* (of the reaction) or the *thermodynamic equilibrium constant*. Relation (6.1) is well known under the name "mass action law." Historically, it is interesting to recall in passing that it has been introduced into the scientific realm by starting from a reasoning which was not at all based on thermodynamic considerations!

The thermodynamic equilibrium constant K° only depends on the temperature and pressure and not on the composition of the system. It is a true constant. This obvious sentence will take all its importance during the reading of the end of this chapter.

The thermodynamic constant must not be confused with the corresponding constant K which is related to the concentrations at the equilibrium of the reactive species, defined for the above reaction by the expression

$$K = [\mathrm{M}]^{\nu M}[\mathrm{N}]^{\nu N}/[\mathrm{A}]^{\nu A}[\mathrm{B}]^{\nu B} \tag{6.2}$$

The terms in brackets in the expression (6.2) are the concentrations at equilibrium. They can be expressed in molalities, molarities, molar fractions … (viz. Chap. 1). The constant K may also be expressed in partial pressures. Each of these cases must be, in principle, distinguished from each other by an index located next to the symbol K. For example, the constant K is symbolized by K_c and K_m when the concentrations are expressed, respectively, in molarities and molalities.

Whereas thermodynamic equilibrium constants are absolutely dimensionless numbers since activities are themselves dimensionless, the equilibrium constants related to the concentrations may be dimensioned according to the stoichiometry of the reaction. The latter equilibrium constants are often called *formal or conditional constants*. They do not only depend on the temperature and total pressure. They also depend on the concentrations of the reactive species.

6.2 Activities and Concentrations

The activity a of a species in a given medium is related to its "concentration" C through the general expression

$$a = \gamma C \tag{6.3}$$

The factor γ is called *the activity coefficient*. The activity of a species and its concentration obey this relation, whatever the concentration scale is. Hence, this relation is general. Let us say that although the activities are dimensionless, the activity coefficients are also dimensionless whatever the scale of concentration C is.

The very big difficulty encountered in the handling of activities lies in the fact that relation (6.3) is not, actually, a true linear relation because the activity coefficient γ does vary with the "concentration" C. Here is the reason why the analogy between relations (6.1) and (6.2) must not mask the fact that the mathematical link between an activity and the corresponding concentration is complex and badly known. It is the matter of this book to somewhat make it clearer.

From another viewpoint, it must not be forgotten that there exist several kinds of activities which are of different numerical values for the same species in the same thermodynamic state according to the chosen standard state (viz. under) and the concentration scale to which they are related to and, eventually, according to the conditions defining the state of the system.

6.3 Chemical Potential and Activity of a Compound

We know (viz. Chap. 5) that one of the most central quantities of chemical thermodynamics is the chemical potential. Let us recall also that, essentially, its change governs the tendency of a system to change its thermodynamic state through a chemical or physical process.

One of the possible definitions of the activity of a species consists in using the relation (6.4) linking it to its chemical potential:

$$\mu = \mu^\circ + RT\ln a \tag{6.4}$$

where R is the perfect gas constant and T the absolute temperature of the system. μ° is an *arbitrary* constant. We see that it is the chemical potential of the compound when its activity equates to unity. μ° is called the *standard chemical potential* of the species or more properly its *chemical potential in the standard state*.

6.4 Standard State and Activity

Relation (6.4) is only a formal definition. Hence, further, the standard state must be defined in terms of experimental variables defining this particular thermodynamic state.

Owing to the arbitrary character of a standard state, which is one of the characteristics of this quantity, it is clear that there exists an infinity of choices for it. However, it turns out that some choices are easier to handle than others. Precisely, these choices can change according to the state of the matter of the compound (gaseous, liquid, solid), according to whether it is pure or in a solution and also according to the concentration scale of the species to which it is related to through relation (6.3).

The result of these considerations is that the notion of activity cannot be dissociated from that of standard state.

6.5 On the Arbitrary Character of the Choice of the Standard State

A puzzling point of the concept of the chemical activity lies in the arbitrary character of the choice of the concentration scale to which the chemical activity of the species is related to. One must realize that, for example, it is as correct to choose the molar fraction as to choose its molality or its molarity to express its concentration. Then, one can rise the legitimate question of the validity of the equilibrium constant value, which evidently varies with the choice of the retained scale of concentration, since the numerical values of the "concentrations" are then different. With this question in mind, it is quite admissible that the conclusions stemming from the study of a chemical equilibrium through the value of the equilibrium constant may be doubtful.

6.6 Activity and Fugacity

Although this book is mainly devoted to the concept of activity, it also mentions some aspects of the quantity called the fugacity.

Both notions are actually intimately linked. It is true that they can be separately introduced in the realm of classical thermodynamics without any mention of the other. This is not astonishing since the concept of fugacity was introduced to study the behavior of imperfect gases whereas that of activity was introduced mainly for the study of solutions. However, as we shall see it later, both can apply to every kind of phase.

There exist some simple mathematical relations linking them. Besides, they permit us to better grasp their significances. In particular, let us mention the occurrence of a very important one which, purely and simply, is one of the definitions of the chemical activity. According to it, the chemical activity is the ratio of the fugacity of the species of concern and of its fugacity in the standard state.

6.7 Ideal Character of a System and Interactions Between the Particles Constituting It

In the general introduction of this book, we have already recalled that the notion of chemical activity has been introduced by G.N. Lewis in order to treat the nonideal systems (in particular solutions) by using a formalism very close to that expressing the chemical potentials of species in ideal systems.

The ideal character of a system is related to the occurrence (or not) of interactions between particles constituting it. It has a somewhat different meaning according to the fact whether it is a gaseous phase or a solution which is considered. Even in the latter case, the conditions of "ideality" differ whether electrolyte or nonelectrolyte solutions are considered.

A pure gas is said ideal if no interaction does exist between its particles. It is the case when its pressure is very weak. Its behavior remains ideal as long as these interactions cannot be felt. It is the same thing for a gaseous mixture. Its behavior remains ideal as long as there do not exist interactions between the particles of the mixture whatever their component identity is.

It is different in the case of solutions. At least, there exist two components, the solute and the solvent, the particles of which are in interactions. Let us recall, indeed, that the gaseous state is a very "expansed" one in which the volume occupied by the particles is negligible with respect to that of the container. Hence, one can consider that it is only occasionally that two particles are sufficiently close to give rise to intermolecular forces. One can consider that the gas molecules move freely. This is not the case of liquids and solutions. Concerning the latter, the total volume of molecules quasi-fully occupies the whole volume of the system. The intermolecular forces are strong. However, they cannot preclude the easy movement of the particles in the medium. This is not the case for the other compact state of the matter which is the solid state. As a result, one can say that evoking the "ideality" notion to liquids, as it applies to the case of gases, is absurd, because of the occurrence of the remaining interactions between solvent and solute particles, even in highly dilute solutions.

A particularly interesting case of solutions is that of those containing ions. For the latter, the interactions between solute particles still exist at distances much higher than those separating two uncharged species when, precisely, the interactions in the latter case are vanishing. Hence, deviations from "ideality" appear for concentrations in charged molecules much weaker than with the uncharged ones. For example, in an aqueous solution of sodium chloride, deviations from thermodynamic laws expressing the ideal behavior by more than 5 % do appear once their concentration attains 2×10^{-3} mol L^{-1}. In solutions only containing uncharged particles, the concentration of at least 1 mol L^{-1} must be reached to obtain such deviations.

At once, let us notice that the more dilute the solutions are, the weaker the interactions between the solute molecules or between the ions are and the more the activity values do approach those of the corresponding concentrations. It is the same for gases. The weaker their partial pressures, the closer their fugacity values approach those of the latter. These properties are very interesting since they provide us with a strategy for the determination of equilibrium thermodynamic constants. It consists in determining them in very dilute solutions or at very weak partial pressures. It is at this level of quantities of matter that the reliability of the values of the obtained thermodynamic equilibrium constants may be expected to be good.

6.8 Intermolecular Forces

Intermolecular forces that operate between the molecules of a pure substance or between the molecules of a mixture command the thermodynamic properties of the system constituted by them. Since it is these intermolecular forces that are responsible for the deviations from “ideality” exhibited by a system and since the chemical activities have been introduced to overcome the problem, it is interesting to briefly evoke these operating intermolecular forces. The intermolecular forces give rise to potential energy functions. This term is often used to explicit the force.

Several intermolecular forces are operating and, hence, they can be classified in several different manners. The different retained classifications are purely arbitrary. For our own part, we distinguish:

- The electrostatic forces they exert between charged particles (ions) and between permanent dipoles and quadrupoles.
- The induction forces they exert between a permanent dipole (or quadrupole) and an induced dipole. The latter is induced in a molecule with polarizable electrons.
- The forces of attraction called dispersion forces and the forces of repulsion between nonpolar molecules.
- The chemical forces (or specific forces) responsible for association and solvation phenomena: Among them, we can mention the formation of hydrogen bonds and association complexes called charge-transfer complexes.

Further considerations of these intermolecular forces are given in Chap. 46.

6.9 Determination of Activities

The determination of activities of all types of compounds is experimentally possible *except* in the case of ions. This is a fact: the activity of an individual ion is not measurable. However, fortunately, its value can be approached, at least in some well-defined conditions, by using theoretical expressions which permit the calculation of activity coefficients.

6.10 Genesis of the Chemical Activity Concept

G.N. Lewis has successively introduced the concepts of fugacity (1901) and activity (1907). According to his own comments, two strategies were in this period followed in order to study chemical equilibria.

The first one, followed in particular by Gibbs, Duhem, Planck, and other authors, consisted in forecasting the evolution of systems by using the properties of their entropy and also those of their thermodynamic potentials (viz. Chap. 2).

The second strategy, followed by Van't Hoff, Ostwald, Nernst, Arrhenius, and others, consisted in using equilibrium constants, *calculated through the concentration values at the equilibrium* because the notion of intangibility of the values of the equilibrium constants was already sensed since some years.

Today, we know that handling the thermodynamic potentials is perfectly legitimate, but it is complicated in the realm of chemistry, by far more complicated than in mechanics. This is the reason why the second method is more used than the previous.

But using the second strategy, at that time, led to the following conclusion:

> Equilibrium constants calculated by using concentrations at equilibrium are not truly constant.

This conclusion was followed by a series of numerous discussions and works essentially devoted to the case of electrolytes. The question was the following one: Do the equilibrium constants vary because of an incomplete dissociation of the electrolyte or because of another phenomenon? The hypothesis of an incomplete dissociation of actually strength electrolytes has been ruled out, notably with the help of conductometric experiences and thanks to the Debye–Hückel relations. Today, we know that the changes in the equilibrium constant values, when they are obtained only from concentrations at equilibrium, are the result of interactions between the species and not to an incomplete dissociation. Because of their occurrence, it is said that the system no longer exhibits an *ideal* behavior.

It is in order to mathematically take into account this phenomenon that Lewis has empirically introduced the notion of chemical activity. Likewise, he had introduced the fugacity concept some years before. It was, of course, in order to take into account the interactions between molecules of gas.

It is important to notice that taking into account the interactions between the particles by the introduction of both notions of fugacity and activity stems from a purely phenomenological reasoning. A rigorous theoretical study which would take perfectly into account these phenomena of "nonideality" would require that the term of the potential energy of the Schrödinger's equation of the whole system would contain all the terms describing the interactions between all the particles. This is quite impossible to do, because on the one hand one cannot know how we can perfectly modelize the interactions between these moving particles and because, on the other hand, if we did know how to do, it would be an insuperable work to carry out it, owing to the great number of particles.

Hence, it appears that the introduction of the notion of chemical activity is a genial trick permitting to overcome this colossal problem.

Chapter 7
The Fugacity Quantity

Abstract This chapter is devoted to the notion of fugacity. It is developed entirely under the standpoint of classical thermodynamics. The fugacity quantity has been introduced in order to describe the behavior of imperfect gases. It permits to express the molar Gibbs energy of a pure imperfect gas and, also, to express the chemical potential (the molar partial Gibbs energy) of a gas in a mixture of imperfect gases with a formalism analogous to that used in the case of perfect gases. For this reason, it can be said that the chemical potential which is an abstract notion can be, through the use of the fugacity, expressed in terms of a new function which is more easily identified with the physical reality than the chemical potential is. The chapter mentions the definition of the fugacity of a pure gas, the chemical potential of a perfect or real pure gas in terms of it, the fugacity of liquids and solids, the notion of fugacity coefficient of a real gas, a coming back to the notion of reference state, and the changes in fugacity with the temperature and the pressure. It also mentions the expressions of the chemical potential of a component of a mixture of perfect gases, the fugacities of real gases in mixtures, and their changes with pressure and temperature together with their determination. From another viewpoint, the values of the fugacity of a species present in different phases may assert or not the state of partition equilibrium.

Fugacity and activity are two intimately linked quantities. This is the reason why an introductory study of the notion of fugacity is necessary to understand well that of activity.

Keywords Fugacity • Fugacity coefficient Lewis–Randall's rule • Molal Gibbs energy • Molar enthalpy • Molar volume • Partial molal quantities • Perfect gases • Reference state

The fugacity quantity has been introduced by G.N. Lewis as soon as 1901 in order to describe the behavior of imperfect gases. More precisely, fugacity permits (as we shall see it) to express the molar Gibbs energy of an imperfect pure gas and, also, to express the chemical potential (the molar partial Gibbs energy) of a gas in a mixture of imperfect gases with a formalism analogous to that used in the case of perfect gases. For this reason, it can be said that the chemical potential which is an abstract notion can be, through the use of the fugacity notion, expressed in terms of a new function which is more easily identified with the physical reality than the chemical

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potential is. We shall see that the chemical activity is also a quantity like the fugacity function permitting to relate the chemical potential to the physical reality.

From another viewpoint, the values of the fugacity of a species present in different phases may assert or not the state of partition equilibrium.

Fugacity and activity are two intimately linked quantities. This is the reason why an introductory study of the notion of fugacity is necessary to understand well that of activity.

7.1 Definition of the Fugacity of a Pure Gas

Although the fugacity notion has been overall used in the case of systems constituted by gas mixtures, it is firstly important to begin with by the definition of the fugacity f of a pure gas. Lewis did that by setting up the expressions

$$dG = RT\,d\ln f \tag{7.1}$$

or

$$G_{\mathrm{m}} = RT\ln f + C(T) \tag{7.2}$$

$C(T)$ is the integration constant. It is already important to notice that constant $C(T)$ depends only on the nature of the substance and temperature (vis Chap. 34). G_{m} is the molar Gibbs energy of the gas.

Expression (7.2) is, according to some authors, incorrect from the mathematical standpoint since the logarithm of a quantity which is dimensioned does not possess any sense, since the fugacity is a quantity endowed with a dimension![1]

On the other hand, relation (7.1) is correct since the ratio df/f is dimensionless.

It is interesting to notice the analogy between relations (7.1) and (7.3) under

$$dG = RT\,d\ln \mathbf{p} \tag{7.3}$$

which links the molar Gibbs energy of a perfect gas and its pressure **p**. It results from the application to the case of perfect gases of the general expression

$$dG_{\mathrm{m},T} = V_{\mathrm{m}}d\mathbf{p} \tag{7.4}$$

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[1] By virtue of the famous aphorism

$$\ln(3\text{apples}) = \ln 3 + \ln\text{apples} \quad !$$

3 and apples are mathematical objects from different nature.

applicable to every reversible, isothermal transformation, only involving an expansion work. V_m is the molar volume of the substance (vis Chap. 5).

Definitions (7.1) and (7.2) are not sufficient for the determination of absolute values of the fugacity since they do not specify how the value of the constant $C(T)$ is fixed at a given temperature. Without any supplementary specification, they only define the ratio between the fugacities f_f and f_i of the gas in the final and initial states defining an isothermal transformation. Given the molar Gibbs energies G_{mf} and G_{mi} in both states, the expression of the change in the Gibbs energy ΔG accompanying it is

$$\Delta G = G_{mf} - G_{mi}$$

$$\Delta G = RT \ln (f_f / f_i)$$

A supplementary specification is necessary. That put forward by Lewis is universally adopted. It is based on the following reasoning.

Let us again consider the previous transformation and suppose that the gas is perfect. The notion of fugacity is, by definition, a general one. Hence, it also applies to perfect gases. In these conditions, one can write

$$\Delta G = RT \ln (f_f / f_i) \tag{7.5}$$

and since the gas is perfect by hypothesis, one can also write

$$\Delta G = RT \ln (\mathbf{p}_f / \mathbf{p}_i) \tag{7.6}$$

$\mathbf{p}_f$ and $\mathbf{p}_i$ being the pressures in the final and initial states of the process under study. Since the Gibbs energy is a state function, it results from the comparison of expressions (7.5) and (7.6), in which in the case of a perfect gas the fugacity must be in linear relation with the pressure.

Since no gas is, from the standpoint of the absolute scientific accuracy, perfect but since, also, the behavior of every gas tends to be ideal when its pressure tends toward 0, a judicious choice (in order to fix the integration constant) is such that the value of the fugacity of pure gas goes over that of its pressure when the latter tends toward 0, that is to say

$$f/\mathbf{p} \to 1 \quad \text{when} \quad \mathbf{p} \to 0$$

This is the choice that Lewis has done. Figure 7.1 exemplifies this specification.

The state in which the fugacity is asserted to be equal to the pressure is called the *reference state*. Thus, the fugacity of a gas equates its pressure in the reference state. The fact that the fugacity of every gas is set up to be equal to the value of its pressure in the reference state permits to evaluate its fugacity at every other pressure. Hence, the proportionality constant between the fugacity and the pressure of a gas in the reference state, evoked above, has been fixed to 1 by Lewis.

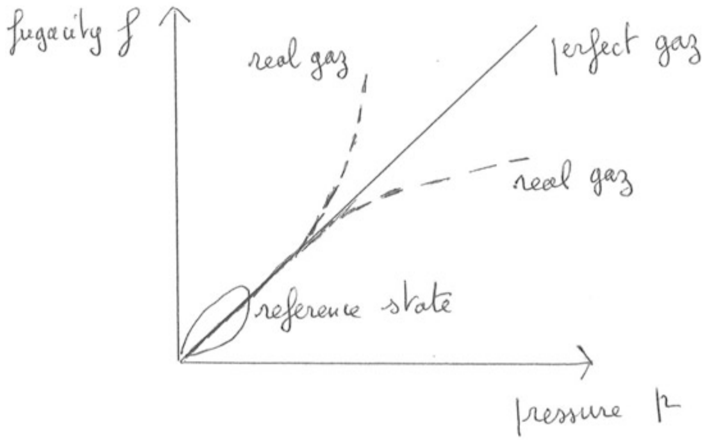

Fig. 7.1 Differences between the fugacity and the pressure of a pure gas

An outcome of the previous choice is that the fugacity of a perfect gas equates its pressure whichever the latter is, on the contrary of a real gas. We have seen, indeed, that in the case of a perfect gas, the fugacity is proportional to the pressure. By adopting the convention that the fugacity is equal to the pressure when the latter is very weak (in the reference state), it is clear that it remains as such in the whole range of pressures in the case of a perfect gas. In order to convince ourself, it is sufficient to consider the transformation described by relations (7.5) and (7.6) in which the initial pressure is very weak. As a result

$$\mathbf{p}_\mathrm{i} = f_\mathrm{i}$$

since

$$RT\ln(f_\mathrm{f}/f_\mathrm{i}) = RT\ln(\mathbf{p}_\mathrm{f}/\mathbf{p}_\mathrm{i})$$

Hence

$$\mathbf{p}_\mathrm{f} = f_\mathrm{f}$$

As a result of what is previously described, it appears that the fugacity must be endowed with the same unities as the pressure. (Most values of fugacities are still expressed in atmospheres in the literature for historical reasons.)

7.2 Chemical Potential of a Perfect or Real Pure Gas in Terms of Fugacities

1. In the case of a perfect gas, we know (vis Chaps. 3 and 5) that its molar Gibbs energy (or, equivalently in this case, its chemical potential) is partially defined by the expression

$$dG = RT\,d\mathbf{p}/\mathbf{p}$$

After integration, we obtain

$$G_{\mathrm{m}} = \mathrm{Cte} + RT\ln\mathbf{p}\ \text{ or}$$
$$\mu = \mathrm{Cte} + RT\ln\mathbf{p}$$

where Cte is the integration constant. (These expressions are incorrect from the mathematical standpoint for the reason given above.)

We know that the correct expression is (vis Chaps. 3 and 5)

$$\mu = \mu^\circ + RT\ln(\mathbf{p}/\mathbf{p}^\circ)$$

in which μ° is the chemical potential in an arbitrarily chosen state of the gas where it is at the pressure P°. We shall see (vis Chaps. 9 and 10) that this state is called the *standard state*. It may be temporarily defined as the state of the gas in which it exhibits a perfect behavior at pressure $\mathbf{p}^\circ$. Usually, $\mathbf{p}^\circ = 1$ pressure unit (historically 1 atm).

2. For a real gas, analogous considerations can be carried out:

We have seen just before that

$$dG = RT\,d\ln f$$

or for its molar Gibbs energy

$$\mu = \mu^\circ + RT\ \ln(f/f^\circ) \tag{7.7}$$

μ° is the integration constant. It is the chemical potential of the gas when its fugacity f is equal to its fugacity f°. f° is its fugacity in the standard state. Hence, μ° is the chemical potential of the gas in its standard state. It is arbitrarily chosen. Let us, at this point, anticipate one definition of the chemical activity a (vis Chap. 9) by already giving the following relation:

$$a = f/f^\circ$$

It expresses the chemical activity of a gas when its fugacity is f in the considered state of chemical potential μ and f° its fugacity in the arbitrary standard state of chemical potential μ°.

7.3 Fugacity of Liquids and Solids

The definition of the fugacity applies to liquid and solid states as to the gaseous state as well. Every substance in principle, indeed, exhibits a finite pressure vapor, even if in some cases it is exceedingly weak.

When the pure solid (or the liquid) is at the equilibrium with its vapor (at a given temperature), the molar Gibbs energy (chemical potential of the species) is the same for both phases. As a result, we can set up by virtue of (7.7)

$$\mu^\circ{}_\mathrm{s} + RT\ln(f_\mathrm{s}/f_\mathrm{s}{}^\circ) = \mu^\circ{}_\mathrm{g} + RT\ln\left(f_\mathrm{g}/f_\mathrm{g}{}^\circ\right) \quad \text{(case of a solid)}$$

or

$$\mu^\circ{}_\mathrm{l} + RT\ln(f_\mathrm{l}/f_\mathrm{l}{}^\circ) = \mu^\circ{}_\mathrm{g} + RT\ln\left(f_\mathrm{g}/f_\mathrm{g}{}^\circ\right) \quad \text{(case of a liquid)}$$

$\mu^\circ{}_\mathrm{s}$, $\mu^\circ{}_\mathrm{l}$, and $\mu^\circ{}_\mathrm{g}$ are the standard chemical potentials of the chemical species in solid, liquid, and vapor phases. f_s, f_l, and f_g are their fugacity in the same conditions. Let us recall that the choice of a standard state is arbitrary. Nothing precludes to choose the same standard state in order to quantify the fugacity of the species in solid or in liquid phase as that being the standard state in phase vapor. Then, of course, the fugacities in the standard states for the solid and liquid phases are no longer $f_\mathrm{s}{}^\circ$ or $f_\mathrm{l}{}^\circ$ but $f_\mathrm{g}{}^\circ$. Under these conditions, the equilibrium is expressed by the two following relations:

$$\mu^\circ{}_\mathrm{g} + RT\ln\left(f_\mathrm{s}/f_\mathrm{g}{}^\circ\right) = \mu^\circ{}_\mathrm{g} + RT\ln\left(f_\mathrm{g}/f_\mathrm{g}{}^\circ\right)$$
$$\mu^\circ{}_\mathrm{g} + RT\ln\left(f_\mathrm{l}/f_\mathrm{g}{}^\circ\right) = \mu^\circ{}_\mathrm{g} + RT\ln\left(f_\mathrm{g}/f_\mathrm{g}{}^\circ\right)$$

As a result, at equilibrium

$$f_\mathrm{s} = f_\mathrm{g}$$
$$f_\mathrm{l} = f_\mathrm{g}$$

The fugacity of the pure compound in the solid (or liquid) state is equal to its fugacity in the vapor state provided that the standard state adopted to quantify the fugacities is the same for both phases, i.e., that chosen for the vapor phase.

7.4 Fugacity Coefficient of a Real Gas

Figure 7.1 shows that the fugacity may be greater or weaker than the pressure of the gas.

One defines the fugacity coefficient ϕ_B of the gas B by the relation

$$\phi_B = f_B/p_B$$

It is sometimes called the activity coefficient of the gas. In the literature, there exist several values of ϕ permitting to calculate the fugacities of gases in given experimental conditions, notably of pressure. They are sometimes found with the help of approximations.

The fugacity coefficient is a pure number. It is dimensionless.

7.5 Coming Back to the Reference State

In order to prepare the future discussion concerning the reference and standard states (viz. the following chapters), it is important to recall the fact that the *reference state is a real state*.

Moreover, we have already mentioned that the reference state is a (real) state in which its fugacity equals its pressure. Hence, we can deduce that the reference state may be defined as a real state in which its fugacity coefficient is equal to its unity. This is the usually adopted definition for the reference state, in any case for gases. Later, we shall see that the notion of reference state is also linked to the notion of activity (viz. Chaps. 9, 10, and 11).

Henceforth, we shall annotate every quantity considered at a very weak pressure (that is to say in the reference state[2]) by the symbol * located in exponent.

7.6 Changes in Fugacity with the Temperature and the Pressure

- The fugacity changes with temperature. These changes are accessible. We give here only the principle of their determination at constant pressure. Let us consider two states of the gas, the molar Gibbs energy and the fugacities G_m, f and $G_m{}^*, f^*$. The state to which the quantities $G_m{}^*, f^*$ are related to is a state of very weak pressure in which the behavior of the gas is ideal (it is the state of reference). The change in the molar Gibbs energy accompanying the path from one state to the other is

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[2] In thermodynamics, for the definition of the reference state, one sometimes finds that it is the state attained from the standard state through a change in pressure. We shall not use this definition.

$$\Delta G_{\mathrm{m}} = G_{\mathrm{m}} - G_{\mathrm{m}}{}^{*}$$

$$\Delta G_{\mathrm{m}} = RT \ln f/f^{*}$$

or equivalently

$$R \ln\left(f/f^{*}\right) = G_{\mathrm{m}}/T - G_{\mathrm{m}}{}^{*}/T$$

whence after derivation with respect to the temperature at constant pressure

$$R\,(\partial \ln f/\partial T)_P - R\left(\partial \ln f^{*}/\partial T\right)_P = \partial[(G_{\mathrm{m}}/T)/\partial T]_P - \partial\left[\left(G_{\mathrm{m}}{}^{*}/T\right)/\partial T\right]_P$$

We know that (viz. Chap. 2—Gibbs–Helmholtz relation)

$$\partial((G_{\mathrm{m}}/T)/\partial T)_P = -H_{\mathrm{m}}/T^2$$

where, in this equation, H_{m} is the molar enthalpy of the system at the pressure P and G_{m} its molar Gibbs energy. In the relation before the latter, the second term of the left member is null since, in the reference state, the fugacity f^{*} is equal to the pressure P^{*} and since the derivation is carried out at constant pressure. Both latter relations immediately lead, after derivation, to

$$(\partial \ln f/\partial T)_P = \left(H_{\mathrm{m}}{}^{*} - H_{\mathrm{m}}\right)/RT^2 \tag{7.8}$$

where $H_{\mathrm{m}}{}^{*}$ is the molar enthalpy of the gas at null pressure. The difference $(H_{\mathrm{m}}{}^{*} - H_{\mathrm{m}})$ is the change in the enthalpy accompanying the "compression" of the gas from the pressure P until the null one at constant temperature. For the easiness of the calculations, it is a fact that the curves $(H_{\mathrm{m}}{}^{*} - H_{\mathrm{m}})/RT^2$ as functions of the temperature are experimentally accessible either by the study of the diagrams **p**–V–T of the gases or by using the appropriate state equations. After this step, the obtention of f is carried out by integration.

- The influence of the pressure on the value of the fugacity of a gas at constant temperature is expressed by the relation

$$(\partial \ln f/\partial \mathbf{p})_T = V_{\mathrm{m}}/RT$$

since, by definition of the fugacity, $dG = RTd \ln f$ and since, in a general manner (viz. Chap. 2),

$$(\partial G/\partial \mathbf{p})T = V_{\mathrm{m}}$$

Let us recall that V_{m} is the molar volume of the substance whatever the phase under which it is and whatever its behavior is, perfect or not.

7.7 Physical Significance of the Fugacity

According to what is previously mentioned, it is evident that the fugacity of a gas is a kind of a fictitious pressure or of a corrected pressure. Statistical thermodynamics (Chap. 34) permits to grasp a deeper knowledge of the relation existing between the fugacity and the pressure.

7.8 Expressions of the Chemical Potential of a Component of a Mixture of Perfect Gases

Before considering the fugacity notion applied to the case of a mixture of real gases, case where it exhibits all its importance, it is convenient, at the beginning, to mention different relations expressing the chemical potential of a component of a mixture of ideal gases.

Generally speaking, we know that the change in the chemical potential μ_{B} of every component B of a gaseous mixture with pressure, at constant temperature T and molar fraction y, is given by the relation (vis Chap. 5)

$$(\partial \mu_B / \partial \mathbf{p})_{T,y} = \overline{V_{\mathrm{mB}}} \tag{7.9}$$

where $\overline{V_{\mathrm{mB}}}$ is the partial molar volume of the component B.

In the case of a mixture of perfect gases, the law of perfect gases applies to the whole mixture. It is written as

$$V = (n_I + n_2 + \cdots + n_{\mathrm{B}} + \cdots) RT/P \tag{7.10}$$

where $n_1, n_2, \ldots$ are the numbers of moles of species 1,2,... in the gaseous mixture, P the total pressure, and V the total volume of the system. Since, by hypothesis, each gas of the mixture exhibits a behavior different from that of any other (of the mixture), the partial pressure of each one p_{B} is given, by definition, by the relation

$$p_{\mathrm{B}} V = n_{\mathrm{B}} RT \tag{7.11}$$

The partial molar volume of the component B being given by the expression

$$\overline{V_{\mathrm{mB}}} = (\partial V / \partial n_{\mathrm{B}})_{T,P,nj}$$

we obtain through derivation of (7.10)

$$\overline{V_{\mathrm{mB}}} = RT/P$$

and hence, after using (7.9),

$$d\mu_B = RT\,(dP/P)_{T,nj} \quad \text{or} \quad d\mu_B = RT\,(d\ln P)_{T,nj}$$

Then, according to (7.10) and (7.11),

$$p_B = n_B(RT/V) \quad \text{and} \quad P = \sum n_B(RT/V)$$

Since n_B and n (n total number of moles in the mixture: $n = \sum n_B$) are constant, the following equality is satisfied:

$$d\ln p_B = d\ln P$$

That is,

$$d\mu_B = RT\,d\ln p_B$$

After integration, we obtain

$$\mu_B = \mu_B{}^* + RT\ln p_B \tag{7.12}$$

$\mu_B{}^*$ is the integration constant. Its value depends only on the nature of the gas and on the temperature as it is justified by statistical thermodynamics (viz. Chap. 34). It is clear that $\mu_B{}^*$ is the chemical potential of the gas B, at the given temperature, when its partial pressure is equal to unity. Let us also recall that in order to obtain this result, the underlying hypothesis was that the mixture should behave ideally.

Hence, the chemical potential of every constituent of an ideal mixture of gases is determined by its partial pressure.

There exist other expressions of the chemical potential μ_B equivalent to the previous one.

Let us notice that relation (7.12) may be considered as being not satisfactory since the logarithm of a dimensioned quantity is under consideration. However, it can be written according to the following one which is perfectly correct:

$$\mu_B = \mu_B RT \; + \; \ln(p_B/1)$$

where 1 is a quantity which is endowed with the same dimension as that adopted for p_B. Therefore, 1 is the unity of pressure.

Let us also notice the chemical potential μ_B of a constituent of an ideal mixture of gases, as every other compound in every system may be expressed under different manners according to the used concentration scales and also according to the retained standard states. (We shall again consider this subject, but then at greater length, when we shall discuss the expressions of the chemical potentials with respect to the adopted standard states in order to define the different kinds of activities in solutions—viz. Chap. 11.)

Let us confine ourselves to mention that by introducing the molar fraction $y_B = (n_B/n)$ of B in the gaseous mixture, the expression of its chemical potential is

$$\mu_{\mathrm{B}} = \mu_{y\mathrm{B}}{}^{*} + RT\ln y_{\mathrm{B}} \tag{7.13}$$

where

$$\mu_{y\mathrm{B}}{}^{*} = \mu_{\mathrm{B}}{}^{*} + RT\ln P$$

We notice that, this time, the integration constant $\mu_{yB}{}^{*}$ depends not only on the nature of B and on the temperature, but also on the total pressure P. The reasoning leading to this expression is based on the fact that the chemical potential of a component in a given thermodynamic state is an invariant quantity, whatever the expression of its quantity of matter is.

7.9 Fugacities and Mixtures of Real Gases

7.9.1 Expressions of the Chemical Potential of the Components

The above considerations taking into account the partial pressures are no longer correct once we are facing mixtures of real gases. Again, in this case, introducing the fugacity notion simplifies the problem. In an analogous manner as that followed in the case of a pure real gas, one partially defines the fugacity of the constituent B in the mixture, at a given constant temperature, by the relation

$$d\mu_{\mathrm{B}} = RT\,d\ln f_{\mathrm{B}} \tag{7.14}$$

that is to say, after integration, by

$$\mu_{\mathrm{B}} = \mu_{\mathrm{B}}{}^{*} + RT\ln f_{\mathrm{B}} \tag{7.15}$$

$\mu_{\mathrm{B}}{}^{*}$ depends on the nature of the gas and on the temperature of the system.

The chemical potential of the gas B is also given by the expression

$$\mu_{\mathrm{B}} = \mu_{\mathrm{B}}{}^{\circ} + RT\ln f_{\mathrm{B}}/f_{\mathrm{B}}{}^{\circ} \tag{7.16}$$

where $\mu_{\mathrm{B}}{}^{\circ}$ is the standard potential of B and $f_{\mathrm{B}}, f_{\mathrm{B}}{}^{\circ}$ the fugacities of B in the state of the system and in the chosen standard state. The reference state to which is linked the standard state $\mu_{\mathrm{B}}{}^{\circ}$ (which has been just evoked) is the same as that which is retained for a gas alone or in the case of an ideal mixture since, as it has been demonstrated above, the behavior of each gas tends to be perfect when the total pressure tends to be null. Hence, $\mu_{\mathrm{B}}{}^{\circ}$ is the standard chemical potential of B, alone, at the same temperature as that of the system. In these conditions, we shall see (viz. Chap. 10) that the chemical potentials in the standard and reference states are equal.

One of the advantages that presents the introduction of the fugacity lies in the fact that the chemical potential of a component of a mixture of real gases may be expressed by the relation (7.15) which is formally analogous to that expressing the chemical potential of a component of a mixture of perfect gases. Such expressions enlighten the significance of the chemical potential since the significance of a corrected pressure is by far closer to a physical reality than is a chemical potential which is essentially an abstract mathematical notion.

7.9.2 Change of the Fugacity of One Component of a Gaseous Mixture with the Pressure

The change of the fugacity of the constituent of a gaseous mixture with the pressure is obtained from the following relation:

$$(\partial \ln f_{\mathrm{B}}/\partial P)_{T,y} = \overline{V_{\mathrm{B}}}/RT \tag{7.17}$$

where $\overline{V_{\mathrm{B}}}$ is the partial molal volume of the constituent (viz. Chap. 4). This relation immediately follows from (7.9) and (7.15) after derivation with respect to P at constant temperature and pressure and by taking into account the fact that in these conditions $\mu_{\mathrm{B}}{}^{*}$ is a constant. Before proceeding to the integration, let us subtract the term $RT\,d\ln \mathbf{p}_{\mathrm{B}}$ from both members of the expression (7.17). We obtain

$$RT\,d\ln(f_{\mathrm{B}}/\mathbf{p}_{\mathrm{B}}) = \overline{V_{\mathrm{B}}}\,dP - RT\,d\ln \mathbf{p}_{\mathrm{B}}$$

But

$$\mathbf{p}_{\mathrm{B}} = y_{\mathrm{B}}P$$

The molar fraction y_{B} being a constant, since we are searching for the fugacity change with the pressure at constant temperature and composition, the preceding relation becomes

$$RT\,d\ln(f_{\mathrm{B}}/\mathbf{p}_{\mathrm{B}}) = \left(\overline{V_{\mathrm{B}}} - RT/P\right)dP$$

The change of the fugacity f_{B} with the total pressure is obtained by integration from $P = 0$ to $P = P'$, that is to say

$$\ln(f_{\mathrm{B}}/\mathbf{p}_{\mathrm{B}}) = \int_0^{P'} \left(\overline{V_{\mathrm{B}}}/RT - 1/P\right)\,dP$$

Let us recall that in the reference state, $f_{\mathrm{B}}{}^{*} = \mathbf{p}_{\mathrm{B}}{}^{*}$. Of course, the integration entails that we know the partial molal volume as a function of the pressure. As a special case, we shall see (viz. the following chapter) that for a mixture of ideal gases, the molal partial volume of a constituent is equal to its molar volume when it is pure.

7.9.3 Change in the Fugacity of a Component of a Mixture of Real Gases with the Temperature

The change in the fugacity of the component with the temperature is given by the relation

$$(\partial \ln f_{\mathrm{B}}/\partial T)_P = \left(H_{\mathrm{B}}{}^{*} - \overline{H_{\mathrm{B}}}\right)/RT^2 \tag{7.18}$$

where $\overline{H_{\mathrm{B}}}$ is the partial molal enthalpy of the component in the mixture at the given pressure and temperature and $H_{\mathrm{B}}{}^{*}$is the molar enthalpy of the gas at the same temperature in the reference state. The relation is obtained as follows. According to (7.15)

$$R\ln f_{\mathrm{B}} = \mu_{\mathrm{B}}/T - \mu_{\mathrm{B}}{}^{*}/T$$

and according to the general properties of the chemical potential (viz. Chap. 5)

$$[\partial(\mu_{\mathrm{B}}T)/\partial T]_P = -\overline{H_{\mathrm{B}}}/T^2$$

$$R(\partial \ln f_{\mathrm{B}}/\partial T)_P = -\overline{H_{\mathrm{B}}}/T^2 + \overline{H_{\mathrm{B}}{}^{*}}/T^2$$

$\overline{H_{\mathrm{B}}}$ is the partial molar enthalpy of the gas at the pressure P. $\overline{H_{\mathrm{B}}{}^{*}}$ is that in the state of reference, that is to say at a null total pressure. In these conditions the behavior of the gas is the same as that of a gas which should be alone, at a very weak pressure. Then its molar partial enthalpy in the reference state equates its molar enthalpy when it is in pure state, at a very weak pressure $H_{\mathrm{B}}{}^{*}$:

$$\overline{H_{\mathrm{B}}{}^{*}} = H_{\mathrm{B}}{}^{*}$$

7.10 Determination of the Fugacity of a Gas in a Gaseous Mixture

The determination of the fugacity of a gas in a gaseous mixture is possible. It is carried out after obtention of the diagrams: total pressure/volume of the mixture and subsequent determinations of partial molar volumes. The knowledge of the couples of experimental data *P*–*V* for the mixture permits to determine the molar partial volumes of the components of the mixture. Then, one carries out the integration by graphical means. It can also be carried out by approached calculations.

7.11 Fugacity and Heterogeneous Equilibria

Under some conditions, the values of the fugacities may be a criterion of equilibrium between different phases. We give two examples of this possibility here.

From a general standpoint, this criterion applies when one considers a closed system constituted by two phases (or more). The whole system is closed but the constituting phases are open systems. In principle, the general equilibrium concerns three processes: the heat transfer, the changes in the limits of the phases (due to a mechanical work), and the transfer of matter from one phase into the other. We are only concerned here by the transfer of matter.

As a first example, let us consider the transfer of the species i from the phase α (its solution) into the phase β (its vapor) at constant temperature and pressure. A first criterion of equilibrium is the equality of the chemical potential of i in both phases (viz. Chap. 5):

$$\mu_i{}^{\alpha} = \mu_i{}^{\beta} \quad \text{(equilibrium)}$$

By replacing the chemical potentials by their expressions (7.16), we obtain

$$\mu_{\mathrm{B}}{}^{\circ\alpha} + RT\ln f_{\mathrm{B}}{}^{\alpha}/f_{\mathrm{B}}{}^{\circ\alpha} = \mu_{\mathrm{B}}{}^{\circ\beta} + RT\ln f_{\mathrm{B}}{}^{\beta}/f_{\mathrm{B}}{}^{\circ\beta} \tag{7.19}$$

The reasoning is the same as that followed in paragraph 3. Nothing precludes to adopt the standard state of the vapor as the unique one for both phases. As a result, we obtain

$$\mu_{\mathrm{B}}{}^{\circ\beta} + RT\ln f_{\mathrm{B}}{}^{\alpha}/f_{\mathrm{B}}{}^{\circ\beta} = \mu_{\mathrm{B}}{}^{\circ\beta} + RT\ln f_{\mathrm{B}}{}^{\beta}/f_{\mathrm{B}}{}^{\circ\beta}$$

that is to say

$$f_{\mathrm{B}}{}^{\alpha} = f_{\mathrm{B}}{}^{\beta}$$

The equality

$$f_{\mathrm{B}} \ \text{(solution)} = f_{\mathrm{B}} \ \text{(vapour)}$$

is the condition of this equilibrium (at constant temperature) provided that the reference states of the species are the same in both phases.

Let us consider, now, the equilibrium, at constant temperature, of a species B present in two immiscible solvents, as a second example. At the equilibrium, the expression (7.19) is still verified. Let us suppose, now, that the standard potentials in both phases $\mu_{\mathrm{B}}{}^{\circ\alpha}$ and $\mu_{\mathrm{B}}{}^{\circ\beta}$ are equal. The condition of equilibrium is still

$$f_{\mathrm{B}}{}^{\alpha} = f_{\mathrm{B}}{}^{\beta}$$

The common standard potential may be that of the vapor phase which would simultaneously be in equilibrium with both solutions.

The criterion of equality of fugacities (in some conditions) is easier to handle than that of the chemical potentials.

7.12 Other Use of the Fugacities

Outside what has been mentioned just previously about the theoretical interests exhibited by the notion of fugacity, it also exhibits a strong practical one. We confine ourselves to mention the fact that taking into account the fugacities in order to study the equilibria between imperfect gases is essential.

A striking example is provided by us with the values of the equilibrium constant of the reaction of synthesis of ammoniac by starting from dihydrogen and dinitrogen. The equilibrium constant, determined at 450 °C from measurements of partial pressures, does not cease to enhance with the total pressure. Its values are, respectively, 6.59×10^{-3} atm under 10 atm and 23.28×10^{-3} under 1000 atm. At 600 atm, it is 12.94×10^{-3}. Taking into account the fugacities instead of partial pressures, the equilibrium constant remains more and less constant ($6.51–7.42 \times 10^{-3}$ atm). At 1000 atm, it has the value 10.32×10^{-3} atm. But, it must be noticed that this latter is somewhat abnormal. This is probably not due to the failure of the concept of fugacity but may be rather attributed to the simplifying rule of Lewis and Randall used to calculate the fugacities. Hence, the last result does not question the interest of the introduction of the fugacity in this field.

(The Lewis–Randall's rule consists in setting up that the fugacity f_i of the species in the mixture is equal to the product of its molar fraction y_i in the vapor phase by its fugacity in the pure state at the temperature and total pressure of the system f_i. It is not reliable because it is based on a simplification which may or may not by far be justified.)

7.13 Fugacity and the Gibbs–Duhem Relation

The Gibbs–Duhem equation can also be expressed in terms of fugacities. It can be written (viz. Chap. 5) as

$$(\partial\mu_1/\partial \ln x_1)_{T,P} = (\partial\mu_2/\partial \ln x_2)_{T,P} \tag{7.20}$$

Let us recall the fact that as such it is written above, it applies to a binary solution at constant temperature and pressure. In order to express it in fugacity terms, it is sufficient to use the relation (7.14) above. The relation being searched for is

$$(\partial f_1/\partial \ln x_1)_{T,P} = (\partial f_2/\partial \ln x_2)_{T,P} \tag{7.21}$$

Chapter 8
Ideal Solutions

Abstract In this chapter, some properties of solutions are recalled, especially those of ideal solutions are mentioned. The notions of "ideality" and of "nonideality" of solutions are central for the purpose. The considerations developed here, solely from the viewpoint of classical thermodynamics, are important in order to provide the reader with a good understanding of the chemical activity of every component of a solution. Actually, here, the case of the solutions of nonelectrolytes is only considered. That of the solutions of electrolytes is studied later. Also, the case of the nonideal solutions is only tackled by opposition to that of the ideal solutions.

Definitions of perfect, ideal, and dilute solutions are given in relation to Raoult's and Henry's laws by applying Gibbs–Duhem relation. Finally, the study of the osmotic pressure as an example of a colligative property is carried out. The study of colligative properties entails the knowledge of the properties of ideal solutions. The properties of osmotic pressure are encountered several times in the book.

Keywords Ideal solutions • Perfect and sufficiently dilute solutions • Raoult's law • Gibbs–Duhem relation • Henry's law • Colligative properties • Osmotic pressure • Non-ideal solutions • Margules relations • Van Laar relations

In this chapter, we recall some properties of solutions. More specifically, we are particularly interested in the ideal solutions. As we shall see it, the notions of "ideality" and of "nonideality" of solutions are central for our purpose. The considerations developed here are important in order to provide us with a good understanding of the chemical activity of every component of a solution.

Ideal solutions have been the matter of a great attention, but their definition is somewhat imprecise. Some authors, indeed, distinguish two kinds of ideal solutions: the perfect solutions and the sufficiently diluted ones.

In this chapter, we only consider the case of the solutions of nonelectrolytes, and that of the solutions of electrolytes will be studied later. In this chapter, that of the nonideal solutions is only tackled by opposition to that of the ideal solutions.

Finally, we study the osmotic pressure as an example of a colligative property. The study of colligative properties entails the knowledge of the properties of ideal solutions. We focus ourselves on the study of osmotic pressure because it is encountered several times in this book.

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8.1 Definition of Ideal Solutions

A solution is ideal when the chemical potential μ_i of all its components is a linear function of the logarithm of its molar fraction x_i, according to

$$\mu_i = \mu_i{}^*(T, \mathbf{p}) + RT \ln x_i \tag{8.1}$$

$\mu_i{}^*$ is a constant, the value of which only depends on the temperature, pressure, and identity of the component and is independent of the composition. Its physical meaning is given below. However, at this point of the development, we can already notice that $\mu_i{}^*(T, \mathbf{p})$ is the chemical potential of the component i when it is pure $(x_i = 1)$.

The formalism of this definition looks like the following ones, already mentioned (viz. Chap. 7):

$$\mu = \mu^\circ(T) + RT \ln \mathbf{p} \quad \text{(pure perfect gas)} \tag{8.2}$$

$$\mu_i = \mu_i{}^\circ(T) + RT \ln p_i \quad \text{(component of a perfect gaseous mixture)} \tag{8.3}$$

which express the chemical potential of a pure perfect gas or that of a component of a perfect gaseous mixture. (Let us notice, once more, that in the denominators of the arguments of the logarithms of relations (8.2) and (8.3), the pressures of 1 unity or that of p° or $p_i{}^\circ$ are omitted.)

A still greater analogy between relation (8.1) and another expression of the chemical potential of gases—relation (8.4) just below and relation (8.13) of the preceding chapter—does exist:

$$\mu_i = \mu_{yi}{}^*(T, \mathbf{p}) + RT \ln y_i \tag{8.4}$$

It is interesting to notice that relation (8.1) is simply an integral solution of the following differential relation:

$$d\mu_i = RT\, d \ln x_i \tag{8.5}$$

Expression (8.5), actually, constitutes the same definition of an ideal solution as that expressed by (8.1). However (8.5) is interesting because it explains the distinction between ideal, perfect, and sufficiently diluted solutions which can be considered as differing, as we shall see it, by the values of their integration constants (viz. paragraph 4 below).

8.2 Ideal, Perfect, and Sufficiently Diluted Solutions

Some authors consider that the ideal solutions are constituted on the one hand by the perfect solutions and, on the other, by the sufficiently diluted ones:

- The perfect solutions: They are ideal ones in the whole domain of concentrations. In order that is the case, their different components must be chemically similar. They obey Raoult's law (viz. below). This kind of solution is rather scarce. As an example, let us mention some mixtures of saturated hydrocarbons.
- The sufficiently diluted solutions: They are solutions in which their solute (s) exhibit(s) an ideal behavior only in a limited domain of "concentrations." The solute obeys Henry's law (viz. below). As soon as the solution is not sufficiently diluted, its behavior is no longer ideal. The case of the sufficiently diluted solutions occurs systematically, provided that the solutions are sufficiently diluted.

In both kinds of solutions, the criterion of ideality is the subscription to the relation (8.1), at least in some domain of concentrations.

8.3 Raoult's Law

8.3.1 Raoult's Law (Strictly Speaking)

In its original version, Raoult's law stipulated that in a liquid solution so-called ideal, the partial vapor pressure p_i of each of its components i is proportional to its molar fraction x_i in the solution and to its vapor pressure $p_i{}^\circ$ when it is pure at the pressure of the system, i.e.,

$$p_i = x_i\, p^{\square} \tag{8.6}$$

This relation must be obeyed in the whole domain of "concentrations" of the solution. As we shall see it, the subscription to Raoult's law, actually, defines a perfect solution (viz. paragraph 3.2). According to this law, also, the expression (8.6) must be verified at every temperature and at constant total pressure. (However, when the pressure remains moderated, the vapor pressures are quasi-independent of the external pressure.)

It is more judicious, however, to use the generalized form of Raoult's form in which the vapor pressures are replaced by the corresponding fugacities in order to take into account the fact that the vapors may no longer obey the perfect gas law. Therefore, we obtain the following definition:

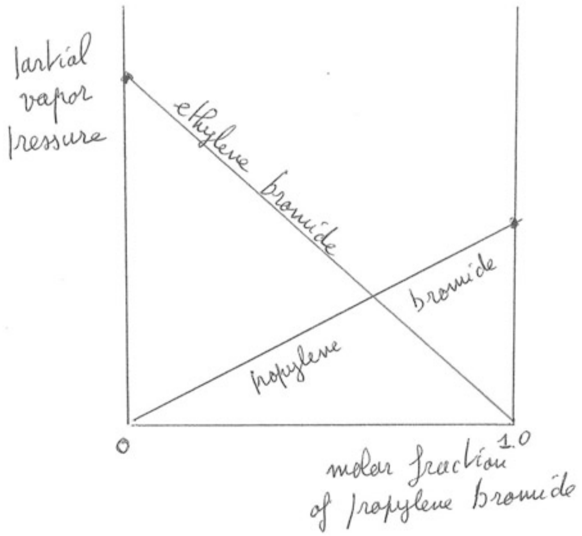

Fig. 8.1 Dependence of the partial vapor pressures (or fugacities) of the components of an ideal perfect solution on their molar fractions: case of the mixture of ethylene bromide and propylene bromide (*according to G.N. Lewis and M. Randall in "Thermodynamics and the free energy of chemical substances," Ed McGraw-Hill Book Company, Inc, New York and London, 1923*)

$$f_i = x_i f^{\square} \tag{8.7}$$

where f_i is the fugacity of every component i in the vapor state and in solution at equilibrium of both phases as well (since they are identical for the same reference state—see the preceding chapter) and $f^{\square}$ is its fugacity in the pure state at the same temperature and pressure.[1]

Hence, the idealized Raoult's law stipulates that in an ideal solution, actually perfect, the fugacity of every component is proportional to its molar fraction for all the concentrations.

The dependence of the partial vapor pressure and hence of the fugacities of both components of a binary ideal solution on their molar fractions is given in Fig. 8.1.

8.3.2 Equivalence of the Definition of Perfect Solutions and the Fact That the Solution Obeys Raoult's Law

Actually, the subscription of a solution to the Raoult's law is equivalent to the definition (relation (8.1)) of the perfect solutions.

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[1] The fugacity in the standard state f_i°—viz. Chap. 9—must not be confused with the fugacity $f_i^{\square}$ introduced in Raoult' law. The latter is the fugacity of the constituent in pure state at some temperature and at the pressure of the system, whereas the former is that of the component in pure state under a well-defined standard pressure, usually 1 atm. They become identical, of course, under the pressure unity. $f_i^{\square}$ depends on the total pressure. It is not the case of f_i°. This remark also applies to partial pressures.

Let us suppose that the gaseous phase above the perfect solution exhibits an ideal behavior. (This hypothesis has no incidence on the accuracy of the following result. It is only adopted for the sake of simplification. If it were not verified, it should be necessary to reason with fugacities.) The equilibrium condition for the component i of both phases (viz. Chap. 5) is

$$\mu_i \, \text{solution} = \mu_i \, \text{vapor}$$

Starting from the expressions (8.1) and (8.3), we obtain

$$\mu_i{}^*(T, \mathbf{p}) + RT \ln x_i = \mu_i{}^\circ(T) + RT \ln p_i \tag{8.8}$$

In the case of a perfect solution, the expression $\mu_i{}^*(T, \mathbf{p}) + RT \ln x_i$ applies to any value of x (obligatorily, of course, located between 0 and 1). When the compound is pure ($x_i = 1$), its partial pressure p_i is nothing different from its vapor pressure in the pure state $p_i{}^{\circ}$. According to (8.8), we obtain

$$\mu_i{}^*(T, \mathbf{p}) = \mu_i{}^\circ(T) + RT \ln p_i{}^\square \tag{8.9}$$

Subtracting of expressions (8.9) from (8.8) leads to Raoult's law (8.6).

From a more general viewpoint, equality (8.8) can be written as

$$\mu_i{}^*(T, \mathbf{p}) + RT \ln x_i = \mu_i{}^\circ(T) + RT \ln (p_i / p_i{}^\circ)$$

where $p_i{}^\circ$ is the partial pressure in the state of chemical potential $\mu_i{}^\circ$.

Hence, another definition of a perfect solution may be based on the agreement of the behavior of the solution with Raoult's law.

8.4 Behavior of the Second Component of a Binary Liquid Mixture When the First One Obeys Relation (8.7) in the Whole Range of Concentrations

We shall demonstrate that, in this case, the second component may also obey the same kind of relation. The demonstration is founded in the Gibbs–Duhem relation.

- Relation of Gibbs–Duhem

  We know (cf. Chap. 5) that for a system consisting in a solution composed of two components in equilibrium with their vapor at constant temperature and pressure, the Gibbs–Duhem relation provides us with information concerning the changes in the chemical potentials of the components with their "concentrations" in solution. This information is accessible through the following relation:

$$(\partial \mu_1 / \partial \ln x_1)_{T,P} - (\partial \mu_2 / \partial \ln x_2)_{T,P} = 0 \tag{8.10}$$

- Demonstration

The proposition is demonstrated as follows. According to the relation (7.14) of Chap. 7

$$d\mu_i = RT\,d\ln f_i$$

and according to (8.10), we obtain

$$(\partial \ln f_1/\partial \ln x_1)_{T,P} = (\partial \ln f_2/\partial \ln x_2)_{T,P} \tag{8.11}$$

When the vapor has the behavior of a perfect gas, we can replace the fugacity of a component by its vapor pressure; thus we obtain

$$(\partial \ln p_1/\partial \ln x_1)_{T,P} = (\partial \ln p_2/\partial \ln x_2)_{T,P}$$

where p_1 and p_2 are the vapor pressures of components 1 and 2 when there is equilibrium between the solution of composition x_1 and x_2 and the vapor.

Since the Raoult's law applies to compound 1 by hypothesis, we can write

$$f_1 = x_1 f_1^{\square}$$

Taking the logarithms and derivating with respect to x_1, at constant temperature and pressure, we obtain

$$d\ln f_1 = d\ln x_1$$

or

$$(\partial \ln f_1/\partial \ln x_1)_{T,P} = 1$$

since $f_1^{\square}$ is constant for a given pressure and temperature. According to (8.11), we immediately find

$$(\partial \ln f_2/\partial \ln x_2)_{T,P} = 1 \tag{8.12}$$

After integration, we obtain

$$f_2 = kx_2 \tag{8.13}$$

where k is the integration constant. From this result, we can distinguish two cases:

- When $x_2 = 1$ the component (8.2) is pure. The fugacity f_2 becomes equal to $f_2^{\square}$. As a result,

  $$f_2 = x_2 f_2^{\square}$$

  This means that the Raoult's law also applies to component 2. The solution is a perfect one.
- When the relation (8.13) is not verified up to $x_2 = 1$, the constant k is no longer equal to $f_2^{\square}$. Nevertheless, it is true that, according to (8.13), there remains a linear relation between the fugacity of component 2 and its molar fraction somewhere in the domain $0 < x_2 < 1$. The solution is no longer perfect, but it is still ideal. We can remark that relation (8.12) may be obtained directly from

the definition (8.5) of an ideal solution, owing to the existing general expression of the chemical potential as a function of the fugacity (viz. Chap. 7). This result is again considered during the study of Henry's law.

8.5 Diluted Solutions: Henry's Law

In the case of diluted solutions, the difference in the behaviors of the solute and of the solvent must be stressed. Usually, one names solvent and solute the components which are, respectively, in the larger and lesser quantities. Their molar fractions are x_1 and $x_{2.}$ in a binary solution.

8.5.1 Henry's Law

Experimentally, it is found that in a diluted solution:

- The behavior of the solvent tends toward that described by Raoult's law, even if it is less marked when the solution under study becomes more and more concentrated in solutes. More precisely, the more diluted the solution is, the more the solvent tends to have a perfect behavior, that is to say

$$f_1 \to x_1 f_1^{\circ} \quad \text{for } x_1 \to 1 \ (\text{diluted solution}) \tag{8.14}$$

- Simultaneously, the behavior of the solute is not that of a solute in a perfect case. It is experimentally found that in a diluted solution, at constant temperature, the vapor pressure (fugacity) of a solute is proportional to its molar fraction, as it is the case in a perfect solution, but the proportionality constant is not the same. These points are expressed by Henry's law.

The proportionality constant is called the Henry's constant $k_{\mathrm{H}.}$ The more diluted the solution is, the more the law verified is (Fig. 8.2). It is symbolized by

$$f_2 \to k_{\mathrm{H}} x_2 \ \text{when } x_2 \to 0 \tag{8.15}$$

in which the index 2 designates the solute, with the index 1 designating the solvent. The law expressed in terms of vapor pressure is

$$p_2 = k_{\mathrm{H}} x_2 \ \text{when } x_2 \to 0$$

In order to illustrate these points, we give some numerical values of Henry's constant for dinitrogen k_{H} (19.4 °C) = 8.32×10^4 atm, oxygen k_{H} (23 °C) = 4.59×10^4 atm, and dihydrogen k_{H} (23 °C) = 7.76×10^4 atm. These values have been obtained for a partial pressure of 2.6 atm for each gas.

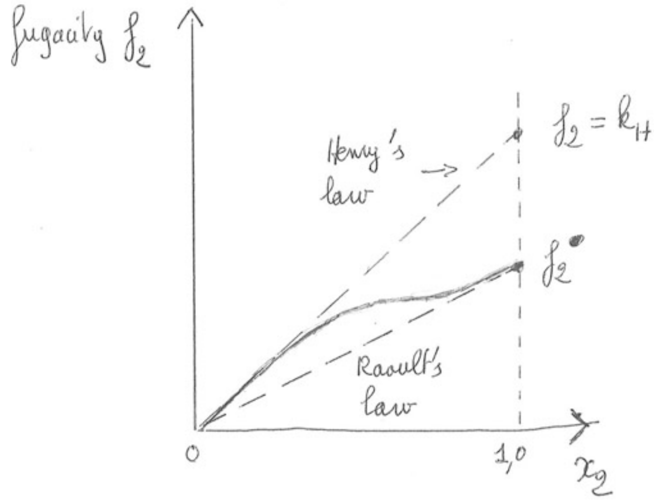

Fig. 8.2 Differences between Raoult and Henry laws

Henry's law applies to all diluted solutions.

From a vivid and purely qualitative standpoint, one can consider that Henry's law is verified when the solution is sufficiently diluted such as each molecule of solute only sees molecules of solvent all around it. In these conditions, the "escaping tendency" of the solute becomes proportional to its molar fraction.

8.5.2 *Henry's Law and Other Expressions of the Composition of the Solution*

Henry's law can be settled with other unities than the molar fraction x. For example, the expression of Henry's law in terms of molalities is found after the following reasoning. For the solute in a binary solution

$$x_2 = n_2/(n_1 + n_2)$$

where n_i is the number of moles of each species. Since the law only applies to very dilute solutions, n_2 is negligible in the denominator, whence

$$x_2 \approx n_2/n_1$$

Since also the molality m_2 of the solute is its number of moles for 1000 g of pure solvent (viz. Chap. 1), we find

$$m_2 = 1000 n_2/(n_1 M_1)$$

where M_1 is the molar mass of the solvent in g mol^{-1}. The relation (8.15) may be written as

$$f_2 = k'_{\rm H}\, n_2/n_1$$
$$f_2 = k''_{\rm H} m_2$$

$k'_{\rm H}$ and $k''_{\rm H}$ being composite constants grouping the previous ones.

(*Remark*: Other interpretation of Henry's law: it is often presented in literature as governing the equilibria involving the solubilities of gases in liquids.)

8.6 About the Differences Between Henry's and Raoult's Laws

Let us recall that in terms of fugacity Raoult's law is expressed by

$$f_2 = f_2^{\square} x_2 \tag{8.16}$$

whichever the component is (here it is the solute). The comparison of relations (8.15) and (8.16) shows that the values of the proportionality constants between the fugacity and the molar fraction differentiate both types of behaviors: $k_{\rm H} \neq f_2{}^{\square}$. The "slopes of the Raoult and Henry" are not the same. Figure 8.2 illustrates this point.

One may consider that a dilute solution is an ideal solution since there is linearity between the fugacities of the components and their molar fractions. But it is only ideal and not perfect because this linearity is verified in an only limited range of composition, that of great dilution, in any case for the solute. It is an ideal solution said sufficiently diluted.

Finally, other difference, in a perfect solution: the behaviors of the components are perfectly analogous.

These definitions and properties are based on experimental results obtained within the framework of classical thermodynamics. Later, we shall reconsider these points under the light of statistical thermodynamics.

8.7 Fundamental Interest of Raoult and Henry's Laws

The principal difficulty encountered in the study of solutions lies in the fact that classical thermodynamics provides us with no information concerning the dependence of the chemical potential of a solute on its "concentration" in the solution. The only one very interesting relation in this field is that of Gibbs–Duhem which applies to a homogeneous phase (viz. Chap. 5 and above). It is evident that Raoult and Henry's laws bring us supplementary precious information.

However, we must notice that these laws are empirical. Besides, there exist some mathematical expressions, not founded on theoretical basis, which satisfactorily describe changes in vapor pressures of solutes as a function of the "composition" of the solution. They are Margules and van Laar laws (viz. paragraph 9 under).

8.8 Consequences of the Ideal Character: Partial Molal Enthalpies and Partial Molal Volumes of the Components of an Ideal Solution

In this chapter, let us confine ourselves to notice that:

- The partial molal enthalpy $\overline{H_{\mathrm{m}\ i}}$ of every component i in an ideal solution is equal to its molal enthalpy in the pure state $H_{\mathrm{m}\ i}{}^{\square}$. As a result, the relation

$$H = n_1\overline{H_{\mathrm{m}\ 1}} + n_2\overline{H_{\mathrm{m}\ 2}} + \cdots$$

which is always valid (viz. Chap. 4) becomes in the case of an ideal solution

$$H = n_1 H_{\mathrm{m}\,1}{}^{\square} + n_2 H_{\mathrm{m}\ 2}{}^{\square} + \cdots$$

  The total enthalpy of the solution H is equal to the sum of the enthalpies of the pure compounds. Hence, there is no thermal effect when a mixture of the components of an ideal solution is realized.
- There is no volume change when the liquid components of an ideal solution are mixed. This result comes from the fact that the partial molal volumes $\overline{V_{\mathrm{m}\ i}}$ of every component of the ideal solution are equal to their molal volumes $V_{\mathrm{m}\ i}{}^{\square}$ in pure state, at the same temperature and pressure.
- The entropy change ΔS resulting from the mixture of two pure components by forming one mole of ideal solution is given by the expression

$$\Delta S = -\, x_1 R \ln x_1 - x_2 R \ln x_2$$

  where x_1 and x_2 are the molar fractions of both components in the mixture and R the perfect gas constant. It is particularly noticeable that the entropy of mixing is inevitably positive.

8.9 Colligative Properties

The above lines of arguments concerning Raoult and Henry's laws are very close to those rationalizing the colligative properties of solutions.

The latter ones essentially depend on the quantities of matter rather than on their nature. They are accompanied by some phenomena such as the boiling point elevation of solutions, the lowering of freezing point of a solution, and the occurrence of the osmotic pressure. They can be used for the determination of the activities.

In this chapter, we confine ourselves to the study of the osmotic pressure because it has been the matter of several works which relate it to the activities. We shall encounter the osmotic pressure several times in this book. (In Chaps. 13 and 14 we shall give the principle of the method of determination of activities based on the measure of the depression of the freezing point of the solvent in a solution.)

8.10 The Osmotic Pressure

Let us consider the apparatus with the form of a U shown in Fig. 8.3. It is made up of two compartments separated by a membrane M. At the beginning of the experience, both compartments are filled by the pure liquid 1 which will play the part of the solvent. This liquid can permeate the membrane. One of the compartments (on the left side for example) is equipped with an aperture allowing the addition of a solute. The solute cannot pass through the membrane and when it is added it will be confined in the compartment on the left.

At the beginning, the solute is not added. The level of the liquid is the same in both compartments because they are under the same pressure P_0. Hence, we can set up the equality (which is a condition of equilibrium at the same temperature and pressure—see Chap. 7):

$$f_1^\bullet(\text{left}) = f_1^\bullet(\text{right})$$

where $f_1^\bullet$ is the fugacity of the pure solvent.

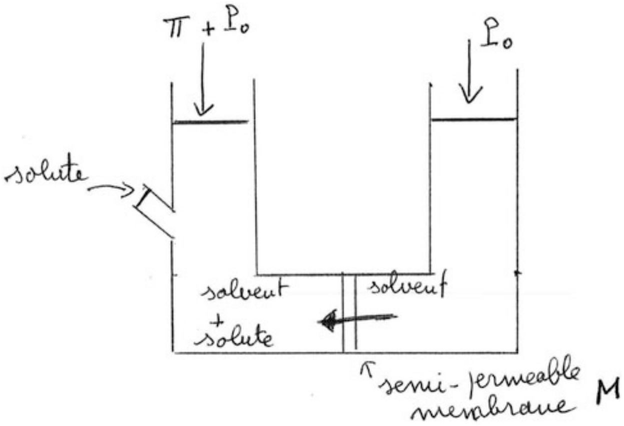

Fig. 8.3 Apparatus to display the occurrence of an osmotic pressure (end of the experience: same level of solvent recovered)

When the solute is added into the left compartment, we notice an enhancement of its level. There has been a moving of the solvent from the right to the left, through the membrane. The chemical potential of the liquid in the right compartment has not changed because its thermodynamic state has not varied. As a result, its chemical potential remains the same, with the value $f_1^{\bullet}$ (right). The conclusion which can be drawn is the following one: because of the addition of the solute, the fugacity of the solvent in the left compartment f_1 (left) has decreased (since there has been a spontaneous transfer of the solvent from the right to the left):

$$f_1(\text{left}) < f_1^{\bullet}(\text{right})$$

f_1 (left) is the fugacity of the solvent in the left compartment after addition of the solute, before the subsequent equilibrium has been established. In order to bring back an identical level of liquid in both compartments, a supplementary pressure π, called osmotic pressure, must be applied on the compartment containing the solute. One can draw an expression relating π to the concentration of the solute.

The reasoning leading to it is the following. For the equilibrium to be brought back, the new, nonequilibrium fugacity f_1 (left) must be modified so that the following equality is satisfied again:

$$f_1(\text{left}) = f_1^{\bullet}(\text{right})$$

At constant temperature, f_1 depends on the pressure and concentration of the solute. Hence, we can write (the index 2 corresponding to the solute)

$$d\ln f_1 = (\partial \ln f_1/\partial \mathbf{p})_{T,\ x2}d\mathbf{p} + (\partial \ln f_1/\partial x_2)_{P,T}dx_2$$

When the identical level of liquid in both compartments is brought back, there no longer exists a change in f_1 and

$$d\ln f_1 = 0$$

whence

$$(\partial \ln f_1/\partial \mathbf{p})_{T,\ x2}d\mathbf{p} = -(\partial \ln f_1/\partial x_2)_{P,T}\,dx_2 \tag{8.17}$$

Owing to the general relation (viz. Chap. 7)

$$(\partial \ln f/\partial \mathbf{p})_T = \overline{V_{\mathrm{m}}}/RT \tag{8.18}$$

that is to say, in the occurrence

$$(\partial \ln f_1/\partial \mathbf{p})_T = \overline{V_{\mathrm{m}\,1}}/RT$$

where $\overline{V_{\mathrm{m}\,1}}$ is the partial molal volume of the solvent. Equation (8.17) may, hence, be written as

$$\overline{V_{\mathrm{m}\,1}}\,/RT = -(\partial \ln f_1/\partial x_2)_{P,T}\,dx_2 \tag{8.19}$$

The partial derivative of the right-hand side of (8.17) can be simplified provided that the solution in the left compartment is sufficiently diluted. Since it is the case for our reasoning, the solvent obeys the Raoult's law:

$$f_1 = f_1{}^{\bullet} x_1$$

and

$$\begin{aligned} f_1 &= f_1{}^{\bullet}(1 - x_2) \\ \ln f_1 &= \ln f_1{}^{\bullet} + \ln(1 - x_2) \\ d\ln f_1 &= d\ln(1 - x_2) \\ d\ln f_1 &= d(1 - x_2)/(1 - x_2) \\ d\ln f_1 &= -dx_2/(1 - x_2) \end{aligned}$$

As the solution is diluted,

$$(1 - x_2) \approx 1$$
$$(\partial \ln f_1/\partial x_2)_{P,T} = -1$$

Reporting this relation into (8.19), it results in

$$\left[\overline{V_{\mathrm{m}\,1}}/RT\right] d\mathbf{p} = dx_2 \tag{8.20}$$

In very dilute solution, the partial molal volume $\overline{V_{\mathrm{m}\,1}}$ does not differ appreciably from its molar volume in the pure state $V_{\mathrm{m}\,1}{}^{\bullet}$:

$$\overline{V_{\mathrm{m}\,1}} \approx V_{\mathrm{m}\,1}{}^{\bullet}$$

Taking into account this approximation and integrating equation (8.20) from the pressure P_0 to the total pressure P acting on the left compartment, once the equilibrium is brought back it leads to the expression

$$P - P_0 = [RT/V_{\mathrm{m}\,1}{}^{\bullet}]x_2$$

or

$$\pi = [RT/V_{\mathrm{m}\,1}{}^{\bullet}]x_2 \tag{8.21}$$

This is the expression searched for, called the Van't Hoff's relation. It is possible to go further into the approximations by considering, again, that the solution is sufficiently diluted so that the following approximation should be valid:

$$x_2 \approx n_2 / n_1$$

and hence

$$\pi = [RT\, n_2 / \, n_1 v_{\mathrm{m}\ 1}{}^{\bullet}] \tag{8.22}$$

By taking into account the total volume of solvent (in the left compartment)

$$V = \, n_1 v_{\mathrm{m}\ 1}{}^{\bullet}$$

we obtain

$$\pi = n_2 (RT/V) \tag{8.23}$$

Relation (8.23) is formally identical to that of perfect gases. Relations (8.22) and (8.23) are also named Van't Hoff's relations.

For indicative purpose, for molar concentrations in saccharose equal to 0.098 and 1.000 mol L^{-1} in water, osmotic pressures of 2.60 and 26.64 atm are observed.

Relation (8.23) shows that the measured properties are rather a functional of the number of moles than of their nature.

The quantity osmotic pressure indirectly plays an important part in the domain of the determination of activities and also in that of their physical meaning as we shall see it later.

8.11 Nonideal Solutions

Aside from the Gibbs–Duhem's relation which is based on theoretical foundations and which also applies well to nonideal solutions, there also exist relations from purely empirical origin relating the fugacities of liquid components of binary nonideal solutions to their molar fractions. Two examples are those of Margules and van Laar. They are capable of representing the positive and negative deviations of their vapor pressures with respect to the ideal behavior. There exist several other relations of this kind which, even, may reasonably describe the behavior of some nonideal solutions which are more complex than the binary ones (viz. Chap. 16).

8.11.1 Margules' Relations

Margules' relations are, respectively, for the solvent and the solute:

$$f_1 = x_1 f_1{}^{\square} \exp\left[1/2\beta_1 x_2^2 + 1/2\gamma_1 x_2^3 + \cdots\right] \tag{8.24}$$

$$f_2 = x_2 f_2{}^{\square} \exp\left[1/2\beta_2 x_1^2 + 1/2\,\gamma_2\, x_1^3 + \cdots\right] \tag{8.25}$$

$f_1{}^{\square}$ and $f_2{}^{\square}$ are, respectively, the fugacities of both liquids in their pure state. Constants β_1, β_2, γ_1, and γ_2 are obtained experimentally from measurements of values of partial vapor pressures at different molar fractions. These constants are not independent from each other.

8.11.2 Van Laar Relations

Van Laar relations constitute an interesting alternative to those of Margules. They are for both components of a binary solution:

$$f_1 = x_1 f_1{}^{\square} \exp\left[\alpha_1 x_2^2/(\beta_1 x_1 + x_2)^2\right] \tag{8.26}$$

$$f_2 = x_2 f_2{}^{\square} \exp\left[\alpha_2 x_1^2/(x_1 + \beta_2 x_2)^2\right] \tag{8.27}$$

The constants are not, of course, the same as those of the Margules' relations.

Remark: There exist other Margules and van Laar relations which are more complicated than those given above.

Chapter 9

Definitions of an Activity

Abstract A way to express the chemical potential of a compound consists in using the quantity named activity.

It will be seen that the handling of activities necessarily requires the choice of thermodynamic standard states, choice which is fully arbitrary. But, actually, some choices are quasi-systematically done rather than others, according to whether the studied species is either in gaseous state or into a solution and, also, according to the studied system. Hence, it is not surprising that a great part of the considerations concerning the activities is devoted to the standard states and to their choice.

In this chapter, the examination of the definitions of an activity is carried out, since an activity of a compound can be defined according to two ways, one through its fugacity and the other directly without involving the notion of fugacity. The consequences of the arbitrary character of the choice of the standard states are considered later. Finally, some general properties of the activities are mentioned. It is the case of their changes with the temperature and pressure.

Keywords Activity/definitions • Standard states • Standard chemical potential • Arbitrary character of the chemical potential • Activity coefficient • Activity and temperature • Activity and pressure

A way to express the chemical potential of a compound, distinct from that which involves directly the notion of fugacity, consists in using the quantity named activity. Generally speaking, it is easier to handle than the activity in the case of solutions whereas it is the converse in the case of gases. However, both notions can apply to each of the two phases. In addition, they are intimately linked.

We shall see that the handling of activities necessarily requires the choice of thermodynamic standard states, choice which is fully arbitrary. But, actually, some choices are quasi-systematically done rather than others, according to whether the studied species is either in gaseous state or into a solution and, also, according to the studied system. Hence, it is not surprising that a great part of the considerations concerning the activities is devoted to the standard states and to their choice. In this chapter, we also examine the consequences of the arbitrary character of their choice. Finally, we mention some general properties of the activities, i.e., their changes with the temperature and pressure.

J.-L. Burgot, *The Notion of Activity in Chemistry*,
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9.1 Definitions of the Activity

Before all, we must distinguish the activity a_B or (B) of a species B from its absolute activity $\lambda_{B.}$ This last notion is only used in statistical thermodynamics. It will be defined in Chap. 24. Now, we focus our attention on the notion of activity as it is usually understood. It is also named *relative fugacity* and even *relative activity* as opposed to the absolute activity.

We may consider that there exist two definitions of the activity of a compound. In the first one, it is defined by starting from its fugacity. In the second, it is defined from the chemical potential of the species that it must characterize.

9.1.1 Starting from the Notion of Fugacity

The activity a_i of the species i in a given thermodynamic state is defined as being equal to the ratio of its fugacity f_i in this state and of its fugacity f_i° in another state called the standard state, generally chosen at the same temperature than the previous one, that is to say

$$a_i = f_i / f_i^\circ \tag{9.1}$$

At first glance, we see that an activity is a dimensionless number. (Let us notice that IUPAC defines the notion of activity without any mention of that of fugacity.)

9.1.2 Starting from the Notion of the Chemical Potential

The handling of relation (9.15) of Chap. 7 permits to express the chemical potentials μ and μ° of the studied compound in the state of the system and in the standard state by the relations

$$\mu_i = \mu_i{}^* + RT \ln f_i$$

$$\mu_i^\circ = \mu_i{}^* + RT \ln f_i^\circ$$

This kind of expressions apply to only one species present in the system and to a mixture as well since a chemical potential is a partial molal quantity. Subtracting the latter expression from the former gives

$$\mu_i - \mu_i^\circ = RT \ln \left(f_i / f_i^\circ\right)$$

$$\mu_i - \mu_i^\circ = RT \ln a_i \tag{9.2}$$

If we consider the previous definition, the activity gets naturally through the operation. Nevertheless, this is not a definition but it suggests the following one.

There is nothing which can stop the setting up of a new quantity, the activity, which characterizes the chemical potential of a compound, the change of which is in linear relation with its logarithm, that is to say which obeys to the expression

$$d\mu_i = RT\, d\ln a_i \tag{9.3}$$

After integration, relation (9.3) gives an expression of the following kind (where Cte is the integration constant):

$$\mu_i = \text{Cte} + RT \ln a_i \tag{9.4}$$

Hence, the second definition of an activity consists, without any consideration of the notion of the fugacity, in setting up that the activity is related to the chemical potential of the solute, which is measured by it, through relation (9.4). (Let us notice that IUPAC, in agreement with what is just said, defines the notion of activity without any mention of fugacity.)

The definition (9.4), of course, is incomplete because of the occurrence of the integration constant which can take any value. Since, in a given thermodynamic state, there is only one value of the chemical potential of a species and given the fact it is given by the expression (Chap. 7)

$$\mu_i = \mu_i^\circ + RT \ln \frac{f_i}{f_i^\circ}$$

it results from its comparison with (9.4) that

$$\text{Cte} = \mu_i^\circ$$

whence the expression

$$\mu_i = \mu_i^\circ + RT \ln a_i \tag{9.5}$$

μ_i° is called *the standard chemical potential* of i. It is a constant which only depends on the nature of i and on the temperature. The relation (9.5) may also be written as

$$a_i = \exp[\mu_i - \mu_i^\circ/RT] \tag{9.6}$$

It is interesting to realize that the standard potential μ_i° is, in principle, different from the integration constant $\mu_i{*}$ of the relation (9.15) in Chap. 7. Actually, it is the introduction of the notion of activity which imposes the notion of standard potential μ_i°. Moreover, according to the two ways through which an activity is defined, it appears that both definitions of an activity are in full agreement.

Remark: The different expressions expliciting the second definition of an activity also involve the fact that an activity must be a dimensionless number since it arises in the argument of a logarithm.

9.1.3 Consequence of the Arbitrary Character of the Standard State

The immediate consequence of the arbitrary character of the choice of the integration constant of relation (9.4), i.e., of the standard state, is that different choices must lead to different values of the activity of a compound in the same thermodynamic state! This is the reality.

This point is significantly unknown since, actually, some standard states are more judicious in their using than others and, because of that, they are quasi-universally chosen. In such conditions, the problem may not arise.

9.1.4 Definition of the Standard Chemical Potential of a Species

By considering the relation (9.5), it appears that the standard chemical potential of a species is its chemical potential when its activity is equal to unity. This definition of the standard chemical potential is general, but it is purely formal (viz. paragraph 4).

9.2 The Activity Coefficient

Let us recall (vis Chap. 6) that the activity of a species is related to its "concentration" by a general relation of the kind

$$\gamma_i = a_i/C_i \tag{9.7}$$

γ_i is the activity coefficient of the species.

An activity coefficient is defined as being a dimensionless number whichever the "concentration" unit is, if ever it does possess one. When this is the case, in order to respect this definition, the activity coefficient must be defined by an expression of the type

$$\gamma_i = a_i/(C_i/C_i{}^\circ)$$

where $C_i{}^\circ$ is the "concentration" of the species in a particular state (viz. under), with $C_i{}^\circ$ being expressed with the same units as C_i.

(Let us notice in passing that in the case of a gas (viz. Chap. 7), since the partial pressure of a gas is an expression of the number of moles of the species in the mixture, one can consider that the fugacity coefficient has the significance of an activity coefficient.)

We shall see in the following chapters that there exist several kinds of activities. A particular symbolism takes this point into account.

9.3 A First Sight of the Physical Significance of the Quantities Activity and Activity Coefficient

We have seen in Chap. 8 that, in the case of a perfect solution, the chemical potential μ_i of every component obeys the expression

$$\mu_i = \mu_i^{\mathrm{p}} + RT \ln x_i$$

where $\mu_i{}^{\mathrm{P}}$ is its chemical potential in its pure state and x_i its molar fraction. Let us also recall that for every mixture exhibiting an ideal behavior, the chemical potential of every component depends on its "concentration" according to the expression

$$\mu_i = \mathrm{Cte} + RT \ln C_i \tag{9.8}$$

where Cte is a constant.

When the mixture is not ideal, that is to say when the electrostatic interactions between the species are not negligible—viz. Chap. 6—G.N. Lewis has introduced the quantity activity in such a manner that the chemical potential of every component may be written as

$$\mu_i = \mathrm{Cte} + RT \ln a_i \tag{9.9}$$

where the constant Cte in both last relations is the same (viz. relation 6.4—Chap. 6).

- We see that the significance of the activity a_i is that of a virtual concentration (sometimes, we speak of a pseudo-concentration or of a corrected concentration). It confers the same chemical potential to the component i as that it would have if it were at the concentration C_i in the mixture of the same composition, should it be ideal.
- Another physical significance of the activity appears after consideration of relation (9.2). It is absolutely compatible with the previous one. We can note that, through its logarithm, it measures the Gibbs energy difference between the considered and standard states. It is a measurable quantity by measuring the work which must be developed in order to perform this change (viz. Chap. 2). Hence, we can deduce that an activity is a measurable quantity (see, however,

the case of ions—Chap. 12). The following reasoning confirms this point. Let us write the chemical potentials of the compound expressed as functions of the fugacities:

- In the standard state

$$\mu_i = \mu_i^\circ + RT \ln f_i^\circ$$

- In every state

$$\mu_i = \mu_i^\circ + RT \ln f_i$$

  The crossing from the first to the second state is endowed with the change in the molar Gibbs energy ΔG°:

$$\Delta G = RT \ln f_i / f_i^\circ$$
$$\Delta G = RT \ln a_i$$

  Since the chemical potential is a molar quantity (viz. Chap. 5), it appears that an activity is endowed with a meaning of a change in the molar Gibbs energy accompanying a process evolving from the standard state till some other state.

- In order to grasp the meaning of the activity coefficient, it is sufficient to write (9.9) again and to introduce the expression (9.7) of the activity into it and, finally, to compare the obtained relation (9.10) with (9.8). We obtain

$$\mu_i = \text{Cte} + RT \ln \gamma_i + RT \ln C_i \tag{9.10}$$

At once, we realize that the term $RT \ln \gamma_i$, that is to say the activity coefficient, represents the part of the chemical potential (belonging to the compound *i*) due to its electrostatic interactions. In a way, this term quantifies the gap in “ideality.”

9.4 A First Return to the Standard State

We have seen that the standard chemical potential of a species is its chemical potential when its activity is equal to unity. This definition is only a purely formal one because it does not specify the thermodynamic state in which the species is endowed with an activity unity, that is to say its standard state. It remains to specify it.

Let us begin by stressing the fact that there exists no particular temperature recommended to define a standard state. More precisely, standard states are defined for a given temperature, arbitrarily chosen by the experimenter but, for practical reasons, chosen as being that of the studied process.

The two following chapters devoted to the activities of gases and to the solutions of nonelectrolytes will explicit this notion of standard state.

9.5 Consequences of the Arbitrary Character of the Standard State

The arbitrary character of the choice of the standard state induces the legitimate question of the credibility of the numerical values of the thermodynamic quantities obtained through the handling of the activities. Here, we give a first answer. A first answer is that the arbitrary character of the choice of the standard state has no impact on the value of the Gibbs energy change accompanying a process and, also, has no impact on the changes of other thermodynamic state functions. We will go deeper into the discussion with the help of the consideration of some equilibria taking into account activities (viz. Chap. 19).

In order to conclude this point, we must first have in mind that the activity of a species is a direct measure of the difference of the partial molal Gibbs energies (chemical potentials) accompanying the crossing of the compound i from the chosen standard state to that studied (viz. paragraph 1), that is to say

$$\mu_i - \mu_i{}^\circ = RT\ln a_i$$

The very fact that the change in the Gibbs energy is constant is demonstrated as follows.

Let us consider the crossing of one mole of gas from a gaseous mixture 1 to a gaseous mixture 2 at constant temperature and pressure. Let us study this transfer in two cases. The first one consists in choosing the state α as standard state (process 1), and the second consisting in choosing the state β as the standard state (process 2). For the process 1, the Gibbs energy change ΔG_{12} is (using the function fugacity—viz. Chap. 7)

$$\begin{aligned}\Delta G_{12}{}^{\alpha} =& [RT\ln f_2 + C(T)] - [RT\ln f_{\alpha}{}^\circ + C(T)] - \\ & \{[RT\ln f_1 + C(T)] - [RT\ln f_{\alpha}{}^\circ + C(T)]\}\end{aligned}$$

and for the process 2

$$\begin{aligned}\Delta G_{12}{}^{\beta} = & [RT\ln f_2 + C(T)] - \left[RT\ln f_{\beta}{}^\circ + C(T)\right] \\ & - \left\{[RT\ln f_1 + C(T)] - \left[RT\ln f_{\beta}{}^\circ + C(T)\right]\right\}\end{aligned}$$

These relations are justified by the fact that fugacities of the solute f_2 and f_1 remain the same whatever the chosen standard state. Once the reference state is chosen and maintained, indeed, the fugacities do possess a well definite value. However, they are different in mixtures 1 and 2 since, owing to the process(es), the state(s) of the system have changed. Both standard states, quite evidently, exhibit the different fugacities $f_{\alpha}{}^\circ$ and $f_{\beta}{}^\circ$. According to these relations

$$\Delta G_{12}{}^{\alpha} = RT\ln f_2 - RT\ln f_{\alpha}{}^{\circ} - RT\ln sf_1 - RT\ln f_{\alpha}{}^{\circ}$$
$$\Delta G_{12}{}^{\alpha} = RT\ln f_2/f_{\alpha}{}^{\circ} - RT\ln f_1/f_{\alpha}{}^{\circ}$$
$$\Delta G_{12}{}^{\alpha} = RT\ln a''_{\alpha} - RT\ln a'_{\alpha}$$

and also a''_{α}, a'_{α}, a''_{β}, and a'_{β} are the activities in the mixtures 2 and 1 according to the standard states α and β. The difference in the molar Gibbs energy accompanying the crossing from the states 1 to 2 (same final and initial states) is obligatorily the same, whatever the standard state; thus we obtain

$$\Delta G_{12}{}^{\alpha} = \Delta G_{12}{}^{\beta}$$
$$\Delta G_{12}{}^{\beta} = RT\ln a''_{\beta} - RT\ln a'_{\beta}$$

It can be deduced from this thought experiment that the difference in the molar Gibbs energy is independent from the standard states, whence the proposal.

One consequence of this fact is that the ratio of the activities in the same experimental conditions a and a' based on two different standard states is constant whatever its concentration is. Since the standard states are different, the fugacities in them are f° and $f^{\circ\prime}$ and the activities based on them are

$$a = f/f^{\circ} \quad \text{and} \quad a' = f/f^{\circ\prime}$$

The ratio of activities is

$$a/a' = f^{\circ\prime}/f^{\circ}$$

since the fugacity f is the same. The ratio of activities is evidently a constant at a given temperature.

We shall see later, especially when we shall consider the case of the electrolytes and also the equilibria in which they take part, that the last sentence must be somewhat shaded. Let us anticipate this point *by saying that if the arbitrary choice of the standard states does not change the value of the Gibbs energy of an equilibrated process*, *it does change the value of the equilibrium constant.*

9.6 Some Properties of the Activity Function

9.6.1 Dependence of the Activity on the Pressure

The fugacity in the standard state is defined at a constant pressure. As a result

$$\partial \ln f^{\circ}/\partial \mathbf{p} = 0$$

and concerning the activities

$$\begin{aligned}(\partial \ln a/\partial \mathbf{p})_{T,x} &= [\partial \ln(f/f^\circ)/\partial \mathbf{p}]_{T,x}\\(\partial \ln a/\partial \mathbf{p})_{T,x} &= (\partial \ln f/\partial \mathbf{p})_{T,x}\\(\partial \ln f/\partial \mathbf{p})_{T,x} &= \overline{V_m}/RT\end{aligned} \tag{9.11}$$

because of the properties of the fugacity function (viz. Chap. 7, paragraph 5). $\overline{V_m}$ is the partial molal volume of the solute in the solution and in the conditions of the experience.

9.6.2 Dependence of the Activity on the Temperature

Let us again consider one of the definitions of an activity and divide the corresponding relation (9.2) by T. We obtain

$$\begin{aligned}R \ln a &= \mu/T - \mu^\circ/T\\\mu/T &= \mu^\circ/T + R \ln f - R \ln f^\circ\end{aligned} \tag{9.12}$$

Let us differentiate this relation with respect to T. Owing to the properties of the fugacity function (viz. Chap. 7), we obtain

$$[\partial(\mu/T)/\partial T]_{P,\,x} = -\overline{H_m}/T^2 \tag{9.13}$$

$$[\partial(\mu^\circ/T)/\partial T]_{P,x} = -\overline{H_m{}^*}/T^2 \tag{9.14}$$

Let us recall that $\overline{H_m}$ is the partial molal enthalpy of the component at the pressure and temperature of the system.

Now, it is interesting to anticipate the considerations concerning the standard states which are in the following chapter. They mention that $\overline{H_m{}^*}$ is the partial molal enthalpy of the solute when its behavior is perfect at the pressure of one unity, that is to say in the standard state and that $\overline{H_m{}^*}$ is also equal to $H_m{}^*$ in the reference state, as it is indicated by the superscript. Since the behavior is ideal both in the reference and ideal states, we obtain

$$\overline{H_m{}^*} = H_m{}^*$$

The molal enthalpy $H_m{}^*$ in the reference state is equal to its molal standard enthalpy, that is to say in the pure state $H_m{}^\circ$, under the pressure unity (viz. course in thermodynamics)

$$H_{\mathrm{m}}{}^{*} = H_{\mathrm{m}}{}^{\circ}$$

As a result, according to (9.14)

$$(\partial \ln a / \partial T)_{P,x} = \left(H_{\mathrm{m}}{}^{\circ} - \overline{H_{\mathrm{m}}}\right)/RT^2 \tag{9.15}$$

The difference $\left(H_{\mathrm{m}}{}^{\circ} - \overline{H_{\mathrm{m}}}\right)$ is the change in enthalpy accompanying the transfer of one mole of species from the solution to the pure state under the pressure unity.

Chapter 10
Activities of Gases

Abstract Although equilibria in gaseous state are the most often studied by handling fugacities, they can also be studied by handling activities. With the study of solutions in mind, it is however interesting, in a first step, to introduce the notions of activity and of standard states in the case of gases. This first approach is easier to grasp than that followed directly for the study of solutions and may be used for an introduction of the latter ones.

The considerations mentioned in the chapter show that several standard states can be indifferently chosen for the definition of the activities of gases; some are easier to handle than others. The fact that several standard states can be chosen leads to the conclusion that, actually, there are several kinds of activities characterizing the same compound. Moreover, the chapter contains a comparison between reference states and standard states.

Keywords Standard state • Activity of a pure gas • Activity of a gas in a gaseous mixture • Reference state • Chemical potential of a gas • Other standard states

Although equilibria in gaseous state are the most often studied by handling fugacities, they can also be studied by handling activities.

With the study of solutions in mind, it is however interesting, in a first step, to introduce the notions of activity and of standard states in the case of gases. This first approach is easier to grasp than that followed directly for the study of solutions and may be used for an introduction of the latter ones.

10.1 Usual Standard State and Activity of a Pure Gas

The standard state of a pure gas is that in which it would exhibit an ideal behavior under a well-definite pressure, called the standard pressure, at the chosen temperature. The standard pressure most often retained is the pressure unity (historically: 1 atm). It is a hypothetical state since gases are no longer ideal at this pressure (with the exception of dihydrogen in some conditions).

- Perfect gas

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Since the fugacity of a perfect gas is equal to its pressure (viz. Chap. 7), its standard state is usually that of fugacity unity ($f^\circ = 1$ atm) at the chosen temperature. But, we must pay attention. This is true only if the gas is perfect. One gas, indeed, the behavior of which is nonideal, may exhibit one fugacity equal to the unity by numerical accident. However, it is not its standard state.

According to the general definition of an activity (viz. Chap. 9)

$$a = f/f^\circ$$

If in this state, $f^\circ = 1$ unity,
whence

$$a = f/1 \quad \text{(perfect gas)} \tag{10.1}$$

In other words

$$a = f \quad \text{(perfect gas : numerical values)} \tag{10.2}$$

Hence, with the choice of the standard state such as $f^\circ = 1$ unity, the activity of a perfect gas is equal to its fugacity. Moreover, since its fugacity is equal to its pressure, its activity is also equal to its pressure:

$$a = p$$

It is interesting to notice that, since the gas is perfect, its fugacity is always equal to its pressure, including its pressure in the standard state, whence the above expression of its activity. When the pressure in the standard state is different from 1 unity

$$a = \mathbf{p}/\mathbf{p}^\circ \quad \text{(perfect gas)} \tag{10.3}$$

It is also interesting to notice that with the standard state such as $f_i^\circ = 1$ unity, we can write

$$\mu_i = \mu_i^\circ + RT\ln f_i/f_i^\circ$$

$$\mu_i = \mu_i^\circ + RT\ln f_i \quad \text{(numerical values)}$$

and, also, since (viz. Chap. 7)

$$\mu_i = \mu_i{}^* + RT\ln f_i \quad \text{(numerical values)}$$

As a result

$$\mu_i^\circ = \mu_i{}^* \quad (\text{perfect gas; } f_i^\circ = 1\,\text{unity})$$

Owing to this choice of standard state, the chemical potential of the perfect gas *i* is equal to the integration constant of the equation permitting the introduction of the fugacity of a gas (viz. Chap. 7).

It is demonstrated in Chap. 26, relation (26.11), that

$$\mu_i{}^{\circ} = -kT\ln\left[\left(2\pi mkT/h^2\right)^{3/2}kT\right] \quad \text{(perfect monoatomic gas)}$$

This relation, stemming from a reasoning of statistical thermodynamics (viz. Chap. 26), is interesting since it provides us with an expression, in concrete molecular parameters, of the standard chemical potential. When it is introduced only in classical thermodynamics, as it has been done up to now, the latter, indeed, appears to be a rather mysterious quantity.

- Real gas

  The usual standard state is the same as previously. It is the hypothetical state in which the gas would exhibit an ideal behavior at the standard pressure $P^{\circ} = 1$ atm, at the chosen temperature.

  In the standard state, because of the (hypothetical) *ideal* behavior of the gas, $f^{\circ} = \mathbf{p}^{\circ}$. With $\mathbf{p}^{\circ} = 1$ atm, we find

$$f^{\circ} = 1\,\text{atm}$$

The standard state remains that for which the numerical value of its activity a is equal to the value of its fugacity f°, at a given temperature, that is to say to the unity

$$a = f^{\circ}/1 \quad \text{(standard state)} \tag{10.4}$$

$$a = 1 \quad \text{(standard state)} \tag{10.5}$$

However, in every state of the gas, its fugacity is different from its pressure (if it were the contrary, it would be no longer real on the contrary of the hypothesis). The fugacity coefficient is different from 1. But, owing to the general definition of the activity

$$a = f/f^{\circ}$$

the latter remains equal to its fugacity (with $f^{\circ} = 1$ atm)

$$a = f \quad (\text{real gas with } f^{\circ} = 1\,\text{atm}) \tag{10.6}$$

as a perfect gas. But, since $f \neq \mathbf{p}$

$$a \neq \mathbf{p}$$

or more generally

$$a \neq \mathbf{p}/\mathbf{p}^\circ \quad \text{(real gas)}$$

There exists one exception in what is just mentioned, that is to say: the fact that the fugacity of a real gas is different from its pressure. It is a reality in the whole domain of concentrations. The exception is when the pressure is very weak, when no longer interactions between atoms or molecules of gas do exist. (Besides, it is in this domain of interactions that the relation has been set up:

$$f/\mathbf{p} \rightarrow 1 \quad \text{for} \quad \mathbf{p} \rightarrow 0$$

in order to fix the values of the fugacities.)

In these conditions

$$a = \mathbf{p}/\mathbf{P}^\circ \quad \text{(real gas : very weak pressure)} \tag{10.7}$$

Finally, the interest of the choice of such a standard state ($f^\circ = 1$ atm) lies in the fact that the value of the activity of a gas is equal to the value of its fugacity.

10.2 Usual Standard State and Activity of a Gas in a Gaseous Mixture

- Ideal mixture

Let us consider the component i. We have already seen that (viz. Chap. 7) its chemical potential is related through its partial pressure p_i through the following relation:

$$d\mu_i = RT\,d\ln p_i$$

We shall see (viz. paragraph 4) that its chemical potential μ_i may be expressed as

$$\mu_i = \mu_i^\circ + RT\ln p_i/\,p_i^\circ \quad \text{(ideal gas or gaseous mixture)}$$

where p_i° is the partial pressure of i in the standard state and μ_i° its chemical potential in the same state. p_i° is an arbitrary pressure with respect to which μ_i is based. It is expressed in the same units as p_i. (We immediately check that when $p_i = p_i^\circ$, $\mu_i = \mu_i^\circ$.)

Usually, the standard state of the gas i is chosen in such a manner that its partial pressure p_i° is equal to 1 atm at the temperature of the system. Since the mixture also exhibiting a perfect behavior by hypothesis, all the components also exhibit this "ideality" (viz. Chap. 8). The notion of fugacity applying to the perfect gases and to the real ones as well results in the following equalities:

$$f_i = p_i$$

and especially

$$f_i^\circ = p_i^\circ$$

As a result,

$$a_i = f_i / f_i^\circ$$

as it must be, and

$$a_i = p_i \quad (\text{perfect mixture—} p_i^\circ = 1\,\text{unity}) \tag{10.8}$$

and more generally

$$a_i = p_i / p_i^\circ \quad (\text{perfect mixture}) \tag{10.9}$$

- Nonideal mixture of gases
  The activity of gas *i* in the gaseous mixture is, of course, defined by the general relation

$$a_i = f_i / f_i^\circ$$

where f_i is its fugacity in the considered state and f_i° its fugacity in the standard state.

Usually and as previously, the chosen standard state is that in which, at the given temperature, the gas would behave ideally at the partial pressure $p_i^\circ = 1$ atm. It is a hypothetical state in which, the mixture behaves ideally,

$$f_i^\circ = \mathbf{p}_{\mathrm{i}}^\circ$$

The same considerations as the previous ones lead to the following facts:

$$f_i \neq p_i$$
$$a_i \neq p_i / p_i^\circ$$

As previously, it results that the numerical value of the activity is equal to its fugacity:

$$a_i = f_i / f_i^\circ$$

This comes from the choice of the adopted standard state, and one finds

$$a_i = f_i \quad (\text{numerical values}\, f_i^\circ = 1\,\text{unity})$$

and that, at very weak total pressure P, the fugacity values tend toward those of the partial pressures:

$$a_i/p_i \to 1 \quad (P \to 0) \quad (\text{numerical values})$$

Finally, with the chosen standard state ($\boldsymbol{p}_i^\circ = 1$ *atm, ideal behavior), the value of the activity of the gas is equal to that of its fugacity, whether it be pure or real.*

10.3 Reference State and Standard State

Through consideration of real gases, we saw that there exists a real state, hence experimentally accessible, in which the properties of the gas, except one, are the same in it as in the hypothetical standard state. The communal properties are due to the ideal behavior exhibited by both the considered real state and the standard state. This real state is that in which the total pressure of the mixture (or that of the sole gas) is very weak. We saw that the interactions between the gas molecules are then negligible. Its behavior becomes ideal. This state is the reference state.

The reference state is a real state of a very weak "concentration" in order that the interactions between the particles constituting the system are negligible.

The property of a gas which is not the same in the reference state as in the standard one is, evidently, the value of its fugacity or of its activity. Their values are, by far, much weaker in the reference state than in the standard one, since its fugacity and in the occurrence its activity (in numerical values) tend toward the value of its pressure or toward that of its partial pressure (both being then very weak) whereas, concerning now the activity in the standard state, it is equal to unity by definition.

It is interesting to notice that in the communal properties of both states, there is the fugacity coefficient which is equal to the unity. By definition of the fugacity, indeed, it is equal to the unity in the reference state. In the standard state, owing to the ideal character it exhibits its pressure is then equal to its pressure.

The reference and standard states must not be confused. In brief, one can define the reference state of a gas as a real *state in which its fugacity coefficient is equal to the unity. (We shall see that, in the case of solutions, the activity coefficient in the reference state is also equal to unity.) Its standard state is a* virtual *state in which not only its fugacity coefficient but also its activity are equal to the unity.*

The fact that a reference state is real has the interesting and fruitful following consequence: the properties of the standard state are obtainable by extrapolation until the value unity of the pressure, of the properties exhibited truly in the reference state, which are experimentally accessible (see later).[1]

10.4 General Expression of the Chemical Potential of a Gas

The choice of the usual standard state permits to express the chemical potential of a gas, perfect or real, pure or in mixture, under the following general relations:

$$\mu = \mu^{\circ} + RT \ln a \tag{10.10}$$

or

$$\mu_i = \mu_i^{\circ} + RT \ln a_i \tag{10.11}$$

We shall justify the generality of this expression in the case of a mixture of perfect or real gases. That of a pure gas is nothing else than a particular case of the mixture one.

- In the case of a mixture of perfect gases, we have already demonstrated (viz. Chap. 7) that the chemical potential of the component i is related to its partial pressure by the two relations:

  $$d\mu_i = RT\, d \ln p_i$$

  and after integration

  $$\mu_i = \mu^* + RT \ln p_i \tag{10.12}$$

  μ^* is the integration constant. It only depends on the nature of the gas and on the temperature. (The fact that μ^* is characteristic of the sole gas i and not of the mixture is an evidence. When the total pressure of the mixture is very weak and when, then, it subsists quasi-alone, the above relation must still be verified).

  After adoption of the usual standard state, we have

  $$\mu_i = \mu^* + RT \ln p_i\,/1$$

  This relation is satisfied at very weak pressure, that is to say in the reference state. Hence μ^* is also the chemical potential in the reference state. Given the fact that we are considering a mixture of perfect gases, the last relation may also be written (partial pressures are equal to the activities) as

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[1] A possible confusion between the reference and the standard states comes from the fact that, in literature, states called "reference standard states" are sometimes mentioned for which a particular reference pressure is stipulated at a given temperature. We shall not use this term.

$$\mu_i = \mu^* + RT \ln a_i \tag{10.13}$$

When $p_i = 1$, $a_i = 1$. By definition, we are in the standard state and

$$\mu_i = \mu_i^\circ$$

and as a result

$$\mu_i^\circ \equiv \mu_i^* \quad \text{(mixture of perfect gases—}f_i^\circ = 1\,\text{unity)}$$

The standard chemical potential of the gas is identical to that it exhibits in its reference state. Then, the relation (10.11) is, actually, satisfied.

- In the case of a real mixture, the reasoning is strictly analogous. It is based on the following relations:

$$\mu_i = \mu^* + RT \ln f_i \tag{10.14}$$

$$\mu_i^\circ = \mu^* + RT \ln f_i^\circ \tag{10.15}$$

where f_i° is the fugacity in the standard state:

$$\mu_i - \mu_i^\circ = RT\, lnf_i/f_i^\circ$$

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

The relation (10.11) is also satisfied. One must remark that this demonstration is based on the fact that the fugacity of i in the mixture is equal to its partial pressure in the reference state. This permits to set up both relations (10.14) and (10.15) and to introduce the chemical potential μ^* of the gas in the pure state.

10.5 Other Standard States

There are two manners to choose the standard states. The first consists in varying the numerical values of the parameters defining the state. This is legitimate because the choice of a standard state is arbitrary. For example, the value $P^\circ = 2$ atm and not the value 1 atm as previously may be chosen. The second manner consists in choosing another physical quantity to which one assigns an arbitrary numerical value. For example, one chooses to relate an activity to its molar concentration instead of its pressure. In this paragraph, we are only interested in the second manner.

Let us notice that the following considerations are valid for all kinds of systems (gaseous, liquid, and solid).

As an example, we choose to express the activity of a gas with respect to its molar concentration c_i°. In this case, the activity of a gas in an ideal mixture when it is at the concentration c_i is defined by the expression

$$a_{\mathrm{c}i} = c_i/c_i^\circ \tag{10.16}$$

where c_i° is its concentration in the standard state. Its chemical potential is

$$\mu_i = \mu_{\mathrm{c}\,i}{}^\circ + RT\ln\, a_{\mathrm{c}\,i} \tag{10.17}$$

(The index c indicates that the chemical potentials and activities are related to the scale of molar concentrations.) The chosen standard state in this case is the state in which the behavior of the gas is that of an ideal one at the molar concentration c_i°, for example 1 mol L^{-1}. Then, its chemical potential is expressed by

$$\mu_i = \mu_{\mathrm{c}\,i}{}^{\mathrm{o}} + RT\ln(c_i/1) \tag{10.18}$$

The dimension of 1 is the mol L^{-1} and, hence, 1 represents 1 mol L^{-1}. $\mu_{\mathrm{c}i}{}^\circ$ is the chemical potential that the gas would possess if its behavior was ideal at the 1 molar concentration (or, possibly, at the concentration c_i°). When the concentration is such that

$$c_i = 1\,\mathrm{mol\,L^{-1}} \quad \text{or} \quad C_i = C_i^\circ\ \mathrm{mol\,L^{-1}}$$

we find again

$$a_{\mathrm{c}\ i} = 1$$

It is, as awaited, the standard state (corresponding to the scale of molar concentrations) since it obeys to the general but formal definition according to which the activity of a species in its standard state is equal to unity.

It is interesting, at least from the theoretical standpoint, to relate the activity $a_{\mathrm{c}\ i}$ to the fugacity of the gas f_i. The followed reasoning permitting to find the correspondence is based on the invariancy of the chemical potential of a species in a given thermodynamic state. It is demonstrated that the expressions being searched for are (see Appendix B)

$$a_{\mathrm{c}\ i} = f_i/RT \quad \text{and} \quad a_{\mathrm{c}\ i} = a_i/RT \tag{10.19}$$

They are only valid in numerical values. With this new standard state, the proportionality factor relating the fugacity to the activity is now 1/*RT*.

Chapter 11
Activities of Nonelectrolytes in Liquid Solutions

Abstract This chapter shows that the notion of activity in solution is more complicated than in the gaseous state, although its introduction obeys the same general principles. Notably, it also involves the choice of standard states. Among the causes of complexity, let us first notice the obligatory occurrence of the solvent in the system, in addition to that of solutes. To be more precise, from the strict standpoint of the activities, the chosen standard states for the solutes differ from those chosen for the solvent for practical reasons. Moreover and secondly, the standard states chosen for a solute differ not only from those of the solvent but also according to the scale of "concentrations" adopted for it, even when the solute remains in the same thermodynamic state. As a result, the introduction and the handling of activity coefficients differ from each other according to the scale of "concentrations" of the species.

In this chapter, the most often encountered standard states adopted by the community of chemists are mentioned. Temporarily, the case of nonelectrolytes as solutes is only studied. That of electrolytes is still more complicated and is considered in later chapters.

Keywords Standard states/pure solids • Liquids • Liquids in mixtures • Solvent and solutes • Rational and practical standard states • Activity coefficients • Relations between different activity coefficients

The notion of activity in solution is more complicated than in gaseous state, although its introduction obeys the same general principles. Notably, it also involves the choice of standard states. Among the causes of complexity, let us first notice the obligatory occurrence of the solvent in the system, in addition to that of solutes. To be more precise, from the strict standpoint of the activities, the chosen standard states for the solutes differ from those chosen for the solvent for practical reasons. Moreover and secondly, the standard states chosen for a solute differ not only from those of the solvent but also according to the scale of "concentrations" adopted for it, even when the solute remains in the same thermodynamic state. As a result, the introduction and the handling of activity coefficients differ from each other according to the scale of "concentrations" of the species.

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In this chapter, we mention the most often encountered standard states adopted by the community of chemists. Temporarily, we only study the case of nonelectrolytes as solutes. That of electrolytes is still more complicated and will be considered later.

11.1 General Definition of an Activity

Let us recall that the activity a of a species in a given thermodynamic state is equal to the ratio of its fugacity f in the latter and of its fugacity in its standard one f°:

$$a = f/f^\circ \tag{11.1}$$

It is at this point that the fact that every substance, whichever the physical state under which it is (gaseous, liquid, or solid), does possess a fugacity (and also a partial pressure even if the latter is very weak) takes all its importance. It permits an identical definition of an activity in every circumstance.

11.2 Standard States of Pure Liquid or Solid Compounds

It turns out that, during the study of chemical reactions in which pure solids and liquids are forming or disappearing, it is convenient to adopt these pure compounds under the pressure of 1 atm and at the temperature of the system, as standard states. According to this convention, the activity a_{pure} of a pure liquid or solid compound at the pressure unity is taken to be *the unity*. Then, their molar fraction is, of course, equal to $1 (x = 1)$:

$$a_{\text{pur}} = 1 \text{ (pure liquid or solid)}$$

Evidently, they only form one phase.

11.3 Standard States of Liquids in Mixtures

In this paragraph, we consider the case of fully miscible liquids, such as the binary mixture of water and methanol. Usually, the chosen standard state is that of the component in its pure state, at the temperature of the system, under the unit pressure. This choice presents the interest to maintain the symmetry of the theoretical treatment of both components. Let us designate them by the indices 1 and 2:

$$a_1 = 1 \text{ standard state of compound } 1 \ (x_1 = 1)$$
$$a_2 = 1 \text{ standard state of compound } 2 \ (x_2 = 1)$$

11.4 Standard States in Solutions

We successively consider the cases of the standard states of the solvent and of the solute.

Let us begin to recall that the distinction between the solvent and the solute is not evident. We confine ourselves to name the component of the solution which is in excess, as being the solvent. In the following chapters, it will be marked by the index 1 whereas the solute will be marked by the index 2. We essentially consider binary solutions. From another side, the "concentrations" in solute are related to the anhydrous matter. Except particular mention, we only consider binary solutions.

11.5 Standard State, Activity, and Activity Coefficient of the Solvent

- The first point to mention is that the quasi-unanimously adopted scale of "concentration" for the solvent is that of molar fractions. It is particularly convenient from the practical standpoint since the values x_1 are only located in the domain 0 - 1.

  The standard state quasi-systematically retained for the solvent is the pure solvent at the pressure of the solution and at the chosen temperature. Its fugacity $f_1{}^{\circ}$ is given by the relation:

  $$f_1{}^{\circ} = f_1^{\bullet}$$

  where $f_1{}^{\bullet}$ is its fugacity in the pure state $(x_1 = 1)$ in the same conditions. The pressure is often, except hazard, very different from 1 atm. Figure 11.1 which represents the fugacity of the solvent as a function of its molar fraction illustrates this choice.

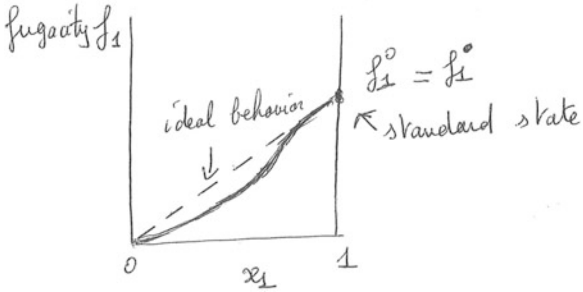

Fig. 11.1 Representation of the fugacity of the solvent and of its standard state as a function of its molar fraction

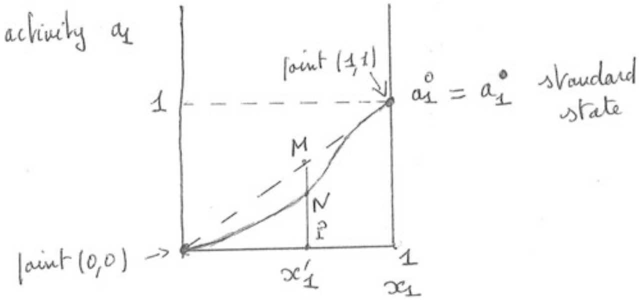

Fig. 11.2 Activity of the solvent as a function of its molar fraction

- Given the general definition of an activity—relation (11.1)—the activity of the solvent in the pure state is, as it must be, equal to unity since the fugacity in the pure state is equal to that in the standard state:

  $$a_1{}^\circ = 1$$

  The activity of the solvent cannot be larger than unity, given the upper limit of its fugacity which is that it possesses in the pure state. Figure 11.2 shows the activity of the solvent, the fugacity of which is given, as a function of its molar fraction, in Fig. 11.1.

  Quite evidently, both curves exhibit the same appearance since values of activities stem from that of fugacities by division of each point of the latter by the constant $f_1{}^\circ$. Notice that the activity of the solvent at its molar fraction $x_1^{\prime}$ is given by the ratio NP/MP.
- It is interesting to consider the behavior of the solvent in a perfect solution. According to Raoult's law (viz. Chap. 8) and according to the definition of the standard state, when the solution is perfect

  $$f_1 = x_1 f_1^\bullet$$
  $$f_1 = x_1 f_1^\circ$$

  and as a result

  $$a_1 = x_1 f_1^\circ / f_1^\circ$$
  $$a_1 = x_1$$

  In a perfect solution, the activity of the solvent is in linear relation with its molar fraction. Let us remark, before studying analogous but different cases, that there is no problem of dimension in the last equality, both quantities being dimensionless. The slope of the line is 1 since it goes through the points of coordinates $(0, 0)$ and $(1, 1)$. The curve in dots of Fig. 11.2 is an illustration of this fact. That in dots of Fig. 11.1 shows the fugacity of the solvent in the ideal case. Its slope is no longer necessarily equal to 1 since its fugacity in the pure state is not equal to unity apart by a numerical accident.

From the practical viewpoint, the choice of this standard state is justified by the fact that the more diluted the solution is, the closer to unity the solvent activity is (factor, of course, easily handled).

- *Two examples of the incidence of this choice of standard state on chemical equilibria are found in analytical and physical chemistry. They are encountered when the solvent simultaneously plays two parts in a process. The first is that of solvent and the second that of a reactant. In this case, its activity is taken equal to unity in the standard state and this explains why, generally, the activity of the solvent most often does not appear in the expression of the mass law.*

  The first example is that of the definition of the constant K_a of acid dissociation of the acid HA in water. The equilibrium is

$$\mathrm{HA} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{A^-}$$

At equilibrium, the thermodynamic constant $K°$ is expressed by

$$K^\circ = a_\mathrm{A} \cdot a_{\mathrm{H_3O^+}} / \, a_\mathrm{HA} \cdot a_{\mathrm{H_2O}}$$

or equivalently

$$K^\circ a_{\mathrm{H_2O}} = a_\mathrm{A} \cdot a_{\mathrm{H_3O^+}} / a_\mathrm{HA}$$

$$K^\circ 1 \;=\; a_\mathrm{A} a_{\mathrm{H_3O^+}} / a_\mathrm{HA} \quad \text{(sufficiently diluted solution)}$$

or usually

$$K^\circ \;=\; a_\mathrm{A} a_{\mathrm{H_3O^+}} / a_\mathrm{HA} \quad \text{(sufficiently diluted solution)}$$

In sufficiently diluted solution, indeed, given the choice of this standard state,

$$x_1 \approx 1$$

$$a_{\mathrm{H_2O}} \approx 1$$

and by definition

$$K_\mathrm{a} = \; K^\circ a_{\mathrm{H_2O}} \approx 1$$

The second example is provided by some global electrochemical reactions, such as

$$Zn_{(\mathrm{s})} \;+\; \mathrm{Cu}^{2+} \rightleftharpoons \mathrm{Zn}^{2+} \;+\; \mathrm{Cu}_{(\mathrm{s})}$$

$Zn_{(s)}$ and $Cu_{(s)}$ mean in the solid state. They are the electrodes. Each of them constitutes a pure solid phase. Their activity is, by convention, taken to be the unity (viz. paragraph 2). Usually, they do not appear in the expression of the mass action law.

- The values of the activity coefficient of the solvent stem from the previous considerations.

  The activity coefficient γ_r, called the rational activity coefficient, is, by definition, given by the expression[1]

  $$\gamma_r = a_1/x_1$$

  Since the ordinate of each point of the line in dots of Fig. 11.2 is equal to its abscissa (slope = 1), it appears that the activity coefficient is equal to the ratio of both segments NP and MP. In the example shown in Fig. 11.2, the ratio is systematically lesser than 1. It is not inevitably the case. In any way, for a real solution, the ratio is different from the unity. When the solvent is pure, it is equal to the unity.

11.6 Standard States, Activities, and Activity Coefficients of the Solutes

Among all the possible standard states, two are particularly used in the case of solutes: the rational and the practical ones. There exists only one rational standard state. It is that in which the "concentration" of the solute is expressed in molar fractions. But there are two practical standard states whether the "concentration" of the solute is expressed in molality or in molarity.

11.6.1 Rational Standard State

The concentration of the solute is expressed in molar fractions.

- It is wise that the standard state would be chosen in such a way that the value of the solute activity tends toward that of its molar fraction in very dilute solution, at the temperature of the solution. Hence, it is as follows:

$$a_2/x_2 \rightarrow 1 \quad \text{when} \quad x_2 \rightarrow 0 \tag{11.2}$$

---

[1] The index *r* recalls the word rational resulting from an ancient name (see paragraph 6). Actually, according to IUPAC, in the present case, the symbol of the activity coefficient should be symbolized by *f* since the standard state is obtained according to the Raoult's law and since the different "concentrations" are expressed in molar fractions. We do not use this symbol since a confusion with the fugacity would be possible:

$$\gamma_r = NP/MP$$
$$\gamma_r = NP/x'_1$$

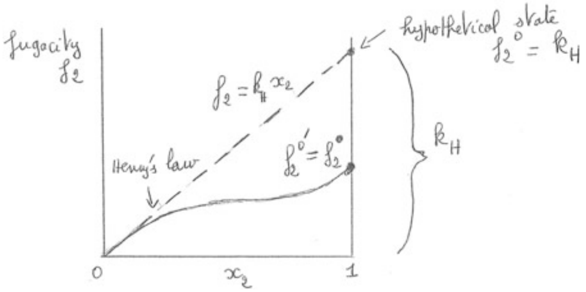

Fig. 11.3 Possible standard states of a solute (scale of molar fractions)

The interest of this choice lies in the fact that Henry's law is obeyed in this case. Let us take the example of a solute, the fugacity of which is known in the whole domain of the molar fractions (Fig. 11.3).

We notice that for the very weak molar fractions, Henry's law is obeyed. The curve of the fugacity is tangent to the line of equation for the low values of x_2:

$$f_2 = k_H x_2 \tag{11.3}$$

Since, in the standard state, the solution is by definition ideal and since then its activity coefficient and its activity tend toward 1 (viz. Chap. 10), we can write

$$\left(f_2/f_2^\circ\right)/x_2\right) \rightarrow 1 \;\text{ when }\; x_2 \rightarrow 0 \tag{11.4}$$

The value of the fugacity f_2° in the chosen standard state is obtained after comparison of relations (11.3) and (11.4). We immediately find

$$f_2^\circ = k_H$$

The fugacity in the standard state is equal to the value of the constant of Henry's law. It is marked on the Henry' s line for the abscissa $x_2 = 1$. This point (and then the standard fugacity) is experimentally accessible by extrapolation up to $x_2 = 1$ of the measures of fugacities for very weak values of molar fractions. Here is the interest of the choice of this standard state.

It is clear that the chosen standard state is a hypothetical one. We notice, indeed, that the real fugacity $f_2^{\circ\prime}$ of the solute in pure state (at the same temperature) (viz. curve in full line) is different from f_2°. Actually, as a rule, we can choose either the standard state of fugacity f_2° or that of fugacity $f_2{}^{\circ\prime} = f_2{}^\bullet$. From the practical viewpoint, the choice of the latter is awkward and even impossible, since it involves the knowledge of the fugacity of the solute in the whole domain of the molar fractions that is often impossible for a solubility reason. On the contrary, it is not the case for the first possibility since the Henry's law is all the more obeyed as the molar fraction is weaker. Quite evidently, it is the domain of concentrations where there is less risk of solubility problems.

- Figure 11.4 represents the activity of the solute as a function of its molar fraction, its fugacity being the same as in Fig. 11.3 and the standard state being obtained by extrapolation of Henry's law.

  We notice that the activity tends toward the molar fraction only for the weak values of the latter. It is clear that the values of the activities obtained with the pure compound of fugacity $f_2^{\circ\prime}$ as standard state differ considerably from the previous ones ($a_2^{\bullet} < a_2^{\circ}$).

  Hence, we can already see that the choice of the standard states governs the values of the equilibrium constants (viz. Chap. 17).
- The activity coefficients γ_x are given by the ratios NP/MP. They are dimensionless numbers, since the activities and the molar fractions are dimensionless numbers. It is very interesting for our purpose to note that their values may change according to the chosen standard states, as it is shown in Figs. 11.4 and 11.5. We see that in the first case (the hypothetical one based on Henry's law), the activity coefficient is less than unity, whereas it is the inverse in the second case, where it is also given by the ratio NP/MP.

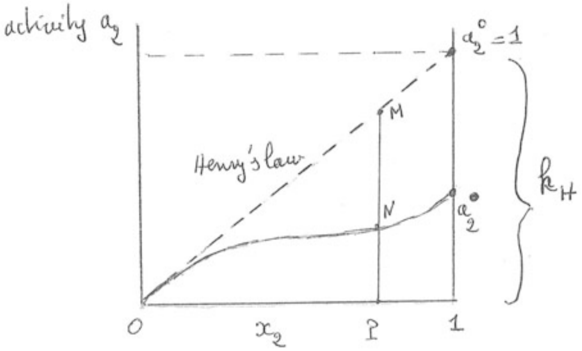

Fig. 11.4 Activity and activity coefficient of the solute when the standard state is based on Henry's law (scale of molar fractions)

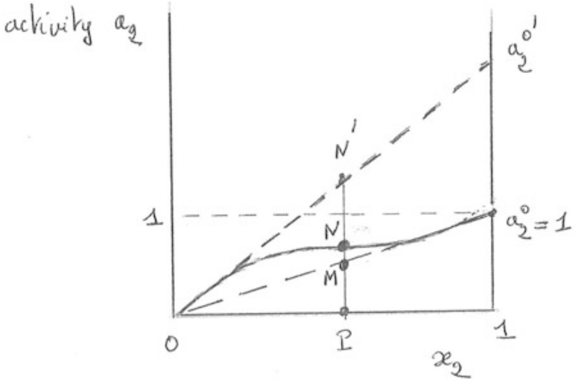

Fig. 11.5 Activity and activity coefficient of the solute when the standard state is the pure solute (scale of molar fractions)

11.6.2 Practical Standard States

This subtitle means that the “concentration” of the solute is expressed either in molalities or in molarities (viz. Chap. 1).

The choice of these units must be preferred to that of molar fractions as soon as we consider the behavior of the solute. This is the present case. This assertion is explained by the fact that when we use the former unities, the numerical values x_2 are very weak and, hence, difficult to handle since, usually, the “concentrations” of the solutes are weak. Expressed in molalities and molarities, the obtained values for the same quantities of matter in the solution are larger than with the molar fractions. Furthermore, as already mentioned, the weak solubilities encountered in practice may be sufficient, then, to determine the activities.

- “Concentrations” of solutes expressed in molalities:

  Figure 11.6 shows the fugacity of the solute as a function of the “concentration” of the solute expressed in molalities m_i related to the molality m_i° in the standard state, m_i and m_i° being expressed in mol kg^{-1}. Most often, $m_i^\circ = 1$ mol kg^{-1}. In diluted solutions, Henry’s law is satisfied. Although, in principle, it expresses a linear relation between the fugacity and the molar fraction of the solute, for the very diluted solutions, the linear relation of the fugacity with the molality remains obeyed. This is not a surprise since, at very weak concentrations, the molalities are proportional to the molar fractions (viz. Chap. 1). It is the same thing with the molar concentrations. The proportionality constants, of course, change from a scale of “concentration” to another. Hence, Henry’s law can be written in this case as

  $$f_2 = k_H{}' m_2 \quad \text{when} \quad m_2 \rightarrow 0$$

  - Again, for the same reasons as previously, it is convenient to choose the standard state in such a way that in diluted solution at the temperature of the system and at the atmospheric pressure

    $$a_{m2^\circ} / m_2 \rightarrow 1 \quad \text{when} \quad m_2 \rightarrow 0$$

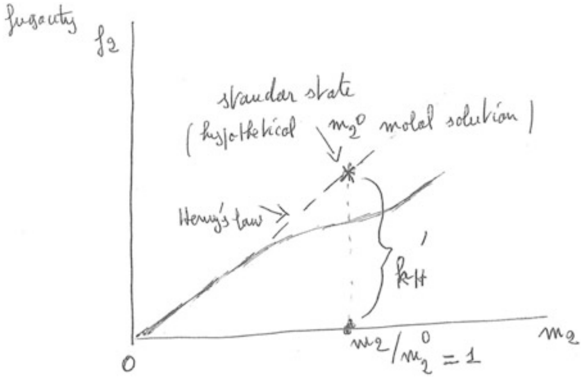

Fig. 11.6 Definition of the standard state of a solute (practical scale of concentrations expressed in molalities)

Obeying simultaneously the last two relations directly leads to the fugacity f_2° in the standard state:

$$f_2^\circ = k_H' \quad \text{(standard state)}$$

This relation is only valid in numerical values since the fugacity is expressed in atmospheres whereas the constant k_H' is expressed in atm/kg mol^{-1}. It is evident that the standard state is hypothetical. It is the state of a solution obeying Henry's law, the concentration of solute being, most often, 1 mol kg^{-1}.

- The activity of the solute a_2 is defined as previously and, as it must be, by the expression

$$a_{m2} = f_2/f_2^\circ$$

Figure 11.7 shows the activity as a function of the molality related to the standard molality.

It is interesting to notice that a real state, exhibiting an activity unity, may exist. In Fig. 11.7, it is the point marked on the activity curve for the molality m_2'. However, it is not the standard state because it is not located on the limit line stemming from that of Henry.

- The activity coefficient γ_{m2} is defined by the expression

$$a_{m2} = \gamma_{m2}(m_2/m_2^\circ)$$

It is clear that it is a dimensionless number. It is easily accessible by considering the diagram in Fig. 11.7. Let us consider, indeed, the point of molality m_2'' and of activity a_{m2}''. Let us draw the line which joins it to the origin. Its slope is a_{m2}''/m_2''. It is by definition endowed by the slope γ_{m2}.

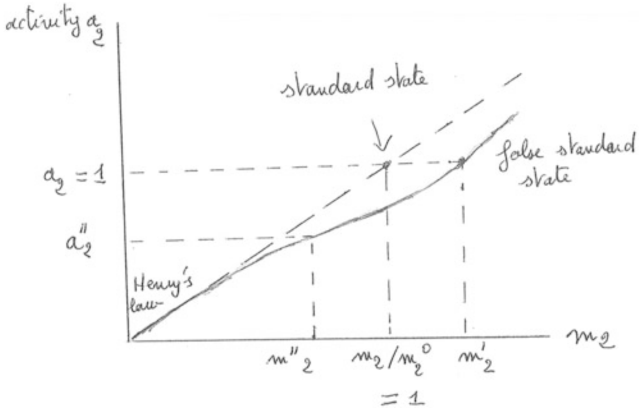

Fig. 11.7 Activity and activity coefficient of the solute (scale of molalities)

- "Concentrations" of the solute in molarities:

  The considerations are here strictly analogous to those concerning the molalities. They are based on Henry's law. The standard state is the hypothetical one in which the fugacity of the solute is equal to the constant of Henry's law for a concentration of 1 mol L^{-1} at the temperature of the system and at the atmospheric pressure. The concentration c° in the standard state may differ from 1 mol L^{-1}. The activity coefficient of the solute γ_{c2} is defined by the relation

  $$a_{c2} = \gamma_{c2}(c_2/c_2{}^\circ)$$

  It is a dimensionless number. For the same solution, the activities of the solute obtained according to the scales of molalities and molarities exhibit very close numerical values, since the values of the "concentrations" themselves also are very close to each other. As an example, let us consider 1 L of an aqueous solution containing 192.6 g of potassium nitrate. Its molar fraction is 0.0348, its molarity is 1.906 mol L^{-1}, and its molality is 2.004 mol kg^{-1}. However, we must notice that this solution cannot, actually, be considered as being very diluted, at least according to the analytical chemists.

11.7 Relations Between Activity Coefficients of the Same Solute, the "Concentrations" of Which Are Expressed According to the Different Scales of Concentrations

It is the matter of this paragraph to set up the relations between the activity coefficients of a solute in the same thermodynamic state when its concentrations are related to the scales of molar fractions, molalities, and molarities.

For one solution of molality m_2, the number of moles of solute is m_2 and the number of moles of solvent is $1000/M_1$, M_1 being the molar mass of the latter. The factor 1000 comes from the fact that M_1 is expressed in g mol^{-1}, whereas the molality is expressed in mol kg^{-1}. As a result, a first expression of the molar fraction of the solute x_2 is

$$\begin{aligned} x_2 &= m_2/(m_2 + 1000/M_1) \\ x_2 &= m_2M_1/(m_2M_1 + 1000) \end{aligned} \tag{11.5}$$

For a solution of molarity c_2, the number of moles of solute is c_2. The number of moles of the solvent is $(1000\rho - c_2M_2)/M_1$. M_2 is the molar mass of the solute and ρ is the density of the solution. 1000ρ is the mass of 1 L of solution whereas c_2M_2 is the mass of the solute it contains. The molar fraction as a function of the molarity is given by the expression

$$x_2 = c_2/[c_2 + (1000\rho - c_2M_2)/M_1]$$

or equivalently by

$$x_2 = c_2M_1/[c_2(M_1 - M_2) + 1000\rho] \tag{11.6}$$

From (11.5) and (11.6), we obtain

$$x_2 = m_2M_1/(m_2M_1 + 1000) = C_2M_1/[C_2(M_1 - M_2) + 1000\rho] \tag{11.7}$$

For a very dilute solution for which we symbolize the molality by m_2*, the molarity by c_2*, and the molar fraction by x_2*, the density becomes that of the pure solvent, that is to say, $\rho°$. Equation (11.7) changes and becomes

$$x_2{}^* = m_2{}^*M_1/1000 = c_2{}^*M_1/1000\rho° \tag{11.8}$$

The difference in the chemical potential of the solute in the solution where its concentrations are x_2, m_2, and c_2 and in that where they are x_2*, m_2*, and c_2* is given by the ratio of the activities in both states, that is to say, by a_2/a_2* (viz. Chap. 10). The activities in the less dilute state are, respectively, $x_2\gamma_x$, $m_2\gamma_m$, and $c_2\gamma_c$. In the dilute state, we know that with the chosen standard states, the activities are equal to the concentrations expressed according to their scale of concentrations. As a result, given the physical meaning of the ratio of two activities which corresponds to the change in the Gibbs energy accompanying the path from a state to another (viz. Chap. 10) which is the same whatever the scale of "concentration," we can write

$$x_2\gamma_x/x_2{}^* = m_2\gamma_m/m_2{}^* = c_2\gamma_c/c_2{}^* \tag{11.9}$$

By using relations (11.7) and (11.8), relation (11.9) leads to

$$\gamma_x = \gamma_m(1 + 0.001m_2M_1) = \gamma_c[\rho + 0.001c_2(M_1 - M_2)]/\rho° \tag{11.10}$$

The relation (11.10) is those we search for. In sufficiently dilute, when the values c_2 and m_2 are weaker than 0.1 and 0.1 mol kg^{-1}, the values of the three activity coefficients are quasi-identical. Handling in the same manner (as just previously) the relation (11.10) by taking into account relations (11.7) and (11.8), we obtain

$$\gamma_m = \gamma_c\,(\rho - 0.001c_2M_2)/\rho° \tag{11.11}$$

This relation is useful from the practical standpoint since it permits the passing from the activities based on the scale of molalities to that based on the scale of molarities and inversely.

When all is said and done, we observe that if it is an indisputable fact that for the same thermodynamic state the activity of a species does vary with the adopted scale of "concentrations," it appears that it is essentially due to changes in the values of the "concentrations" themselves rather than changes in the values of activity coefficients, as it is demonstrated just above.

In relation with this point, let us recall that in physical chemistry it is the scale of molalities which is generally used whereas in analytical chemistry, it is that of molarities.

11.8 Dependence of the Activity Coefficients on Temperature and Pressure

It is interesting to know the changes of the activity coefficients with temperature and pressure, whatever the scale of the “concentration” to which the activity is related to.

11.8.1 With the Temperature

- Concerning the scale of molar fractions:

$$a_x = \gamma_x x$$

whence, since x does not change with the temperature (x and T are independent variables),

$$(\partial \ln a_x/\partial T)_{P,x} = (\partial \ln \gamma_x/\partial T)_{P,x}$$

According to relation (9.15) (viz. Chap. 9)

$$(\partial \ln a/\partial T)_{P,x} = \left(H_m{}^\circ - \overline{H_m}\right)/RT^2$$

As a result

$$(\partial \ln \gamma_x/\partial T)_{P,x} = \left(H_m{}^\circ - \overline{H_m}\right)/RT^2 \qquad (11.12)$$

- It is the same for the scale of molalities, since the molality does not change with the temperature. We find

$$(\partial \ln \gamma_m/\partial T)_{P,x} = \left(H_m{}^\circ - \overline{H_m}\right)/RT^2$$

- Concerning now the scale of molarities, the demonstration is not the same since the molarity of a species changes with the temperature since the volume of the solution, that is to say, its density, changes with the temperature. In order to set up the change in the coefficient γ_c with the temperature, let us consider relation (11.11):

$$\gamma_c = \gamma_m \rho^\circ / (\rho - \ 0.001 c_2 M_2)$$

Neglecting the term $0.001c_2M_2$ with respect to the density ρ of the solution (this is a reasonable approximation), we obtain

$$\gamma_c \ = \ \gamma_m \rho^\circ / \rho$$

whence

$$(\partial \ln \gamma_c / \partial T)_{P,x} \ = \ \left(H_m{}^\circ - \overline{H_m}\right)/RT^2 \ + [\partial \ln(\rho^\circ/\rho)/\partial T]_{P,x}$$

11.8.2 With the Pressure

In Chap. 9 (relation (9.11)), we have set up the relation which gives the change of the activity of a species with the pressure at constant temperature and molar fraction:

$$(\partial \ln a / \partial \mathbf{p})_{T,x} \ = \left(\overline{V_m}\right)/RT$$

where $\overline{V_m}$ is the molar partial volume of the species. Since

$$a_\mathrm{m} \ = m \gamma_\mathrm{m}$$

as a result

$$(\partial \ln \gamma_\mathrm{m} / \partial \mathbf{p})_{T,x} = \left(\overline{V_m}\right)/RT$$

Remark:

It is an experimental fact that the activity coefficients of nonelectrolytes also vary with the charge of the ions in solution and, particularly, with what is called the *ionic strength* of the solution. This point will be studied in Chap. 16.

Chapter 12
Activities of Electrolytes

Abstract The consideration of the solutions of electrolytes by using the notion of activity is that which, very highly, has been the matter of the largest number of studies, in any case in the realm of the study of activities. The handling of the activities is quasi-imperative as soon as one is faced with solutions of electrolytes since, among all the solutions, the latter are those which exhibit the most strong nonideality effects. This is due to the charges brought by ions. For example, even when the "concentrations" of electrolytes are weak, equilibria constants in which ions intervene are not constant, on the contrary to the solutions of nonelectrolytes. Then, it is imperative to work with very weak "concentrations" so that these constants can be considered as being constant.

Therefore, as soon as a solution does contain ions, the chemical potentials of the different solutes must be the matter of supplementary theoretical and practical considerations with respect to the solutions of nonelectrolytes. One is induced, indeed, not only to define the activity and the activity coefficient of the whole electrolyte but also for the ions coming from its dissociation.

The chapter is focused on the setting up of relations linking all these kinds of activities. However these relations are fundamentally the same in the cases of strong and weak electrolytes. Actually, it is clearer to successively treat both kinds rather than to do that simultaneously. The study shows that a parameter of great importance is the electric charge of the different intervening ions.

Keywords Activity of strong electrolytes/univalent and multivalent • Activity of an ion • Non-dissociated part of a weak electrolyte

The consideration of the solutions of electrolytes by using the notion of activity is that which, very highly, has been the matter of the largest number of studies, in any case in the realm of the study of activities. The handling of the activities is quasi-imperative as soon as we are faced with solutions of electrolytes since, among all the solutions, the latter are those which exhibit the most strong nonideality effects. This is due to the charges brought by the ions. For example, even when their "concentrations" are weak, equilibria constants in which ions intervene are not constant, on the contrary to the solutions of nonelectrolytes. It is, therefore, imperative to work with very weak "concentrations" so that these constants remain constant.

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Actually, as soon as a solution does contain ions, the chemical potentials of the different solutes must be the matter of supplementary theoretical and practical considerations with respect to the solutions of nonelectrolytes. One is induced, indeed, not only to define the activity and the activity coefficient of the whole electrolyte but also for the ions coming from their dissociation.

To define these notions, we focus ourselves on setting up relations linking all these kinds of activities. Although these relations are fundamentally the same in the cases of strong and weak electrolytes, it appears that it is clearer to successively treat the two kinds rather than to do that simultaneously.

12.1 General Considerations

- Given the electrolyte of general formula $M_{\nu+}A_{\nu-}$, it ionizes in solution according to the equilibrium

  $$M_{\nu+}A_{\nu-} \rightleftharpoons \nu_+M^{z+} + \nu_-A^{z-} \tag{12.1}$$

  z_+ and z_- are the charges of the ions (z_+ and z_- are not necessarily equal in absolute values) and ν_+ and ν_- the stoichiometric coefficients. The ionization is total in the case of strong electrolytes. We shall study the notion of activity in the case of:

  - The electrolyte taken as a whole. It is the species $M_{\nu+}A_{\nu-}$.
  - Its ions M^{z+} and A^{z-}.

- As in the case of the nonelectrolytes, the activity of every species (whatever it is the electrolyte or one of its ions) is defined as being equal to the ratio of its fugacities f in the studied solution and $f°$ in the standard state, that is to say,

  $$a = f/f° \tag{12.2}$$

In the literature, in a quasi-systematic manner, the activity a of the different species of concern is chosen in such a way that its value tends toward the one of its concentration m expressed in molality or in molarity at infinite dilution, whether the electrolyte is strong or weak. Let us recall that in the standard state, not only the fugacity of the species is $f°$, but its activity is also equal to unity by definition. Let us also recall that in the standard state the properties of the species are the same as in infinite dilution. (These definitions do not differ from those applying to nonelectrolytes.) Hence, the previous considerations can be summarized by the following symbolism:

$$a/m \rightarrow 1 \quad \text{when} \quad m \rightarrow 0$$

The origin of this choice is from practical origin. The solubility of the electrolyte in the solvent may be, indeed, limited, and, of course, it is only with a weak dilution that it is possible to have experimental data on their fugacities (vapor pressures) in solution. (It must be well understood, however, that their "concentrations" may also be expressed in molar fractions, in molarities, or in molalities as well.) It is of a quasi-general use in physical and analytical chemistry to, respectively, choose the molalities and the molarities, the molalities presenting the advantage to be nonsensitive to the temperature. Let us remark that for the same "composition" in solute, the numerical values of the molar fractions are weaker, than those of the molalities and molarities, whence there is the preferential use of the two latter since they permit to gain a better precision on the drawing of the Henry's line. Here, we only consider the "concentrations" of the different species expressed in molalities m. The reasonings, obtained then, can also be applied without any difficulty to the other scales of "concentrations."

Hence, given these considerations, it appears that the strategy which must be followed in order to define the activity of a strong electrolyte and consequently in order to choose its standard state seems to be, as a rule, quite similar to that followed in the case of a solute nonelectrolyte. Hence, it would be sufficient to draw the Henry's line, that is to say, to draw the diagram fugacity (vapor pressure) of the species as a function for example of its molality, to prolong until the value unity of the molality and, hence, to determine its fugacity in the standard state and to obtain the activity for each point. Unfortunately, there exists a major difficulty in applying such a strategy as soon as there is dissociation. It is the following one: the fugacity of the electrolyte tends toward 0 when the molality tends toward 0, and that *with a null slope (viz. Fig. 12.1 which shows the case of hydrochloric acid).*

Hence, with the electrolytes, it is impossible to proceed as with the nonelectrolytes.

Fig. 12.1 Diagram of the relative fugacity (activity) of one electrolyte (hydrochloric acid) as a function of its molality. Curve calculated by I.M. Klotz from data cited by G.N. Lewis and M. Randall (*According to I.M. Klotz, Chemical thermodynamics, basic theory and* ***methods****, Ed W.A. Benjamin, Inc., New York, 1964 and G.N. Lewis and M. Randall in "Thermodynamics and the free energy of chemical substances," Ed McGraw-Hill Book Company, Inc, New York and London, 1923*)

12.2 Activity of a Strong Electrolyte

In this case, reaction (12.1) goes to completion when it occurs from the left to the right.

12.2.1 *Case of the Univalent Electrolytes*

- Choice of the standard state
  It is an experimental fact that in the case of a univalent strong electrolyte MA, the diagram of its fugacity as a function of the square of its molality shows a line of finite slope when its molality tends toward 0 (Fig. 12.2).

  A good example is provided by a solution of hydrochloric gas in water. Hence, according to experimental data, we can set up the following relation:

$$f_2 = k_H m^2 \ \text{when} \ m^2 \rightarrow 0 \tag{12.3}$$

  where f_2 is the fugacity of the whole electrolyte and m its molality.

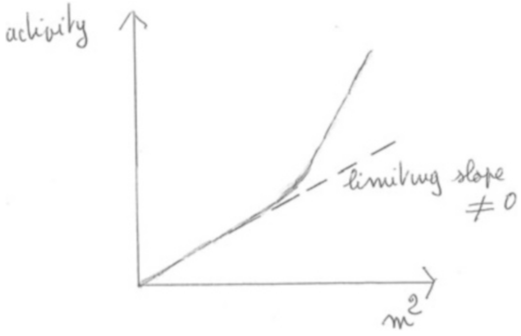
  k_H is the proportionality constant of Henry's line. Since k_H possesses a finite value, it is convenient to choose the standard state in such a manner that the ratio of the activity of the (whole) electrolyte a_2 and of the square of molality m^2 tends toward 1 when m tends toward 0, that is to say,

$$a_2/m^2 \rightarrow 1 \ \text{when} \ m \rightarrow 0 \tag{12.4}$$

The activity a_2 remaining is defined by the general expression

$$a_2 = f_2/f_2{}^{\circ} \tag{12.5}$$

Fig. 12.2 Fugacity of an univalent electrolyte as a function of the square of its molality (same comments as for Fig. 12.1)



where $f_2°$ is the fugacity of the whole electrolyte in the standard state. The expressions (12.3), (12.4), and (12.5) must be simultaneously verified. A very simple reasoning, starting from the last relations, shows that it is the case when

$$f_2{}^{\circ} = k_{\mathrm{H}} \tag{12.6}$$

The fugacity in the chosen standard state is equal to the constant of Henry's law in numerical values. It is obtained experimentally by extrapolating Henry's line until the value $m^2 = 1$. Hence, the standard state of an electrolyte 1–1 is the hypothetical one which would exhibit the value of the Henry's law constant (at the pressure of 1 atm and at the temperature of the system) for the value of its fugacity. The chemical potential μ_2 of the whole electrolyte is given by the expression

$$\mu_2 = \mu_2{}^{\circ} + RT\ln a_2 \tag{12.7}$$

- Activity coefficient:
  We can define the activity coefficient γ_2 of the whole electrolyte through the relation

$$a_2 = \gamma_2 m_2 \tag{12.8}$$

The comparison of this relation with the equalities (12.4) and (12.6) shows that, in the standard state and also in very dilute solutions, $\gamma_2 \to 1$.

12.2.2 Case of the Multivalent Electrolytes

- Choice of the standard states:
  Whatever the kind of electrolyte is, the most convenient standard state is that the choice of which has the consequence that the ratio of the activity a_2 of the electrolyte and its concentration tends toward 1 (in numerical value) when the molality tends toward 0.
  - In the case of a symmetrical electrolyte (in which the ions constituting it bring the same charge in absolute value), the fugacity of the electrolyte in the standard state is equal to the slope of Henry's line:

$$f_2{}^{\circ} = k_{\mathrm{H}}$$

Henry's line is drawn by writing the fugacity of the electrolyte as a function of the square of its molality m^2 (viz. the case of $MgSO_4$ in Table 12.1). The reasoning behind this choice is strictly the same as that followed in the case of the univalent electrolyte.

Table 12.1 Equations of Henry's lines according to the kind of electrolyte

	NaCl	$MgSO_4$	Na_2SO_4	$AlCl_3$	$M_{\nu+}A_{\nu-}$
$f_2=$	k_Hm^2	k_Hm^2	k_Hm^3	k_Hm^4	$k_Hm^{(\nu++\nu-)}$

- In the case of the dissymmetrical multivalent electrolytes, it turns out that, according to their kind, the experimental Henry's lines have the expressions mentioned in Table 12.1 for mathematical equations.

  In the same line of view as previously, it seems, at first sight, that one must choose the standard states in which the fugacity $f_2°$ does possess the value of the Henry's law constant k_H, obtained by extrapolation of its line until the value $m^n = 1$ where n would be equal to 1, 2, 3,…($\nu_+ + \nu_-$) according to the stoichiometry of the electrolyte.

  Actually, there is a choice which proves to be more interesting than the preceding one. It takes into account the fact that the concentrations of the ions coming from the dissociation of these electrolytes are no longer equal (viz. paragraph 3).

- Activity coefficient:

  As usual, the activity coefficient of the solute γ_2 is defined by the expression (12.9), formally identical to (12.8):

$$\gamma_2 = a_2/\, m_2 \tag{12.9}$$

It tends toward 1 when m_2 tends toward 0. It is equal, of course, to 1 in the standard state corresponding to the electrolyte.

12.3 Activity of Ions Resulting from the Dissociation of Strong Electrolytes

We name strong electrolytes those which are fully dissociated. Others are named weak electrolytes.

Until now, we did not take into account the dissociation of the electrolyte. However, we were able to set up thermodynamic relations concerning the behavior of the latter without having to take into account its dissociation. This lack of taking into account is not at all surprising since the very structure of classical thermodynamics is independent of the notions of atoms or molecules. However, the dissociation is an experimental fact, the occurrence of which suffers no doubt. Hence, it appeared interesting to give a thermodynamic framework to the ionic theory, given its great importance.

Given the fact that classical thermodynamics do not take into account the phenomenon of dissociation in its foundations, we can, already, forecast that a thermodynamic theory of it must stem from some arbitrary choices.

12.3.1 Monovalent Electrolyte MA

By hypothesis, the electrolyte is fully dissociated. As a result, naming m_+ and m_- the molalities of the ions M^+ and A^-, the following equalities are satisfied:

$$m_+ = m \text{ and } m_- = m$$

Since for the dilute solutions, the fugacity of the electrolyte MA is proportional to the square of its molality (Henry's line), that is to say,

$$f_2 = k_\mathrm{H} m^2$$

According to what is preceding, we can set up the equivalent relation

$$f_2 = k_\mathrm{H}(m_+)(m_-) \tag{12.10}$$

In other words, it is logical to relate the fact that the fugacity of the electrolyte is proportional to the square of its molality in dilute solution to its dissociation in two ions, in the occurrence of same "concentrations."

- Chemical potentials and activities of the ions:
  Since the existence of the ions is an unquestionable reality, it appeared interesting to assign a proper chemical potential and a proper activity to every one. Let μ_+, a_+ and μ_-, a_- be the symbols of these individual quantities. In the same spirit as what is preceding, the activities of the ions are defined in such a manner that they approach their molality at infinite dilution, in absolute values, that is to say,

$$a_+/m_+ \to 1 \text{ and } a_+/\,m \to 1 \text{ when } m \to 0 \tag{12.11}$$

Concerning the definition of the chemical potentials of the ions, one sets up

$$\mu_+ = \mu_+{}^\circ + RT \ln a_+ \text{ and } \mu_- = \mu_-{}^\circ + RT \ln a_- \tag{12.12}$$

A first choice, which is arbitrary but intuitive, consists in laying down the chemical potential μ_2 of the whole electrolyte as being equal to the sum of the chemical potentials of both ions, that is to say,

$$\mu_2 = \mu_+ + \mu_- \tag{12.13}$$

Let us compare the expression (12.7) and the expression (12.14) just under (the latter resulting from (12.12) and (12.13))

$$\begin{aligned} \mu_2 &= \mu_2{}^\circ + RT \ln a_2 \\ \mu_2 &= \mu_+{}^\circ + \mu_-{}^\circ + RT \ln (a_+)(a_-) \end{aligned} \tag{12.14}$$

It is evident that a second arbitrary choice, consistent with the first one, consists in setting up

$$\mu_2{}^\circ = \mu_+{}^\circ + \mu_-{}^\circ \tag{12.15}$$

The result is the equality

$$a_2 = (a_+)(a_-) \tag{12.16}$$

One may remark that it is possible to recover the relation (12.16) according to another reasoning starting from the definitions (12.11). At infinite dilution, indeed, starting from the latter ones, we can write

$$a_+ = m_+ \quad \text{and} \quad a_- = m_- \quad \text{(numerical values)}$$

and according to (12.10)

$$f_2 = k_\text{H}(a_+)(a_-)$$

Moreover, by definition

$$a_2 = f_2/f_2{}^\circ$$

and with the standard state chosen for the electrolyte

$$a_2 = f_2/k_\text{H}$$

whence relation (12.16) is derived. This reasoning demonstrates that choosing the standard states such as the activity values that are equal to the concentrations in dilute solutions permits to automatically set up relation (12.15).

Relation (12.16) is often used in order to calculate the activity of an electrolyte by starting from the activities of its ions. We shall see (viz. considerations under) that these relations can be generalized to all types of electrolytes, including the weak ones.

- Activity coefficients of ions stemming from the dissociation of strong electrolytes:

  The introduction of the activity of ions induces the notion of the activity coefficient of an ion. By analogy with other systems and in consistency with the definitions of the activities of ions usually adopted, the activity coefficients of ions are defined so that they obey the following relation, such as for a binary electrolyte, through

$$\gamma_{m_+} = a_+/m_+ \ \text{and} \ \gamma_{m-} = a_-/m_- \tag{12.17}$$

Given the adopted definitions of the activities, it is evident that γ_+ and γ_- tend toward unity at infinite dilution:

$$\gamma_{m_+} \rightarrow 1 \quad \text{when} \quad m \rightarrow 0$$
$$\gamma_{m_-} \rightarrow 1 \quad \text{when} \quad m \rightarrow 0$$

γ_{m_+} and γ_{m_-} are the activity coefficients on the scale of molalities. If the activities had been related to the molarities or to molar fractions, the symbols of the coefficients would have been γ_{c_+}, γ_{c_-} or γ_{x_+}, γ_{x_-} and their values different. (The coefficients γ_m, γ_c, and γ_x are sometimes named molal, molar, and rational coefficients.[1])

The activity coefficients of the ions as others are dimensionless numbers. From a rigorous mathematical standpoint, relations (12.17) are incomplete. They should be written as

$$\gamma_{m_+} = a_+/(m_+/m^\circ{}_+) \quad \text{and} \quad \gamma_{m_-} = a_-/(m_-/m^\circ{}_-)$$

where $m^\circ{}_+$ and $m^\circ{}_-$ are the molalities in the standard states, for example 1 mol L^{-1}.

It is of utmost importance to already notice that the activities of the ions and their coefficients cannot be determined experimentally. This is due to the fact that an ion cannot be alone in a solution. It must be obligatorily accompanied by a counterion in order that the electrical neutrality of the solution should be satisfied. The result is, actually, that every experimental information coming from the solution is only an emanation from the whole electrolyte and not from the only ion under study. However, their values can be approached, at least in some conditions, by calculations, for example through the use of Debye–Hückel's equations (viz. Chap. 15).

- Mean activity coefficient:

  This is the reason why the notion of mean activity coefficient $\gamma_\pm$ of an electrolyte has been introduced. It is experimentally accessible. This is not a surprise since it takes into account the occurrence of both ions of opposed charges. It is defined as being the geometrical mean of the coefficients of the ions. In the case of an univalent electrolyte, it is given by the expression

$$\gamma_\pm = \left(\gamma_+\gamma_-\right)^{1/2}$$

or

$$\gamma_\pm = [(a_+/m_+)(a_-/m_-)]^{½}$$

and according to (12.16)

$$\gamma_\pm = (a_2)^{1/2}/m$$

---

[1] In the following pages of this chapter, we use the lightened symbols γ_+ (and γ_-) for the scale of molalities.

Defining meaning activity $a_{\pm}$ by the relation

$$a_{\pm} = [(a_{+})(a_{-})]^{1/2}$$

we obtain the relation

$$\gamma_{\pm} = a_{\pm}/m \tag{12.18}$$

It is clear that

$$a_{\pm} = (a_2)^{1/2}$$

We notice, according to relation (12.18), that by introducing the mean activity coefficients and the mean activities, one obtains a relation between them which is of the same type as that which is obtained with a non-dissociated derivative.

- On the physical meaning of the chemical potential of an ion:
For some authors, the chemical potential of an ion is nothing else than a fiction. The argument is the following one. Let us, again, consider the case of a strong univalent electrolyte MA. By the general definition of a chemical potential

$$\mu_{+} = (\partial G/\partial m_{\mathrm{M}})_{T,P,\ n1,mA}$$
$$\mu_{-} = (\partial G/\partial m_{\mathrm{A}})_{T,P,n1,mM}$$

m_{M} and m_{A} are the molalities of the ions M^{+} and A^{-}, and n_1 the number of moles of the solvent. G is the Gibbs energy of the whole system, and T and P are its temperature and pressure. The fictitious aspect comes from the fact that the chemical potential is a partial derivative. For example, the potential μ_{+} is the change in the Gibbs energy of the system dG when the molality of M^{+} is changed by the differential dm_{M}, all the other variables defining the state of the system being constant. In particular, it is the case of the molality of the counterion. Now, from an operational standpoint, it is impossible to add an ion into the system without adding one counterion since the electroneutrality must be verified. Moreover, even admitting that this addition is possible, the simple addition of an electrical charge, alone, would confer a supplementary electrical energy to the system, supplementary energy by far larger than that which is of interest for our purpose concerning the activities. In brief, the notion of the chemical potential of an ion is doubtful.

Some authors somewhat shade the previous reasoning but their conclusion is the same. They consider that since the differential dm_{M} is an infinitely (fixed) weak quantity, as every differential, it is not necessary to add the counterion for the respect of the electroneutrality. But, in this case, the change dG is immensely weak and, hence, is imperceptible and the integration which permits to obtain the change in Gibbs energy is impractical. In other words, the differentiation process permitting the definition of the chemical potential of an ion, even if it is possible, cannot lead to measurable results, but according to this standpoint, it remains conceivable.

12.3.2 Multivalent Ions

- Definitions of the chemical potentials and of the activities of multivalent ions: The chemical potentials and the activities of the ions constituting the corresponding electrolytes are defined as previously.
- Standard states in the case of symmetrical bivalent electrolytes:
  There exist more convenient standard states for dissymmetrical electrolytes than those retained for the symmetric ones.
  - Concerning the symmetrical bivalent electrolytes, for example $MgSO_4$, the reasoning is strictly identical to that followed in the case of monovalent ones. Relations (12.15) and (12.16) apply without any difficulty. As it was mentioned in Table 12.1, the Henry's law line is of the type

$$f_2 = k_{\mathrm{H}} m^2 \ \text{ or } f_2 = k_{\mathrm{H}}(m_+)(m_-)$$

  The standard state quasi-unanimously retained is the hypothetical one, in which the fugacity of the electrolyte is equal to the Henry's constant at the unit pressure and at the temperature of the system. One can verify that, as it is wanted by the formal definition of an activity, its activity in this state is equal to 1 since m_+ and m_- must be equal to the unity in order for $f_2 = k_{\mathrm{H}}$, while the ideal character is satisfied.
- Standard state in the case of multivalent dissymmetric electrolytes:
  Let us consider the case of an electrolyte 2-1 such as sodium sulfate which dissociates in two cations and one anion. By a reasoning identical to that adopted in the case of symmetrical electrolytes, that is to say, by setting up that the chemical potential of the electrolyte is equal to the sum of the chemical potentials of both ions, we obtain the equality

$$\begin{aligned} a_2 &= (a_+)(a_+)(a_-) \\ a_2 &= (a_+)^2(a_-) \end{aligned} \tag{12.19}$$

The demonstration is very simple. The chemical potential $\mu(\mathrm{Na_2SO_4})$ of the electrolyte, taken as a whole, is given by the expression

$$\mu(\mathrm{Na_2SO_4}) = \mu^\circ(\mathrm{Na_2SO_4}) + RT \ln a(\mathrm{Na_2SO_4})$$

The chemical potentials of the ions sodium and sulfate are given by the expressions

$$\mu(\mathrm{Na^+}) = \mu_+{}^\circ + RT \ln a(\mathrm{Na^+})$$
$$\mu\left(\mathrm{SO_4{}^{2-}}\right) = \mu_-{}^\circ + RT \ln a\left(\mathrm{SO_4{}^{2-}}\right)$$

The first possible choice which can be done is to admit the following relation:

$$\mu(\mathrm{Na_2SO_4}) = 2\mu(\mathrm{Na^+}) + 1\mu\left(\mathrm{SO_4{}^{2-}}\right)$$

We obtain relation (12.19), provided that we admit the following equality:

$$\mu^\circ(\mathrm{Na_2SO_4}) = 2\,\mu_+{}^\circ(\mathrm{Na^+}) + 1\,\mu_-{}^\circ\left(\mathrm{SO_4{}^{2-}}\right)] \tag{12.20}$$

It is very interesting to notice that if the standard potentials $\mu_+{}^\circ$ and $\mu_-{}^\circ$ are not endowed with a physical significance, their linear combination above (12.20) *does have*, as it is the case of the combination, $2\,\mu(\mathrm{Na^+}) + 1\mu\left(\mathrm{SO_4{}^{2-}}\right)$.

- Activities and mean activity coefficients:
  The mean ionic activity $a_\pm$ is defined as previously as being the geometrical mean of the individual activities, that is to say,

$$a_\pm = \left[(a_+)^2(a_-)\right]^{1/3} \tag{12.21}$$

or, in principle (viz. relation 12.19),

$$a_\pm = (a_2)^{1/3} \tag{12.22}$$

These two relations lead to an inconsistency.

When the solution is very diluted, it is once more interesting that the value of the activity of each ion would be equal to that of its concentration, that is to say,

$$a_+ = m_+ = 2m \tag{12.23}$$

$$a_- = m_- = m \tag{12.24}$$

where m is the molality of the whole electrolyte. Let us replace a_+ and a_- by their expressions (12.23) and (12.24) into (12.21). We obtain

$$a_\pm = (4)^{1/3}m \tag{12.25}$$

or, in an equivalent way,

$$\begin{aligned} a_2 &= (a_\pm)^3 \\ a_2 &= 4\,m^3 \end{aligned} \tag{12.26}$$

We notice that for the dilute solutions, the mean activity tends no longer toward m but rather toward the factor $(4)^{1/3}m$. In other words

$$\gamma_\pm = a_\pm/m \to (4)^{1/3} \quad \text{when} \quad m \to 0$$

There is no major drawback that it would be the case, but this is not consistent with the case of symmetrical electrolytes. Here is the new fact.

In this context, it is interesting to notice that the fugacity in the standard state, that is to say, the variable defining the value of the activity can still be obtained

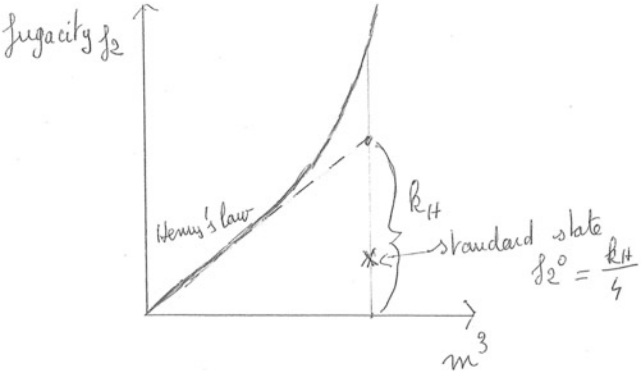


Fig. 12.3 Determination of the standard state for a ternary electrolyte (for example: Na_2SO_4)

exactly as in the case of symmetrical electrolytes, but it leads to a result which is not consistent with relations (12.25) and (12.26). The usual extrapolation process of the Henry's line (in the present case—viz. Table $1 - f_2 = k_H m^3$ of equation so that the value $m = 1$ leads by setting up $f_2{}^\circ = k_H$, to the fact

$$a_2 \rightarrow m^3 \quad \text{when} \quad m \rightarrow 0 \tag{12.27}$$

The only manner to make relations (12.26) and (12.27) self-compatible is to adopt the quantity

$$f_2{}^\circ = k_H/4$$

for the fugacity in the standard state.

Hence, the standard state is the hypothetical state in which the fugacity is equal to the Henry's constant divided by 4 in the present case, at the unit pressure and at the temperature of the system. With this value, the coherence between the mean activity of the ions and the activity of the electrolyte is reached. From the graphical standpoint, it is sufficient to prolong the Henry's straight line until the molality unity and to divide the corresponding ordinate by 4 in order to obtain the standard fugacity (viz. Fig. 12.3).

12.3.3 Generalization to Every Strong Electrolyte

Let us consider the electrolyte $M_{\nu+}A_{\nu-}$ which ionizes by giving ν_+ ions M^{z+} and ν_- ions A^{z-} according to reaction (12.1).

- Its fugacity f_2 in very dilute solution is given by the expression

$$f_2 = km^{(\nu_+ + \nu_-)}$$

or

$$f_2 = km^{\nu}$$

with

$$\nu = (\nu_+ + \nu_-)$$

The individual activities of the ions are related to the activity a_2 of the electrolyte by the relation

$$(a_{\mathrm{M}})^{\nu_+}(a_{\mathrm{A}})^{\nu_-} = a_2 \tag{12.28}$$

It is obtained through the chemical potentials as in the case of the sodium sulfate (viz. above). The chemical potentials of the ions are defined by the expressions

$$\mu(\mathrm{M}^{z+}) = \mu^\circ(\mathrm{M}^{z+}) + RT \ln a(\mathrm{M}^{z+}) \tag{12.29}$$

$$\mu(\mathrm{A}^{z-}) = \mu^\circ(\mathrm{A}^{z-}) + RT \ln a(A^-) \tag{12.30}$$

One arbitrary sets up the two following expressions:

$$\mu^\circ\left(\mathrm{M}_{\nu_+}\mathrm{A}_{\nu_-}\right) = \nu_+\mu_+{}^\circ(\mathrm{M}^{z+}) + \nu_-\mu_-{}^\circ(\mathrm{A}^{z-})$$

and

$$\mu(M_{\nu+}A_{\nu-}) = \nu_+\mu_+(M^{z+}) + \nu_-\mu_-(A^{z-})$$

whence the following is derived:

$$a_2(M_{\nu+}A_{\nu-}) = (a_+)^{\nu+}(a_-)^{\nu-} \tag{12.31}$$

- The mean ionic activity $a_\pm$ is given by the expression

$$a_\pm = \ a_2{}^{1/(\nu_+ \ +\nu_-)} \tag{12.32}$$

or

$$a_\pm = \left[(a_{\mathrm{M}})^{\nu+}(a_{\mathrm{A}})^{\nu-}\right]^{1/\nu}$$

- The mean activity coefficient $\gamma_{\pm}$ is given by the expression

$$\gamma_{\pm} = \left[(\gamma_{+})^{\nu+}(\gamma_{-})^{\nu-}\right]^{1/\nu} \tag{12.33}$$

Given relations (12.31) and (12.33) and since $m_{+} = m\nu_{+}$ and $m_{-} = m\nu_{-}$, we obtain the following relation:

$$ln\, a_{\pm} = \; ln\, m_{\pm} + \; ln \gamma_{\pm} \tag{12.34}$$

$m_{\pm}$ is named the mean molality, defined by the expression

$$m_{\pm} = \left(m_{+}{}^{\nu+} m_{-}{}^{\nu-}\right)^{1/\nu}$$

- The fugacity in the standard state is given by the expression

$$f_2{}^{\circ} = k_{\mathrm{H}} / \left[(\nu_{+}m)^{\nu+}(\nu_{-}m)^{\nu-}\right]$$

12.4 Activities of Weak Electrolytes

In this case, it is necessary to consider the existence of a supplementary species, the non-dissociated form. We shall see that, contrary to what may be perhaps intuitively forecast, the fact that the electrolyte is not fully dissociated does not change the preceding considerations.

- On the one hand the activity a_2 of the electrolyte $\mathrm{M}_{\nu+}\mathrm{A}_{\nu-}$, taken as a whole, is equal to the product of the activities of the ions taken at the power equal to their stoichiometric coefficients. In other words, relation (12.28) is still legitimate:

$$(a_{\mathrm{M}})^{\nu+}(a_{\mathrm{A}})^{\nu-} = a_2 \tag{12.28}$$

- On the other, the activity a_{nd} (nd: non-dissociated) of the non-dissociated fraction is equal to the activity a_2 of the whole electrolyte:

$$a_{\mathrm{nd}} = a_2 \tag{12.35}$$

The demonstration of the result that weak electrolytes obey equation (12.28) is a consequence of the equality (12.35) which, firstly, must be demonstrated.

Let us consider a solution containing the electrolyte $\mathrm{M}_{\nu+}\mathrm{A}_{\nu-}$ as a solute, which partially dissociates according to equilibrium (12.1). Let n_1 be the number of moles of the solvent, n the total number of moles of solute, n_{nd} the number of moles of the non-dissociated solute, n_{+} that of the ions M^{z+}, and n_{-} that of the ions A^{z-}.

Starting from the stoichiometry of the dissociation reaction (12.1), we can draw the following relations:

$$n_+ = \nu_+(n - n_{\mathrm{nd}}) \tag{12.36}$$

$$n_- = \nu_-(n - n_{\mathrm{nd}}) \tag{12.37}$$

An infinitesimal change dG of the Gibbs energy of the solution, at constant pressure and temperature, is given by (viz. Chap. 5)

$$dG = \mu_{\mathrm{nd}} dn_{\mathrm{nd}} + \mu_+ dn_+ + \mu_- dn_- + \mu_1 dn_1 \tag{12.38}$$

According to (12.36) and (12.37)

$$dn_+ = \nu_+ dn - \nu_+ dn_{nd}$$
$$dn- = \nu - dn - \nu - dn_{nd}$$

By replacing dn_+ and dn_- by the last two relations into (12.38), we obtain

$$dG = \left(\mu_{\mathrm{nd}} - \nu_+\mu_+ - \nu_-\mu_-\right)dn_{\mathrm{nd}} + \left(\nu_+\mu_+ + \nu_-\mu_-\right)dn + \mu_1 dn_1 \tag{12.39}$$

The global equilibrium condition is such as

$$dG = 0$$

We immediately notice that in order to be reached, we must simultaneously have the factors of (12.39) involving the differentials d_{nd}, dn, and dn_1 equal to 0.

The numbers of moles n and n_1 may be changed independently from each other. The numbers n_{nd} and n_+ and n_- also, since each position of the dissociation equilibrium is possible. Hence, in order that the equilibrium should be reached in these conditions, we must have:

$$(dG/dn_{\mathrm{nd}})_{T,P,n,n1} = 0$$

The result of this condition is

$$\mu_{\mathrm{nd}} = \nu_+\mu_+ + \nu_-\mu_- \tag{12.40}$$

Equation (12.39) becomes

$$dG = \left(\nu_+\mu_+ + \nu_-\mu_-\right)dn + \mu_1 dn_1 \tag{12.41}$$

Otherwise, at equilibrium

$$(\partial G/\partial n)_{T,P,n1} = 0$$

The partial derivative $(\partial G/\partial n)_{T,P,n1}$ is, by definition, the chemical potential μ of the electrolyte, taken as a whole:

$$(\partial G/\partial n)_{T,P,n1} = \mu \tag{12.42}$$

After comparison of (12.42) and (12.41), since n_1 and n are independent from each other, we obtain

$$\mu = \nu_+\mu_+ + \nu_-\mu_- \tag{12.43}$$

Moreover, the comparison of (12.40) and (12.43) shows that

$$\mu_{\text{nd}} = \mu$$

The chemical potential μ_{nd} of the undissociated electrolyte is equal to the chemical potential of the whole electrolyte.

Let us remark that relation (12.40) is no more nor less than the classical expression of equilibrium of reaction (12.1).

The setting up of relation (12.28) is realized as it follows. The chemical potentials of the ions are defined exactly as in the case of the strong electrolytes (viz. (12.29) and (12.30)). The chemical potential and the standard one of the undissociated electrolyte are those of the electrolyte taken as a whole, as we have just seen. Let us reason with one mole of $M_{\nu+}A_{\nu-}$.

Chapter 13
Determination of the Activity of the Nonelectrolytes

Abstract The most used methods of determination of the activities of the nonelectrolytes are mentioned in this chapter. In addition, they may also be applied to solutions of electrolytes. This aspect will be studied in the next one. At its beginning, the principle of the determination of an activity of one component from that of the other component of a binary solution is recalled. It is founded on the Gibbs–Duhem's relation. The mentioned methods are those based on the determination:

Of vapor pressures
Of the activity of the solvent from the determination of its freezing point
Of the osmotic pressure
Of electromotive forces of suitable electrochemical cells
From gas chromatography
From excess functions and empirical relations

Values of some activities of this kind of solutes are given in this chapter. The very important fact to know is the following one: the determination of the activities of nonelectrolytes is a possible task.

Keywords Henry's law • Gibbs–Duhem relation • Activity of one compound from that of the other • Freezing point depression • Electrochemical cell • Gas chromatography • Excess function

In this chapter, we mention the most used methods of determination of the activities of the nonelectrolytes. In addition, they may also be applied to solutions of electrolytes. This aspect will be studied in the next chapter. After having recalled the principles of these methods, we shall give some results and values of some activities of this kind of solutes.

J.-L. Burgot, *The Notion of Activity in Chemistry*,
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13.1 Activity of One of the Components of a Binary Solution from That of the Other Component

Once the activity of a component of a binary solution, solvent, or solute is determined, it is possible to calculate the activity of the other component starting from the value of the former. The calculation is founded on the Gibbs–Duhem's relation, one form of which is (viz. Chap. 5)

$$x_1 d\mu_1 + x_2 d\mu_2 = 0$$

Given the definition of an activity from the chemical potential

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

the Gibbs–Duhem's relation becomes

$$x_1 d\ln a_1 + a_2 d \ln a_2 = 0 \tag{13.1}$$

This expression is applicable at constant pressure and temperature whatever the adopted standard states since the chemical potential of a species in a given state is constant for a given temperature. The rearranged relation (13.1) is

$$d\ln a_1 = -(x_2/x_1) d \ln a_2 \tag{13.2}$$

$$d\ln a_2 = -(x_1/x_2) d \ln a_1 \tag{13.3}$$

13.1.1 Activity of the Solvent from That of the Solute

The integration of relation (13.2) gives

$$\ln\left(a_1/a_1'\right) = -\int_{x_2'}^{x_2} (x_2/x_1) d \ln a_2 \tag{13.4}$$

a_1 and $a_1^{'}$ are the activities of the solvent in the two solutions where the molar fractions of the solute are x_2 and $x_2^{'}$. The ratio $a_1/a_1^{'}$ is calculated by drawing the curve (x_2/x_1) in ordinates as a function of the values ln a_2 in abscissas and by determining the area under the curve between the limits $x_2^{'}$ and x_2.

Actually, this process is poorly convenient from the standpoint of the precision of the results. since, when the solution is very dilute, ln a_2 exhibits very large negative values and, as a result, the evaluation of the area under the curve is not precise. It is based on expression (13.5) below, similar to (13.4). An interesting variant of this integration process has been proposed.

It involves the activity coefficients rather than the activities themselves. Its principle stems from the following reasoning. For a binary solution:

$$x_1 + x_2 = 1$$

$$dx_1 + dx_2 = 0$$

$$x_1(dx_1/x_1) + x_2\left(dx_{2/}x_2\right) = 0$$

$$x_1 d\ln x_1 + x_2 d\ln x_2 = 0$$

Subtracting this expression from (13.1), we obtain

$$d\ln(a_1/x_1) = -(x_2/x_1)d\ln(a_1/x_2)$$

and after integration

$$\ln(a_1/x_1) - \ln\left(a_1'/x_1'\right) = -\int_{x1}^{x2} (x_2/x_1)d\ln(a_2/x_2) \tag{13.5}$$

This relation can be simplified. At infinite dilution, $x_1^{'} = 1$ and $x_2^{'} = 0$; the activity $a_1^{'}$ of the solvent is equal to unity because of the choice of the standard state usually done (the unity of "concentration" is the molar fraction). The second term of the left member vanishes and we obtain

$$\ln(a_1/x_1) = -\int_0^{x2} (x_2/x_1)d\ln(a_2/x_2) \tag{13.6}$$

The area under the curve limited by the values $x_2 = 0$ and x_2 gives the value $\ln\gamma_1$ at the concentration x_2.

As examples, Table 13.1 provides the necessary experimental data in order to calculate the activity of mercury in the case of the amalgam of thallium at 20 °C. They are stemming from the electromotive force of appropriate electrochemical cells (viz. paragraph 5). In this table, x_2 is the molar fraction of thallium, a_2 its activity, and a_1 the activity of mercury being searched for.

Table 13.1 Activity coefficients of mercury in some amalgams by applying relation (13.6) (According to G.N. Lewis and M. Randall: Thermodynamics and the free energy of chemical substances: McGraw-Hill company, Inc, New York, 1923)

x_2	x_2/x_1	a_2/x_2	a_1/x_1
0	0	1	1
0.005	0.00502	1.06	0.9998
0.01	0.0101	1.15	0.999
0.05	0.0526	1.80	0.986
0.1	0.111	2.84	0.950
0.2	0.250	4.98	0.866
0.3	0.428	6.60	0.790
0.4	0.667	7.57	0.734
0.5	1.000	7.98	0.704

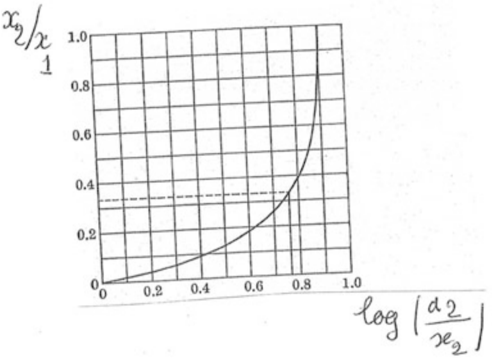

Fig. 13.1 Example of curve $(x_2/x_1)/\log(a_2/x_2)$ permitting the obtention of the activity of the solvent as the function of that of the solute (case of thallium amalgams) (viz. Table 13.1 and paragraph 5)

Figure 13.1 shows the corresponding curve $(x_2/x_1)/\log(a_2/x_2)$, the appropriate area determination of which permitting the calculation of the activity coefficients a_1/x_1.

13.1.2 Activity of the Solute as a Function of That of the Solvent

The determination is based on relation (13.3) or on the following one:

$$d\ln(a_2/x_2) = -(x_1/x_2)d\ln(a_1/x_1)$$

or

$$\ln(a_2/x_2) = -\int_0^{x_2}(x_1/x_2)d\ln(a_1/x_1) \tag{13.7}$$

Table 13.2 mentions the experimental data necessary to calculate the activity of thallium from the activity values a_1 of mercury in a thallium amalgam, through relation (13.7) (determination at 325 °C).

The curve $(x_1/x_2)/\log(a_1/x_1)$ built with the values of Table 13.2 is presented in Fig. 13.2. (The indexes 1 and 2 remain affected, respectively, to mercury and thallium.)

Actually, the graphical integration of (13.7) is difficult since for the solutions very dilute (in solute), the ratio x_1/x_2 tends toward infinite. Hence, this process entails to possess very precise data at high dilutions. (Among others, there exists a means to overcome this problem by a process of graphical extrapolation. Another consists in carrying out a fit of an algebraic function on some experimental points which are not endowed with a great imprecision.)

Table 13.2 Activity coefficients of mercury in some amalgams by applying relation (13.7) (According to G.N. Lewis and M. Randall: Thermodynamics and the free energy of chemical substances: McGraw-Hill Company, Inc, New York, 1923)

x_2	$\frac{a_1}{x_1}$	$\frac{a_2}{x_2}$
0	1	1
0.10	0.98	1.53
0.20	0.95	1.86
0.30	0.92	2.05
0.40	0.80	2.17
0.50	0.87	2.23
0.60	0.85	2.28
0.70	0.83	2.30
0.80	0.82	2.31
(1.00)	(0.80)	(2.32)

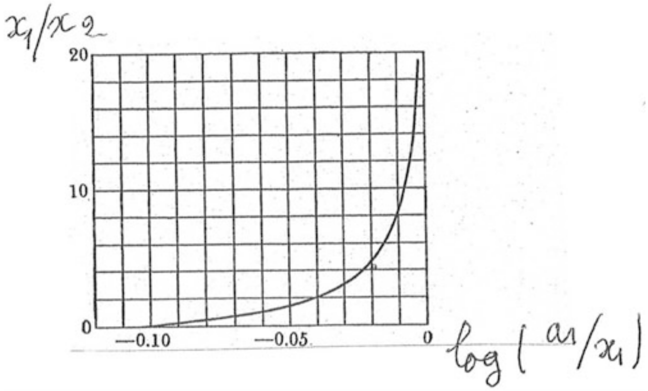

Fig. 13.2 Example of curve $x_1/x_2/\log(a_1/x_1)$ permitting the calculation of the thallium activity in some amalgams

13.2 Determination by Measurements of Vapor Pressures

Given the fact that the activity of every component of a solution is equal to the ratio of its fugacity in the studied state and of its fugacity in the standard state and given the links existing between the fugacity and the vapor pressure, it is intuitive that measurements of partial pressure vapors may permit to approach the values of the activities. The first condition is that the partial pressure vapor must be sufficiently large in order to be measurable. However, it must not be too large in order to be assimilated to its fugacity. That is to say, its partial pressure must obey the perfect gas law. In these conditions

$$a = f/f^\circ$$

$$a \approx p/p^\circ$$

According to these considerations, we can determine the activity either of the solvent or of the solute.

13.2.1 Activity of the Solvent $\mathbf{a}_1$

The method of determination is based on the relation

$$a_1 \approx p_1/p_1{}^{\circ}$$

p_1 is the vapor pressure of the solvent in equilibrium with the solution where its activity is a_1. $p_1{}^{\bullet}$ is its vapor pressure in the standard state. The effect of the external pressure may be considered as being negligible. Let us recall (viz. Chap. 11) that the standard state of the solvent is unanimously chosen is the pure solvent at the temperature and pressure of the system. Then, we can write

$$a_1 \approx p_1/p_1{}^{\bullet}$$

$p_1{}^{\bullet}$ is the vapor pressure in the pure state at the same temperature and approximately at the same pressure as the solution.

This method of determination of the activities of the solvents has been used for aqueous and organic solutions.

13.2.2 Activity of the Solute $\mathbf{a}_2$

If the solute is sufficiently volatile in such a manner that the determination of its vapor pressure above its solution is possible, its activity can be determined in the same conditions as above through the measurement of its vapor pressure p_2 in the state of the system and in the standard state $p_2{}^{\circ}$ through the relation

$$a_2 = p_2/p_2{}^{\circ}$$

$\mathbf{p}_2{}^{\circ}$ is not, usually, the vapor pressure of the pure solute. $\mathbf{p}_2{}^{\circ}$ is the vapor pressure which would be exhibited by the solute in the hypothetical standard state consisting in a molal solution where it would obey Henry's law. We have seen (viz. Chap. 11) that

$$p_2{}^{\circ} = k_{\mathrm{H}}$$

The fugacity and, hence, the vapor pressure of the solute in the standard state are equal to the constant k_{H} of Henry's law in the conditions mentioned above.

We know that in order to determine the latter, we linearly extrapolate the Henry's law until the molality unity.

From a practical standpoint, it may happen that the value of the vapor pressure appreciably deviates from a line as soon as the molalities are very weak. In this case, we must use another process to determine the constant k_{H}. It is also a graphical one. It consists in drawing the diagram solute pressure p_2 as a function of its

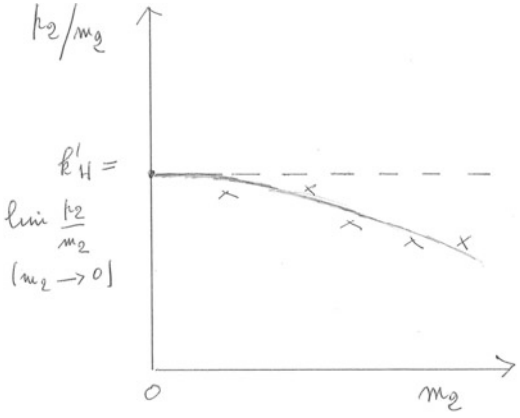

Fig. 13.3 Graphical determination of the partial pressure of the solute in its standard state

molality m_2. The obtained curve is extrapolated until down to the molality m_2 null—Fig. 13.3.

At null molality, the ratio p_2/m_2 is equal to the Henry's constant, that is to say, to the fugacity in the standard state. At null molality, indeed

$$p_2 \rightarrow f_2 \quad \text{and} \quad a_2 \rightarrow m$$

As a result

$$(p_2{}^{\circ}/m)_{m=0} = f_2/a_2$$

and since $a_2 = f_2/f_2{}^{\circ}$

$$(p_2{}^{\circ}/m)_{m=0} = f_2{}^{\circ}$$
$$(p_2{}^{\circ}/m)_{m=0} = k_{\mathrm{H}}$$

Graphical processes may also be used when the "concentration" scales to which are related the activities are those of molarities and of molar fractions. Molalities are simply replaced by the molar fractions and molarities in the drawing of diagrams.

Another approach is possible, but it is more rarely used than the previous one because of the fact that it is only practised when the solvent and the solute are essentially miscible in the whole range of concentrations. Then, for the standard state of the solute, one can choose it in its pure state. Then, we are again in the case in which it remains to determine the activity of the solvent. In this new standard state, the vapor pressure of the solute is roughly equal to its vapor pressure in the pure state. An interesting example of this double possibility of choice of a convenient standard state is provided by the solutions of dibromine in carbon tetrachloride. The diagram of the vapor pressure p_2 of dibromine as a function of its molar fraction is shown in Fig. 13.4.

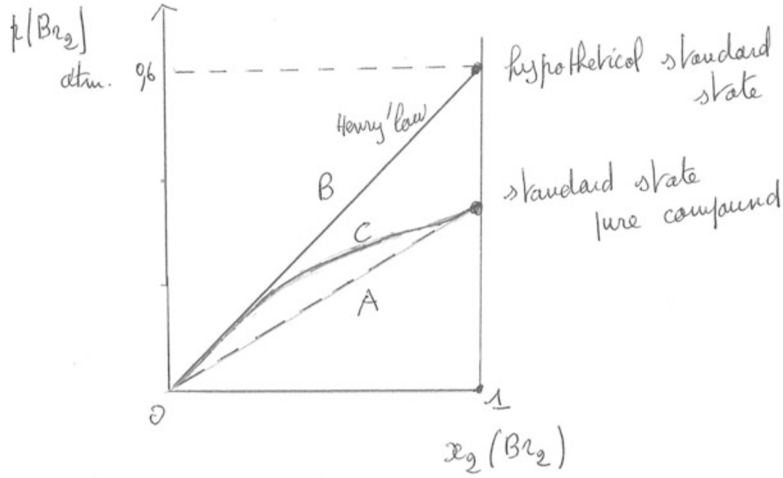

Fig. 13.4 Vapor pressure of dibromine as a function of its molar fraction in a solution of carbon tetrachloride (According to G.N. Lewis and M. Randall: Thermodynamics and the free energy of chemical substances: McGraw-Hill company, Inc, New York, 1923)

The line B is that of Henry. The pressure of bromine in this hypothetical standard state is 0.539 atm. The line A shows the calculated values of the pressure if the solution was perfect, the pure dibromine exhibiting a value of 0.280 atm. Hence, it is the pressure in the real standard state defined as being the pure compound. The curve C is the experimental one. The fugacity of the dibromine at each molar fraction being equal to its vapor pressure p_2 whatever the chosen standard state, it is evident that both activities according to the two standard states ax_2 (Henry) and ax_2 (real) are in the ratio

$$a_{x_2}(\text{Henry})/a_{x2}(\text{real}) = 0.280/0.539$$

This is an excellent illustration of the fact that in the same thermodynamic state, the activity of a compound may exhibit different values according to the adopted standard state.

13.3 Activity of the Solvent from the Determination of Its Freezing Point

This process is very general. Although it is, in principle, a method of determination of the activity of the solvent, it also permits to obtain that of the solute in the case of the binary solution. Then, the activity of the solute is determined through the use of the Gibbs–Duhem's relation once the activity of the solvent is known (viz. paragraph 1 above). In this chapter, essentially we set up a general relation between the solvent activity and the depression of the freezing point. Supplementary precisions will be given in the next chapter devoted to the determination of the activities of electrolytes.

13.3.1 General Considerations

The matter of the whole paragraph is the depression of the freezing point of the solvent of a binary dilute solution. The phenomenon is a consequence of the equilibrium solid–liquid.

When a solid is separating from a binary solution, three cases may exist according to the nature of the solid phase. The latter can be constituted by:

- The pure solute: In this case, the composition of the solution is purely and simply the solubility of the solute at the pressure and temperature of the system.
- The pure solvent: The temperature of the system is then named freezing point of the solvent at the composition and pressure of the system.
- A solid solution of both constituents.

For our purpose, the most interesting point is the second one. This is the reason why we limit our study to it.

From the qualitative standpoint, when a solute is dissolved in a liquid phase, initially pure, the fugacity of the latter is lowered. It becomes weaker than that of the pure solid solvent which was that of the initial pure liquid phase in equilibrium with it. There is a break of the initial liquid–solid equilibrium. In order to recover it, the temperature of the system must decrease. It is the reason why, in this case, the freezing point of the solvent is always lower than the normal freezing point.

13.3.2 Mathematical Expression Linking the Solvent Activity to the Depression of the Freezing Point

In this paragraph, we are seeking for a mathematical expression relating the activity a_1 of the solvent in every solution to the lowering of its freezing point due to the presence of the solute into it. Having this relation in our hands, it is possible to obtain the solvent activity once the freezing point is determined.

In order to set up the relation, one relates the chemical potential μ_s of the solvent in the solid state, at the temperature T, to its activity a_s in the solid pure state through the standard chemical potential $\mu°_1$ of the solvent *in the liquid state*. The relation is

$$\mu_s = \mu_1{}^\circ + RT\ \ln a_s \tag{13.8}$$

Reasoning in such a manner is unusual but is perfectly legitimate, given the arbitrary character of the definition of an activity. As we shall see it immediately, with this choice, the activity of the pure solvent in the solid state is equal to its activity in solution, the latter varying with the temperature:

$$a_s = a_1$$

It is true that this result may appear to be surprising since with the usually chosen standard states, the activity of a pure compound is constant at given temperature and pressure. This is not the case here as we shall see it. This result apparently paradoxical is due to the fact that the fugacity of the solvent is identical (at constant pressure and for a given temperature in both phases (solid pure and solution)). We have already said that this is a condition of equilibrium (viz. Chap. 7). As a result, since the fugacity of the solvent varies with the temperature and with the composition of the solution, the fugacity of the solid also varies. This is the base of the phenomenon.

Concerning, now, the equality of the activities in both phases, it results from the same reasoning. The activity a_s is according to the general definition of an activity:

- For the solid phase (s: solid, l: liquid) $a_s = f_{1(\text{solid})}/f_1{}^\circ{}_{(\text{liq})}$
- For the liquid phase $a_1 = f_{1(\text{liq})}/f_1{}^\circ{}_{(\text{liq})}$

with $f_{1(\text{solid})} = f_{1(\text{liq})}$ (equilibrium). The fugacity $f_1{}^\circ{}_{(\text{liq})}$ is the same in both phases. This is the result of the arbitrary choice of the same standard state. As a result $a_s = a_1$.

13.3.3 Relation Between the Activity of the Solvent and the Temperature of the System

Let us divide the expression (13.8) by T. We obtain

$$R \ln a_s = \mu_s/T - \mu_1{}^\circ/T$$

Now, let us derivate this expression with respect to T at constant pressure. Given the general expression of the partial derivate with respect to T of the ratio μ/T at constant pressure and composition (viz. Chaps. 2, 5 and 9)

$$[\partial(\mu_i, T)/\partial T]_{p,x} = -\overline{H_i}/T^2$$

we obtain

$$(\partial \ln a_s/\partial T)_\text{p} = (H_1{}^\circ - H_s)/RT^2$$

In this expression, the partial molal enthalpies have disappeared because μ_s and $\mu_1{}^\circ$ are related to the pure solvent in the solid and liquid states. Hence, they are replaced by the molal quantities (viz. Chap. 8, paragraph 8). The enthalpy difference $(H_1{}^\circ - H_s)$ is nothing else than the molal fusion heat ΔH_{fusion} of the solvent at the temperature and the pressure of the system:

$$H_1{}^\circ - H_s = \Delta H_{\text{fusion}}$$

in which

$$(\partial \ln a_s / \partial T)_p = \Delta H_{\text{fusion}} / RT^2$$

We have seen that with the chosen standard state, the activity of the pure solvent in the solid state and its activity in solution are equal. As a result

$$(\partial \ln a_1 / \partial T)_p = \Delta H_{\text{fusion}} / RT^2 \tag{13.9}$$

This relation gives the change in the activity of the solvent with the temperature at the freezing point at constant pressure. The change varies with the composition. Hence, the expression relating the activity of the solvent at the freezing point can be obtained by integration of this relation.

The integration of (13.9) is performed in the following way. It entails to know the change in ΔH_{fusion} with the temperature. The Kirchhoff's relation (which relates the heat accompanying a chemical or a physical process at a given temperature to that produced by the same process at another temperature) is written in the present case, since the heat of fusion ΔH_{fusion} is referred at constant pressure:

$$\begin{aligned} [\partial(\Delta H_{\text{fusion}})/\partial T]_P &= (C_P)_1 - (C_P)_s \\ [\partial(\Delta H_{\text{fusion}})/\partial T]_P &= \Delta C_P \end{aligned} \tag{13.10}$$

$(C_P)_1$ and $(C_P)_s$ are the molar calorific capacities at constant pressure of the solvent in the pure liquid state and in the pure solid state. One can admit that, for a break change in temperature, the calorific capacities are constant. Then, the integration of equation (13.10) gives

$$\Delta H_{\text{fusion}} + L_0 + \Delta C_P(T\text{-}T_0) \tag{13.11}$$

L_0 is the integration constant. It is the molar latent heat of fusion at temperature T_0, freezing temperature of the pure solvent.

It is simpler, for the sake of simplification of the calculations, to change the variable in order to continue the mathematical development. We adopt the variable θ such as

$$T_0 - T = \theta$$

θ is the depression of the freezing point. Equation (13.11) becomes

$$\Delta H_{\text{fusion}} = L_0 - \theta \Delta C_P \tag{13.12}$$

The expression which must be integrated is

$$d \ln a_1 = \left[(L_0 - \theta \Delta C_P)/RT^2\right] dT$$

Since $dT = -d\theta$ and $T = T_0 - \theta$, it becomes

$$-d \ln a_1 = \left[(L_0 - \theta \Delta C_P)/R(T_0 - \theta)^2\right] d\theta \tag{13.13}$$

The integration can be performed by developing the term $1/(T_0 - \theta)^2$ according to Newton's binomial. This term can also be written as $1/{T_0}^2(1 - \theta/T_0)^{-2}$, in which

$$1/(T_0 - \theta)^2 = 1/T_0^2\left(1 + 2\theta/T_0 + 3\theta^2/T_0^2 + \cdots\right)$$

Equation (13.13) becomes

$$-d \ln a_1 = 1/RT_0^2[L_0 + (2L_0/T_0 - \Delta Cp)\theta +] d\theta \tag{13.14}$$

The integration is performed in the domain of the values of θ going from 0 until the value of θ, respectively, corresponding to the limits $a_1 = 1$ and a_1. The integration is immediate and gives, after having neglected the terms in θ^3, θ^4, ... since the weak value of θ:

$$-\ln a_1 = L_0\theta/RT_0^2 + \theta^2/RT_0^2(L_0/T_0 - \Delta Cp/2) \tag{13.15}$$

The expression (13.15 permits to determine the activity of the solvent a_1 knowing the depression of the freezing point.

Let us recall that the relation (13.15 gives the activity of the solvent at temperatures which vary with the solute concentration of the solution. It is desirable to transform the results obtained in this way into results at the same temperature. This point is studied in Chap. 14.

Broadly speaking, the depression of the freezing point θ is of the order of the 1/10 °C for solutions, the concentrations in solutes of which are lower than 0.5 mol kg $^{-1}$. (Let us notice that it is relatively easy to measure differences of temperature of the order of 10^{-4} °C between an aqueous solution in equilibrium with ice and pure water.)

13.4 Activity of the Solvent and Osmotic Pressure

In principle, the measurement of the osmotic pressure permits the determination of the activity a_1 of the solvent of a binary solution. It is based on the existence of a relation between the solvent activity and the osmotic pressure.

One knows (viz. Chap. 8) that, in order to recover the initial equilibrium, after the system has given rise to the phenomenon of osmosis, one must apply a supplementary pressure $\pi = P - P_0$, called osmotic pressure, to the solution constituting the system. P is the pressure above the solution before the initial equilibrium has been recovered. P_0 is the pressure above the compartment containing the pure solvent. (Let us recall that the osmotic pressure must be applied at constant temperature and number n_2 of moles of the solute.) Let μ_{01} and μ_1 be the chemical potentials of the pure solvent and of the solution before the initial equilibrium (broken by the addition of the solute) is recovered. After it is the case, the following equality is satisfied:

$$\mu_{01} = \mu_1 + \int_{p_0}^{P} (\partial\mu_1/\partial P)_{T,n2} dp$$

The partial derivative $(\partial\mu_1/\partial P)_{T,n2}$ is equal to the partial molal volume of the solvent in the solution (viz. Chap. 5):

$$(\partial\mu_1/\partial P)_{T,n2} = \overline{V_1}$$

Thus

$$\mu_{01} = \mu_1 + \int_{p_0}^{p} \overline{V_1} dp \tag{13.16}$$

The chemical potentials are related to the fugacities in the pure state $f_1{}^\circ$ and in the solution f_1 at the pressure P_0 by the relations (viz. Chap. 9)

$$\mu_{01} = \mu_1^* + RT \ln f_1{}^\circ \quad \text{and} \quad \mu_1 = \mu_1^* + RT \ln f_1$$

After substitution into (13.16), we obtain

$$RT \ln(f_1{}^\square / f_1) = \int_{p_0}^{p} \overline{V_1}\, dP \tag{13.17}$$

By definition, the inverse of the above ratio of the fugacities is the activity a_1 of the solvent:

$$a_1 = f_1/f_1^{\square}$$

in which

$$-RT \ln a_1 = \int_{p_0}^{p} \overline{V_1}\, dP$$

In order to set up the relation between the activity of the solvent and the osmotic pressure, it remains, evidently, to know the changes of $\overline{V_1}$ with the external pressure. Assuming that they are linear, one can write at every pressure

$$\overline{V_1} = \overline{V_0}\,[1 - \alpha(P - P_0)]$$

where $\overline{V_0}$ is the partial molal volume at the pressure p_0 (1 atm) and α is a constant. Introducing this hypothesis, we obtain

$$-RT \ln a_1 = \overline{V_0}\int_{p_0}^{p} [1 - \alpha(P - P_0)]dP$$

$$-RT \ln a_1 = \overline{V_0}(P - P_0)[1 - (1/2)\alpha(P - P_0)]dP$$

and finally

$$-RT \ln a_1 = \overline{V_0}\,\pi[1 - (1/2)\alpha\pi] \tag{13.18}$$

This is the relation being searched for. In several cases, the partial molal volume $\overline{V_0}$ at pressure P_0 is purely and simply replaced by the molal volume V_0 of the pure solvent in the preceding relation.

In practical use, the process consisting in determining the activity a_1 through the measurement of π is not satisfactory. One of the difficulties it encounters is that it is difficult to have a true semipermeable membrane at our disposal. Another difficulty lies in the knowledge of the change in the partial molal of the solvent with the pressure and the concentration. This is the reason why using the process based on the osmotic coefficients is preferred. Its study is deferred to Chap. 14 since it is overall used to determine the mean ionic activity coefficients.

13.5 Determination of the Activities of Nonelectrolytes by Measurements of the Electromotive Forces

13.5.1 General Considerations

Let us recall that the determination of the activities of nonelectrolytes (and of electrolytes) is possible through the measurements of electromotive forces (emf) of judiciously designed electrochemical cells (viz. Chap. 5). The emf of a cell may depend on the activities of the species participating in the reactions occurring onto the electrodes or on the activities of the species chemically reacting with the preceding ones (viz. Chap. 14). In some galvanic cells, the emf may also depend on the composition of the electrolyte in the cell. Finally, there still exist cells in which the emf only depends on the state of the electrode. It is the case of some concentrations of galvanic cells without a liquid junction (viz. Chap. 14). It is the case of the galvanic cells equipped with electrodes constituted by metallic solutions of changing concentrations such as metallic alloys or amalgams of different compositions. This kind of cell is represented, for example, by

$$\mathrm{Me(Hg)}, x_2'\big|\mathrm{Me\,X}\big|\mathrm{Me(Hg)},\, x_2$$

Both electrodes are amalgams of different concentrations x_2' and x_2 in the metal Me. In these caculations, they dip into the same solution of the electrolyte MeX. The experience shows that an emf creates, the value of which does not depend on the concentration of the electrolyte but depends on the activities of the metal in the amalgams, whence the used process.

13.5.2 Example of the Determination of the Activity of Thallium in an Amalgam

An example of the previous process is provided by the use of the cell, the electrodes of which are constituted by two thallium amalgams of different concentrations. The measurements of the emf in some conditions permit to obtain the activities of thallium (and even of the mercury—viz. above and later in this chapter) in both metallic solutions constituting the electrodes.

Let us consider a galvanic cell, the electrodes of which are thallium amalgams of different molar fractions, x_2 and x_2'. The electrolyte is an aqueous solution of a thallous salt. The cell is represented by the following scheme:

$$\mathrm{Tl}\left(\text{amalgam } x_2'\right)\big|\text{thallous salt}\big|\mathrm{Tl}\,(\text{amalgam } x_2)$$

Both electrochemical reactions are as follows:

- For the electrode on the left (in the occurrence the electrode playing the part of the anode since we are faced with a pile):

$$\mathrm{Tl} \rightleftharpoons \mathrm{Tl}^+ + 1\mathrm{e}^-$$

– For the cathode:

$$\mathrm{Tl^+ + 1e^- \rightleftharpoons Tl}$$

There is no global reaction of cell. The sole net process occurring is the transformation

$$\mathrm{Tl}(\mathrm{amalgame}, x_2') \rightarrow \mathrm{Tl}(\mathrm{amalgame},\ x_2)$$

The difference in Gibbs energy ΔG accompanying the transfer of one mole of thallium from the anode to the cathode is equal to the difference of the chemical potentials μ_2 and μ_2' of thallium in both amalgams, that is to say,

$$\begin{aligned} \Delta G &= \mu_2 - \mu_2' \\ \Delta G &= RT\ \ln(a_2/a_2') \end{aligned} \qquad (13.19)$$

The crossing of one mole of thallium from one electrode to the other involves the crossing of one faraday of electricity. The "increase" of the Gibbs energy of the system ΔG accompanying the transfer is given by the expression

$$\Delta G = -1FE \qquad (13.20)$$

F is the faraday ($1\,F = 96{,}485\ \mathrm{C\ mol^{-1}}$) and E the observed potential difference in the conditions of the determination. 1 is the number of electrons exchanged between the two redox couples intervening in the global (virtual) reaction (of cell). The measurement of E (at null current—viz. Chap. 5) permits to obtain the ratio of activities. The comparison of the expressions (13.19) and (13.20) shows that

$$E = -(RT/F)\ln(a_2/a_2') \qquad (13.21)$$

13.5.3 Determination of the Activity of the Metal in the Amalgam

Actually, the measurement of E also permits to reach the activity of the metal in the amalgam and not only the ratio of both activities, but this is solely possible after the standard state of the metal has been fixed.

For the sake of illustration of the whole previous considerations, the activity of the metal is determined after having chosen two different standard states.

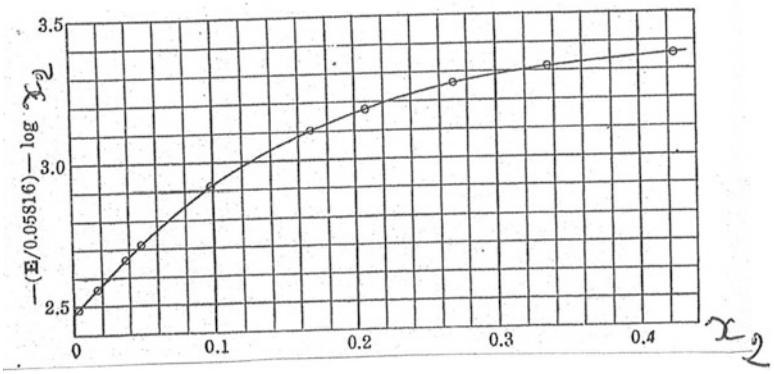

Fig. 13.5 Determination of the activity of thallium in the amalgams at 20 °C and $x'_2 = 0.00326$ *(According to G.N. Lewis and M. Randall: Thermodynamics and the free energy of chemical substances: McGraw-Hill company, Inc, New York, 1923)*

- Let us choose the standard state in such a way that the activity coefficient a_2/x_2 is equal to 1 at infinite dilution.

  Equation (13.21) can be equivalently written as

$$\ln a_2 = -EF/RT + \ln a'_2$$

Let us subtract $\ln x_2$ from the two members of the equality. We obtain

$$\log(a_2/x_2) = (-EF/2.303RT - \log x_2) + \log a'_2 \tag{13.22}$$

In order to apply this relation, one builds a series of cells in which the composition x_2 of the electrode on the right varies, whereas the concentration x'_2 of the electrode on the left is constant. The emf E of the different cells is measured and the different values of the term in the brackets in relation (13.22) are brought on a diagram as a function of the concentration x_2. The curve is shown in Fig. 13.5.

When $x_2 = 0$ (infinite dilution), according to the choice of the standard state, $a_2/x_2 = 1$ $\log(a_2/x_2) = 0$. (*It is at this point that we can recognize that we adopt this standard state*.) The value of the term in brackets is then equal to $-\log a'_2$. It is at the value (2.4689) that the previous curve cuts the ordinates axis. Its corresponds to the value $a'_2 = 0.003396$. Then, one can determine the ratio a_2/x_2 and hence a_2 in each of the amalgams by applying (13.21). The different obtained values are mentioned in Table 13.2.

We notice that as soon as the amalgams are no longer sufficiently dilute, the activities considerably move away from the concentrations x_2 as it is indicated by the values $a_2/x_2 = \gamma_2$. It is understood that the deflection with respect to unity of the coefficient γ_2 quantifies the deviation of the system with respect to Henry' law, given the standard state.

- Let us now choose the pure liquid thallium at 20 °C. In that case, the electrochemical used is symbolized by

$$\text{Tl}\left(\text{pure liquid}, x_2' = 1\right)\left|\text{Thallous salt}\right|\text{Tl}\left(\text{amalgam}, x_2\right)$$

Let us notice that the standard state is already chosen by setting up $x_2' = 1$ in the electrode on the left. Now, the relation (13.21) is

$$E = -(RT/F)\ln(a_2/1) \tag{13.23}$$

The thallium activity in the amalgam can be directly calculated from measurements of E. However, there is a difficulty; thallium melts at 302 °C and the cell symbolized above cannot exist. The difficulty can be overcome as follows. The process consists in extrapolating the values a_2/x_2 as a function of x_2 (viz. Table 13.3) until $x_2 = 1$ which defines a new standard state, differing from the previous one. Given the fact that all the values used for the extrapolation are obtained by working with liquid amalgams at 20 °C, the obtained value 8.3 corresponds to the pure thallium in supercooling. Since $a_2/x_2 = 8.3$, in the standard state and since $x_2 = 1$, the result is that the activity of thallium is $a_2 = 8.3$. But, given the fact that the values a_2/x_2 used above to perform the extrapolation have been established starting from the previous standard state based on Henry's law, the value $a_2 = 8.3$ is that of pure thallium in supercooling *based on the standard state defined in such a way that at infinite dilution the activity is equal to its molar fraction.*

However, adopting a standard state entails the fact that the activity of the species must be equal to unity in it. To sum up, we can write:

a_2 (pure supercooled thallium, 20 °C) = 8.3 (standard state: infinite dilution, 20 °C)

a_2 (pure supercooled thallium, 20 °C) = 1 (standard state: pure supercooled thallium 20 °C)

Let us recall that the ratio of the activities of the same species (in the same thermodynamic state), based on two different standard states, is constant. Once more, these results constitute an illustration of the fact that the activity of a substance, in a given thermodynamic state, exhibits different numerical values according to the choice of the standard state. As a result, the values of the constants of equilibria involving these substances present different numerical values (viz. Chap. 17). In continuation of the previous reasoning, the values of the activities a_2 in the different amalgams of Table 13.3, based on the standard state at infinite dilution, must be, of course, systematically divided by the factor 8.3 in order to obtain their values in the new standard state.

The method, just described above, has been used in order to determine the activity of a metal in another one, that is to say, in a liquid alloy or in other

Table 13.3 Activity of thallium in some amalgams at 20 °C

x_2	$-E$	$\frac{-E}{0.05816} - \log x_2$	$\frac{a_2}{N_2}$	a_2
0	$-\infty$	2.4689	1	0
0.003259	0	2.4869	1.042	0.003396
0.01675	0.04555	2.5592	1.231	0.02062
0.03723	0.07194	2.6660	1.574	0.05860
0.04850	0.08170	2.7184	1.776	0.08624
0.0986	0.11118	2.9177	2.811	0.2772
0.1680	0.13552	3.1045	4.321	0.7259
0.2074	0.14510	3.1780	5.118	1.061
0.2701	0.15667	3.2610	6.196	1.674
0.3361	0.16535	3.3159	7.031	2.363
0.4240	0.17352	3.3558	7.707	3.268
0.428 (sat.)[1]	0.17387	3.3580	7.75	3.316
Tl (liquid, supercooled)			8.3	8.3

amalgams. Let us mention the determination of lead in an alloy of lead and bismuth, of bismuth or cadmium or potassium in amalgams.

13.5.4 *Activity of the Mercury*

As it has been said above, the previous process also permits to determine the activity of the other component of a binary mixture. In the case of amalgams such as that of thallium, the values of the activities of thallium, obtained as described, permit to reach those of mercury by using the Gibbs–Duhem's relation (viz. the beginning of this chapter).

13.6 Determination of the Activities of Nonelectrolytes with Varied Instrumental Methods

Here, we confine ourselves to the description of a method based on the use of the chromatography in vapor phase. It is named "inert gas stripping and gas chromatography." It consists in determining the decrease of the concentration of the solute (the activity of which being asked for) in the gaseous phase as a function of time as its elimination from the liquid phase is in progress because of the bubbling of the inert gas into it. The concentration in the vapor phase is of course determined by gas chromatography.

The activity coefficients determined in such a manner are those at infinite dilution. The method exhibits the advantage to be a kinetic one. The values are extracted from the decreasing curve. Hence, we can cast off the value of the initial concentration which is at least quite uncertain, given the high dilutions used.

13.7 Determination of Activities Through Excess Functions and Calculation of Activities Through Empirical Relations

Thermodynamic properties of solutions, in particular those of mixtures of nonelectrolytes, are frequently studied through consideration of excess functions. They are quantities by which the Gibbs energy, entropy, and other thermodynamic functions differ from the corresponding ones of an ideal solution of same composition. In particular, the excess Gibbs energy is related quasi-directly to the activity coefficients, where there is the existence of another process of determination of activities. Otherwise, we know that there exist empirical relations of the type of those of Margules and van Laar (viz. Chap. 8). They permit to fairly well calculate the fugacities and hence the activities of the components of nonideal solutions.

Let us slightly anticipate what is described in Chap. 16. Of utmost importance is the notion of excess Gibbs energy G^{E} which is experimentally accessible. It permits to determine the activity coefficients. One of the methodologies consists in finding mathematical relations between this quantity and the molality m (or the molar fraction x) of the solutes. This is done by starting from experimental data. Most of the time, these relations are polynomial.

For example, in the case of only one nonelectrolyte solute, the following relation is satisfactory:

$$\left(G^{\mathrm{E}}/w_{\mathrm{s}}RT\right) = \lambda m^2 + \mu m^3 + \cdots$$

w_{s} is the mass of the solvent and λ and μ are fitting parameters. We shall see that, after derivation, one can obtain the activity coefficient of the solute γ and the practical osmotic coefficient ϕ_{m} (viz. Chap. 14) according to the relations

$$\ln \gamma = 2\lambda m + 3\mu m^2 + \cdots$$

$$\phi_{\mathrm{m}} - 1 = \lambda m + 2\mu m^2 + \cdots$$

λ and μ must be, of course, known. This is realized by fitting the experimental data of G^{E} to the molalities or molar fractions.

We defer the study of these means of calculation of activities to Chap. 16.

Table 13.4 Activities of saccharose and water in aqueous solutions as a function of the molality of saccharose (*According to R.A. Robinson, R.H. Stokes, Electrolyte Solutions,* 2nd *Ed, Dover Publications Inc, 2002, New York)*

M	a_w	ϕ	$\log \gamma$
0.1	0.99819	1.0072	0.0062
0.3	0.99449	1.0226	0.0193
0.5	0.99068	1.0393	0.0333
0.7	0.98676	1.0569	0.0479
0.9	0.98272	1.0754	0.0631
1.2	0.97641	1.1044	0.0868
1.6	0.96755	1.1447	0.1197
2.0	0.95818	1.1857	0.1535
3.0	0.93284	1.2863	0.2382
4.0	0.90560	1.3761	0.3185
5.0	0.8776	1.4500	0.3906
6.0	0.8496	1.5084	0.4541

13.8 Some Results

At concentrations lower than 0.1 mol kg^{-1}, the difference between the activity of a non-charged species does not differ from its concentration by a deflection larger than 1 p 100. This is the reason why in dilute solutions, the activity coefficients are taken to be equal to unity during, for example, the calculations involving chemical equilibria. In Table 13.4, we give the activities of water and saccharose as a function of the molality of the latter. The activity coefficients of uncharged molecules are generally higher than unity.

Chapter 14
Determination of the Activities of the Electrolytes

Abstract As a rule, the determination of the activity of electrolytes obeys the same principles as the ones of nonelectrolytes. However, electrolytes exhibit a particular behavior. This induces the using of some particular methods of determination.

It must be borne in mind that the matter, here, is the determination of the activity of the whole electrolyte and not that of each of the ions constituting it, which is theoretically impossible.

The book is primarily devoted to the determinations in aqueous solutions. In addition, water is, given its physical properties, a solvent particularly interesting in order to study the behavior of electrolytes and ions. The described methods are those based on the determinations of the freezing-point depression of the solvent, isopiestic principle, osmotic coefficients, excess Gibbs energies, electromotive forces, and solubilities.

Keywords Freezing-point depression • Isopiestic method • Osmotic coefficient (rational and practical) • Excess Gibbs energies • Electrochemical cell • Activities and electromotive forces • Activities and solubility • Solubility product

As a rule, the determination of the activity of the electrolytes obeys the same principles as the ones of nonelectrolytes. However, electrolytes exhibit a particular behavior. This induces the using of some particular methods of determination of their activities.

Let us recall that the matter is to determine the activity of the whole electrolyte and not the determination of each of the ions constituting it, which is impossible.

In this book, we are primarily interested in the determinations in aqueous solutions. In addition, water is, given its physical properties, a solvent particularly interesting in order to study the behavior of electrolytes and ions.

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14.1 Activity of the Electrolytes by the Measurement of the Freezing-Point Depression of the Solvent

The method is based on the use of relation (13.14) of Chap. 13 that we can write under the form

$$-d\ \ln a_1 = 1/RT_0^2\left[L_0 + b\theta + c\theta^2 + \ldots.\right]d\theta \tag{14.1}$$

where b and c are constants and L_0 the molar latent heat of fusion of the pure solvent at the freezing point of the solvent under 1 atm. It relates the freezing-point depression θ of the solution to the activity of the solvent a_1. The activity of the whole electrolyte is obtained from that of the solvent by using the Gibbs-Duhem relation

$$d\ln a_2 = -\ (x_1/x_2)\,d\ln a_1 \tag{14.2}$$

as we have seen in Chap. 13. It is convenient to modify somewhat the relation (14.1) in order for it to become easier to handle.

The basic reasoning of the method of determination is the following. Relation (14.2) may, for solutions sufficiently diluted, be written as

$$d\ln a_2 = -(n_1/n_2)\,d\ln a_1 \tag{14.3}$$

since in the denominator $(n_i + n_1)$, n_i is negligible with respect to n_1, given the high dilution. Let us set up that n_1 moles correspond to 1 kg of solvent. In this case

$$n_1 = 1000/M_1$$

where M_1 is the molar mass of the solvent. n_2 is then the number of moles of electrolyte in 1 kg of solvent. Hence, it is its molality m. Now, relation (14.3) is written as

$$d\ \ln\ a_2 = -\ (1000/\mathrm{mM}_1)\ d\ \ln\ a_1$$

This last relation combined with (14.1) leads to

$$d\ln a_2 = 1000/\left[RT_0^2M_1\right]\left[L_0 + b\theta + c\theta^2\ + \ldots\ \right]d\theta/m \tag{14.4}$$

The expression $(RT_0^2M_1/1000L_0)$ is exactly the molal cryoscopic constant of the solvent λ (viz. thermodynamics). Consequently, the relation (14.4) becomes

$$d\ln a_2 = d\theta/\lambda m + \alpha\theta d\theta/m \tag{14.5}$$

where the symbol λ is introduced in order to simplify the writing with

$$1\ /\lambda = \left(1000/RT_0^2M_1\right)L_0$$

and by setting up

$$\alpha = 1000/\left[RT_0{}^2M_1\right](b + c\theta\ + \ldots\ldots)$$

Before integrating the relation (14.5), we must express the activity of the whole electrolyte a_2 as a function of the mean activity $a_\pm$ of its ions. One knows (viz. Chap. 12) that

$$a_2 = a_\pm^v$$

where ν is the total number of ions given into the solution per mole electrolyte ($\nu = \nu_+ + \nu_-$). The result is

$$d\ln a_\pm = d\theta/v\lambda m + \alpha\theta\, d\theta/vm \tag{14.6}$$

The integration of this expression is not immediate. We confine ourselves, here, to only giving the result. Details concerning it are given in Appendix C. It involves the intermediary function j defined by the relation

$$j = 1 - \theta/v\lambda m$$

It leads to the expression

$$\ln\gamma_\pm = -\int_0^m j d\ln m\ - j + (\alpha/v)\int_0^m (\theta/m)\, d\theta \tag{14.7}$$

The first integral of relation (14.7) is graphically evaluated by drawing the function j, which is known (it is obtained from the freezing point of the solvent) as a function of $\ln m$, and by determining the area under the curve. The second integral is also evaluated graphically by drawing θ/m as a function of θ. For the solutions of concentrations lower than 0.1 mol kg^{-1}, the latter is negligible. For the solutions of concentrations lower than 10^{-2} mol kg^{-1}, the first integral can be calculated by using an empirical relation between j and m.

It must be noticed that the values found in such a manner are those of the activities at the freezing point of the solution. For solutions more concentrated than 0.1 mol kg^{-1}, one must consider that there is a change of the activity coefficient with the temperature. This is done by taking into account the change of the relative partial molar heat content of the solvent with the temperature through the Kirchoff's relation which relates its change to the difference of molal calorific capacities (at constant pressure) of the liquid and of the solid (viz. Chap. 13).

14.2 Isopiestic Method

This is one of the simplest methods of determination of the activity of electrolytes. It has been especially used in the case of aqueous solutions. It can be applied to nonelectrolytes as well, but it has been the matter of the most applications in the first case.

Its principle is the following one. The method consists in comparing the properties of two solutions, each containing a nonvolatile solute. The activity of the solvent of one of them has been, beforehand, determined with a great precision. When both solutions in the same solvent, maintained isothermal, are placed in an evacuated container, the solvent of the solution of higher vapor pressure (that is to say the solution of higher fugacity (hence activity)) will evaporate and condensate into the solution of lower vapor pressure, until the equilibrium is attained. Then, the solutions will have the same vapor pressure. The solvent has the same fugacity and, hence, the same activity in each (the reference state is the same in both solutions). They are said isopiestic. Let us suppose that one of these solutions contains a reference substance and that its mean ionic activity coefficients are known at different molalities, after having used a suitable method of determination. Hence, with such data, a calibration curve has been built. The molality of the solute in each solution is measured. That of the solution of reference, once known, is reported on the calibration curve. Hence, we obtain the activity of the solvent in the solution under study which is identical to that of the reference solution.

Finally, the activity of the solute in the studied solution is determined by applying the Gibbs-Duhem relation. The isopiestic method is an indirect one.

From the quantitative standpoint, the method is based (at its end of application) on the relation (viz. (13.2) Chap. 13)

$$d\ln a_1 = -(x_2/x_1)\, d\ln a_2$$

which in terms of the solvent molality becomes

$$(\mathrm{mM}_1/1000)\, d\ln a_2 = -\, d\ln a_1$$

since $x_2/x_1 \approx n_2/n_1$ and since for 1000 g of solvent $n_1 = 1000/M_1$ and then $n_2 = m$.

In the case of an electrolyte, according to the relation (12.32) (viz. Chap. 12)

$$d\ln a_2 = v d\ln a_\pm$$

Hence

$$(v\mathrm{mM}_1/1000)\, d\ln a_\pm = -\, d\ln a_1 \tag{14.8}$$

$a_\pm$ is the mean activity of the ions in the solution and m the molality of the electrolyte. For the electrolyte of reference, one can write

$$(v_{\text{ref}} m_{\text{ref}} M_1/1000)\, d\ln a_{\text{ref}} = -\, d\ln a_1 \tag{14.9}$$

At equilibrium, according to (14.8) and (14.9)

$$v_{\text{ref}}\; m_{\text{ref}} d\,\ln a_{\text{ref}} = vm\, d\ln a_{\pm} \tag{14.10}$$

According to relation (12.34) of Chap. 12,

$$d\ln a_{\pm} = d\ln m_{\pm} + \; d\ln \gamma_{\pm}$$

Hence, we can write

$$v_{\text{ref}}\; m_{\text{ref}} d\ln m_{\text{ref}}\gamma_{\text{ref}} = v\,m\,d\ln m_{\pm}\;\gamma_{\pm} \tag{14.11}$$

γ_{ref} being the mean activity coefficient of the reference electrolyte. Let us suppose for sake of simplification that $\nu_{\text{ref}} = \nu$ (by no means does this simplification change the generality of the reasoning) (14.11) becomes

$$m\,d\ln m_{\pm}\;\gamma_{\pm} = m_{\text{ref}} d\ln m_{\text{ref}}\gamma_{\text{ref}} \tag{14.12}$$

Relation (14.12) can be equivalently written as

$$d\ln\gamma_{\pm} = d\ln\gamma_{\text{ref}} + d\ln\left(m_{\text{ref}}/m_{\pm}\right) \; + \left(m_{\text{ref}}/m_{\pm} - 1\right) d\ln m_{\text{ref}}\,\gamma_{\text{ref}}$$

or by introducing the ratio $r = m_{\text{ref}}/m_{\pm}$ of both solutions said isopiestic or isotonic:

$$d\ln\gamma_{\pm} = d\ln\gamma_{\text{ref}} + d\ln\; r + (r-1)\, d\ln m_{\text{ref}}\;\gamma_{\text{ref}} \tag{14.13}$$

After integration, we obtain

$$\ln\gamma_{\pm} \;=\; \ln\gamma_{\text{ref}} + \ln\; r + \int_0^{a_{\text{ref}}} [(r\;-\;1)/a_{\text{ref}}] da_{\text{ref}} \tag{14.14}$$

since $\gamma_{\pm}$ and γ_{ref} are equal to unity and, hence, their logarithms equal to zero when m and m_{ref} are equal to zero, that is to say, at infinite dilution. The integral is evaluated by a graphical means. The area under the curve $(r-1)/a_{\text{ref}}$ as a function of a_{ref} is determined. a_{ref} varies from 0 until the point corresponding to the solution of molality m_{ref} isopiestic with that of molality m. Another graphical means is proposed for the sake of precision of the results. It is founded on the determination of the following integral equivalent to the previous one:

$$2\int_0^{a'} [(r\;-\;1)/a'] da'$$

with

$$a' = a_{\mathrm{ref}}^{1/2} \text{ et } da\text{'} = da_{\mathrm{ref}}^{1/2}.$$

The power ½ which occurs above is a remnant of the Debye–Hückel relations (viz. Chap. 15).

It is an evident fact that the comparative nature of the method is a drawback because its use entails that the calibration curve (vapor pressure of the solvent/electrolyte concentration of the reference solution) must be known with a great accuracy. But, it is a fast method. The determinations are easier to do with solutions rather concentrated, the only limit being the saturation of one of the solutions. The lowest limit for which the method is no longer workable seems to be 0.1 mol kg^{-1}.

In some cases, the method is jointly used with that involving the osmotic coefficients (viz. the next paragraph).

14.3 Activities from Osmotic Coefficients

This is a method of determination of activity coefficients. From the purely experimental viewpoint, it finally involves the determination of the vapor pressure of the solvent of the solution of the electrolyte. It may be direct or involve the isopiestic method. It involves the notion, of rational and practical osmotic coefficients.

14.3.1 Rational Osmotic Coefficient

One knows that the chemical potential of the solvent of the solution containing the electrolyte is

$$\mu_1 = \mu_1{}^{\circ} + RT \ln a_1 \tag{14.15}$$

or

$$\mu_1 = \mu_1{}^{\circ} + RT \ \ln x_1 \gamma_1 \tag{14.16}$$

$\mu_1{}^{\circ}$ is its standard chemical potential, a_1 its activity, and γ_1 its activity coefficient. It is said rational *since* the concentration is expressed in this case in molar fraction x_1.

The chemical potential of the solvent can also be expressed in terms of rational osmotic coefficient ϕ_x. It is defined by the following relation:

$$\mu_1 = \mu_1{}^{\circ} + \phi_x RT \ \ln x_1 \tag{14.17}$$

It is a dimensionless number. The comparison of (14.17) and (14.16) leads to the following relation between the activity coefficient of the solvent and its osmotic coefficient ϕ_x:

$$\ln\gamma_1 = (\phi_x - 1)\ln x_1 \tag{14.18}$$

The osmotic coefficient ϕ_x is a quantity which permits to evaluate the deflection from the "ideality" of the solvent and to obtain the activity coefficients of the solute by repercussion.

14.3.2 On the Physical Significance of the Rational Osmotic Coefficient

The rational osmotic coefficient ϕ_x is roughly equal to the ratio of the osmotic pressure of the solution and that of the corresponding ideal system. According to relation (13.18) of Chap. 13, indeed

$$-RT\ \ln a_1 \approx \overline{V_0}\pi$$

or

$$-RT\ln x_1 - RT\ln\gamma_1 \approx \overline{V_0}\pi$$

For an ideal solution in the same conditions of temperature, pressure, and concentrations, for which the osmotic pressure is π', we can write

$$-RT\ln x_1 \approx \overline{V_0}\pi'$$

whence, taking into account (14.18),

$$\pi/\pi' = \phi_x$$

It appears that ϕ_x approaches unity at infinite dilution since, then, the solvent follows the Raoult's law.

14.3.3 Practical or Molal Osmotic Coefficient ϕ_m

One also uses the practical or molal osmotic coefficient ϕ_m (m means related to the molalities) defined by the expression

$$\mu_1 \ = \ \mu_1{}^\circ - \phi_m RT(M_s/1000)\Sigma \ m_i$$

$\Sigma\, m_i$ is the sum of the molalities of all the nonelectrolyte species and all the present ions and M_1 the molar mass of the solvent. When there is only one electrolyte and if one mole of the latter provides ν ions, one has $\Sigma\, m_i = \nu\, m$ and the previous equality becomes

$$\mu_1 = \mu_1{}^\circ - \phi_m RT(v\,\mathrm{mM_1}/1000) \tag{14.19}$$

The comparison of (14.15) and (14.19) leads to

$$\ln\ a_1 = -\ \phi_m v\,\mathrm{mM_1}/1000 \tag{14.20}$$

Relations (14.19) and (14.20) link the solvent activity a_1 (and its chemical potential μ_1) and the practical osmotic coefficient ϕ_m.

14.3.4 Relation Between Rational and Practical Osmotic Coefficients

We note that (by definition of ϕ_x)

$$\ln\ a_1 \ = \ \phi_x\ \ln x_1 \tag{14.21}$$

with

$$x_1 = n_1/(n_1 + n_2)$$

(the index 1 is that of the solvent and index 2 that of the solute). In order to simplify the reasoning, let us suppose that the solute is a strong electrolyte, the molality of which is m. It gives νm ions in solution:

$$n_2 = vm$$

Now, we can write

$$n_1 = 1000/M_1$$

whence (since $n_2 = \nu m$)

$$x_1 = 1/(1 + vmM_1/1000)$$

and according to the definition of ϕ_x

$$\ln a_1 = \phi_x \ln[1/(1 + vmM_1/1000)]$$

or

$$\ln a_1 = \phi_x [-\ln(1 + vmM_1/1000)]$$

After having expanded in series the logarithm of the right-hand member and after having only kept the first two terms, we obtain

$$\ln \mathrm{a}_1 = -\phi_\mathrm{x}\left\{ [\mathrm{vmM}_1/1000)] - [\mathrm{vmM}_1/1000)]^2/2 + \ldots.\right\}$$

with (relation (14.20) l)

$$\ln a_1 = -\phi_m vmM_1/1000$$

it results in the equality:

$$1 - \phi_m/\phi_x = v\mathrm{mM}_1/2000$$

Hence, in very dilute solution, the rational and practical osmotic coefficients tend to be equal:

$$\phi_m \rightarrow \phi_x \text{ (very dilute solution)}$$

14.3.5 Theoretical Interest of Handling the Practical Osmotic Coefficient

The interest of handling the practical osmotic coefficient lies in its relation with the mean ionic activity coefficient of an electrolyte. Let us differentiate the relation (14.20), m and ϕ_m being the variables. We obtain

$$d\ln a_1 = -(vM_1/1000)\,(\phi_m dm + m d\phi_m)$$

Let us combine this relation with (14.8). We obtain

$$m\,d\ln a_\pm = \phi_m dm + m\,d\phi_m$$

or

$$d\ln a_\pm = \phi_m d\ln m + d\phi_m$$

or (viz. paragraph 2 of this chapter)

$$d\ln a_{\pm} = d\ln m + d\ln \gamma_{\pm}$$

It follows the relation between the mean ionic activity coefficient $\gamma_{\pm}$ and the molality m in terms of osmotic coefficients:

$$d\ln \gamma_{\pm} = (\phi_m - 1)\, d\ln m + d\phi_m \tag{14.22}$$

14.3.6 Determination of the Activity Coefficient Starting from the Practical Osmotic Coefficient

It results from the integration of relation (14.22). The utilization of (14.22) entails, in a first step, to determine ϕ_m.

- Measurement of ϕ_m
  - ϕ_m can be measured by starting from measurements of vapor pressures by using the relation (14.20) knowing that by definition

$$a_s = f_s/f_s{}^{\square}$$

and approximately

$$a_s \approx p_s/\, p_s{}^{\square}$$

p_s is the vapor pressure of the solvent above the solution and $p_s{}^{\square}$ that of the pure solvent at the same temperature. It is the same for the corresponding fugacities. As a result, relation (14.20) becomes

$$\phi_m \approx -(1000/v\,\mathrm{mM_1})\ \ln\,(p_1/p_1{}^{\square})$$

The measurement of the vapor pressure can be performed directly by the isopiestic method (viz. immediately under).

- Another way for the determination of the mean ionic activity coefficients, also based on the determination of osmotic coefficients, is as follows. Its consists in determining the osmotic coefficients of a reference substance in some domain of concentrations. Then, the activity coefficients of another electrolyte may be found through the isopiestic method.
- The practical osmotic coefficient can also be obtained from the measurement of freezing point of the solvent. Here, we take advantage of the great accuracy of

this measurement, especially when the solvent is water. The practical osmotic coefficient is related to the depression of the freezing point of the solution through the relation

$$\phi_m = \left(\Omega\Delta_{\text{fus}}H^\circ / R{T^2}_{\text{fus}}\right)\left[\theta/m + \left(1/T_{\text{fus}} - \Delta C_p/2\Delta_{\text{fus}}H^\circ\right)\theta^2/m + \ldots\right] \quad (14.23)$$

where $\Omega = 1000/M_1$ is the number of moles of solvent in 1 kg of pure solvent. Relation (14.23) results from the juxtaposition of relations (13.20) and (13.15)—Chap. 13.

- Integration of (14.22).

The integration is performed through the introduction of the following function h:

$$h = 1 - \phi_m$$

Let us already recall that $\phi_m = 1$ and $h = 0$ at infinite dilution. With the introduction of the function h, (14.22) becomes

$$d\ln\gamma_\pm = -h\, d \ln m - d\, h$$

After integration between the limits 0 and m and because of the properties of h and ϕ_m at infinite dilution

$$\ln\gamma_\pm = -\int_0^m h\, d\ln m - h \quad (14.24)$$

The integral is evaluated graphically by drawing h as a function of ln m and by determining the area under the curve. Another option which may in some cases be more precise than the previous one consists in handling the equivalent equation under (with $m' = m^{1/2}$)

$$\ln\gamma_\pm = -2\int_0^{m'} (h/m')\, dm' - h$$

By comparing the relations (14.24) and (14.7), it appears that

$$h = J$$

since in (14.7), in sufficiently dilute solution, the last integral is negligible. As a result, since we have seen that, at infinite dilution, j tends toward 0, it is the same for h. (This is a result that we have already used in the above integration.) Hence, at infinite dilution

$$\phi_m = \theta/\nu\lambda m$$

Table 14.1 Practical osmotic coefficients of aqueous solutions of potassium chloride at 25 °C

m	0.1	0.2	0.3	0.5	0.7	1.0	1.5
ϕ	0.926	0.913	0.906	0.900	0.808	0.899	0.906

According to R.A. Robinson, R.H. Stokes, Electrolyte Solutions, 2nd Ed., Dover Publications, Inc., 2002, New York

The practical osmotic coefficient is equal to the ratio of the depression of the freezing point and the quantity $\nu\lambda m$ (viz. paragraph 1).

14.3.7 Practical Interest of the Introduction of Osmotic Coefficients

It is an experimental fact that the activity coefficient of the solvent differs very weakly from unity. In the case of dilute solutions, it may differ from unity by only 1/10,000th whereas that of the solute may differ from some 1/100th. The osmotic coefficients are by far more sensitive. Hence, the measurements of the deflections with respect to the ideal character are more significant with the latter. For example, a solution 2 mol L^{-1} of potassium chloride in water exhibits for the latter an activity of 0.9364 at 25 °C. Its molar fraction being 0.9328, its activity coefficient is 1004. At first sight, this value does not permit to take into account the deflection with respect to the ideal character whereas it is the case with the mean ionic activity coefficient of the solute ($\gamma_2 = 0{,}614$).

As further examples, Table 14.1 mentions some values of the practical osmotic coefficients obtained with some aqueous solutions of potassium chloride at different molalities at 25 °C.

14.4 Determination of the Solute Activity Coefficients from Excess Gibbs Energies

We have already recalled, in the case of the nonelectrolytes, that it is possible to determine the activity coefficients from excess Gibbs energies (viz. Chap. 13). It is the same with electrolytes (viz. Chap. 16).

14.5 Determination of the Activity Coefficients of the Electrolytes by Measurements of emf

Let us recall that a " concentration galvanic cell" is a cell, which provides electric energy spontaneously due to the Gibbs energy change accompanying the transfer of one substance from one electrode to the other (from that with the larger concentration to the other). There does not exist a global chemical reaction in such cells. Finally, let us recall that there exist galvanic cells, the working of which involves transference of ions from a compartment into another one. In this case, in order to avoid a too fast mixture, one uses an appropriate device called a liquid junction. Cells with a liquid junction are, hence, cells with transference. (It is understood, of course, that the "concentration" in the compartment can be expressed with any scale of "concentration.")

The activity coefficients of electrolytes can be determined with cells without liquid junction or with cells with transference (viz. Chaps. 5 and 13).

14.5.1 *Determination with Cells Without Liquid Junction*

Examples of this kind are given in Chap. 18 devoted to the determination of thermodynamic constants of equilibria which involves, by definition, the use of activities. The method permits the direct measurement of the mean activity coefficient of an electrolyte. Let us anticipate the results given in Chap. 18 by mentioning the fact that the global reaction of these cells involves the formation of the compound at the mean activity that is, actually, required. For example, with the cell

$$\mathrm{Pt}\big|\mathrm{H_2(1\ atm)}\big|\mathrm{HCl\ (m)}\big|\mathrm{AgCl(s)}\big|\mathrm{Ag}$$

the cell reaction is

$$1\ /2\mathrm{H_2(1\ atm.)} + \mathrm{AgCl(s)} \rightarrow\ \mathrm{H^+(m)} + \mathrm{Cl^-(m)} + \mathrm{Ag(s)}$$

The cell emf only depends on the activities of ions hydrogen and chloride since the silver halide, silver, and dihydrogen are in their standard state in the conditions of the experiment.

This method of determination may be, in principle, generalized to every electrolyte.

14.5.2 *Determination with Cells with Transference*

The determination of activities is also possible with cells with transference (viz. Chap. 13 and Appendix D). An example is provided by the determination of the mean ionic activity of a solution of hydrochloric acid with the following cell:

$$\mathrm{Pt}\left|\mathrm{H_2}(1\,\mathrm{atm.})\right|\mathrm{HCl}(\mathrm{m'})\left|\right|\mathrm{HCl}(\mathrm{m})\left|\mathrm{H_2}(1\,\mathrm{atm.})\right|\mathrm{Pt}$$

Two solutions of hydrochloric acid of different molalities are in contact through a device, symbolized by ‖ permitting the flow of current and avoiding the mixture of the solutions.

The principle of the determination is based on the fact that, once the transference number of an ion is known as a function or its "concentration," its activity coefficient can be obtained from the emf of a suitable cell with transference. (The transference number of an ion is the fraction of the total current transported by this ion—viz. electrochemistry).

Let us suppose that the galvanic cell has debited 1 faraday and evaluate the processes occurring without forgetting the fact that ions cross over the junction, thus ensuring the flow of current. The occurring electrochemical reactions are

$$\text{at the anode}\quad \frac{1}{2}\mathrm{H_2} \rightleftharpoons \mathrm{H^+} + 1\ \mathrm{e^-}$$
$$\text{at the cathode}\quad \mathrm{H^+} + 1\mathrm{e^-} \rightleftharpoons \frac{1}{2}\mathrm{H_2}$$

Finally for 1 faraday debited and for the electroneutrality to be respected, there is a gain of t_- moles of HCl by the left compartment and for the right one a loss of t_- moles of HCl in order to respect the electoneutrality of both.

One demonstrates (viz. Appendix D) that

$$dE/t_- = (2RT/F)\,(d\ln m + d\ln\gamma_\pm) \tag{14.25}$$

m is the molality of the solution, E the emf of the cell, t_- the transference number of the anion, and $\gamma_\pm$ the mean activity coefficient.

For the integration, we introduce the function δ through the following equality:

$$1/t_- = 1/t_R + \delta \tag{14.26}$$

t_R is the transference number (here of the anion) at the molality reference m_R. The transference number, indeed, varies with the concentration. With this introduction, (14.25) becomes

$$d\ln\gamma_\pm = (F/2t_R RT)dE - d\ln m + (F/2RT)\delta dE$$

After integration between the limits m_R and m, the mean activity coefficients γ_R and $\gamma_\pm$ play a part in the following expression:

$$\ln(\gamma_\pm/\gamma_R) = (FE/t_R 2RT) + \ln(m_R/m) + (F/2RT)\int_0^E \delta dE \tag{14.27}$$

The first two terms are immediately calculated from the experimental values, once the reference concentration is chosen. The last term is obtained by graphical integration by drawing the δ values as a function of E. The δ values are calculated by using relation (14.26), since, according to the principle of the method, the transference number values t_- are known as a function of molalities m.

The experimental measurements consist in performing a series of measurements of the emf of a cell with transference, the molality of one compartment being fixed to m', that m of the other compartment being variable. The emf is related to the activity coefficients, molalities, and transference numbers through the preceding relation. One draws the curve ln ($\gamma_\pm/\gamma_R$) as a function of m for the fixed m_R. The value of the molality of the studied solution reported on this curve provides the value of the corresponding term ln ($\gamma_\pm/\gamma_R$). In order to know $\gamma_\pm$ it remains to determine γ_R. The value γ_R is obtained after extrapolation of the curve ln ($\gamma_\pm/\gamma_R$) as a function of m at $m = 0$. In these conditions, for $m = 0$, $\gamma_\pm = 1$. This entails that we choose as the standard solution that which has the same properties as the infinite dilute solution. A better method from the viewpoint of the accuracy of the result is to proceed to the extrapolation at $m = 0$ of the function stemming from Debye and Hückel's theory (viz. Chap. 15)

$$\log \gamma_\pm/\gamma_R + 0.5107\sqrt{}\mathrm{m}/\left(1 + 1.350\sqrt{}\mathrm{m}\right)$$

in order to obtain the value of ln γ_R.

The activities of several metallic chlorides have been determined in this manner, by using a cell sensitive to the ion chloride:

$$\mathrm{Ag}\left|\mathrm{AgCl}\right|\mathrm{NaCl}\ (\mathrm{m}')\left|\right|\mathrm{NaCl}(\mathrm{m})\left|\mathrm{AgCl}\right|\mathrm{Ag}$$

For example, it is the case of alkali and alkaline earth metals chlorides and lanthanide chlorides. In these cases, it is the transference number t_+ and not t_- which must be now considered and moreover the sign of ΔG (related to E) must be modified.

14.6 Determination of the Activities of the Electrolytes from Measurements of Their Solubilities

The activity and the activity coefficient of a poorly soluble electrolyte may be obtained from measurements of its solubility when it is in mixture with other electrolytes, once its solubility product is known.

Let us consider the electrolyte $M_{\nu+}A_{\nu-}$ which dissociates according to the equilibrium (symbol (s) meaning in solid state):

$$M_{\nu+}A_{\nu-}(s) \rightleftharpoons \nu_+M^{z+} + \nu_-A^{z-}$$

We shall see (viz. Chap. 18) that the equilibrium condition is

$$K = a_M^{v+} \, a_A^{v-} / a_{Mv+Av-}$$

According to the usual conventions concerning the activities, that of a solid at atmospheric pressure and forming only one phase is chosen to be equal to unity. Here, it is the case of $a_{M\nu+A\nu-}$. Hence, we can write

$$K_s = a_M^{v+} a_A^{v-}$$

The equilibrium constant is named solubility product and is symbolized by K_s. a_M and a_A are the activities of both ions at saturation of the solution, at atmospheric pressure, and at the chosen temperature. According to what is preceding

$$K_s = m_+^{v+} \, m_-^{v-} \, \gamma_+^{v+} \gamma_-^{v-}$$

or

$$K_s = (m_\pm \gamma_\pm)^v$$

where $m_\pm$ and $\gamma_\pm$ are the ionic molalities and the mean activity coefficient in the saturated solution and where $\nu = \nu_+ + \nu -$. One deduces that

$$\gamma_\pm = K_S^{1/v} \, / \, m_\pm \tag{14.28}$$

Hence, the mean activity coefficient of a poorly soluble electrolyte can be determined provided that its solubility product is known together with its mean ionic molality in the solution saturated with the electrolyte.

In order to perform the determination, one begins by obtaining the solubility product K_s by measuring the mean ionic molalities at saturation of the electrolyte in the presence of variable quantities of other electrolytes. (Other electrolytes may have or not one ion in common with the electrolyte under study. Even if only two ions are formed in solution by dissolution of a salt, their activities depend on the presence of other salts. One must, of course, take into account the concentration of the ions in common with those of the electrolyte in the calculations.)

Figure 14.1 mentions the solubility of silver chloride in the presence of sodium perchlorate in variable concentrations.

We notice that the solubility slightly increases with the concentration of the added salt. This effect takes its roots in the fact that activity coefficients decrease while the concentration of the added salt is increasing (viz. Chap. 15). As a result, the only way to make sure that the solubility remains constant is such as the solubility product of both ions increases.

The determination consists in drawing the obtained mean ionic molalities obtained as a function of variable amount of ions (actually and usually as a function of the ionic strength—of the solution (viz. Chap. 15)). The value $\mathrm{m}_\pm$ obtained after

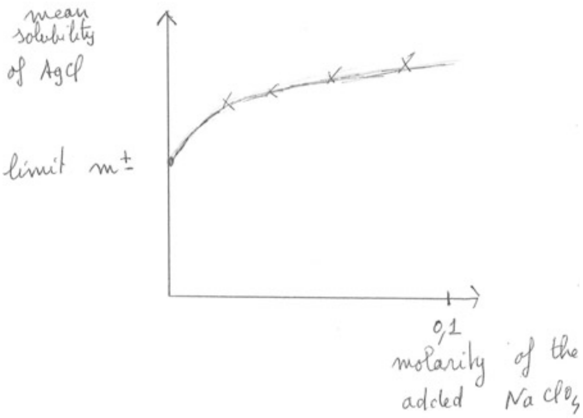

Fig. 14.1 Solubility of silver chloride as a function of the concentration of added sodium perchlorate

extrapolation until a null value in added ions into the solution permits to reach the solubility product. The simple consideration of relation (14.28), indeed, shows that K_s is accessible since, then at infinite dilution, the mean activity coefficient is equal to 1, given the usual convention on the standard state.

The calculation of the mean activity coefficient entails, then, to know the mean ionic molality of the electrolyte at saturation in the studied solution. Then, the calculation becomes immediate. However, we must pay attention to the fact that in the calculation of the mean molality of the concentration of the ions, there are some of them which can eventually be in common with those of the added electrolyte. (They are brought by the other salts added in the solution.) This fact must be taken into account in the calculations.

Then, for example, the solubility product of thallous chloride is $K_s = 2.02 \times 10^{-4}$ and its solubility in a solution 0.025 mol kg^{-1} of potassium chloride is 0.00869 mol kg^{-1}. The concentrations in thallous ions are

$$[\mathrm{Cl}^-] = 0.025 + 0.00869 = 0.03369 \quad \mathrm{mol} \quad \mathrm{kg}^{-1}$$
$$[\mathrm{Tl}^+] = 0.00869\,\mathrm{mol}\ \ \mathrm{kg}^{-1}$$

Thallous chloride giving two ions, $\nu = 2$:

$$m_{\pm} \ = (0.00869 + 0.03369)^{½}\ \ \mathrm{mol}\ \ \mathrm{kg}^{-1}$$
$$m_{\pm} = 0.01711\,\mathrm{mol}\ \ \mathrm{kg}^{-1}$$

and

$$\gamma_{\pm} = \sqrt{}2.02 \times 10^{-4} / \ 0.01711$$

$$\gamma_{\pm} = 0.831$$

In this chapter, we have not mentioned some methods of determination that can be qualified as being more marginal as the previous ones given the limited number of applications they have given.

Chapter 15

Debye–Hückel Relations and Neighboring Relations: Calculation of the Activity Coefficient of an Ion

Abstract The value of the activity of an ion cannot be determined experimentally, contrary to that of an uncharged species. However, it is accessible through a calculation, at least in some conditions of concentrations. Hence, this possibility is of utmost importance from the theoretical standpoint and, also, from the practical one as well. An example of such an importance is provided by the most commonly and quasi-universally used scale of pH which is based on the estimation of the *activity* of the solvated proton in the studied medium.

The calculation of the activity of ions is performed by applying Debye–Hückel or a very neighboring relation.

The chapter is focused on the presentation of these relations and on the results and conclusions to which they lead. (Their setting up is described in another chapter.) Here are also mentioned the properties of the mean activity coefficients of electrolytes which, contrary to those of their constitutive ions, can be measured. They have the great virtue to permit to indirectly verify the Debye–Hückel relations. However, the using of these relations imposes to know the ionic strength of the solution. This notion is introduced at the beginning of the chapter but, just before, the impossibility of the measurement of the activity of an ion is explored.

Keywords Ion activity (determination?) • Ionic strength (influence on the nonelectrolytes) • General behavior of the activity coefficient of the whole electrolyte • Guntelberg's relation • Guggenheim's relation • Davies' relation • Broomley's relation • Debye–Hückel's relation • pH scale

The value of the activity of an ion cannot be determined experimentally, contrary to that of an uncharged species. However, it is accessible through a calculation, at least in some conditions of concentrations. Hence, this possibility is of utmost importance from the theoretical standpoint and, also, from the practical one as well. An example of such an importance is provided by the most commonly and quasi-universally used scale of pH which is based on the estimation of the *activity* of the solvated proton in the studied medium.

The calculation of the activity of ions is performed by applying Debye–Hückel relations. In this chapter, we not only focus ourselves on their presentation but also on the results and conclusions to which they lead. Here, we also mention the properties of the mean activity coefficients of electrolytes which, contrary to

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those of ions, can be measured. They permit to indirectly verify the Debye–Hückel relations.

Using these relations imposes to know the ionic strength of the solution. We introduce this notion at the beginning of the chapter. But, just before, we come back on the notion of impossibility of measurement of the activity of an ion.

15.1 Impossibility of an Experimental Measurement of the Activity of an Ion

As we have already and briefly said it (viz. Chap. 6) and as we shall specify it below, activity coefficients quantify the electrostatic interactions between the chemical species constituting the studied system, notably the interaction ions/ions. Let us also mention the interaction ions/dipoles, dipoles/dipoles, etc. They result in a Gibbs energy change of the whole solution under study for a mole of ions added to it. It is impossible to determine this Gibbs energy change because of the following two reasons:

- We do not have a chemical species constituted by only one kind of ions at our disposal. This is for a reason of electroneutrality. A salt is always neutral from the electrical standpoint. It is also the case of a solution. In brief, an ion is always accompanied by a counterion to ensure the electroneutrality of the medium. Hence, it is quite impossible to add an ion into the studied solution and as a result to determine the change in the chemical potential during this virtual process.
- The second reason is that, if even the previous process was possible, the corresponding measured change in Gibbs energy would then comprise a supplementary term from electrostatic origin which adds to the search for one concerning the interactions of the ions, which is only of interest for our purpose. It would correspond to the work necessary to perform (in the conditions of reversibility) in order to add a charged particle to an already charged solution.

Hence, in order to measure the activity coefficient of an ion, it should be necessary to think up a process which would be able not only to add only one kind of charged ion but also to evolve at a constant electrical charge of the solution.

Hence, all that is possible from the experimental viewpoint consists in adding an ion and its counterion together. Certainly, while doing that, the studied ion is added at the constant charge (null) of the solution, but the measured Gibbs energy change is vitiated by the proper Gibbs energy of addition of the counterion. Actually, here, one finds the same impossibility as that encountered for the measurement of the solvation heat of one ion. It is, indeed, impossible to add only one kind of ions without adding its counterion.

However, the opinion of some authors is that the activity of an ion is potentially measurable but only when an infinitely weak number of ions would be transferred into the solution and, that, provided that the net electrical charge of the solution would be measured at every moment. For some others (Guggenheim), the very notion of activity of an ion is devoid of any physical significance.

To sum up, only some mathematical combinations of activities of ions can be measured (viz. Chap. 12, paragraph 3). Fortunately, if the activity of an ion cannot be experimentally measured, its value can be approached through calculations, at least in some conditions.

From the historical viewpoint, it is interesting to know that the physico-chemical literature is endowed with writings asserting that this determination is possible.

15.2 Ionic Strength

A rapid mention concerning the notion of ionic strength has already been given (viz. Chap. 12). It has been introduced in 1921 by Lewis and Randall on purely empirical bases but its introduction into the realm of the study of solutions has been theoretically justified some years later within the framework of Debye–Hückel theory (viz. Chap. 46).

The ionic strength is a function, the value of which expresses the charge "in ions" of a solution. It is defined as being the half sum of the terms obtained by multiplying the molality m_j of each ion present in solution by the square of its relative charge z_j that is to say

$$I_m = 1/2\sum_j m_j z_j^2 \tag{15.1}$$

where I_m is the ionic strength of the solution on the scale of molalities. The index j indicates that the sum is over all the ions of the solution. It is expressed in mol kg^{-1}. It can also be defined in terms of molarities:

$$I_c = 1/2\sum_j c_j z_j^2 \tag{15.2}$$

Then, it is expressed in mol L^{-1}. Given the fact that the notion of ionic strength is only handled in the cases of dilute and very dilute solutions and since, then, the numerical values of molalities are very close to those of molarities, the numerical values of the ionic strengths expressed in both unities are very close to each other:

$$I_m \approx I_c \text{ (dilute solutions)}$$

(The symbol μ has also been used formerly in order to symbolize the ionic strength. It is no longer recommended.)

It is very important to highlight the fact that the "concentration" m_j or c_j is the true "concentration" of the ions and not their total "concentration." As a result of this point, the calculation of the ionic strength entails to take into account the incomplete dissociation of some electrolytes. This is not without setting up some calculation problems (viz. Chap. 19).

Let us confine ourselves, at the present time, to deduce the following conclusions relative to the fully dissociated electrolytes from relations (15.1) and (15.2):

- For those of the type 1/1, the ionic strength is equal to its molar concentration. For example, for a solution c molar of sodium chloride

$$I = 1/2\left([\mathrm{Na}^+]1^2 + [\mathrm{Cl}^-]1^2\right)$$
$$I = c\,\mathrm{mol\,L}^{-1}$$

- For the multivalent ones, it is larger than the molar concentration. Its value is larger all the more the charges of the ions are themselves larger, since there are changes with the square of these ones. For example, for 1 M solution of magnesium sulfate

$$I = 1/2\left(\left[\mathrm{SO}_4^{2-}\right]2^{\mathbf{2}} + \left[\mathrm{Mg}^{2+}\right]2^{\mathbf{2}}\right)$$
$$I = 4c\,\mathrm{mol\,L}^{-1}$$

In direct relation with the use of all Debye–Hückel relations (viz. under), the question coming in mind is this: What are the ions which must be into account in order to calculate the ionic strength of the solution containing the ion under study. The answer is simple: *all*.

15.3 Influence of the Ionic Strength on the Activity of Nonelectrolytes

We know that, in dilute solutions, the activity coefficients of nonelectrolytes are quasi-equal to 1 and hence their activities are quasi-equal to their concentrations in numerical values (viz. Chap. 13). Although the principal subject of this chapter is the solutions of electrolytes, it is interesting, in passing, to study the influence of the ionic strength on the activity coefficients of the nonelectrolytes. We are concerned, here, with aqueous solutions.

It is an experimental fact that one finds the following relation:

$$\ln(\gamma/\gamma_0) = kI_m \tag{15.3}$$

where γ is the activity coefficient of the nonelectrolyte when its solubility is m when it is in presence of some quantity of electrolyte and γ_0 its activity coefficient in pure water in which its solubility is m_0. This relation is found by measurements of solubilities of numerous nonelectrolytes in the presence of electrolytes. I_m is the ionic strength of the solution based on the scale of molalities. Hence, ln γ appears as being proportional to the ionic strength of the solution. The relation seems to be obeyed up to large ionic strengths such as 5 mol kg^{-1}. The value of the proportionality coefficient k depends on the nature of the nonelectrolyte and also of that of the electrolyte added in order to fix the ionic strength. For the major part of electrolytes, the k value is located between 0 and 0.1. For an ionic strength such as $I_m < 0.1$ mol kg^{-1}, the ratio γ/γ_0 changes in the range of 1000–1023. This result justifies the fact that, as a rule, one attributes the value 1 to the activity coefficient of a nonelectrolyte or of the undissociated part of a weak electrolyte in calculations, even when they must be refined (viz. Chap. 19).

An interesting point to underline is that the solubility m of a nonelectrolyte in the presence of an electrolyte is weaker as that m_0 it exhibits in the presence of pure water. This is a point easy to justify. Let us compare two solutions of the same nonelectrolyte, one in pure water where its solubility is m_0 and its activity coefficient γ_0 and the other in water containing an electrolyte where its solubility is m and its activity coefficient γ. At saturation, in both solutions, there is equilibrium between the nonelectrolyte in the solid pure state and itself in solution. Moreover, its fugacity is the same in the solid state, whatever the solution is and the standard state in solution (necessary to quantify whether its activity is the same in both solutions).

Hence, the fugacity in the standard state is the same for both solutions. As a result, the activity of the nonelectrolyte is the same in both solutions. By introducing the activity coefficients, we obtain

$$m_0\gamma_0 = m\gamma$$

and

$$\gamma = (m_0/m)\gamma_0$$

Since the ratio γ/γ_0 is larger than 1, it is also the case of the ratio m_0/m.

The solubility of a nonelectrolyte in water is weakened by the addition of an electrolyte in the solution. It is the base of the phenomenon called “salting out” which is one of the processes used to resolve liquid phases into their constituents in proximate analysis.

It is also interesting to notice that, according to relation (15.3), ln γ is proportional to the ionic strength. This is not the case for the electrolytes as it is evidenced by the Debye–Hückel relations (viz. under).

15.4 General Behavior of the Mean Ionic Activity Coefficients of Electrolytes

In Table 15.1, we mention the experimental values of the mean ionic activity coefficients of several electrolytes in water at 25 °C as a function of their molalities. (Their methods of determination have been described in Chap. 13.)

Table 15.1 Mean ionic activity coefficients in aqueous solutions at 25 °C

Molality	0.001	0.005	0.01	0.05	0.1	0.2	0.5	1.0	2.0
HCl	0.966	0.928	0.905	0.830	0.796	0.767	0.757	0.809	1.009
NaCl	0.966	0.929	0.904	0.823	0.778	0.732	0.679	0.656	0.670
NaBr	0.966	0.934	0.914	0.844	0.800	0.740	0.695	0.686	0.734
KCl	0.965	0.927	0.901	0.815	0.769	0.717	0.650	0.605	0.575
$CaCl_2$	0.888	0.789	0.732	0.584	0.531	0.482	0.457	0.509	0.807
Na_2SO_4	0.887	0.778	0.714	0.530	0.450	0.360	0.270	0.200	–
$ZnSO_4$	0.734	0.477	0.387	0.202	0.148	0.104	0.063	0.044	0.035
$LaCl_3$	0.853	0.716	0.637	0.417	0.356	0.298	0.303	0.387	0.954

According to S. Glasstone, Thermodynamics for chemists, 11th ed., D. Van-Nostrand, Inc., 1960, Princeton

These values clearly show the following points:

- When the molalities are weak, the numerical values of the activity coefficients decrease all the more quickly as the electrolyte is constituted by the most charged ions. This result justifies the definition and introduction of the ionic strength. For example, for a molality of 0.01 mol kg^{-1}, the activity coefficient of lanthanum chloride is 0.637, whereas for sodium chloride at the same molality, it is 0.904. The lanthanum chloride activity is $a_{\mathrm{LaCl3}} = 0.637 \times 0.01 = 6.37 \times 10^{-3}$. Its value falls very quickly with respect to its concentration. From the standpoint of its thermodynamic behavior, the occurrence of interactions from several origins, in particular due to the interaction ions/ions in the bulk solution (viz. Chap. 6), decreases its *effective* presence.
- The mentioned values show that when the molality of the electrolyte is weak, the activity coefficients of the same kind of electrolytes (from the standpoint of the charges of the ions constituting them) are quasi-equal.
- When the molality of the electrolyte increases, the values of the mean ionic activity coefficients begin decreasing, then reach a minimum, and after end up increasing.

The general behavior of the mean ionic activity coefficient is shown in Fig. 15.1 where it is exemplified by three kinds of electrolytes.

Sometimes, when the concentration of the electrolyte is very large, the mean ionic activity coefficient may take incredibly large numerical values. For example, for a molality $m = 20$ mol kg^{-1} of lithium bromide in water, the value of its activity coefficient $\gamma_{\pm}$ reaches 485!

It is interesting to notice that there exists one concentration (more rigorously: ionic strength) at which the activity coefficient exhibits the value unity, as if the solution would be ideal. This particular concentration varies with the nature of the electrolyte. In aqueous solution at 25 °C, it is located in the range about 3–4 mol kg^{-1}. This phenomenon has a practical application. Some authors take it into account in order to quickly approach the values of the equilibrium thermodynamic constants. Let us recall (viz. Chap. 6) that the latter are expressed in terms of activities. By fixing

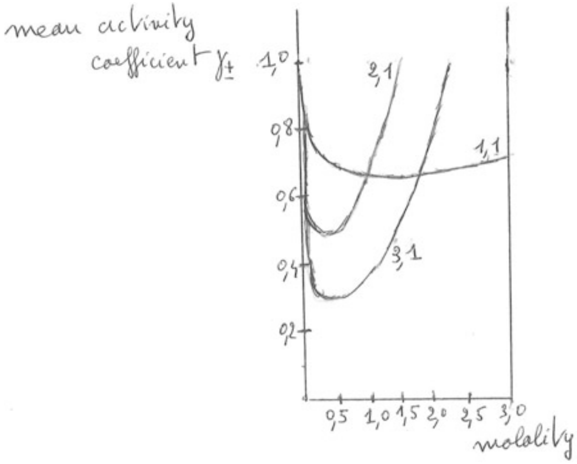

Fig. 15.1 General behavior of the mean ionic activity coefficients as a function of their molalities and according to the kind of electrolyte (symbolism *i*, *j*: *i* metallic ion charge, *j* anion charge)

the ionic strength of the solution under study in the above range of molalities, the different activity coefficients are close to unity and hence the values of equilibrium constants calculated by handling concentrations may not frankly differ from the thermodynamic ones. Calculations taking into account the activities, as they must do in all scientific rigor, may be indeed tedious (viz. Chap. 19). With such a trick, they can be, at least in part, avoided.

Let us also notice in passing that all these behaviors in water we have already mentioned are also recognized in nonaqueous media (ethanol, methanol) and in hydro-organic ones such as the mixtures ethanol-water and dioxan-water.

The Debye–Hückel theory and the equations resulting from it, at least in part, account for these results.

15.5 Debye–Hückel's Relations

Usually, one distinguishes the limit Debye–Hückel relation (1923) and the extended Debye–Hückel one and some others which are very close to the previous ones.

15.5.1 *The Limit Equation Law*

In this chapter, let us confine ourselves to mention that in order to obtain the limit equation, Debye and Hückel have adopted the hypothesis that ions are electrically charged points dispersed in a continuous medium, the permittivity of which is constant and equal to that of the pure solvent. In these conditions, the equation stemming from it, called the limit Debye–Hückel law, is for a binary electrolyte, the charges of its ions being z_+ and z_-:

$$-\log \gamma_{\pm} = A\left|z_{+}z_{-}\right|\sqrt{I} \tag{15.4}$$

where I is the ionic strength of the solution expressed in molalities or molarities. This distinction does not matter given the conditions in which the relation can legitimately be used (viz. under). A is a constant, the value of which only depending on the temperature and on the solvent permittivity ε, according to the relations[1]

$$\begin{aligned} A &= 1.825\,10^{6}\,(\varepsilon \mathrm{T})^{-3/2} \\ A &= 0.509\,\mathrm{mol}^{-1/2}\mathrm{l}^{1/2} \quad (\text{water}:\ 25\,°\mathrm{C}) \end{aligned}$$

The comparison of the calculated values through the expression (15.4) with those experimentally found for the mean ionic activity coefficients shows that the limit law is only verified for ionic strengths lower than 10^{-3} mol L^{-1}.

The Debye–Hückel theory also provides us with the relation (15.5) which permits the calculation of the activity coefficient of one ion only of charge z in a sufficiently dilute solution:

$$-\log \gamma = A\,z^{2}\sqrt{I} \tag{15.5}$$

As it has been already said, the expression (15.5) cannot be directly compared with an experimental measurement, but it can be indirectly compared (viz. Chap. 46). However, indirectly, it confirms what has been experimentally found by studying the behavior of the whole electrolyte (viz. the paragraph 4 above). The activity coefficient of an ion, cation, or anion only depends on the ionic strength of the solution. This assertion is exact for the sufficiently diluted solutions. It has been proposed, once in 1923, by Lewis and Randall.

15.5.2 Extended Debye–Hückel Relation

The previous Debye–Hückel's relation (15.4) leads to markedly too weak values of the activity coefficients for the intermediary concentrations of electrolytes. A change in the limit equation enhancing the range of its applications is obtained by adopting the hypothesis that ions are spheres of finite radius, the other hypothesis prevailing in the setting up of the limit law remaining the same. For a binary electrolyte, the new Debye–Hückel's relation, called the extended Debye and Hückel's law, is

$$-\log \gamma_{\pm} = A\left|z_{+}z_{-}\right|\sqrt{I}/\left(1 + \mathrm{Ba}\sqrt{I}\right) \tag{15.6}$$

---

[1] Other numerical values (but close to the latter ones) may be found in the literature. The discrepancy depends on the chosen value of the solvent permittivity (viz. Chap. 46).

and for only one ion

$$-\log \gamma = Az^2\surd\mathrm{I}/\left(1+\mathrm{Ba}\surd\mathrm{I}\right) \tag{15.7}$$

In both expressions, B is a function of the temperature and of the permittivity ε of the solvent. B has for expression

$$\begin{aligned}B &= 50.3\ (\varepsilon\mathrm{T})^{-1/2}\\ B &= 0.328\,10^8\ \mathrm{cm}^{-1}\,\mathrm{mol}^{-1/2}\,\mathrm{l}^{1/2}\quad (\text{water}:\ \ 25\,^\circ\mathrm{C})\end{aligned}$$

In (15.6) and (15.7), a is an adjustable parameter approximately corresponding to the effective radius of the hydrated (solvated) ion, measured in Å (10^{-10} m). The a parameter is called "ion size parameter" or "minimal approach distance" by the other ions of the solution of the ion, the activity coefficient of which is considered. The parameter A of both limit and extended relations is the same. In the case of a binary electrolyte constituted by monovalent ions, the extended Debye–Hückel's relation is

$$-\log \gamma = Az^2\surd m\ /\left(1+\mathrm{Ba}\surd m\right)$$

given $m = I$.

As a first rule, we can conceive that the parameter a is related to the radius r of the ions. By comparing the expressions (15.5) and (15.7), one can notice that it is the presence of the denominator in (15.7) which differentiates them. This finding may be correlated to the fact that, when the concentration of the ion (the ionic strength of the solution) increases, the electronic cloud gets closer to the considered ion, as it is shown by the Debye–Hückel's theory itself (viz. Chap. 46). As a result, the electrical interactions called "long-range interactions" are no longer the only ones to be efficient. "Short-range interactions" are then added to the previous ones. One author (Kielland) has compiled the values of the parameter a for 136 inorganic and organic ions in water. They have not been, of course, directly measured. The values result from the comparison of mean ionic activity coefficients already known, adjusted according to an empirical manner in such a way that the activity coefficient of an electrolyte can be forecasted in a mixture of other electrolytes. A calculation of the activity of a given ion can, then, be possible (viz. Appendix E). It is interesting to notice, through the values of the Kielland's table, that the activity coefficients do vary few little with the parameter a.

The extended Debye–Hückel is satisfactory for ionic strengths varying up to 0.1 mol L^{-1}.

The calculations of the mean ionic activity coefficients of binary monovalent electrolytes lead to accurate values at the level of 1 p 100 whereas the use of the limit equation leads to errors of the order of 10 p 100 in the same conditions.

According to several authors, it seems that the meaning of hydrated radius of the ion under study given to the parameter a is devoid of any thermodynamic base. In addition, inverse calculations of the parameter a as a function of $\sqrt{m}$ by introducing experimental values of $-\log \gamma_\pm$ show that a is not a constant.

The worst is that for some concentrations, a is endowed with fully aberrant values. For examples, for molalities of 1.8 mol kg^{-1} in HCl and 2.5 mol kg^{-1} in lithium chloride, the respective values of a are -41.12 nm and -14.19 nm!!

This is the reason why, today, a is only considered as being an adjustable parameter permitting to obtain the best fit between the experimental values of the mean activity coefficients and the extended Debye–Hückel relation.

Finally, from another viewpoint, it must be noticed that, for some authors, it seems that the activity coefficients calculated through the Debye–Hückel relations are related to the scale of molar fractions, although the ionic strength values used for their calculations are expressed in molalities or molarities.

15.5.3 Other Relations Permitting the Calculation of the Mean Activity Coefficient of an Electrolyte

Numerous relations which are more and less related to those of Debye–Hückel have been proposed. Either they stem from minor modifications of the extended Debye–Hückel equation or they differ from the extended relation by the presence of supplementary terms. In connection with this subject, it is interesting to notice that from the mathematical standpoint, the Debye–Hückel relations (both limit and extended) cannot, at all, explain the occurrence of minima in the curves $-\log \gamma_\pm/\text{I}$ or $-\log \gamma_\pm/c$ or m, as it can be proved definitively by an elementary calculation of derivatives.

Let us mention, like other equations, the

- Guntelberg's relation

By adopting the unique numerical value $a = 3.0$ Å for all the ions, Guntelberg, starting from the extended Debye–Hückel relation, leads to the expression

$$-\log\gamma_\pm = A\left|z_+z_-\right|\left[\sqrt{\text{I}}/\left(1+1\sqrt{\text{I}}\right)\right] \tag{15.8}$$

The factor unity of $\sqrt{\text{I}}$ in the denominator is a real stroke of luck since at 25 °C, $B = 0.328$ whence $\text{Ba} \approx 1$ with $a = 3$ Å. The Guntelberg's relation seems to give too weak values $\gamma_\pm$, even in the range of ionic strength values less than 0.1 mol L^{-1}. Another relation very close to that of Guntelberg plays a fundamental part in the anchoring of the pH scale of the National Bureau of Standards (pH scale of Bates and Guggenheim).

- Guggenheim's relation (1935)

$$-\log \gamma_{\pm} = A\left|z + z - \right|\left[\surd \mathrm{I}/\left(1 + \surd \mathrm{I}\right)\right] - \mathrm{bI} \tag{15.9}$$

In this relation, there exists the empirical linear term—bI. For ionic strengths larger, supplementary linear terms may be added to the Guggenheim's equation, whence the relations of the kind are derived:

$$-\log \gamma_{\pm} = A\left|z + z - \right|\left[\surd \mathrm{I}/\left(1 + \surd \mathrm{I}\right)\right] + \mathrm{bI} + \mathrm{cI}^2 + \mathrm{dI}^3 \tag{15.10}$$

Quite evidently, the greater the number of terms added, the better the fit between the calculated and experimental values is. But, then, the latter added terms cI^2, dI^3, etc. do possess a statistical weight which is less and less.

A more elaborate form of the Guggenheim's relation is

$$\log \gamma_{\pm} = -A\left|z + z - \right|\left[\surd \mathrm{I}/\left(1 + \surd \mathrm{I}\right)\right] + \left[2\nu_{+}\nu_{-})/(\nu_{+} + \nu_{-})\right](2\beta m)$$

Its applies to only one electrolyte. m is the molality of the electrolyte and ν_+ and ν_- the charges of the cation and of the anion. β is a parameter specific of each electrolyte. This relation is exact for an ionic strength up to 0.1 mol l^{-1} with univalent, bi-univalent, and uni-bivalent electrolytes. The coefficient β of the linear term is adjustable according to the nature of the electrolyte. Guggenheim's equations are semiempirical relations.

- Davies' relation (1938)

Davies' relations are

$$-\log \gamma_{\pm} = A\left|z + z - \right|\left[\surd \mathrm{I}/\left(1 + \surd \mathrm{I}\right)\right] - 0.2\mathrm{I} \tag{15.11}$$

or

$$-\log \gamma_{+} = A\, z^2\left[\surd \mathrm{I}/\left(1 + \surd \mathrm{I}\right)\right] - 0.2\ \mathrm{I} \tag{15.12}$$

It has been largely used in order to estimate the activity coefficients of ions "alone" at ionic strengths relatively large. It seems that for ionic strength of 0.5 mol L^{-1}, the error made by using it on the estimation of the activity coefficient is lower than 8°/°.

Concerning all these relations comprising one or several linear terms, it is interesting to notice that the presence of this term may, mathematically, justify the existence of the minimum of the curves $\gamma_{\pm}/m$.

- Broomley's relation (1972)

According to this theory, the mean activity coefficient of an electrolyte in a binary solution is given by the relation

$$-\log \gamma_{\pm} = A\left|z_{+}z_{-}\right|\left[\surd \mathrm{I}/\left(1 + \surd \mathrm{I}\right)\right] + \mathrm{B}_{12}\mathrm{I}$$

with

$$\mathrm{B}_{12} = [(0.06 + 0.6\,\mathrm{B})(z_1 z_2)]/(1 + (1.5/z_1 z_2)\mathrm{I})^2 + \mathrm{B}$$

B is the Broomley's parameter. z_1 and z_2 are the charges of both ions of the electrolyte. A is the Debye–Hückel's constant A ($A = 0.509$). Broomley's relation is also a semiempirical relation since it is based, on the one hand, on those of Debye and Hückel and on the other on arbitrary terms. Some extensions of Broomley's relation exist. They permit to study some mixtures of electrolytes.

Let us also mention the theory of Meissner and Kusik (1978), the mainspring of which is the reduced activity coefficient Γ_{AC} defined by

$$\Gamma_{\mathrm{AC}} = \gamma_{\pm}(1/z_+ z_-)$$

The idea behind this relation is that the reduced activity coefficient is mainly influenced by the interactions between the anions and cations.

Other relations of Debye–Hückel's kind, but less used than the previous ones, are also proposed (viz. Chap. 46). Others, which are not of Debye–Hückel's kind, are also proposed. The most interesting are those based on the radial distribution functions (viz. Chap. 47). The theory leading to them stems from considerations of statistical thermodynamics.

Chapter 16
Excess Gibbs Energy and Activities

Abstract Besides the fact that the introduction of the activities permits, among other processes, to quantify chemical equilibria when the behaviors of the fluids of the studied system are not ideal, it must be noticed that it also constitutes a means to study nonideal solutions. Another process to study them is to use excess Gibbs functions which are experimentally accessible. For some authors, their handling would be the best and the easiest means to study real (that is to say nonideal) solutions and, even, to study equilibria between fluids. In particular, their measurement would provide the best way to detect an ideal (or not) character. These few lines are sufficient to induce the taking cognizance of the existence of interesting mathematical expressions linking excess functions and activities. As this matter of things stands, it is evident that it is a part of the purpose of this book to study the links between activities and excess Gibbs energy functions. They concern solutions of nonelectrolytes and those of electrolytes as well.

In this chapter, the determination of activities from excess Gibbs energies by using empirical relations is studied. It concerns essentially the solutions of nonelectrolytes, in particular the binary ones. The activity values are found from the excess Gibbs energies through least square regression processes, linear or not linear.

Keywords Mixing Gibbs energy • Ideal mixing energy • Excess Gibbs energy • Activity coefficients from Gibbs energy • Osmotic practical coefficient • Activity determinations from empirical relations • Van Laar and Margules relations

Besides the fact that the introduction of the activities permits, among other processes, to quantify chemical equilibria when the behavior of the fluids of the studied system is not ideal, it must be noticed that it also constitutes a means to study nonideal solutions.

Another process to study them is to use excess functions which are experimentally accessible. For some authors, their handling would be the best and the easiest means to study real (that is to say non ideal) solutions and, even, to study equilibria between fluids. In particular, their measurement would provide the best way to detect an ideal or not character. These few lines are sufficient to induce the taking cognizance of the existence of interesting mathematical expressions linking excess functions and activities.

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As this matter of things stands, it is evident that it is a part of our purpose to study the links between activities and excess Gibbs energy functions. They concern solutions of nonelectrolytes and those of electrolytes as well. In this chapter, we study the determination of activities from excess Gibbs energies by using empirical relations. We are essentially interested in the solutions of nonelectrolytes, in particular by the binary ones.

16.1 Mixing and Excess Gibbs Energies

16.1.1 Mixing Gibbs Energy

Let us consider the process which consists in mixing n_1 moles of species 1 and n_2 moles of species 2 with, for example, formation of a liquid solution. In this case, 1 is the solvent s and 2 the solute i nonelectrolyte or electrolyte. The solvent and the solute are pure, before the formation of the solution (initial state). In the latter, their chemical potentials (molar Gibbs energies, not yet partial ones because they are pure) are given by the expressions

$$\mu_1 = {\mu_1}^\circ + RT\ \ln x_1$$

and since the solvent is pure

$$x_1 = 1$$
$$\mu_1 = {\mu_1}^\circ$$

and likewise

$$\mu_i = {\mu_i}^\circ + RT \ln x_i$$

since i is pure

$$\mu_i = {\mu_i}^\circ$$

The Gibbs energy G^i of the initial system constituted by both components (which are not still in mixture), is given by the expression

$$G^i = n_1 {\mu_1}^\circ + n_i {\mu_i}^\circ \quad \text{initial state}$$

The formation of the mixture is accompanied by a Gibbs energy change for two reasons: the first is due to the change of composition (entropic effect). The second is due to energetic interactions between both kinds of particles, solute and solvent. It is an enthalpic effect. Let μ_1^f and μ_i^f be the chemical potentials of both types of particles, once the mixture is formed. Quite generally, they are given by the expressions

$$\mu_1^f = \mu_1{}^\circ + RT\ln x_1\gamma_1 \text{ and } \mu_i^f = \mu_i{}^\circ + RT\ln x_i\gamma_i$$

where x_1 and x_i are the molar fractions of both components in the mixture and γ_1 and γ_i their activity coefficients (on the scale of the molar fractions). Hence, the Gibbs energy G^f of the system in the final system is

$$G^f = n_1\mu_1^f + n_i\mu_i^f \quad \text{(final state)}$$

or

$$G^f = n_1\mu_1{}^\circ + n_1RT\ln x_1 + n_1RT\ln\gamma_1 + n_i\mu_i{}^\circ + n_iRT\ln x_i + n_iRT\ln\gamma_i$$

The change in Gibbs energy $\Delta_{\text{mix}}G$ accompanying the formation of the mixture starting from the initial system is called the *mixing Gibbs energy*. It is given by the expression

$$\Delta_{\text{mix}}G = G^f - G^i$$

$$\Delta_{\text{mix}}G = n_1RT\ln x_1 + n_1RT\ln\gamma_1 + n_iRT\ln x_i + n_iRT\ln\gamma_I \tag{16.1}$$

16.1.2 Ideal Mixing Gibbs Energy

When the solution is ideal, the activity coefficients are equal to unity. The mixing Gibbs energy becomes the *ideal mixing Gibbs energy* $\Delta_{\text{mix}}G^{\text{id}}$. It is given by the expression

$$\Delta_{\text{mix}}G^{\text{id}} = n_1RT\ln x_1 + n_iRT\ln x_i$$

16.1.3 Excess Gibbs Energy

The excess Gibbs energy is defined by the relation

$$G^E = \Delta_{\text{mix}}G - \Delta_{\text{mix}}G^{\text{id}}$$

i.e.,

$$G^E = n_1RT\ln\gamma_1 + n_iRT\ln\gamma_i \tag{16.2}$$

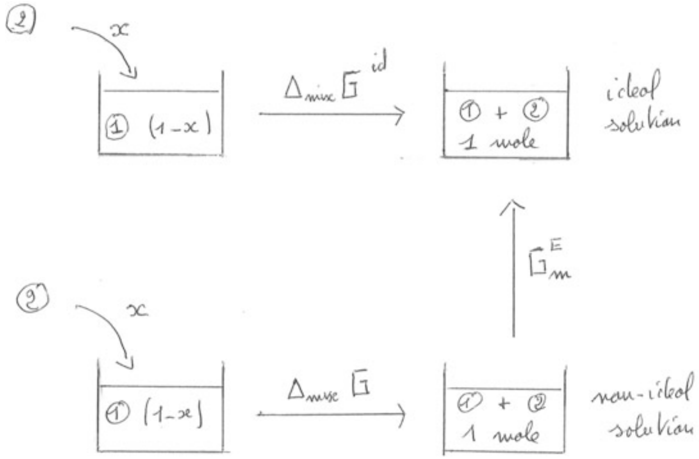

Fig. 16.1 Gibbs energies of mixing: ideal mixing and of excess. [x molar fraction of the solute (16.2) and ($1-x$) that of the solvent (16.1)]

The links between the Gibbs energies of mixing, of ideal mixing, and of excess are shown in Fig. 16.1.

Clearly, the excess Gibbs energy has "something to see" with the activities and with the activity coefficients of the components.

The excess Gibbs energy defined in Fig. 16.1 is for 1 mole of final solution. It is the *molar excess Gibbs energy* G_m^E. The excess Gibbs energy for a total number of moles $n_1 + n_i$ is symbolized by G^E. In this case, of course, the molar excess Gibbs energy G_m^E is given by the expression

$$G_m^E = G^E/(n_1 + n_i)$$

G_m^E is also given by the expression

$$G_m^E = [n_1/(n_1 + n_i)]RT\ln\gamma_s + [n_i/(n_1 + n_i)]RT\ln\gamma_i$$

or

$$G_m^E = x_1RT\ln\gamma_1 + x_iRT\ln\gamma_i$$

16.2 Determination of the Activity Coefficients from the Excess Gibbs Energies

Let us calculate the differential dG^E from relation (16.2) at constant temperature and pressure, the variables being the numbers of moles n_1 and n_i and the activity coefficients γ_1 and γ_i. We obtain

$$dG^E = RT\,n_1 d\ln\gamma_1 + RT\,n_i\,d\ln\gamma_i + RT\ln\gamma_1\,dn_1 + RT\ln\gamma_i\,dn_i$$

Given the Gibbs-Duhem's relation (viz. Chap. 5), it appears that the sum of the first two terms of the right member is null at constant temperature and pressure:

$$dG^E = RT\ln\gamma_1\,dn_1 + RT\ln\gamma_i\,dn_i$$

As a result

$$\left(\partial G^E/\partial n_1\right)_{P,T,n_i} = RT\ln\gamma_1 \quad \text{and} \; \left(\partial G^E/\partial n_i\right)_{P,T,n_1} = RT\ln\gamma_i \qquad (16.3)$$

These relations constitute the theoretical basis on which is founded the determination of activity coefficients from the excess Gibbs energy. Let us mention, without however insisting, that this result can be generalized to the case of solutions constituted by more than two components. This is true because of the fact that the Gibbs-Duhem's relation is verified, in this case also, at constant temperature and pressure. That is to say

$$\sum_j n_j\,d\ln\gamma_j = 0 \quad [(dT = 0 \text{ and } d\mathbf{p} = 0)]$$

16.3 A Variant: Simultaneous Obtention of the Practical Osmotic Coefficient and of the Activity Coefficients of the Solutes from the Excess Gibbs Energy

In this paragraph, we somewhat extend the possibilities of applications of the previous theory.

In the case where there are several solutes (nonelectrolytes and electrolytes), the relation (16.1) applies

$$\Delta_{\text{mix}}G = RT\sum_i n_i \ln\; m_i\gamma_i + n_1 RT\ln a_1 \qquad (16.4)$$

At this point, we must specify that the activity coefficients of the solutes, mentioned just above, are related to the scale of molar fractions. [It is true, however, that concerning the solutes, the values of their activity coefficients vary very little from a scale to another one (viz. Chap. 11).] Given the relation (14.20) of Chap. 14 which is also written (with $\Omega = 1000/M_1$) as

$$\phi_m = -\left(\Omega/\sum m_i\right)\ln\; a_1 \qquad (16.5)$$

we obtain:

$$\Delta_{\text{mix}}G = RT\left[\sum_i n_i \ln m_i \gamma_i - \phi_m (n_1/\Omega)\sum m_i\right]$$

Given the definition of the molarity, the following relation is satisfied:

$$m_i = n_i 1000/n_1 M_1$$

(the factor 1000 being present in order to pass from kilograms to grams). After introduction of this relation into the preceding one, we obtain

$$\Delta_{\text{mix}}G = RT\sum_i n_i \left[\ln m_i \gamma_i - \phi_m\right]$$

We must link this expression to the excess Gibbs energy in order to be able to calculate the values $\ln \gamma_i$ together with the value ϕ_m. With the theory just developed, indeed, it is possible to calculate the activity coefficients of the solutes and of the solvent, the latter through ϕ_m.

We note that if one adds the term $RT\ \Sigma_i\ n_i(1-\ln\ m_i)$ to $\Delta_{\text{mix}}G$, we obtain the following expression for the excess Gibbs energy:

$$G^E = \Delta_{\text{mix}}G + RT\sum_i n_i(1 - \ln m_i) \tag{16.6}$$

The demonstration of this equality is simple. It is sufficient to add all the terms of relation (16.6) term to term, to take into account the expression (16.5) of ϕ_m and to neglect $\Sigma_i\ n_i$ with respect to n_1. Then, we obtain the following relation:

$$G^E = RT\left(\sum_i n_i \ln\ \gamma_i + n_1 \ln\ \gamma_1\right)$$

(Contrary to the case previously mentioned, the present excess Gibbs energy is related to the scale of molalities.)

Expression (16.6) can be, equivalently, also written as

$$G^E = RT\sum_i n_i(1 - \phi_m \ \ + \ln\ \gamma_i)$$

It is practical to use expressions relative to the handling of 1 kg of solvent. If w_1 is the mass of the solvent in kilograms, we have the relation

$$n_i = m_i w_1$$

where n_i is the number of moles of the solute i and m_i its molality in the solution. As a result, the excess Gibbs energy per kilogram of solvent is given by the expression

$$G^E/w_1RT = \sum_i m_i(1 - \phi_m + \ln \gamma_i) \tag{16.7}$$

which can also be written as

$$G^E/RT = \sum_i m_i w_1(1 - \phi_m) + \sum_i m_i w_1 \ln \gamma_i \tag{16.8}$$

- Let us differentiate these relations, taking into account that w_1 is a variable. We obtain

$$dG^E/RT = \sum_i m_i(1 - \phi_m)\,dw_1 + \sum_i m_i \ln \gamma_i\, dw_1$$

As a result,

$$\left[\partial\left(G^E/RT\right)/\partial w_1\right]_{n_i} = \sum_i m_i(1 - \phi_m) + \sum_i m_i \ln \gamma_i$$

The second term of the right member is null (according to the Gibbs-Duhem's relation—viz. above). We obtain

$$\left(1/RT \sum_i m_i\right)\left(\partial G^E/\partial w_1\right)_{n_i} = (1 - \phi_m) \tag{16.9}$$

- Let us differentiate (16.7), m_i being considered as a variable. We obtain

$$\begin{aligned}\left[\partial\left(G^E/w_1RT\right)/\partial m_i\right]_{w_1,\ m_j} &= \ln \gamma_i + (1 - \phi_m) \\ &\approx \ln \gamma_i\end{aligned} \tag{16.10}$$

As a result, if we have an algebraic expression of the excess Gibbs energy (on the scale of molalities) under the form of a function of w_1 and m_i at our disposal, ϕ_m and $\ln \gamma$ can be easily calculated by derivation. Let us notice that the Gibbs-Duhem's is automatically verified since it is involved in the reasoning leading to the above result.

From the mathematical standpoint, these considerations are legitimate because the expressions G^E are homogeneous first-order function of the numbers of moles of components since the function Gibbs energy is an extensive one of the system. This means that if, for example, the numbers of moles of both components is increased twofold, the function G^E is also increased twofold (viz. Appendix A).

Remark Let us, in passing, notice that one introduces and handles other excess functions in thermodynamics such as the molar excess, excess entropy, enthalpy, volumes …. We do not consider them in this book.

16.4 Determination of Activities from Empirical Relations

In Chap. 8, we have seen that, for nonideal solutions, there exist some relations from purely empirical origin which link the fugacities of the liquid components of binary solutions to their molar fractions in solution, such as those of Margules and van Laar.

- Margules's relation is

$$f_1 = x_1 f_1^{\square} \exp\left[1/2\,\beta_1 x_2^2 + 1/2\,\gamma_1 x_2^3 + \ldots\ldots\right]$$
$$f_2 = x_2 f_2^{\square} \exp\left[1/2\beta_2 x_1^2 + 1/2\gamma_2 x_1^3 + \ldots\ldots\right]$$

It pertains to both solvent and solute. Given the general definition of an activity, we immediately obtain

$$a_1 = x_1 \exp\left[1/2\beta_1 x_2^2\right]$$
$$a_2 = x_2 \exp\left[1/2\beta_2 x_1^2\right]$$

after having only kept the first term of each exponential, whence the expressions of the activity coefficients become

$$\gamma_1 = \exp\left[1/2\beta_1 x_2^2\right] \quad \text{and} \quad \gamma_2 = \exp\left[1/2\beta_2 x_1^2\right]$$

Actually, the constants β_1 and β_2 are equal. Let us take, indeed, the logarithms of the above expressions of the fugacities f_1 and f_2. By only retaining the first term of the exponentials, given the fact that $0 \leq x_1, x_2 \leq 1$, we obtain

$$\ln f_1 = \ln x_1 + \ln f_1^{\square} + 1/2\beta_1 x_2^2$$
$$\ln f_2 = \ln x_2 + \ln f_2^{\square} + 1/2\beta_2 x_1^2$$

Derivating the first expression with respect to $\ln x_1$ and the second with respect to $\ln x_2$, we obtain

$$(\partial \ln f_1/\partial \ln x_1)_{T,P} = 1 - \beta_1 x_1 x_2$$
$$(\partial \ln f_2/\partial \ln x_2)_{T,P} = 1 - \beta_2 x_2 x_1$$

As a result, since, in the occurrence, the Gibbs-Duhem's is [viz. Chap. 7 relation (7.20)]

$$(\partial f_1/\partial \ln x_1)_{T,P} = (\partial f_2/\partial \ln x_2)_{T,P}$$

we obtain

$$\beta_1 = \beta_2$$

Setting up $\beta_1 = \beta_2 = \beta$, we can write

$$f_1 = x_1 f_1^{\square} \exp\left[1/2\beta x_2^2\right] \quad \text{and} \quad f_2 = x_2 f_2^{\square} \exp\left[1/2\beta x_1^2\right]$$

When the vapor pressures are not too high, those measured at different molar fractions in solution permit to determine the corresponding activities. General methodologies, such as least square fitting of experimental values to theoretical ones, give the parameter β [viz. Chap. 19]. We can notice that the knowledge concerning the data of one of the components permits to obtain those concerning the other.

- Van Laar's relation is an interesting alternative to that of Margules. For two components, it is written as

$$f_1 = x_1 f_1^{\square} \exp\left[\alpha_1 x_2^2/(\beta_1 x_1 + x_2)^2\right]$$
$$f_2 = x_2 f_2^{\square} \exp\left[\alpha_2 x_1^2/(x_1 + \beta_2 x_2)^2\right]$$

Constants β_1 and β_2 are not the same as those of Margules' equation. In order to determine the activities and the values of the constants involved in van Laar's equations the same reasoning and methodologies as those applied to Margules' relations are applied to partial pressures. They, together with molar fractions, constitute the experimental values on which the methodologies apply provided that their values are not too high. The different constants of van Laar's equations are not independent from each other. A mathematical reasoning shows that

$$\alpha_1 \beta_2 = \alpha_2 \quad \alpha_2 \beta_1 = \alpha_1$$

Van Laar's relations lead to the two following relations expressing the activity coefficients of the components of a binary solution:

$$\log \gamma_1 = A/(1 + A x_1/B x_2)^2 \quad \log \gamma_2 = B/(1 + B x_2/A x_1)^2$$

These van Laar's relations, given at this point, come from other more complex van Laar's relations (see below).

Let us notice that the merits of these relations are confirmed by the existence of other relations, also empirical but more recent. They express excess Gibbs energies of solutions (viz. below).

Kirkwood-Buff's theory also confirms some of these relations (viz. Chap. 45).

16.5 Calculation of Activities from Excess Gibbs Energy Relations

According to the previous reasoning, it would be convenient to find an analytical expression of the excess molar Gibbs energy as a function of the composition of the solution, the word composition being used in its largest acception. It may mean the numbers of moles of its components, their molalities, the mass of the solvent, etc.

Actually, the expressions of the excess Gibbs energy can take the form of empirical series, the number and values of the terms of which they comprise are chosen in such a way that the series give the best fits with varied data. They may also be founded on theoretical models.

From a general standpoint, there exist several expressions of excess Gibbs energy functions in the literature and, probably, their number will continue to increase.

16.5.1 Solutions Without Electrolytes

It is an experimental fact that for the solutions not containing ions or high-molecular-weight polymers, several kinds of empirical series express satisfactorily the excess Gibbs energies of more and less complex solutions as a function of the molar fractions or of the molalities of the components. The polynomial form of these expressions makes easier the calculations of the activity coefficients, by derivation.

- A very simple excess Gibbs energy function for a binary mixture is

$$G_m^E/RT = wx_1x_2 \quad \text{or} \quad G_m^E/RT = wx_1(1-x_1) \tag{16.11}$$

  w is dimensionless. At this point, it is sufficient to know that it is a constant, the value of which depends only on the temperature and on the pressure. (In paragraph 7, we shall give an approach of the significance of this term.)
- As another example, let us mention the series (16.12) and (16.13) which give the excess Gibbs energies of binary mixtures of nonelectrolytes as a function of molar fractions. (The relation (16.13) is equivalent to the previous one.) We briefly discuss its properties and also its using:

$$G^E_m = RT\ x_1x_2\left[A_0\ + A_1(x_2 - x_1) + A_2(x_2 - x_1)^2 + \ldots.\right] \tag{16.12}$$

$$G^E_m = RT\ x(1 - x)\left[A_0\ + A_1(2x - 1) + A_2(2x - 1)^2 + \ldots.\right] \tag{16.13}$$

In relation (16.13), x is the molar fraction of the second component. Using the variable x presents the drawback, however, to mask the respective parts played by both components.

The coefficients A_0, A_1, and A_2 are, by definition, independent from x_1 and x_2 but are dependent on T and, to a lesser extent, on P. Several points deserve further comments:

- The first one is that those series obey the condition, which must be obligatorily satisfied, i.e., they lead to a null value at the null value of G^E_m for $x_1 = 0$ and $x_2 = 0$.
- The second comment is that three terms in the series are often sufficient for the binary solutions. Statistical tests permit, besides, to discuss about the pertinence of the addition of supplementary terms.

Generally, the coefficient A_1 is related to the dissymmetry of the behaviors of both components. The terms bringing higher indices are related to more complex phenomena.

The expressions (16.12) and (16.13) permit to accede to the activity coefficients γ_1 and γ_2 through the relations (16.3). We obtain

$$\ln\gamma_1 = x_2^2[A_0 + A_1(x_2 - 3x_1) + A_2(x_2 - x_1)(x_2 - 5x_1)] \tag{16.14}$$

$$\ln\ \gamma_2 = x_1^2[A_0 + A_1(x_1 - 3x_2) + A_2(x_1 - x_2)(x_1 - 5x_2)] \tag{16.15}$$

It is evident that the terms of the series (16.14) and (16.15) are not, evidently, independent from the others. Given the fact that x_1 and x_2 are linked by the relation $x_1 + x_2 = 1$, we also notice that ln γ_1 and ln γ_2 are, respectively, only functions of molar fractions x_2 and x_1. In order to discover this property, Il is sufficient to replace x_1 by $1 - x_2$ and inversely. Relations (16.14) and (16.15) are hence a generalization of the Margules' equations, the simplified expressions of which having already been given (viz. above).

- Let us also briefly mention another empirical relation. It also permits to study the nonideal solutions. It is

  $$G^E_m/RT = -x_1(\ln x_1 + \Lambda_{12}x_2) - x_2(\ln x_2 + \Lambda_{21}x_1) \tag{16.16}$$

  where $\Lambda_{12} \neq \Lambda_{21}$. Its interest lies in the fact that it is working with only two parameters Λ_{12} and Λ_{21}. In this expression, the ideal character of the solution is evidenced by the values of these parameters which are equal to 1. It is, without any difficulty, generalized to the solutions which are more complex than the binary ones.

- Other Van Laar's relations

In his works devoted to the obtention of expressions of the vapor pressures as a function of the composition of the solutions at equilibrium, van Laar suggested to use four arbitrary parameters a z_1, z_2, b_1, and b_2 linked by the following relations:

$$z_1 = n_1 b_1/(n_1 b_1 + n_2 b_2) \quad \text{and} \quad z_2 = n_2 b_2/(n_1 b_1 + n_2 b_2)$$

where n_1 and n_2 are the numbers of moles of components. (It is proved correct that, when the latter are sufficiently similar from the standpoint of their physical properties, the b_1 and b_2 are roughly equal to their partial molar volumes.) Parameters b_1, b_2, z_1, and z_2 can also be freely adjusted in order to obtain the best fit with the experimental data. The excess Gibbs energy, as a function of these parameters, is

$$G^E = a_{12}\big(b_1 b_2 n_1 n_2/(n_1 b_1 + n_2 b_2) \qquad (16.17)$$

a_{12} is the parameter expressing the interaction between the two different kinds of particles. Hence, it quantifies the nonideal character of the mixture.

- A proposed equation relates the excess Gibbs energy of the solution to the molalities of more than two components. It is

$$\left(G^E/w_1 RT\right) = \sum_i \sum_j \lambda_{ij} m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k + \ldots. \qquad (16.18)$$

w_1 is the mass of solvent in kilogram. The coefficients λ_{ij} take into account the interactions between the two particles i and j which may be identical ($i=j$), whereas the coefficients μ_{ijk} take into account the interactions between three particles which may be identical. This kind of development finds some theoretical foundations in the McMillan-Mayer's theory (viz. Chap. 30). In the case of only one solute, the expression simplifies and gives the following one:

$$\left(G^E/w_1 RT\right) = \lambda m^2 + \mu m^3 \ldots + \ \ldots..$$

There exist numerous other relations of the above kinds.

16.5.2 Case of Electrolyte Solutions

- Let us begin by recalling the fact that the relation

$$\ln a_1 = -\phi_m \nu m M_1/1000$$

(permitting to define the practical osmotic coefficient) together with the above relations (16.9) and (16.10) remains applicable in the case of electrolyte solutions.

- Some semiempirical relations permit to express the activities and osmotic coefficients of the pure electrolytes or those of the components of electrolyte mixtures or, even, those of the components of mixtures of electrolytes and of nonelectrolytes.
  - The first proposed relations of this kind are due to Guggenheim. They are founded, of course, on the taking into account of the interactions between the ions but also on the Brönsted's hypothesis according to which all the ions of the same sign cannot exhibit interactions between them at short distances, given the fact that they repel each other, contrary to the behavior of ions of opposite signs.
  - More recently, Pitzer has proposed some relations relating the excess Gibbs energies to the number of moles of different electrolytes. They are used a lot. They present the following general form in the case where the solvent is water:

$$G^E/RT = w_w f(I) + 1/w_w \sum_{ij} \lambda_{ij}(I)\, n_i n_j + 1/w_w^2 \sum_{ijk} \mu_{ijk} n_i n_j n_k \tag{16.19}$$

    w_w is the weight of the solvent water in the solution; n_i, n_j, and n_k are the number of moles of the species i, j, and k; and $f(I)$ is a function of the ionic strength of the solution (viz. Chap. 15) and also of the nature of the solvent and of the temperature. It takes into account the long-range interactions. From the mathematical standpoint, $f(I)$ can take the form of the term of Debye–Hückel's relation (viz. Chap. 15) or that of a term stemming from the use of the notion of the radial distribution function (viz. Chap. 47). $\lambda_{ij}(I)$ is also a function of the ionic strength of the solution. This parameter takes into account the short-distance interactions, property which is not achieved by the Debye–Hückel's relations (viz. Chap. 46), but let us notice that it only takes into account the interactions between two ions. The parameter μ_{ijk} takes into account the interactions between three particles. Supplementary terms are added when neutral species are also present in the solution. Concerning these relations, it must be noticed that only some combinations of the constants λ_{ij} and μ_{ijk} can be obtained by regression.

    It appears that the arguments prevailing in the development of the expressions (16.17) take their roots in the results of the theories of Debye–Hückel and of McMillan-Mayer (viz. Chap. 38), even more in the notion of radial distribution function (viz. Chap. 42). This is the reason why these relations are named semiempirical ones.

- Another kind of model has been presented. It exhibits the very interesting characteristic to describe the excess Gibbs energy of a solution containing both electrolytes and nonelectrolytes. The model is an extension of that of Pitzer. It splits up the excess Gibbs energy into two groups: one which takes into account the long-distance interactions and the other the short-distance ones. The latter may be due in majority, according to the studied mixtures, to the present nonelectrolytes. The model is based on two hypotheses: on the one hand, there is a total repulsion between ions of the same charge and on the other one, there is electroneutrality all around a molecule of solvent.

Let us finish this paragraph by mentioning the fact there exist informatic programs which permit to study equilibria between phases. Some, such as UNIFAC (universal functional activity coefficient), permit to estimate the activity coefficients in some mixtures. They are based on the allocation of values to some parameters characterizing the groups constituting the studied molecule. The important parameters are those of interactions of the two members of each pair of groups existing in the solution. In principle, the molecule is divided into several functional groups. The molecule-molecule interactions are calculated by doing the ponderated sum of the group-to-group interactions.

16.6 Some Methodological Aspects

The representation as judicious as possible of the excess Gibbs energy by empirical series involves to determine the judicious parameters A_0, A_1, A_2, …, A, B, C, …, Λ_{12}, Λ_{21} … and so forth, together with their numbers. We have already mentioned that there exist statistical tests which permit to assert the pertinence (or not) of the number of parameters to retain. They are most often obtained by least square regressions linear or nonlinear. These determinations are performed by comparing the calculated values G^E (or other functions) to those of the same functions experimentally determined, in the same fixed conditions. To know the calculated values entails to choose the number of parameters to determine at the beginning of the process and also to attribute initial empirical values to them. These values adjust themselves, often automatically according to the algorithms, during the regression process.

The experimental data which are most often retained in the regression process are the total pressure or the partial pressures above the solution.

16.7 On the Very Simple Expression (16.11) of an Excess Gibbs Energy

Let us again consider the very simple excess Gibbs energy (16.21). It gives rise to an interesting theoretical explanation (viz. paragraph 8).

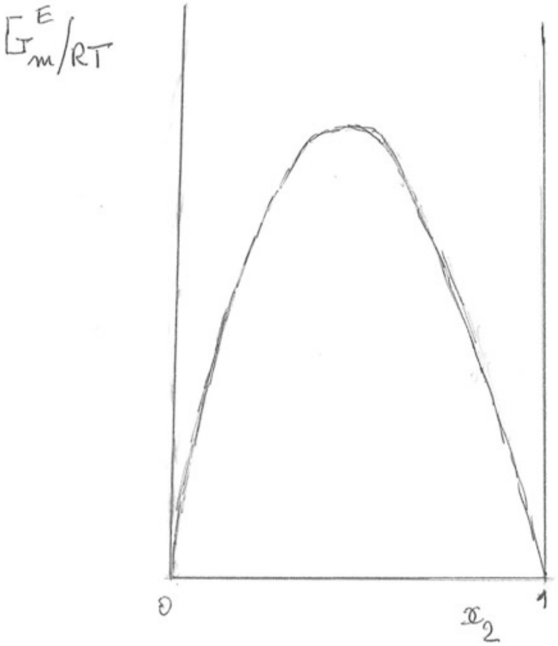

Fig. 16.2 Excess Gibbs energy G_m^E/RT of a binary mixture such as $G_m^E/RT = wx_1x_2$

The diagram $(G_m^E/RT)/x_2$ is a parabola (Fig. 16.2).

For an indefinite number $n_1 + n_2$ moles of mixture, the excess function is

$$G^E/RT = \left(G_m^E/RT\right)(n_1 + n_2)$$
$$G^E/RT = w\,n_1n_2/\,(n_1 + n_2)$$

Given the relations (16.3), we find immediately by derivation that

$$\ln\gamma_1 = wx_2^2 \qquad (16.20)$$
$$\ln\gamma_2 = wx_1^2$$

These expressions are the simplified relations of Margules. Actually, some mixtures exhibit this behavior, by example of the mixture benzene/cyclohexane at different temperatures. It is also the case of mixture of argon and dioxygen. We notice the perfect symmetry of the curve.

It is interesting to express the activities within the framework of this hypothesis, when one of the components (2 for example) is very dilute, that is to say, for $x_2 \rightarrow 0$. According to (16.20)

$$\ln\gamma_1 = \ln\exp\left(w\ x_2^2\right)$$
$$\gamma_1 = \exp\left(w\ x_2^2\right)$$

After the development in series of the exponential and after only retaining the first two terms, since $x_2 \to 0$

$$\gamma_1 \sim 1 + wx_2^2$$

and since

$$a_1 = \gamma_1 x_1$$

we obtain, since $x_1 + x_2 = 1$,

$$a_1 = x_1 + w\left(x_2^2 - x_2^3 + \ldots..\right)$$

The activity of the major component (the solvent) tends toward its molar fraction in pure state (that is to say, toward $x_1 = 1$) when that of the solute tends toward 0. The solvent obeys Raoult's law. Now, concerning the activity of the solute, we can write

$$\begin{aligned}
&\ln \gamma_2 = wx_1^2 \\
&\gamma_2 = \exp\left(wx_1^2\right) \\
&\gamma_2 = \exp\left[w(1 - x_2)^2\right] \\
&\gamma_2 = \exp\left[w\left(1 - 2x_2 + x_2^2\right)\right] \\
&\gamma_2 = \exp\left(w - 2wx_2 + wx_2^2\right) \\
&\gamma_2 = \exp(w)\exp\left(-2wx_2 + wx_2^2\right) \\
&\gamma_2 = \exp(w)\left(1 - 2wx_2 + wx_2^2\right)
\end{aligned}$$

We notice that when $x_2 \to 0$, $\gamma_2 \to \exp(w)$. The activity coefficient tends toward the constant $\exp(w)$ and the activity a_2 is expressed by

$$a_2 = \exp(w)\, x_2$$

Then, there is a linear relation between the activity and the molar fraction of the solute. It obeys Henry's law.

Remark The solutions, the excess Gibbs energies of which are of the kind (16.21), are called simple mixtures (Guggenheim).

16.8 Theoretical Foundation of the Expression of the Excess Gibbs Energy of a Simple Mixture: Meaning of *w*

We have noticed that when both components of a mixture do possess molecules roughly of the same size, the excess Gibbs energy obeys the simple relation already encountered:

$$G_m^E/RT = wx_1x_2 \tag{16.11}$$

The semiqualitative explanation is the following one. It is an experimental fact that liquids retain the structure in lattice of crystals, at least in part (viz. the chapter concerning the measurement of the radial distribution functions g—viz. Chap. 29). This means that the molecules of a component are more and less strongly fixed on the sites of the lattice around a molecule of the same component or of one molecule of the other component. The fact that the molecules of both components are roughly of the same size permits, however, the exchange of both types of molecules on the sites of the lattice. The theory leading to this result is a statistical one.

Let us suppose that the $N_a + N_b$ *molecules are fixed on the sites of the lattice which are also equal to the number* $N_a + N_b$ *and that both types of molecules (similar) possess the same number of the sites of coordination Z (at the number of 12, the most of the time, it seems). If the molecules a were completely separated from the molecules b on the lattice, There would exist on the one hand* ½ ZN_a *pairs a-a and* ½ ZN_b *pairs b–b on the other. The factor 1/2 is introduced in order not to take into account the same pair two times. We must remark that, in this theory, one only takes into account the pairs formed between neighboring molecules, called molecules in direct interaction. After the mixing, the probability that one site does possess one molecule a is equal to its molar fraction* $x_a = N_a/(N_a + N_b)$ *and that it does possess one molecule b is* $x_b = N_b/(N_a + N_b)$*. The probabilities of existence of pairs a–a, a–b, and b–b are then* x_a^2*,* $2x_a x_b$*, and* x_b^2*. The factor 2 is present because there are two manners to obtain the pair a–b (obtentions of a–b and of b–a). Let* w_{aa}*,* w_{ab}*, and* w_{bb} *be the increases of potential energies when two molecules a,a–a, b–b–b form a pair while they were separated at infinity. They are negative values. The potential energy U after mixing is given by the expression*

$$U(\text{after mixing}) = -½Z(N_a + N_b)\left(w_{aa}x_a^2 + 2w_{ab}x_ax_b + w_{bb}\,x_b^2\right)$$

or

$$U(\text{after mixing}) = -½Z\left(w_{aa}N_a^2 + 2w_{ab}N_aN_b + w_{bb}N_b^2\right)/(N_a + N_b)$$

Before mixing, the potential energy was

$$U(\text{before mixing}) = -½Z(N_aw_{aa} + N_bw_{bb})$$

Hence, the change in potential energy due to the mixing ΔU *is*

$$\Delta U = ½\,ZN_aN_b(w_{aa} + w_{bb} - 2w_{ab})/(N_a + N_b)$$

which can also be written as

$$\Delta U = (n_a + n_b)\,x_ax_bw'\,RT$$

after having introduced the quantity w'*:*

$$w' = ZN_A(w_{aa} + w_{bb} - 2w_{ab})/2RT$$

where N_A *is the Avogadro's number (which must be introduced since the previous reasoning involves the molecular scale and does not involve the molar one as it must be because of the presence of the constant R)*[1]*. If we consider an ideal solution,* ΔU *is equal to the mixing Gibbs energy and hence*

$$w' = w$$

Maybe, here lies the meaning of the constant w introduced in the case of simple mixtures.

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[1] *Pay attention, do not confuse* N_A *and* N_a*!*

Chapter 17
Equilibrium Constant, Activities, and Reaction Gibbs Energy

Abstract The concept of chemical equilibrium is intimately linked to that of Gibbs energy change accompanying the studied reaction. According to the value of the latter, one can forecast if, spontaneously, the reaction is possible (or not) in the sense in which it is considered in the given experimental conditions. Likewise, it permits to forecast the position of the equilibrium. Hence, applying the general properties of the quantity Gibbs energy to a chemical reaction leads to the law of the chemical equilibrium, also called "mass action law." It stems from the notion of standard reaction Gibbs energy which is quantified with the aid of the introduction of a constant named the equilibrium constant.

In this chapter, it is demonstrated that the equilibrium constant is truly a constant only when it is calculated in terms of the activities of the reactants and products. This point is a very important one, because it is only at this price that the interactions between the particles of the system are taken into account. The introduction of the activities allows, indeed, to express the chemical potentials of the reactants and products and as a result the mass action law with the same formalism as that used to study the behavior of species in ideal solutions.

The theoretical developments of this chapter lead to the somewhat surprising result that, according to the chosen standard states of the reacting species, the values of the equilibrium constants of a given reaction vary! This is the reason why it is interesting to mention the relations existing between the different equilibrium constants. Finally, the changes of equilibrium constants with temperature and pressure are examined.

Keywords Reaction Gibbs energy • Activities of the reactants and products • Equilibrium constant (constancy) • Usual standard states • Kinds of equilibrium constants • Equilibrium constants/changes with the temperature and pressure

The concept of chemical equilibrium is intimately linked to that of Gibbs energy change accompanying the studied reaction. According to the value of the latter, one can forecast if, spontaneously, the reaction is possible in the sense in which it is envisaged and in the given experimental conditions, or not. Likewise, it permits to forecast the position of the equilibrium. Hence, applying the general properties of the quantity Gibbs energy to a chemical reaction leads to the law of the chemical equilibrium, also called "mass action law." It stems from the notion of standard

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reaction Gibbs energy which may also be quantified with the aid of the introduction of a constant named the equilibrium constant.

It is the goal of this chapter to show that the equilibrium constant is truly a constant only when it is calculated in terms of the activities of the reactants and products. This point is a very important one, because it is only at this price that the interactions between the particles of the system are taken into account. The introduction of the activities allows to express the chemical potentials of the reactants and products with the same formalism as that used to study the behavior of species in ideal solutions.

It is also the goal of this chapter to show that, according to the chosen standard states of the reacting species (participating to the equilibrium), the values of the equilibrium constants of a given reaction vary. It is the reason why it is interesting to mention the relations existing between the different equilibrium constants. We also investigate the changes of equilibrium constants with temperature and pressure.

17.1 Reaction Gibbs Energy

Let us consider a closed system (the system may be constituted of several phases, which are themselves open systems, but the following considerations concern the whole closed system) in which the following reaction takes place:

$$aA + bB + \rightleftharpoons pP + qQ + ... \Rightarrow$$

Let us suppose that an infinitesimal change takes place in the system. The natural variables of the Gibbs energy function T and $\mathbf{p}$ and the numbers of moles n_i $(n_A \ldots n_Q \ldots)$ exhibit the infinitesimal changes dT, $d\mathbf{p}$, and dn_i and the change in the Gibbs energy is given by the expression of the total differential:

$$dG = -SdT + Vd\mathbf{p} + \sum_i^n \mu_i dn_i \tag{17.1}$$

The μ_i are the chemical potentials of the species participating in the reaction; G, S, and V the Gibbs energy, the entropy, and the volume of the system; and $\mathbf{p}$ and T its pressure and temperature. Let us write the above chemical reaction under the most concise form:

$$\sum v_i M_i = 0$$

M_i symbolizes the reactants and products. For the reactants (A, B), the stoichiometric coefficients ν bring the negative sign since their number of moles decreases during the reaction. It is the contrary for the products. Because of the stoichiometry of the reaction, the following equalities are obligatorily satisfied:

$$dn_A/a \; = \; dn_B/b = \; dn_P/p = dn_Q/q = d\xi$$

ξ is the extent of the reaction. With these relations, the change in the Gibbs energy accompanying the reaction is

$$dG = -\, SdT \; + \; Vd\boldsymbol{p} \; + \; \left(a\mu_A \; + \ldots . \, q\mu_Q\right)d\xi$$

At constant temperature and pressure,

$$dG \; = \; \left(a\mu_A \; + \; \ldots . \, q\mu_Q\right) \, d\xi$$

Let us symbolize $\sum \nu_i\mu_i$ the sum $p\mu_p + q\mu_Q + ... - a\mu_A - b\mu_B - ....$:

$$\sum \nu_i\mu_i = p\mu_P \; + \; q\mu_Q \; + \; \ldots . \; - \; a\mu_A \; - \; b\mu_B \; - \; \ldots .$$

The sum $\sum \nu_i\mu_i$ is the reaction Gibbs energy Δ_rG:

$$\Delta_rG \;\; = \sum \nu_i\mu_i \tag{17.2}$$

By examination of the expression Δ_rG, it appears that the reaction Gibbs energy is the change in the Gibbs energy accompanying the reaction *at a given moment of its evolution*, that is to say, for a given extent ξ at which each species i exhibits an instantaneous chemical potential μ_i. The chemical potentials of the species vary with the extent of the reaction and as a result the reaction Gibbs energy does vary with the extent of the reaction.

When the reaction spontaneously takes place, the change dG must be negative because of the proper properties of the function G. As a result, at constant temperature and pressure, the reaction Gibbs energy Δ_rG must be negative:

$$\Delta_rG \; < \; 0 \quad (\text{spontaneous} \quad \text{reaction} \;\; dT = 0, \;\; \mathrm{d}\mathbf{p} = 0)$$

17.2 Expression of the Reaction Gibbs Energy as a Function of the Activities of the Reactants and Products

Let us recall that, from the general standpoint, the chemical potential of a species whatever its thermodynamic state is

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

μ_i° is its standard chemical potential and a_i its activity in the state where it stands. The relation between the reaction Gibbs energy and the activities is obtained by expressing the chemical potentials μ_i present in the relation (17.2) by the above expression. We obtain

$$\begin{aligned}\Delta_r G = &\left(p\mu^\circ{}_P + q\mu^\circ{}_Q + \ldots.. - a\mu^\circ{}_A - b\mu^\circ{}_B\right)\\ &+RT \ln\left(a_P^p a_Q^q / a_A^a a_B^b\right)\end{aligned} \tag{17.3}$$

In this expression, each activity can take every value (except that corresponding to the equilibrium—this point is the matter of the next paragraph). The ratio ($a_P^p\, a_Q^q/a_A^a\, a_B^b$) is called the *reaction quotient* and is symbolized by Q.

17.3 Equilibrium Law: Equilibrium Constant

From the general standpoint (viz. Chap. 5), at equilibrium

$$dG = 0$$

At constant temperature and pressure, according to what is preceding

$$\sum \nu_i \mu_i = 0 \quad (dT = 0 \quad \text{and} \quad d\mathbf{p} = 0) \tag{17.4}$$

For example, for the above reaction, the equilibrium condition (at constant temperature and pressure) is

$$p\mu_P + q\mu_Q + \ldots - a\mu_A - b\mu_B - \ldots = 0 \tag{17.5}$$

Let $\mu_{i\text{eq}}$ be the chemical potentials of the different species at equilibrium. Considering the above example again, the equilibrium condition entails the equality:

$$p\mu_{P_\text{eq}} + q\mu_{Q_\text{eq}} + \ldots = a\mu_{A_\text{eq}} + b\mu_{B_\text{eq}} + \ldots \tag{17.6}$$

Let us replace the chemical potentials at equilibrium by their general expressions where the activities are those at equilibrium:

$$\mu_\text{eq} = \mu^\circ + RT \ln a_\text{eq}$$

Expression (17.6) becomes

$$
\begin{aligned}
&p\left(\mu^{\circ}{}_P + RT \ \ln \ a_{P_{\mathrm{eq}}}\right) + q\left(\mu^{\circ}{}_Q + RT \ \ln \ a_{Q_{\mathrm{eq}}}\right) + \ldots \\
&\quad - a\left(\mu^{\circ}{}_A + RT \ \ln \ a_{A_{\mathrm{eq}}}\right) - b\left(\mu^{\circ}{}_B + RT \ \ln a_{B_{\mathrm{eq}}}\right) - \ \ldots\ldots \ = 0
\end{aligned}
$$

or after rearrangement

$$
\begin{aligned}
&RT \ \ln \left(a_p{}^p aQ^q \ldots./ \ aA^a aB^b \ldots..\right)_{\mathrm{eq}} \\
&\quad = (a\mu^{\mathrm{o}}A + b\mu^{\mathrm{o}}B + \ldots..) - (p\mu^{\mathrm{o}}P + q\mu^{\mathrm{o}}Q + \ldots..)
\end{aligned}
\tag{17.7}
$$

We have seen that the standard potentials $\overset{\circ}{\mu}_A$, $\overset{\circ}{\mu}_B$, etc. are constant at given temperature and pressure. As a result

$$
RT \ \ln \left(ap^p a_Q^q \ldots./ \ a_A^a a_B^b \ldots..\right)_{\mathrm{eq}} = \text{ constant } \quad (dT = \ 0 \ d\mathbf{p} = \ 0)
$$

and evidently

$$
\left(ap^p a_Q^q \ldots./ \ a_A^a a_B^b \ldots..\right)_{\mathrm{eq}} \ = \ K^{\circ} \tag{17.8}
$$

K° is the constant of the chemical equilibrium. It is called standard equilibrium constant (IUPAC) or also thermodynamic equilibrium constant. At equilibrium and at constant temperature and pressure, the activities of the species participating in the reaction obey relation (17.8). Conversely, the fact that this relation is verified means that the chemical equilibrium is reached. Relation (17.8) is the expression of the mass action law.

The relation (17.8) is general. It is satisfied, at constant temperature and pressure, when the equilibrium of every reaction is reached and this assertion is true when it involves only one phase or even several. However, in the latter case, it is true only when the whole closed system is considered. It is not if one considers each phase separately.

17.4 Reaction Standard Gibbs Energy and Reaction Gibbs Energy

Let us consider the right member of relation (17.7), the sign of which has been changed. According to relation (17.3) of Chap. 5, it is clear that it has the significance of the standard molar Gibbs energy change $\Delta_r G^{\circ}$ accompanying the reaction:

$$aA + bB + \ldots\ldots. \quad pP + qQ + \ldots..$$

that is to say, when the reactants and the products are in their standard states:

$$\Delta_r G^\circ = \left(p\mu^\circ{}_P + q\mu^\circ{}_Q + \ldots..\right) - \left(a\mu^\circ{}_A + b\mu^\circ{}_B + \ldots..\right) \tag{17.9}$$

The reaction Gibbs energy $\Delta_r G$, according to (17.3), is

$$\Delta_r G = \Delta_r G^\circ + RT \ln\left(a_P^p a_Q^q / a_A^a a_B^b\right) \tag{17.10}$$

or

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q \tag{17.11}$$

At equilibrium,

$$\Delta_r G = 0$$

and from (17.8), one can deduce that

$$-RT \ln K^\circ = \Delta_r G^\circ \tag{17.12}$$

and

$$\Delta_r G = -RT \ln K^\circ + RT \ln\left(a_P^p a_Q^q / a_A^a a_B^b\right) \tag{17.13}$$

Relation (17.13) is sometimes called the van't Hoff's reaction isotherm.

The notion of reaction standard Gibbs energy $\Delta_r G^\circ$ is endowed with a true practical interest since it permits to calculate the Gibbs energy change $\Delta_r G$ accompanying a chemical reaction between reactants and products when they are in ordinary thermodynamic states, provided that the activities of the different species in the initial and final states are known and provided that the transformation is performed at constant temperature and pressure. Let us, indeed, envisage the following cycle (Cf., Fig. 17.1):

Let us consider the reaction

$$aA + bB \rightarrow mM + nN$$

and calculate the Gibbs energy change $\Delta_r G$ accompanying it. The initial and final states are some given states. It is clear (viz. Fig. 17.1) that

$$\Delta_r G = \Delta G_1(\text{reactants})\text{initial} \rightarrow \text{standard} + \Delta_r G^\circ + \Delta G_2(\text{products})\text{standard} \rightarrow \text{final}$$

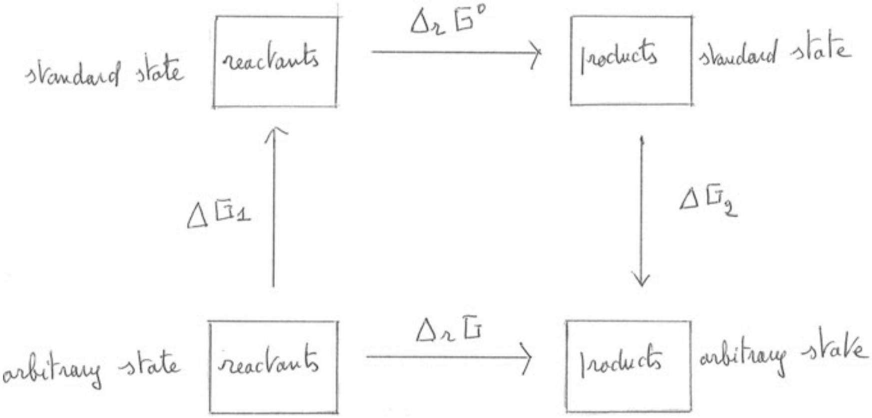

Fig. 17.1 Principle of the calculation of the change in molar Gibbs energy $\Delta_r G$ of a chemical reaction through the standard Gibbs energy when the reactants and products are in an ordinary state at constant temperature and pressure

Since the chemical potentials are molal Gibbs energies and since the activities in the standard states are equal to unity

$$\begin{aligned}\Delta G_1(\text{reactants})\text{initial} \rightarrow \text{standard} &= [a\,\mu_A{}^\circ - a(\mu_A{}^\circ + RT\ \ln\ a_{Ai})] \\ &\quad + [b\mu_B{}^\circ - b(\mu_B{}^\circ + RT\ \ln\ a_{Bi})] \\ \Delta G_2(\text{products})\text{standard} \rightarrow \text{final} &= \left[m\left(\mu_M{}^\circ + RT\ \ln\ a_{Mf}\right) - m\,\mu_M{}^\circ\right] \\ &\quad + \left[n\left(\mu_N{}^\circ + RT\ \ln\ a_{Nf}\right) - n\mu_N{}^\circ\right]\end{aligned}$$

that is to say,

$$\Delta_r G = \Delta G_1 + \Delta_r G^\circ + \Delta G_2$$

We again find the fact that an activity has the meaning of the Gibbs energy change accompanying the crossing of a substance from the standard state into some non-ordinary state (viz. Chap. 9).

Hence, the tabulation of a limited number of standard Gibbs energies permits the calculation of the Gibbs energies of chemical reactions arising whatever the conditions are, but which must evolve at constant pressure and temperature.

Concerning this purpose, it seems interesting for us to briefly recall the main methods of determination of standard Gibbs energies. Let us mention:

- The determination of the equilibrium constants
- That of electromotive forces of galvanic cells
- The measurement of energy intervals in molecules allowing the calculation of molecular partition functions (viz. Chap. 26)
- The use of the third law of thermodynamics

17.5 Usually Chosen Standard States

As a rule, the choice of standard states is arbitrary. It is the same thing for that of the scale of "concentrations" to which the activities are related. Actually, the choice is rather based on practical considerations. Let us recall those which are, by far, most often, adopted. Usually, but in no case obligatorily:

- For ions and molecules in dilute solutions, activities are related to the scale of molar concentrations or to that of molalities (viz. Chap. 1). The numerical values on either of these scales little differ from each other, for dilute solutions.
- For the solvent of a dilute solution, its activity is related to its molar fraction. Its numerical value differs very little from unity in dilute solutions.
- For a pure solid, its standard state is its pure state at atmospheric pressure. Hence, its activity is equal to unity.
- For gases in equilibrium with their solutions, their activities are chosen to be equal to their partial pressures expressed in pressure unity, still often in atmospheres for historical reasons. This is true when the pressures are not too large.
- For liquid mixtures, the activity of each component is related to its molar fraction and its numerical value differs few from the latter.

The qualifier "related to" used above means that the activity a of a species in a given medium is related to its "concentration" C whatever the scale is, by the following relation (viz. Chap. 6):

$$a = \gamma C$$

17.6 Come Back on the Constancy of the Equilibrium Constants

It has been already said, at several steps, that the value of an equilibrium constant may vary according to the chosen standard states. Relation (17.12) above is an indisputable proof of this assertion. When, indeed, one chooses different standard states for the reactants and products of a chemical reaction, quite evidently, the standard Gibbs energy $\Delta_r G^\circ$ changes and according to relation (17.12), the equilibrium constant also. When there is no equilibrium ($\Delta_r G \neq 0$), when one operates with different standard states, relation (17.10) shows that since Gibbs energy changes accompanying the chemical transformation are constant (state function), the reaction quotient differs according to the description mode of the phenomenon. As a result, the activity values of the different species are not the same as those handled with the first set of standard states. In other words, for the reaction Gibbs energy to remain the same, whichever the retained standard states are, there must exist a kind of spontaneous compensation between the values of the standard reaction Gibbs energy and those of the activities. This compensation can be qualified as being subtle.

17.7 Equilibrium Constant in Homogenous Gaseous Medium

By hypothesis, the reaction occurs only in one phase. By adopting the hypothetical state in which it exhibits an ideal behavior at the pressure of 1 atm as standard state, activity is equal to its fugacity in numerical values (viz. Chap. 10):

$$a_i = f_i$$

As a result, the general expression of the equilibrium constant (17.8) is

$$\left(f_P^p f_Q^q \ldots . / f_A^a f_B^b \ldots ..\right)_{\text{eq}} = K_f \tag{17.14}$$

It is, then, specified that the equilibrium constant is related to the fugacities by the use of the index f. Of course

$$K_f = K^\circ$$

when the behavior is ideal. By using the fugacity coefficients ϕ_i (viz. Chap. 7), K_f is expressed by the following relation:

$$K_f = \left(p_P^p p_Q^q \ldots . / p_A^a p_B^b \ldots ..\right)_{\text{eq}} \bullet \left(\phi p^p \phi_Q^q \ldots . / \phi_A^a \phi_B^b \ldots ..\right)_{\text{eq}}$$

Actually, it is little used since there exist few data concerning the fugacity coefficients in literature. The first term of the product of the right member is the equilibrium constant K_p expressed in terms of partial pressures:

$$K_p = \left(p_P^p p_Q^q \ldots . / p_A^a p_B^b \ldots ..\right)_{\text{eq}}$$

It is clear that it does not take into account the interactions between the gas molecules. Hence, it cannot be constant. At high pressures, its value may considerably change.

Another constant K_f' is by far more used than the previous one. It comes from the application of a rule (which actually is an approximation) due to Lewis and Randall. According to it, the fugacity f_i of a gas in a gaseous mixture is related to its fugacity f_i' in the pure state at the total pressure of the mixture studied by the relation

$$f_i = y_i f_i'$$

where y_i is its molar fraction in the gaseous state. After replacement in the expression of K_f above, we obtain

$$K_f{}' = \left(f'^{p}_{p} f'^{q}_{Q} \ldots . / f'^{a}_{A} f'^{b}_{B} \ldots ..\right)_{\text{eq}} \bullet \left(y^{p}_{p} y^{q}_{Q} \ldots . / y^{a}_{A} y^{b}_{B} \ldots ..\right)_{\text{eq}}$$

It is evident that this expression cannot be exact, given the fact that the rule is nothing else than an approximation.

17.8 Equilibrium Constants of Reactions in Homogeneous Solutions Resulting from Mixtures from Several Fully Miscible Liquids

For the case of chemical reactions occurring in a mixture of several fully miscible liquids, the most often chosen standard state of each species is the pure liquid at the temperature of the solution under the pressure of 1 atmosphere. The activity of each species is equal to the product of its molar fraction by its activity coefficient (viz. Chap. 9):

$$a_i = \gamma_{r\,i} x_i$$

The equilibrium thermodynamic constant is

$$K^\circ = \left(x^{p}_{p} x^{q}_{Q} \ldots . / x^{a}_{A} x^{b}_{B} \ldots ..\right)_{\text{eq}} \bullet \left(\gamma_r p^{p} \gamma^{q}_{rQ} \ldots . / \gamma^{a}_{rA} \gamma^{b}_{rB} \ldots ..\right)_{\text{eq}} \qquad (17.15)$$

Evidently, the constant $K_x{}'$ defined by the expression

$$K_x{}' = \left(x^{p}_{p} x^{q}_{Q} \ldots . / x^{a}_{A} x^{b}_{B} \ldots ..\right)_{\text{eq}}$$

is only approximate.

17.9 Reactions in Dilute Solutions

Equilibrium constants are often expressed in terms of molarities and molalities. Let us recall (viz. Chap. 9) that for the dilute solutions, the usually chosen standard states are such that, at the temperature of the solution and under the pressure of 1 atmosphere, in the cases where the "concentration" is expressed in:

- Molalities, the activity coefficient of each substance $\gamma_{m2} = a_{m2}/(m_2/m_2{}^\circ)$ tends toward unity when the molality m_2 tends toward zero,
- Molarities, the activity coefficient $\gamma_{c2} = a_{c2}/(c_2/c_2{}^\circ)$ tends toward unity when the concentration c_2 tends toward zero.

The equilibrium constants can be obtained by starting from relation (17.14) by replacing the molar fractions by the molalities or the molarities in it and also by replacing of course the activity coefficients relative to the molar fractions by those relative to the molalities and molarities.

One knows (viz. Chap. 1) that the number n_2 of moles of the solute is related to its molality m_2 by the relation

$$n_2 = (\mathrm{n}_1 M_1/1000) m_2$$

where n_1 and M_1 are the numbers of moles and the molar mass of the solvent. One can make the following approximation for the dilute solutions. Its molar fraction x_2 is defined by the expression

$$x_2 = n_2/\sum n$$

where Σn is the sum of the number of moles of all the other components of the solution, including the solvent. When the solution is sufficiently diluted, one can set up

$$\sum n \approx n_1$$

By performing this approximation, the two preceding relations lead to

$$x_2 \approx (M_1/1000) m_2$$

By replacing the molar fractions of the solute by the expressions of this kind, we obtain the relation

$$K_m{}' = \left(mp^p m_Q^q \ldots . / \, m_A^a m_B^b \ldots ..\right)_{\mathrm{eq}} \tag{17.16}$$

Actually, the numerical value $M_1/1000$ is already introduced into the value $K_m{}'$. The relation (17.16) is approached for two reasons. The first one lies in the approximations governing the crossing from the molar fractions to the molalities. The second approximation lies in the absence of the factor grouping the activity coefficients. Actually, its presence is not justified given the preceding approximations entailing a very weak number of moles.

By an analogous reasoning, one finds the expression (17.17) of the equilibrium constant $K_c{}'$ expressed in molarity terms:

$$K_c{}' = \left(c_p^p c_Q^q \ldots . / c_A^a c_B^b \ldots ..\right)_{\mathrm{eq}} \tag{17.17}$$

As K_m', K_c' is approximate for the same reasons as above. The crossing from the molar fractions to the molarities is realized thanks to the exact relation (viz. Chap. 1)

$$x_2 = (c_2/1000\rho)\left(\sum nM/\sum n\right)$$

where $\Sigma\ nM$ is the mass of the solution and ρ its density. The approximations performed here are due to the facts that in diluted solutions

$$\sum nM \approx n_1M_1 \quad \text{and} \quad \sum n \approx n_1$$

The equilibrium constants expressed in terms of "concentrations" are often called formal or conditional constants. More generally, the adjective conditional seems to qualify the case where not only the "concentrations" are taken into account but also other experimental conditions are fixed.

17.10 Heterogeneous Cases

Now we consider the case in which the chemical reaction occurs in heterogeneous systems. It is the case, for example, when the equilibrium involves gases and solids, one solution and one solid, etc.

Whichever the case is, the general relation (17.8) can be applied. The important point to notice is that, when the equilibrium involves a pure liquid or solid, its activity is usually chosen, to be equal to unity. This simplifies the writing of the equilibrium constant. As an example, let us again take the case of equilibrium

$$aA + bB + \rightleftharpoons pP + qQ + \ \ldots.. \Rightarrow$$

where A, P, and Q are in solution and where B is a pure solid. Given the corresponding convention for the activity, the chemical potential B is

$$\mu_B = \mu_B{}^\circ + RT \ \ln\ 1$$
$$\mu_B = \mu_B{}^\circ$$

The same reasoning as that which leads to the general relation (17.8) gives the expression

$$\left(a_p^p a_Q^q \ldots./a_A^a 1^b \ldots..\right)_{\text{eq}} = K^\circ$$

systematically written in literature as

$$\left(a_p^p a_Q^q \ldots . / a_A^a \ldots ..\right)_{\text{eq}} = K^\circ$$

If the activity of the solid pure compound does not intervene in the writing of the equilibrium constant (because of the value unity of its activity), its standard potential, however, still intervenes in the standard Gibbs energy change which is still written according to relation (17.9) as it is shown by the reasoning involved in the occurrence. This explains why, for example in an electrochemical cell, when one electrode is constituted by a pure metal (Zn, Cu, and so forth) the activity of which is taken to be equal to unity, when the metal constituting it participates in the chemical equilibrium.

Let us recall that the fact to write down the activity of a pure phase equal to unity is legitimate only under the pressure of 1 atmosphere. When it is not the case, its activity remains constant as previously but is no longer equal to unity. Hence, corrections must be in principle done. However, since the influence of the pressure on the activity of a solid or a liquid is weak, it is neglected in "everyday" practice.

17.11 Change in the Equilibrium Constant with Pressure

The change of the value of the equilibrium constant with the pressure can be grasped through relation (17.12)

$$\ln K^\circ = -\Delta_r G^\circ / RT$$

Let us differentiate with respect to the total pressure **p** at constant temperature. We obtain

$$(\partial \ln K^\circ / \partial \boldsymbol{p})_T = 1/RT[\partial(\Delta_r G^\circ)/\partial \boldsymbol{p}]_T$$

Since the standard states are defined as being independent from the pressure of the system, the reaction standard Gibbs energy does not change with the external pressure:

$$(\partial \ln K^\circ / \partial \boldsymbol{p})_T = 0$$

As a result, the constant K_f is also independent from the external pressure (viz. paragraph 6).

However, the fact that the value of the equilibrium constant does not vary with the pressure does not necessary mean that the equilibrium concentrations of reactants and products remain constant when the pressure increases. Constancy of the equilibrium constant and equilibrium position must not be confused!

– Let us consider the following reaction where the reactants and products are in the gaseous state and are at equilibrium at a given temperature:

$$aA + bB + \rightleftharpoons pP + qQ + \;\ldots.. \Rightarrow$$

The equilibrium constant K_f is given by relation (17.14). The fugacity coefficient of each gas is given by the relation

$$\phi_i = f_i / p_i$$

The partial pressure of the gas i is given by the relation

$$p_i = y_i P$$

where P is the total pressure and y_i the molar fraction of the gas in the mixture. From the last two relations, one deduces

$$f_i = \phi_i y_i P$$

Replacement of the fugacities f_i by this expression into (17.14) leads to

$$K^\circ = \left(y_P^p y_Q^q \ldots . / \, y_A^a y_B^b \ldots ..\right)_{\text{eq}} \bullet \left(\phi_p^p \phi_Q^q \ldots . / \phi_A^a \phi_B^b \ldots ..\right)_{\text{eq}} \bullet P^{(m + n - a - b)} \tag{17.18}$$

After studying this expression, it is evident that the K° constancy entails that when the total pressure P varies, the factor grouping the molar fractions also varies. When the total pressure varies, the equilibrium concentrations adapt themselves in order that the value K° does not change. However, we can notice that when the combination of exponents $(m+n-a-b)$ is null, there is no modification of the equilibrium concentrations with P. The change in the equilibrium position with the pressure is related to Le Chatelier's principle which stipulates that increasing the pressure favors the reaction which is accompanied by a decrease of the number of molecules.

Another point must be taken in mind. In the just above reasoning, the term taking into account the fugacity coefficients has not been considered. But the latter varies with the pressure, very moderately with weak pressures but, very markedly, when they are endowed with large values.

17.12 Change in the Equilibrium Constant with the Temperature

The effect of the temperature on the equilibrium constant can be studied through the differentiation of relation (17.12) with respect to the temperature. Performed at constant pressure, it leads to the expression

$$(\partial \ \ln \ K^\circ/\partial T)_P = -(1/R)\partial(\Delta_r G^\circ/T)/\partial T$$

Thanks to the Gibbs-Helmholtz relation (viz. Chap. 2)

$$[\partial(\Delta G/T)/\partial T]_P = -\Delta H/T^2$$

one can write

$$d\ln K^\circ/dT = \Delta H^\circ/RT^2 \qquad (17.19)$$

This relation is sometimes called van’t Hoff’s equation.

(In passing, let us remark that using partial derivatives is unnecessary, because K° does not depend on the total pressure. A simple differentiation is sufficient.)

ΔH° is the standard enthalpy change accompanying the chemical reaction when it occurs from the left toward the right:

$$\Delta H^\circ = \left(pH^\circ{}_P + qH^\circ{}_Q + \ldots.\right) - \left(aH^\circ{}_A + bH^\circ{}_B + \ldots..\right)$$

The $H^\circ{}_i$ are the molar enthalpies of species i in their standard states, at temperature T. They depend only on the temperature. Of course, the standard states chosen in order to define the chemical potentials and those chosen to define the enthalpies must correspond to each other. Let us confine ourselves to only recall that for a solute, the partial molar enthalpy is always equal to that it possesses at infinite dilution. As a result, the solution of the solute at infinite dilution is the solution of reference.

In short intervals of temperature changes, one can admit the approximation that ΔH does not depend on the temperature. Then, the integration is immediate. We obtain

$$\ln \ K^\circ = -\Delta H^\circ/RT + \text{constant}$$

This relation is very interesting. It shows, indeed, that it is possible to obtain the heat of reaction when the equilibrium constant is known, at least, at two temperatures. Another possibility of its use is the following one: it permits to know the equilibrium constant at every temperature provided that it is known at one temperature and that its enthalpy change is also known.

For larger temperature intervals, corrections through calorific capacities must be done.

Chapter 18

Obtention of Equilibrium Thermodynamic Constant pH: Definitions and Measurement

Abstract The importance of the knowledge of the equilibrium constants of the chemical reactions is considerable. They notably permit to know the position of the equilibrium according to the experimental conditions with a good accuracy, thanks to the use of the activities when the behaviors of reactants and products are not ideal.

The chapter mentions some determinations of thermodynamic equilibrium constants. They entail the use of activities. Here, very classical determinations by potentiometric and conductometric measurements are considered. Some examples are given. They are the potentiometric determinations of the mean activity coefficient of a strong acid, the thermodynamic acidity constant of a weak acid, the ionic product of water, and the conductometric measurement of an acidity constant. It is also devoted to the quantity named pH, the definition and measurement of which being intimately linked to the concept of activity.

Keywords Equilibrium constants (potentiometric and conductometric determinations) • Electrochemical cells • pH • Formal and operational definitions • Thermodynamic acidity constants • Water, tonic product

By way of introduction of this chapter, let us recall the considerable importance of the knowledge of the equilibrium constants of chemical reactions. They notably permit to know the position of the equilibrium with a good accuracy, according to the experimental conditions, thanks to the use of the activities.

In this chapter and in the following, we mention some determinations of thermodynamic equilibrium constants. They entail the use of the activities. In this chapter, we consider very classical determinations by potentiometric and conductometric measurements. We finish with some considerations on the quantity pH, the definition and measurement of which are intimately linked to the concept of activity.

In the following chapter, we shall describe some less conventional determinations while taking into account the activities.

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18.1 Potentiometric Determination of the Mean Activity Coefficient of a Strong Acid

The potentiometry permits to directly determine the mean ionic activity coefficient of one electrolyte (Cf, Chap. 14). The cell reaction involves the formation of the substance (the activity of which is wanted) in solution. Let us take the example of the hydrochloric gas which is a strong acid in water. We want to determine its mean activity when its molality in water is *m*.

Let us consider, for example, the cell

$$\mathrm{Pt}\left|\mathrm{H_2(1\ atm.)}\right|\mathrm{HCl(aq, m)}\left|\mathrm{AgCl(s)}\right|\mathrm{Ag}$$

constituted by a hydrogen electrode (under the pressure of 1 atm.) and by a silver–silver chloride electrode dipped into the solution of hydrochloric acid at the molality *m*. The hydrogen electrode is sensitive to hydrogen ions. It is the indicator (or working) electrode. The spontaneous cell reaction is

$$1/2\ \mathrm{H_2(1\ atm.)} + \mathrm{AgCl\ (s)} \rightarrow \mathrm{H^+(m)} + \mathrm{Cl^-(m)} + \mathrm{Ag(s)} \qquad (18.1)$$

Ions H^+ and Cl^- are at the "concentration" *m* in the solution. The cell reaction (18.1) does not evolve as it is written above. Actually, it evolves according to a fragmented manner through the two simultaneous electrochemical reactions:

$$\text{at the anode}: \quad 1/2\ \mathrm{H_2(1\,atm.)} \rightarrow \mathrm{H^+(m)} + 1\ \mathrm{e^-}$$

$$\text{at the cathode}: \quad \mathrm{AgCl(s)} + 1\ \mathrm{e^-} \rightarrow \mathrm{Ag(s)} + \mathrm{Cl^-(m)}$$

There only exists one solution in the cell in which both electrochemical reactions occur. Hence, the cell does not possess two compartments, the existence of which would involve the existence of a liquid junction (viz. Chaps. 5, 12, and 14).

The cell electromotive force *E* is related to the activities of the different species participating in the cell reaction through the equation

$$E = E^\circ - (RT/nF)\ln\left[a_{\mathrm{HCl}}\, a_{\mathrm{Ag}}/\left(a_{\mathrm{H_2}}\right)^{1/2} a_{\mathrm{AgCl}}\right] \quad (\text{with } n = 1)$$

where E° is the standard electromotive force. According to the usual choices of the standard states (viz. Chap. 17):

- $a_{\mathrm{H_2}} = 1$ since dihydrogen is at the standard pressure and since it exhibits a perfect behavior at this pressure, at usual temperature,
- $a_{\mathrm{Ag}} = 1$ and $a_{\mathrm{AgCl}} = 1$ since both are solid constituting pure phases.

As a result, the cell electromotive force is given by the expression

$$E = E^\circ - (RT\ /\ F)\ln a_{\mathrm{HCl}} \qquad (18.2)$$

The measurement of *E* permits to obtain the activity a_{HCL}.

E is also given by the expression

$$E = E^\circ - (RT / F) \ln (a_{H+} \bullet a_{Cl-})$$

or

$$E = E^\circ - (RT/F) \ln(m_+ \bullet m_-) - RT \quad \ln \gamma_+ \gamma_-$$

In the present case,

$$\gamma_+ \gamma_- = \gamma_\pm^2$$

and

$$m_+ \bullet m_- = m_\pm^2$$

whence

$$E + (2RT/F) \ln \quad m - E^\circ = - (2RT/F) \ln \gamma_\pm$$

We see that the method permits, starting from the measurement of the corresponding electromotive forces E, to evaluate the mean ionic activity coefficient $\gamma_\pm$ when the molality of hydrochloric acid is m. But, in order that it is possible, the standard force electromotive E° must be known. The latter is obtained by extrapolation. The extrapolation is based on a form of the Debye–Hückel's relations which is of the following type for a monovalent electrolyte in very dilute solution (viz. Chap. 15):

$$\ln \gamma_\pm = - A\surd m + Cm$$

where C and A are constants. Putting this relation into the preceding one, we obtain

$$E + (2RT/F) \ln m + A\surd m = E^\circ + Cm$$

We notice that the left member of the last equation is a function of the molality, *which is known*. After measurement of the emf E at each molality m, it is known. The extrapolation of its value down to $m = 0$ gives the value of the standard electromotive force E°.

This principle of determination can be generalized to every electrolyte. The only condition which must be fulfilled in order that the determination would be possible is that one of the electrodes of the used cell reversibly responds to one of the ions of the electrolyte.

For example, for generalization, let us consider the electrolyte $M_{\nu+} A_{\nu-}$. The cell which may be used is

$$M|M^{v+},\ A^{v-}\text{solution}\ (m)|A$$

The electromotive force of the cell is given by the expression

$$E = E^{\circ} - (RT/nF)\ \ln\ a_{+}^{v+}a_{-}^{v-}$$
$$E = E^{\circ} - (v\ \ RT/nF)\ \ln\ \ m_{\pm} - (v\ \ RT/nF)\ \ln\gamma_{\pm}$$

In this expression, $m_{\pm}$ is defined by the expression

$$m_{\pm}^{v} = m_{+}^{v+}m_{-}^{v-}$$

and since

$$m_{+} = v_{+}m \quad \text{and} \quad m_{-} = v_{-}\ m$$
$$m_{\pm}^{v} = m^{v}\left(v_{+}^{v+}v_{-}^{v-}\right)$$

with

$$v = v_{+} + v_{-}$$

and n is the number of exchanged electrons appearing in each of both electrochemical reactions. This methodology of determination of the electrolyte activities has been used in numerous times, in various experimental conditions.

(*On the fringe of this method of determination, it is interesting to answer the following question: Why the cell reaction* (18.1) *does not occur chemically rather than through the electrochemical way, since all the reactants are present together in the same solution as that of the cell. The reason is of kinetic order. With respect to the electrochemical reactions, the chemical reaction is very slow and has no time to evolve.*)

18.2 Potentiometric Determination of the Thermodynamic Acidity Constant of a Weak Acid

Let us take the example of a determination in water. Let HA be the acid. Let us consider the following cell, called the Harned cell:

$$\mathrm{Pt}|\mathrm{H_2}(1\ \mathrm{atm.})|\mathrm{HA, A^{-},\ H^{+},\ Cl^{-}}|\mathrm{AgCl(s)}|\mathrm{Ag}$$

Once more, it is without a liquid junction. The goal is to determine the thermodynamic acidity constant K_{a}° of the weak acid HA in water. It is defined by the expression

$$K_a^{\circ} = a_{H+}\, a_{A-} \,/\, a_{HA} \tag{18.3}$$

where A^- is the conjugated base. A constant concentration of chloride ions is introduced as sodium chloride. The "concentration" in chloride ions, introduced as sodium chloride, is constant.

Generally, the acid HA and its conjugate base A^- are not electroactive in these conditions. The cell reaction is reaction (18.1).

As we have seen it above, the electromotive force of the cell E is given by relation (18.2); that is, it depends on the activity a_{HCl}. The activity of chloride ions being constant, it is evident that the electromotive force depends on the activity a_{H+} which, in turn, depends on the ionization constant through relation (18.3). Hence, one can conceive that E measurements in well-defined conditions allow to reach K_a°.

For example, let us consider the cell without junction:

$$\mathrm{Pt}\left|\mathrm{H_2(1\ atm.)}\right|\mathrm{CH_3COOH\ (m_1),\ CH_3COO^-(m_2),\ NaCl(m_3)}\left|\mathrm{AgCl(s)}\right|\mathrm{Ag}$$

The goal is the determination of the thermodynamic acidity constant of acetic acid. According to what is preceding, the electromotive force of the galvanic cell is given by the expression

$$E = E^{\circ} - (RT/F) \ln \left(m_{H+} m_{Cl-}\ \gamma_{H+} \gamma_{Cl-}\right)$$

Given the definition of the dissociation constant:

$$K_a^{\circ} = \left(m_{H+} m_{CH3COO-} / m_{CH3COOH}\right) \bullet \left(\gamma_{H+} \gamma_{CH3COO-} / \gamma_{CH3COOH}\right)$$

The combination of both expressions is as follows:

$$\begin{aligned} E - E^{\circ} + (RT/F) \ln \left(m_{CH3COOH} m_{Cl-} / m_{CH3COO-}\right) \\ = -(RT/F) \ln\ K_a - (RT/F) \ln \left(\gamma_{CH3COOH} \gamma_{Cl-} / \gamma_{CH3COO-}\right) \end{aligned}$$

The left-hand member of this expression can be calculated. E°, indeed, is already known (viz. the above paragraph) and E is the electromotive force measured with the cell. When its values, obtained for different molalities m_1, m_2, m_3, and so forth, are drawn as a function of the ionic strength of the solution, and when, after, one extrapoles down to a null ionic strength I_m, the obtained value gives K_a°, since the term containing the activity coefficients is then equal to zero:

$$I_m \rightarrow 0 \quad K_a \rightarrow K_a^{\circ}$$

In order to perform this kind of extrapolation, the "concentrations" $m_{CH3COO-}$ and $m_{CH3COOH}$ must be those which truly exist when the acid–base equilibrium is reached. From the kinetic standpoint, this condition does not raise any problem because the equilibria acid–base in aqueous solutions are obtained very quickly.

From the standpoint of the equilibrium, an approached value of the constant is chosen at the beginning of the process in order to calculate a first approached value of the ionic strength and of the constant. This latter value is retained as a first value for a second calculation and so on. For the first approximation, one sets up

$$m_{\mathrm{CH3COOH}} \approx m_1,$$

$$m_{\mathrm{CH3COO-}} \approx m_2,$$

$$m_{\mathrm{Cl-}} \approx m_3.$$

The ionic strength is calculated according to the relation

$$I_m = m_2 + m_3 + m_{\mathrm{H+}}$$

since all the ions are monovalent. The molalities at equilibrium are approached thanks to the approximative chosen ionization constant. Generally, a small number of iterations are necessary. The process of iteration is ended when two successive values K_a are considered as being equal according to the precision of the measurements.

Finally, the value obtained at 25 °C for acetic acid is $K_a^{\circ} = 1754 \times 10^{-5}$.

18.3 Potentiometric Determination of the Ionic Product of Water

This example is quite similar to the previous one. The used cell is the following:

$$\mathrm{Pt}|\mathrm{H_2}(\ 1\ \mathrm{atm.})|\mathrm{MOH}\ (\mathrm{m_1})\ \mathrm{MCl}\ (\mathrm{m_2})|\mathrm{AgCl(s)}|\mathrm{Ag}$$

where M^+ is an alkali metal ion. By definition, the ionic product of water K_w° is given by the relation

$$a_{\mathrm{H+}}\, a_{\mathrm{OH-}} = K_w^{\circ}$$

The electromotive force of the cell is again given by the expression (18.2). A reasoning absolutely analogous to the preceding, followed by considering that the base MOH and the metallic chloride are fully dissociated, leads to the following relation:

$$\begin{aligned} E - E^{\circ} + (RT/F)\ln\left(m_{\mathrm{Cl-}}/\, m_{\mathrm{OH-}}\right) \\ = -(RT/F)\ln\ K_w - (RT/F)\ln\left(\gamma_{\mathrm{Cl-}}/\gamma_{\mathrm{OH-}}\right) \end{aligned}$$

At infinite dilution, the term on the right containing the activity coefficients becomes null. Hence

$$K_w \rightarrow K_w^{\circ}$$

Once more, one proceeds by extrapolation by writing the value of the left term of the above equation as a function of the ionic strength, the value of E° being known from another side. Finally, it has been found that at 25 °C

$$K_w^{\circ} = 1{,}008 \times 10^{-14}$$

This kind of determination has been very often performed.

Let us notice that a junction cell must also be used. Then, the principal uncertainty affecting the result comes from the occurrence of the junction potential (viz. under the pH measurement).

18.4 Conductometric Determination of the Thermodynamic Acidity Constant of a Weak Acid

Let us consider the determination of the thermodynamic acid dissociation constant K_a° of a monoacid HA.

It is an experimental fact that the molar conductivity Λ_m of a weak acid depends on its concentration. It decreases, firstly, very quickly and then more slowly when its concentration increases (Fig. 18.1).

It is admitted that the lowering of the molar conductivity is, in great part, due to the lesser dissociation of the acid with its concentration. This behavior is in accordance with Ostwald's dilution law which stipulates that the more dilute a weak acid is, the more dissociated it is.

- In a simplified treatment of the phenomenon, it is admitted that the value of the dissociation coefficient α of the acid is approached by the coefficient α' given by the expression

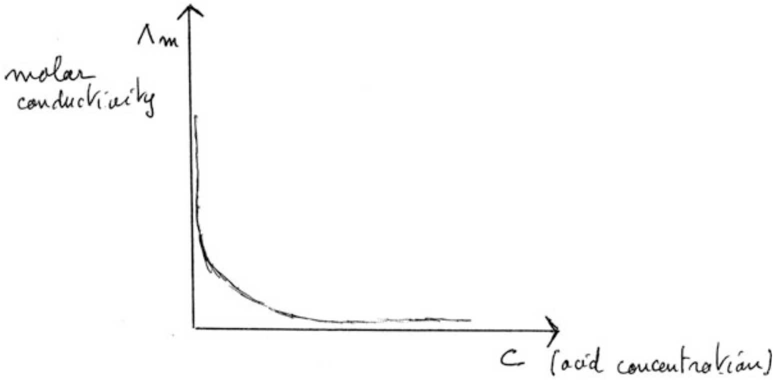

Fig. 18.1 Dependence of the molar conductivity of a monoacid on its concentration

$$\alpha' = \Lambda/\Lambda_o \tag{18.4}$$

where Λ_o is the limit molar conductivity, that is to say, at infinite dilution. α' permits to obtain an approached value of the constant K' being searched for. The reasoning is as follows. Once the coefficient α' is known, it is evident that given the equilibrium

$$\mathrm{HA} \rightleftharpoons \mathrm{H}^+ + \mathrm{A}^-$$

if the analytical concentration of the acid is C, K' obeys the relations

$$\begin{aligned} K' &= (\alpha' C)(\alpha' C)\,/\,(1-\alpha')C \\ K' &= (\Lambda/\Lambda_o)^2 C\,/\,(1-\Lambda/\Lambda_o) \end{aligned} \tag{18.5}$$

For the following operations, Λ being measured, Λ_o must be known.

According to Kohlrausch's law of the independent migration of ions (law of purely experimental origin) (that some authors qualify as being a postulate), the limit molar conductivity of the acid can be calculated by applying the following expression which relates the limit molar conductivities of HCl, NaA, and NaCl:

$$\Lambda_o(\mathrm{HA}\ ) = \Lambda_o(\mathrm{HCL}) + \Lambda_o(\mathrm{NaA}) - \Lambda_o(\mathrm{NaCl})$$

since HCl, the sodium salt of the acid NaA and NaCl are strong electrolytes, that is to say fully dissociated. This relation should be rather written as follows:

$$\Lambda_o(\mathrm{H}^+ + \mathrm{A}^-) = \Lambda_o(\mathrm{H}^+ + \mathrm{Cl}^-) + \Lambda_o(\mathrm{Na}^+ + \mathrm{A}^-) - \Lambda_o(\mathrm{Na}^+ + \mathrm{Cl}^-)$$

- This approach is approximate for two reasons which act in synergy. The first one is that the conductances Λ of the ions, parameters that cannot be rid of since they are inherent to the method, are not truly constant. The conductances vary with the square root of the "concentrations" of the ions, according to an empirical law due, also, to Kohlrausch. The second one is that there is also a ionic strength effect. Hence, both factors are due to ionic interactions and corrections must be done at two levels.
- In order to solve the whole problem, one operates in two steps.

- In the first step, one introduces the notion of effective conductivity Λ_e for each ion (the index e means effective and not equivalent). Λ_e is obtained by a mathematical relation in which intervenes the concentration C_i equal to that of all the ions of the solution where the acid is dissolved. For example, for acetic acid,

$$\Lambda_e = 390.59 - 148.61\sqrt{C_i} + 165.5C_i\left(1 - 0.2274\sqrt{C_i}\right)$$

(Let us mention in passing that this kind of relation, which is from an experimental origin, is justified in part by the Debye–Hückel's relations—viz. Chap. 15.) By generalizing the relation (18.5) to the effective conductivities, one obtains the relation (18.6) permitting an estimation K'' of the constant $K_a{}^\circ$ being searched for:

$$K'' = (\Lambda/\Lambda_e)^2 C\,/\,(\,1 - \Lambda/\Lambda_e) \tag{18.6}$$

or equivalently:

$$K'' = \mathrm{C}''_{\mathrm{H+}}\mathrm{C}''_{\mathrm{A-}}/\mathrm{C}''_{\mathrm{HA}}$$

One can consider that once the approximate value K'' is obtained, one is cast from the first problem which is that of the change of conductivities.

A better approach K''' of the constant being searched for is obtained, then, by resorting the activity coefficients. K''' is given by the expression

$$K''' = \left(C''_{\mathrm{H+}}\mathrm{C}''_{\mathrm{A-}}/\,\mathrm{C}''_{\mathrm{HA}}\right)\left(\gamma_{\mathrm{H+}}\gamma_{\mathrm{A-}}/\gamma_{\mathrm{HA}}\right)$$

Therefore, one can write

$$\ln\ K''' = \ln\ K'' + \ln\gamma_\pm^2/\gamma_{\mathrm{HA}} \tag{18.7}$$

with

$$\gamma_\pm^2 = \gamma_{\mathrm{H+}}\gamma_{\mathrm{A-}}$$

At this point of the reasoning, it seems that one has reached a dead end. In order to know K''', indeed, one must know K'' which depends on Λ_e. Now, to know Λ_e entails to know the concentrations C_i and this knowledge, in turn, entails to know K'''!

The problem is solved by successive iterations. For the first loop turn of the iteration process, one begins by adopting the approximation $\Lambda_e = \Lambda_o$ which permits to obtain a first value α by using the relation (18.8) and hence a value C_i'' and then a value Λ_e. The latter one permits to obtain a new value α through the relation

$$\alpha = \Lambda/\Lambda_e \tag{18.8}$$

The iterative process is continued until the last calculated α value does not differ significantly from the preceding one. The convenient value K'' is then found.

- In the second step, one takes into account the activity problem. The methodology is classical. It consists in drawing the curve ln K'' as a function of the ionic strength of the solution. When the latter is null, the term taking into account the activity coefficients in (18.7) becomes null. Hence, the extrapolation of the curve down to $I = 0$ gives the being searched for constant K_a°. The methodology, of course, entails to have, before, performed measurements of conductances at several analytical concentrations and to have, for every one, done the previous calculations.

18.5 The Quantity pH

The quantity pH involves the determination of the activity of an ion, in the occurrence, the activity of the hydrogen ion. This paragraph gives an example of what a lot of dispositions and precautions must be taken in order to have the best estimation of the activity of an ion.

18.5.1 Generalities: Formal Definition of pH

(We confine ourselves to the study of the notion of pH in water.)

The quantity pH is considered today as being a parameter permitting to evaluate the acidity or the basicity of a medium rather than one parameter exactly quantifying the activity of the solvated proton (also called "hydrogen ion") in the studied medium.

Even so, from a theoretical standpoint, a pH value is conceived in order to quantify the activity of the proton since it is defined as being the decadic antilogarithm of the activity of the solvated proton in the medium ($a_{\mathrm{H+aq}}$ for water):

$$\mathrm{pH} = -\log \; a_{\mathrm{H+aq}}$$

This is the formal definition of pH.

From the historical viewpoint, the authors who have proposed this definition, as early as in 1924, are Sörensen and Linderstrom-Lang.

It results from the conjunction of some experimental results and scientific facts which were, then, already known. Let us mention:

- *The use of hydrogen electrode by Sörensen in order to measure the acidity (in the occurrence, which was considered at this time, as being the proton concentration) of a medium Le Blanc having before demonstrated that its behavior toward the hydrogen ions is reversible,*
- *The fact, however, that Sörensen had found that the hydrogen electrode does not exactly respond to the concentration in ions H^+.*
- *The introduction by G.N. Lewis as early as 1907 of the quantity activity.*

Arrhenius's theory of the electrolytic dissociation and the hypothesis that it is the true concentration of ions H+, rather than the total concentration of an acid, which quantifies the acidity in the best way, indeed, were already known.

Concerning, now, the fact that the quantity pH should be today considered as a parameter permitting to evaluate the acidity of a medium rather than exactly reflecting its activity, as for it, is due to some difficulties inherent to the definition:

- The first one, but not the least, is the true nature of the species "hydrogen ion" in water (and also in other solvents). It is doubtful and we do not insist on it.
- The second is not of less interest than the first one: it results from our impossibility to measure the activity of an ion.
- A third point, which is not truly pejorative but which is very important, is the generalized adoption of the potentiometric assembling in order to measure the pH, in the proper definition of pH (viz. under). It is undoubtedly for measurement facilities. The laterative assembling is constituted by a glass electrode sensitive and selective to the aqueous proton, by a reference electrode, a part such a liquid junction in order to permit the contact of the reference compartment with the solution under study and by an electrometer for the measurement of pH.

The question we now face is the following one: What is the link between the measured electromotive force and the quantity pH?

18.5.2 The Electromotive Force and the Quantity pH

Let us consider the Sörensen's cell schematized by

$$\mathrm{Pt}\left|\mathrm{H_2(g)}\right|\mathrm{solution}\left|\right|\mathrm{KCl\ (aq)}\left|\mathrm{AgCl\ (s)}\right|\mathrm{Ag}$$

It is a cell with a junction, the potential E_j of which is minimized (this fact is symbolized by the presence of the two vertical straight lines in the scheme). We know that the cell reaction is

$$\mathrm{AgCl(s)}\ + 1/2\,\mathrm{H_2(g)} \rightarrow \mathrm{Ag(s)} + \ \mathrm{Cl^-(aq)} + \ \mathrm{H^+(aq)}$$

In the usual conditions, this reaction spontaneously evolves. Hence, the cell is a galvanic one. Its electromotive force is given by the expression (viz. electrochemistry)

$$E = E^\circ - (RT/F)\ln\left[a_{\mathrm{Cl-}}a_{\mathrm{H+}}/\left(a_{\mathrm{H_2}}\right)^{1/2}\right] + E_j$$

E° is the standard electromotive force. $a_{\mathrm{H+}}$ and $a_{\mathrm{H_2}}$ are the activities of the proton and of dihydrogen in the left compartment, whereas $a_{\mathrm{Cl-}}$ is that of the chloride ion in that of the right. E_j is the junction potential between both compartments. This expression takes into account the fact that the activities a_{Ag} and a_{AgCl} are equal to unity, by convention on the activities, because they are solid phases constituted by only one component. At room temperature, for pressures of the order of 1 bar, the dihydrogen behavior is that of a perfect gas. Hence, it is legitimate, according to the unanimously adopted conventions for the activities, to write

$$a_{H_2} = P_{H_2} \quad \text{(in numerical values)}$$

where P_{H2} is the pressure of dihydrogen. Thus, we obtain

$$E = E^\circ - (RT / F) \ln \left[a_{Cl-} a_{H+} / (P_{H_2})^{1/2}\right] + E_j \tag{18.9}$$

Unfortunately, the activities a_{Cl-} and a_{H+} (activities of ions alone) and E_j are not experimentally accessible. Actually, the electromotive force depends on the activity of the solvated proton, but it also depends on the other two unknown quantities. This is the difficulty which must be overcome.

18.5.3 Operational Definition of pH

The operational *definition* of pH is based on the use of the Sörensen cell. It involves two operations. The first one consists in conventionally assigning values of pH to some buffer solutions, called standard buffers. These must be, imperatively, compatible with the formal definition of pH. It is at this level that it is necessary to make one hypothesis on the activity of an ion alone. Such a hypothesis is founded on the Debye–Hückel's relations. In the second operation, one uses a device which, reasonably, allows the measurement of the pH difference between two solutions.

Let us consider the Sörensen's cell above working for two different acid solutions X (unknown solution) and S (standard reference solution). It is quite possible, from the experimental standpoint, to choose experimental conditions such as the dihydrogen pressure P_{H2} and the activity a_{Cl-} of the chloride ions are constant during the whole measurements performed and that they are, each one, in both solutions. a_{Cl-} depends only on the concentration of potassium chloride in the right compartment and one can admit that it is not perturbed by the ions of the liquid junction. The electromotive forces measured in identical conditions with both solutions are, respectively, $E(X)$ and $E(S)$. Admitting the hypothesis that, during the two experiences, the potential of liquid junction E_j remains the same, one immediately finds the following two relations, starting from the relation (18.9) applied to the solutions X and S:

$$E(X) - E(S) = -(RT/F)\ln[a_{H+}(X)/a_{H+}(S)]$$

and by introducing the formal definition of pH:

$$\text{pH}(X) - \text{pH}(S) = F[E(X) - E(S)]/(2.303\ RT)$$

We notice that once one has assigned a pH value to the solution S, that of the solution X is settled once the potential difference is measured.

The measurement of pH may be performed with other reference electrodes than the silver–silver chloride one or with other working electrodes sensitive to the ion hydrogen than the hydrogen electrode, both used in the Sörensen's cell. In practice, most often, one uses the glass electrode as working electrode and the calomel one as the reference.

It remains, now, to assign a pH value, which must be compatible with the formal definition, to the solutions standard S. Several methodologies have been proposed in order to do that. Here, we only mention that proposed by the "National Bureau of Standards (NBS)" in Washington, developed by Bates and Guggenheim.

The assignation of the pH values to the standard solutions is performed, once for all, after studying the electromotive forces of the Harned galvanic cells (viz. the beginning of the chapter) of the kind

$$\text{Pt}|\text{H}_2(\text{g})|\text{buffer solution},\quad \text{Cl}^-|\text{AgCl(s)}|\text{Ag(s)}$$

The standard solutions are those containing the buffer mixture. They also contain known molalities of potassium chloride. Let us recall that these cells are without junction. This characteristic, of course, eliminates the problem of the junction potential. Moreover, let us also notice that the fact that the standard solution should also be a buffer solution is imperative. Thus, in such a manner, the pH value of the solution to which a definitive value must be assigned is stabilized.

The electromotive force of these cells is given by the expression (viz. electrochemistry)

$$E = E^{\circ}(\text{AgCl/Ag}) - \text{RT/F}\ \ln\left[(a_{H+}a_{Cl-})/(a_{H_2})^{1/2}\right]$$

When one operates under a hydrogen pressure of 1 bar and when one introduces the definition of the activity a_{Cl-},

$$a_{Cl-} = m_{Cl-}\gamma_{Cl-}$$

the previous relation becomes

$$\log(a_{H+}\gamma_{Cl-}) = -(E - E^{\circ})F/(2.303\ \text{RT}) + \log\ m_{Cl-}$$

(the "concentration" of the chloride ion being, here, expressed in molalities, $\gamma_{\mathrm{Cl}-}$ should be symbolized by $\gamma_{m\ \mathrm{Cl}-}$—we do not do it for the sake of the simplicity of the writing). It appears that the product $a_{\mathrm{H}+}\gamma_{\mathrm{Cl}-}$ is experimentally accessible. All these facts being taken into consideration, the different steps of the assignation of the pH values to the buffer solutions are the following ones:

- The determination of the value of the term $-\log\,(a_{\mathrm{H}+}\gamma_{\mathrm{Cl}-})$ for several solutions containing the same buffer at the same "concentration" but with different molalities in potassium chloride, by using the cell without junction above.
- The obtaining of the value $-\log\,(a_{\mathrm{H}+}\gamma_{\mathrm{Cl}-})^{\circ}$ by linear extrapolation, down to the molality $m_{\mathrm{Cl}-}$ null, of the preceding values: $-\log\,(a_{\mathrm{H}+}\gamma_{\mathrm{Cl}-})$. This series of handlings is repeated for each buffer solution.
- The calculation of the pH value of the (buffer) solution according to the relation

$$\mathrm{pH} = -\log\left(a_{\mathrm{H}+}\gamma_{\mathrm{Cl}-+}\right)^{\circ} + \log\gamma_{\mathrm{Cl}-}$$

It is in this kind of calculations and, more precisely, in that of $\gamma_{\mathrm{Cl}-}$ that the following relation (in all evidence of Debye–Hückel type and called the Bates-Guggenheim's relation) is used:

$$\log\gamma_{\mathrm{Cl}-} = A\,I^{1/2}/\left(1 + 1.5\ \ I^{1\,/2}\right)$$

where A is the coefficient A of the Debye–Hückel's relations and I the ionic strength of the solution expressed in molalities (I should be symbolized by I_m). The factor 1, 5 comes from the choice of the admitted value of the "size parameter" of the chloride ion, $a = 5$. It is interesting to notice that the linear extrapolation of $-\log\,(a_{\mathrm{H}+}\gamma_{\mathrm{Cl}-})$ down to $m_{\mathrm{Cl}-} = 0$ is justified by the relation

$$-\log\left(a_{\mathrm{H}+}\gamma_{\mathrm{Cl}-}\right) = -\log\left(m_{\mathrm{H}+}\gamma_{\mathrm{H}+}\gamma_{\mathrm{Cl}-}\right)$$

The NBS (National Bureau of Standards—USA) has proposed some buffer standards called primary standards. Some secondary standards have been proposed later.

It is important to recall that the assigning, to the standard solutions, of pH values compatible with the formal definition cannot be directly verified. However, it can be so indirectly. The argument is as follows: if the pH value of a solution is the same whatever the choice of a standard solution, it is highly likely that the formal definition is checked. It is actually the case. In the literature, this favorable check is called the internal coherence of the NBS scale of pH.

The range of validity of the operational scale of pH is limited by the two following constraints in order that the pH value keeps its physical significance, that is to say, so that it is in agreement with the formal definition. The first constraint is that the ionic strength of the solution under study does not exceed 0.1 mol L^{-1} in order that the obtained result remains compatible with the used Bates-Guggenheim's relation. The second is that pH values (which are to be found) must lie between 2 and 12. The last two limits are those beyond which the constancy of the junction potential, probably, is no longer granted, given the high mobility of hydroxide and hydrogen ions of the solution under study.

Chapter 19

General Principles of Calculations Involving the Activities of Ionic Species in Solution

Abstract The chapter describes some methodologies in order to obtain thermodynamic equilibrium constants, but in a manner less conventional and certainly more modern than previously.

The determination of equilibrium constants entails the knowledge of the "at equilibrium activities" of the species participating in it. There is a difficulty. It is the following one. If the determination of the activities of the uncharged substances is possible (but somewhat difficult and lengthy) it is impossible for the ions. As a rule, this impossibility leads to a problem which may appear as being impossible to solve.

The methodologies described in this chapter show how the thermodynamic equilibrium constants involving some ions may be approached by calculations using the Debye–Hückel relations. But, these calculations, in turn, also suffer as a rule from a difficulty which is briefly mentioned in this chapter. To use the "Debye–Hückel" relations, the ionic strength of the solution must be known and its knowledge involves that of the equilibrium constants, one of which, at least, by hypothesis is unknown! The principle and the followed methodology of these calculations are described in this chapter with the examples of the determinations of acidic constants.

Keywords Ion activity (experimental determination) ionic strength • Debye–Hückel relations use • Concentrations of the different species at equilibrium • Non-ideality corrections • Informatic calculations • Absorbance p*K*a determination

In this chapter, we are continuing to describe some methodologies in order to obtain thermodynamic equilibrium constants, but in a manner less conventional and certainly more modern than previously.

We have seen that the determination of equilibrium constants entails the knowledge of the "at equilibrium activities" of the species participating in it. Now, if the determination of the activities of the uncharged substances is possible but somewhat difficult and lengthy, we also know that it is impossible for the ions. As a rule, this impossibility leads to a problem fantastically difficult to solve.

The goal of this chapter is to show how the thermodynamic equilibrium constants involving some ions may be approached by calculations using the

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Debye–Hückel relations. But, these calculations, in turn, as a rule, also suffer from a difficulty that we first briefly mention. Then, we recall the conditions of ionic strengths for which corrections of nonideality must be done. Finally, we mention the principle and the methodology of these calculations.

19.1 Fundamental Difficulty

The fundamental difficulty concerning these calculations lies in the chain of the following facts:

- The ionic strength of the solution must be known in order to calculate the activity coefficients of the ions through the Debye–Hückel relations.
- The knowledge of the ionic strength entails that the extent of dissociation of the electrolytes (which are not obligatorily strong) must be known. The knowledge of this extent, in turn, entails the prior determination of the equilibrium constants ... being searched for!

We shall see how this difficulty may be overcome.

19.2 Nonideality Corrections

For rough calculations, nonideality corrections can be neglected. In these conditions, the found values of the concentrations and those of the obtained equilibrium constants are only approached. Moreover, they vary with the ionic strength of the solution.

For ionic strengths of the solution less than 10^{-2} mol L^{-1}, the calculations are proved to be relatively simple. They are based on the Debye–Hückel limit equation. There is no reason to take into account the identity of the ions, i.e., to use the extended relation.

For ionic strengths ranging in the interval 10^{-2}–10^{-1} mol L^{-1}, it must be used. But, then, the nature of the ions must be taken into account by introducing the "ion-size parameter" a. This complicates the calculations.

Beyond ionic strength forces superior to 10^{-1} mol L^{-1}, Davies' relation (which gives reasonable results up to ionic strengths of the order of 5×10^{-1} mol L^{-1}) may be used.

Roughly, it can be said that the theoretical prediction of the activity coefficients is very satisfactory up to ionic strengths of 0.1 mol L^{-1}. When only electrolytes 1–1 are involved, the activity coefficients may be then obtained with an accuracy of 3 p 100 by founding ourselves on the limit equation. When an adjustable parameter such as the so-called ion-size parameter a, is used, the accuracy may amount up to ± 1 p 100. For the polycharged ions, an accuracy nearly as good as the preceding may be obtained, provided that all the equilibria existing in the solution are taken into account.

We shall see, immediately under, that the calculations of the activities are often necessary to perform at every step of the calculation of the equilibrium concentrations and of equilibrium constants, both types of calculations being, indeed, intimately linked.

19.3 Reasoning Allowing the Calculation of the Concentrations of the Different Species at Equilibrium

Before beginning the calculations (through the Debye–Hückel equations) of the activities and those of the equilibrium constants in which some ions intervene, it is judicious to give the strategy of the calculation of the different species concentrations at equilibrium.

Let us assume, at this moment, that activities are equal to concentrations. The strategy is based on the fact that the species concentrations at equilibrium must, obligatorily, obey some mathematical relations. They are, of course, the reflection of intangible physical laws. It happens that, from an absolute standpoint, they are systematically in a sufficient number in order that the resultant mathematical system is systematically determined. These relations are the following:

- The mass balance of the solution
- Its charge balance
- The equilibrium state

Let us take the example intentionally simple of the dissolution of C_0 moles of acetic acid in water to form 1 L of solution. The matter is to calculate the concentrations of the different species stemming from the ionization of acetic acid, once the equilibria are reached. The two chemical equilibria are the following:

- The revelation of the acid character of acetic acid:

$$\mathrm{CH_3COOH} \rightleftharpoons \mathrm{CH_3COO^-} + \mathrm{H^+}$$

- The ionic product of water:

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H^+} + \mathrm{OH^-}$$

The corresponding mathematical equations, which must be obligatorily satisfied, are the expressions of the equilibria, which we write temporarily (the species concentrations are figured in square brackets):

$$|CH_3COO^-||H^+|/|CH_3COOH| = K_a \tag{19.1}$$

$$|H^+||OH^-| = K_w \tag{19.2}$$

– The mass law:

$$[CH_3COO^-] + [CH_3COOH] = C_0 \tag{19.3}$$

(There is no reason to take into account the water balance because the theory is only valid in dilute aqueous solutions. Since the "concentration" of water is expressed in molar fractions—viz. Chap. 17—it can be considered as being constant and equal to unity.) (Here, the equilibria are written according to the Arrhenius theory, equivalent, in the occurrence, to that of Brönsted.)

– The charge balance:

$$[H^+] = [OH^-] + [CH_3COO^-] \tag{19.4}$$

Hence, for this example, there exist four equations for four unknowns $[H^+]$, $[OH^-]$, $[CH_3COOH]$, and $[CH_3COO^-]$. The system is mathematically determined. It is reduced easily into one equation with only one unknown. It is (19.5) of the third order in $|H^+|$ which must be, finally, solved:

$$[H^+]^3 + K_a[H^+]^2 - (K_w + K_aC_0)[H^+] - K_aK_w = 0 \tag{19.5}$$

Of course, (19.5) depends on the parameters K_a, K_w, and C_0 which govern the system. Once the root $[H^+]$ is found, all the other concentrations are immediately accessible through the handling of the initial relations which are obligatorily satisfied at equilibrium.

19.4 Taking into Account the Activities

The taking into account of the activities is performed by using the Debye–Hückel equations since some ions intervene in the equilibrium. Concerning, now, the uncharged species, one assigns the value unity to their activity coefficients since the solutions are sufficiently dilute in order that this is legitimate.

Let us recall that the problem we face with is that we must know the ionic strength of the solution in order to use Debye–Hückel equations, and consequently we must know the true species concentrations which are, actually, searched for.

Before entering into the problem of the unknown ionic strength, the fact that some relations are expressed in terms of activities and other ones expressed in terms of concentrations must be handled simultaneously. For example, in the above case of acetic acid, (19.1) and (19.2) are expressed, in principle, in activities, that is to say according to (the terms located in round brackets are the activities)

$$(H^+)(CH_3COO^-)/(CH_3COOH) = K_a{}^\circ \quad \text{and} \quad (H^+)(OH^-) = K_w{}^\circ$$

whereas (19.3) and (19.4) are expressed in concentrations. Let us also recall that the conditional constants $K_a{}'$ and $K_w{}'$ are given by the expressions

$$[H^+][CH_3COO^-]/[CH_3COOH] = K_a{}' \quad \text{and} \quad [H^+][OH^-] = K_w{}'$$

and that thermodynamic and conditional constants are linked together by the relations

$$K_a{}^\circ = K_a{}'(\gamma_{CH3COOH}/\gamma_{H+}\gamma_{CH3COO-}) \quad \text{and} \quad K_w{}^\circ = K_w{}'/\gamma_{H+}\gamma_{OH-}$$

According to the retained scale of "concentrations" (molarities or molalities), the constants should, of course, be symbolized by $K_{a\ c}{}'$ or $K_{a\ m}{}'$ (viz. Chap. 11).

19.5 Calculations

The calculations of concentrations and of activities of the species are performed in an iterative way.

Let us suppose that we are interested in the "concentrations" and the activities of the different species at equilibrium and that we have at our disposal the thermodynamic equilibrium constants (in the example of acetic acid $K_a{}^\circ$ and $K_w{}^\circ$). Equations (19.1)–(19.4) are not homogeneous. The first two are expressed in activities, and the latter two in concentrations. Solving the system as it has been done above, that is to say by not taking into account this inhomogeneity, induces the problem of the physical significance of the calculated quantities: Are they activities or concentrations? The answer and the whole problem are overcome by adopting the following iterative process:

- In the first step of iterations, one operates by mixing activities and concentrations, i.e., one supposes that the equations are homogeneous, i.e., one mixes activities and concentrations. The system of the initial equations is reduced to a single one, the unknown of which is $|H^+|$ (it is (19.5) in the case of acetic acid). It is solved. One obtains a first value $|H^+|_1$ which has neither the meaning of an activity nor that of a concentration, since it is obtained from initial equations involving both kinds of quantities. Nevertheless, from this first value, one calculates the other "pseudo-concentrations or activities" $|CH_3COO^-|_1$, $|CH_3COOH|_1$, and $|OH^-|_1$. Thus, one calculates a first pseudo-ionic strength I_1. (Notice the used symbols with vertical lines—and not round or square brackets—which mean that the quantities are a kind of mixture of activity and of concentration.) Once obtained, the value I_1 is introduced into the judicious equation Debye–Hückel equation (that applies for the found I_1). It permits to calculate a first set of pseudo-activity coefficients γ_{H+1}, $\gamma_{CH3COO-\ 1}$, $\gamma_{OH-\ 1}$. The latter ones, in turn, permit to obtain a first set of the values of the conditional constants $K_a{'}_1$ and $K_w{'}_1$ by using the following relations (and by setting up $\gamma_{CH3COOH-} = 1$. This is justified—viz. Chap. 15)—

$$K_{a1}' = K_a{}^\circ/\gamma_{CH3COO-}\gamma_{H+} \quad \text{and} \quad K_{w1}' = K_w{}^\circ/\gamma_{H+}\gamma_{OH-}$$

The first iteration is finished. It is important to notice that the constants $K_a{'}_1$ and $K_w{'}_1$ do not have, yet, the meaning of pure formal constants. But, however, they approach them and, hence, their meaning begins to deviate from that of thermodynamic constants, given the manner which has permitted to obtain them.

- The second iteration is then initiated. It is strictly performed just like the first one, but in the calculations intervene the pseudo-constants $K_a{'}_1$ and $K_w{'}_1$ stemming from the preceding iteration. At the end of the second iteration, we obtain a new set of pseudo-concentrations $|H^+|_2$, …, a new pseudo-ionic strength I_2, new pseudo-activity coefficients γ_{H+2}, and new formal equilibrium pseudo-constants. After this second iteration, constants $K_a{'}_2$ and $K_w{'}_2$ do possess the meaning of formal constants more than did $K_a{'}_1$ and $K_w{'}_1$ obtained at the end of the previous iteration. It is the same thing concerning the activity coefficients of ionic species which tend more and more to the coefficients such as they are defined, that is to say, in such a manner that they transform pure concentrations into pure activities.
- The further iterations evolve strictly in an analogous manner. The process is stopped when the pseudo-ionic strength I_n is equal to the preceding one I_{n-1}. Then, the constants $K_a{'}_n$ and $K_w{'}_n$ are the *true conditional or formal constants*. The equation system is then homogeneous. They are all expressed in terms of *concentrations*. At the end of this *n*nd and definitive loop of iteration, the concentrations of all the species are found. They are no longer a cross of concentrations and activities. The problem is solved.

At this point of the operations, one can immediately calculate the activities of the different species since their concentrations are known and because of the "true ionic strength" also. It suffices to calculate the activity coefficients through the Debye–Hückel equations and to multiply them by their concentrations. Besides, the activity coefficients are known through the calculations performed during the last iteration.

Generally, the convergence of the whole process is fast. The number of iterations is weak, of the order of 3 or 4.[1]

This process is general. The difficulty often lies at the level of the obtention of the suitable root of the single equation stemming from the reduction of the system of initial equations which must be satisfied. Equations of the fourth order are not rare in this realm. Abel's theorem stipulates that there is no general solution to the

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[1] These calculations can be performed on some pocket calculators.

equations with one unknown of order superior to four. However, several informatic routines permitting to obtain the root, with the required precision, exist in the literature.

19.6 Simultaneous Determination of Concentrations, Activities, and Equilibrium Constants Using Computers

We finish this chapter by showing, with the help of an example, that the use of computers may greatly facilitate the handling of activities and the obtaining of equilibrium constants. The chosen example is that of the determination of the successive acidity constants K_{a1} and K_{a2} of the diacid H_2A:

$$\begin{aligned} &H_2A \rightleftharpoons HA^- + H^+ \quad K_{a1} \quad \Rightarrow \\ &HA^- \rightleftharpoons A^{2-} + H^+ \quad K_{a2} \quad \Rightarrow \end{aligned}$$

The analytical instrumental method used is the UV-visible spectrophotometry since, usually, the diacid H_2A and the dibasic A^{2-} forms exhibit spectra clearly distinct from each other. In this case, of course, the use of the spectrophotometry is convenient.

19.6.1 Determination for a Monoacid

In introduction, we recall the principle of the determination of the pK_a of the monoacid HA by spectrophotometry UV-visible. It is founded on the relation

$$pK_a = pH + \log[HA]/[A^-] \tag{19.6}$$

where [HA] and $[A^-]$ are the concentrations of the conjugate forms at a given pH value. The principle of the method consists in fixing the pH of the solution with the help of a buffer and to measure both concentrations by spectrophotometry. Then, relation (19.6) permits to calculate pK_a. Let us already remark, however, that relation (19.6) is not homogeneous since pH is defined as being rather a measurement of the *activity of the proton* whereas [HA] and $[A^-]$ are concentrations, since the UV-visible spectrophotometry responds to the concentrations.

In order to obtain [HA] and $[A^-]$, one uses the Beer-Lambert law which, at a given fixed wavelength, relates the absorbance A of the solution to the concentration(s) of the species. For example, at very acid pH, provided that the pK_a value is not too low,

$$A = \varepsilon_{\mathrm{HA}}\mathrm{C}.\,1.\,[\mathrm{HA}] \qquad \text{(acid pH)}$$

where $\varepsilon_{\mathrm{HA}}$ is the molar extinction coefficient of the form HA, [HA] is its concentration (for example in mol L^{-1}) and 1 the length of the measurement cell. $\varepsilon_{\mathrm{HA}}$ is a constant for a given temperature, wavelength, and solvent. Likewise, in a very basic medium, provided that the pK_a value is not too large,

$$A = \varepsilon_{\mathrm{A}}\mathrm{C}.\,1.\,[\mathrm{A}^-] \qquad \text{(basic pH)}$$

At intermediary pH, that is to say in the pH interval where both forms are present, the total absorbance A of the solution is the sum of the absorbances of both forms since the two are present and also because of the properties of Beer-Lambert's law:

$$A = \varepsilon_{\mathrm{HA}}\mathrm{C}.\,1.\,[\mathrm{HA}] + \varepsilon_{\mathrm{A}}\mathrm{C}.\,1.\,[\mathrm{A}^-] \quad \text{(intermediary pH)}$$

From another side of reasoning, since in the solution

$$[\mathrm{HA}] + [\mathrm{A}^-] = C$$

and

$$K_a = |\mathrm{A}^-||\mathrm{H}^+|/|\mathrm{HA}|$$

by assimilating activities (terms in which the pK_a is expressed) and concentrations, we obtain the two relations:

$$|\mathrm{HA}| = |\mathrm{H}^+|/[|\mathrm{H}^+| + K_a] \quad \text{and} \quad |\mathrm{A}^-| = |\mathrm{A}^-|/[|\mathrm{H}^+| + K_a] \tag{19.7}$$

And by handling the relations (19.6) and (19.7), we obtain

$$\mathrm{p}K_a = \mathrm{pH} + \log(A - \varepsilon_{\mathrm{A}}\mathrm{C}.1)/(\varepsilon_{\mathrm{HA}}\mathrm{C}.1 - A) \tag{19.8}$$

ε_{A}C.1 and $\varepsilon_{\mathrm{HA}}$C.1 are the absorbances of the sole basic and acid forms at the total concentration C of the whole species. These values are easily determined. It is sufficient to "work" at the judicious pH. The measurement of the absorbance A at an intermediary pH immediately gives the pK_a value. The problem of the activities is studied under. In principle, only one measurement is sufficient for the determination, but several ones are indicated in order to take into account a maximum of experimental information and, thus, to obtain an optimal precision. In order to perform the determination, the working wavelength (the "analytical wavelength") must be chosen in such a way that the spectra of the pure acid and basic forms differ as much as possible from each other. This is the "analytical wavelength."

When neither of both forms HA and A^- absorb in the UV-visible domain, of course, the determination is not possible. However, let us notice that when only one form does absorb, the determination remains possible.

19.6.2 Case of the Diacid H_2A

The preceding considerations can be generalized, but a supplementary difficulty may often happen. Both acidities K_{a1} and K_{a2} may, indeed, overlap. Then, it is impossible to experimentally determine the molar absorption ε_{HA} since the intermediary form HA^- cannot exist, alone, contrary to the forms H_2A and A^{2-}. HA^- is always accompanied by one of the two other forms H_2A or A^{2-}, and even by both. This is due to the overlapping of the two constants K_{a1} and K_{a2}. Its spectrum in the pure state is, therefore, inaccessible by an experimental way. However, at the extreme pH values, H_2A and A^{2-} exist, alone, whence the possible registering of their spectra in the "pure" state remains possible.

The absorbance at a given pH_i is the sum of the absorbances of the three present forms:

$$A = \varepsilon_{H2A}[H_2A]_i.1 + \varepsilon_{HA}[HA^-]_i.1 + \left[A^{2-}\right]_i.1 \tag{19.9}$$

The handling of the equations which are obligatorily satisfied

$$K_{a1} = \left|H^+\right|_i\left|HA^-\right|_i/\left|H_2A\right|_i \quad \text{and} \quad K_{a2} = \left|H^+\right|_i\left|A^{2-}\right|_i/\left|HA^-\right|_i$$

and

$$C = [H_2A]_i + [HA^-]_i + \left[A^{2-}\right]_i$$

leads to the following expressions:

$$[H_2A]_i = 1\left\{[H^+]_i^{\,2}C/D; \quad [HA^-]_i = K_{a1}[H^+]_i C/D; \quad \left[A^{2-}\right]_i = K_{a1}K_{a2}/D\right\} \tag{19.10}$$

with

$$D = [H^+]_i^{\,2} + K_{a1}[H^+]_i + K_{a1}K_{a2} \tag{19.11}$$

The examination of (19.9)–(19.11) shows that the absorbance at a given pH depends on the three molar extinction coefficients, on the constants K_{a1} and K_{a2}, on C, and on $|H^+|$, that is to say on the pH.

19.6.3 Determination of Constants K_{a1} and K_{a2} Without Taking into Account the Activities

The two unknowns to determine are both constants K_{a1} and K_{a2}. Their determination entails that the molar extinction coefficient ε_{HA} of the intermediary pure form, which is directly inaccessible by an experimental means, must be known. Therefore, it is the third unknown. On the other hand, the pH is known and, also, the coefficients $\varepsilon_{\mathrm{H2A}}$ and ε_{A} which are, respectively, determined in very acid and very basic media.

The methodology used to determine the three unknowns is a process of informatic simulation (viz. Chap. 47).

In a first step, it consists in choosing the analytical wavelength and in performing absorbance measurements at several $\mathrm{pH_i}$ values. In order to have the best precision, one must choose a number of pH values by far larger than the number of unknowns.

In a second step, one arbitrarily chooses values of the three unknowns K_{a1}, K_{a2}, and $\varepsilon_{\mathrm{HA}}$ and, thanks to these values, one calculates the total absorbance A_{calc} for each retained $\mathrm{pH_i}$. The calculation is performed through relation (19.9). Then, for this set of the three parameters, one calculates the function U defined by the relation

$$U = \sum_i \left(A_{\mathrm{i\ calc}} - A_{\mathrm{i\ exp}}\right)^2$$

where $A_{\mathrm{i\ exp}}$ is the measured absorbance at the same $\mathrm{pH_i}$ as that for which $A_{\mathrm{i\ calc}}$ is calculated. The function U is the cost function . In the following steps, one modifies the values of the three parameters according to some order of logical decisions and one calculates the function U at each time up to obtaining the set of the values of the three parameters leading to the value U as weak as possible. In other words, the process is repeated till the three following conditions are simultaneously satisfied:

$$(\partial \mathrm{U}/\partial K_{\mathrm{a1}})_{K\mathrm{a}_2,\varepsilon_{\mathrm{HA}}} = 0 \qquad (\partial U/\partial K_{\mathrm{a}_2})_{K_{\mathrm{a1}},\varepsilon_{\mathrm{HA}}} = 0 \qquad (\partial U/\partial \varepsilon_{\mathrm{HA}})_{K_{\mathrm{a1}},K_{\mathrm{a2}}} = 0$$

One must also check that, when it is the case, this is not a singular point or a maximum of the function U. The values of the parameters which minimize the cost function are those being searched for. The described methodology is a least square process, in the occurrence of a nonlinear one since the constants K_{a1} and K_{a2} (contrarily to $\varepsilon_{\mathrm{HA}}$) do not intervene linearly in the calculation of $A_{\mathrm{i\ calc}}$. This is a general methodology.

The difficulty, that this methodology may encounter, is that the research of the parameters minimizing the function U may be difficult and lengthy. There exist several described algorithms permitting to point toward the *minimum minimorum*, of the cost function, but none is infallible. There exists no mathematical process permitting to automatically reach this point.

19.6.4 Taking into Account the Activities

As a rule, one could imagine that one can assimilate activities and concentrations when the equilibrium constants are determined by UV-visible spectrophotometry. It is not rare, indeed, to work with concentrations of the order of 10^{-4} to $5\ 10^{-4}$ mol L^{-1}

of the compound with UV-visible spectrophotometry. Quite evidently, the working concentration interval depends on the values of molar extinction coefficients. But there is a data which must be taken into account: the presence of the buffer which fixes the pH values to which the determinations are performed. Even, we know that to be effective, the buffer solutions must be rather concentrated. Let us admit that for the determination of the pK_a value, the concentration 10^{-4} mol L^{-1} is satisfactory. That of the buffer must be of the order of 10^{-2} mol L^{-1} in order to be effective. The ionic strength exhibits about this value, the ions coming from the compound under study contributing for a negligible amount. As a result, the activity coefficients cannot be neglected.

In the chosen example, one converts the retained pH values into concentrations by the following relations:

$$a_{\mathrm{H}+} = 10^{-\mathrm{pH}} \quad \text{and} \quad [\mathrm{H}^+] = a_{\mathrm{H}+}/\gamma_{\mathrm{H}}$$

$\gamma_{\mathrm{H}+}$ is obtained through the Debye–Hückel relations since the ionic strength is known. In these conditions, the calculations are performed with homogeneous equations. Therefore, the K_{a1} and K_{a2} constants are the conditional ones. It is very easy to go back to the thermodynamic constants, since the ionic strength is known.

Part II
The Activity in Statistical Thermodynamics

Chapter 20
Statistical Thermodynamics in Brief

Abstract The object of statistical thermodynamics is to set up a theory at the molecular scale permitting an interpretation of the classical thermodynamics which, itself, applies to the macroscopic level. Statistical thermodynamics is founded on several postulates and, also, on the principles of quantum mechanics. It permits to calculate the mechanical properties of a thermodynamic system. The obtaining of the expressions relating the mechanical properties to molecular quantities is founded on the ensemble theory of Gibbs. Several kinds of ensembles are considered and used according to the thermodynamic environment of the studied system. The most important are the following:

– The canonical ensemble: The canonical ensemble is a closed, isothermal and volume-constant system
– The grand ensemble or the great ensemble, or the grand canonical ensemble: It corresponds to an open, isothermal, and volume-constant system
– The microcanonical ensemble: It corresponds to an isolated system
– The isothermal, isobaric ensemble.

There happens to exist a well-definite mathematical function, characteristic of each kind of ensembles. When it is known, it permits to calculate the other thermodynamic quantities at the macroscopic scale. These mathematical functions are called partition functions.

Keywords Quantum mechanics • Partition function • Canonical ensemble • Grand-ensemble • Isothermal–isobaric ensemble • Microcanonical ensemble

The object of statistical thermodynamics is to provide a theory at the molecular scale permitting an interpretation of the classical thermodynamics which, itself, applies to the macroscopic level. This theory, indeed, concerns systems containing a very great number of molecules of the order of, at least, about 10^{20}. Therefore, the goal of statistical thermodynamics is to calculate macroscopic properties from molecular properties.

Statistical thermodynamics is founded on several postulates and, also, on the principles of quantum mechanics. It permits to calculate the mechanical properties of a thermodynamic system. Mechanical properties are those whose definition does not involve the introduction of the concept of temperature. For example, they are

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pressure, energy, volume, and number of molecules. As examples of nonmechanical thermodynamic quantities let us mention temperature, entropy, the Gibbs and Helmholtz energies (formerly free energies—Gibbs or Helmholtz), the chemical potential . . ..

The obtaining of the expressions relating the mechanical properties to molecular quantities is founded on the ensemble theory of Gibbs. An ensemble is a mental collection of an extremely large number of *macroscopic* systems representing that under study (which is itself, of course, at the macroscopic scale). Although these systems are all identical at the thermodynamic (macroscopic) scale, they are not at the molecular scale. Gibbs' method consists in assimilating the mechanical variable value in the macroscopic system under study to the average of the values of the same mechanical variable that each system of the ensemble takes. The obtaining of the nonmechanical quantity expressions is done by comparing the relations of classical thermodynamics with those stemming from statistical thermodynamics, that is to say by introducing the values of the mechanical quantities stemming from the statistical theory into the classical one.

Several kinds of ensembles are considered and used according to the thermodynamic environment. The most important are the following:

- The canonical ensemble: From the macroscopic standpoint, it is defined by the three quantities N, V, and T, the values of which being given (N number of molecules or species . . ., V the volume, and T the temperature of the system). The canonical ensemble is a closed, isothermal, and volume-constant system.
- The grand ensemble or the great ensemble, or the grand canonical ensemble: It is defined by the values of the volume V and of the temperature T of the system and by the chemical potential μ_i of each constituent i. It corresponds to an open, isothermal, and volume-constant system.
- The microcanonical ensemble: It corresponds to an isolated system, macroscopically defined by the values N, V, and E.
- The isothermal, isobaric ensemble macroscopically defined by the values N, $\mathbf{p}$, and T.

There happens to exist a well-definite mathematical function, characteristic of each kind of each of these ensembles. Each of these functions is a function of the quantities defining these ensembles. When they are known, they permit to calculate the other thermodynamic quantities (at the macroscopic scale). These mathematical functions are called *partition functions*. Most of the time, they are determined, by calculations, from spectroscopic data. Partition functions are dimensionless numbers.

Incidentally, it seems interesting for us to recall that there exist several strategies to tackle statistical thermodynamics. We confine ourselves to only mentioning them. They essentially differ from each other by the averaging method and by the step at which it is performed:

The strategies differ in the following respects:

- Whether the averaging process is carried out over the collection of the quanto-energetic states of the species or over the quanto-energetic states of the macroscopic systems (which must also obey the principles of quantum mechanics (quanto-energetic states: energy states allowed by quantum mechanics principles)). The quanto-energetic states of the species must be distinguished from those of the systems constituting an ensemble.
- Either the obtained averages are the true average values or the most probable.
- Or the kind of system under study. It may possess:
  - Fixed values of its energy, and composition, that is to say it is an isolated system.
  - Fixed values of its volume, composition, and temperature (the last condition being provided with the help of a heat source at constant temperature). That is to say, it constitutes a canonical ensemble.
  - A fixed value of its volume whereas it is in equilibrium with a heat source at constant temperature and also with reservoirs containing the substances it possesses. The latter equilibrium is obtained through the use of semipermeable membranes. In other words, the system is opened. Its corresponds to the grand ensemble.

Concerning this book, the mentioned averages are related to the collections of the quanto-energetic states of the *macroscopic* systems and the retained values are the most *probable ones*.

Chapter 21
Concept of Ensembles and Postulates

Abstract The followed strategy in order to introduce statistical thermodynamics into the classical one is the one devised by Gibbs. It is based on the consideration of ensembles of systems. It entails the adoption of two postulates permitting to relate the average in time of a mechanical variable to the average of the same variable calculated over one ensemble of systems.

According to:

- The first postulate, the value of the mechanical property in the thermodynamic system under study is equal to its average over the ensemble of the systems, when the number of systems $\rightarrow \infty$.
- The second postulate, in a representative ensemble ($\aleph \rightarrow \infty$) of an isolated system, the systems are uniformly distributed, and, hence, they have the same probability of existence.

The energy levels of the systems are given by the Schrödinger's equation.

Keywords Ensemble • System • Mechanical variable • Closed system • Stationary energy state • Quantum mechanics • Quanto-energetic state • Schrödinger's equation • Wave function • Isolated system • Open system • Ergodic theory of matter • Thermodynamic system

The methods of thermodynamics are fully independent of the notions of atomic and molecular structures as they also are of the notions of reaction mechanisms. The results to which thermodynamics leads do not bring any direct piece of information concerning these aspects of chemistry. Actually, thermodynamics only permits to predict some relations and interconnections between variables describing macroscopic systems which can be directly observed or which can be deduced from quantities which themselves are experimentally directly accessible.

The object of statistical thermodynamics is to provide classical thermodynamics with a theoretical justification founded on the study of phenomena evolving at the molecular level.

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21.1 Strategy: Ensembles and Postulates

The goal consists in finding the expressions of thermodynamics describing the behavior of macroscopic systems at equilibrium by starting from atomic and molecular properties of matter.

Solving this problem is tremendously difficult: it is to deduce these relations by starting from the properties of a huge number of particles, of the order of 10^{20}, at least! As an example of the difficulty, let us regard the case of the pressure. In principle, if we want to calculate the pressure of a system through purely molecular considerations, we must calculate the force exerted *per* area unit upon the partitions of the system. The force is calculated according to the laws of classical or quantum mechanics (viz. next paragraph) . Given the huge number of particles constituting the system, it is absolutely unthinkable to perform the calculation by following this way. This is all the more inconceivable as the system evolves at every moment, because all the particles are in interactions. Hence, in addition to the huge number of particles, calculations should be performed by taking into account the incessant changes with time of the state of the system.

However, one characteristic of the problem simplifies the matter. It is the fact that given the inconceivably large number of particles, it is legitimate to admit that the average values of some physical quantities of the systems are perfectly representative of its (classical) thermodynamic properties.

The followed strategy in order to introduce statistical thermodynamics into the classical one is the one devised by Gibbs. It is based on the consideration of *ensembles of systems*. It entails the adoption of two postulates permitting to relate the average in time of a *mechanical* variable to the average of the same variable calculated over one ensemble of systems (viz. paragraph 3).

21.2 Quantum Mechanics: Schrödinger's Equation—Quanto-Energetic States

The goal of statistical thermodynamics being to calculate the properties of macroscopic systems by starting from those of the particles constituting them, it is an evidence that the latter must be known, including the nature of their interactions. In principle, they are obtained by applying the principles of quantum mechanics.

For our purpose, we must take into consideration the fact that these particles and the *s macroscopic systems putting them together* can only take some discrete energetic levels of values $E_0, E_1, E_2, \ldots, E_j$, often called stationary quanto-energetic states. Theoretically, they are obtained by resolution of the Schrödinger's equation corresponding to the system which applies to the particles and to the macroscopic systems as well.

Let us consider a particle i (molecule, atom) present in a container. Its mass is m_i, its cartesian coordinates x_i, y_i, and z_i, and its momenta are p_{xi}, p_{yi}, and p_{zi}. From the standpoint of quantum mechanics, the system is described by a function Ψ, called *wave function*, possessing the following property: the probability that the particle possesses its coordinates located in the intervals $x_i + dx_i$, $y_i + dy_i$, and $z_i + dz_i$ is given by the expression

$$\Psi^2 dx_i dy_i dz_i$$

In other words, Ψ^2 plays the part of a probability density. Let us suppose that the particle is in a state which is independent of time (it is often the case in chemistry, the species being, most of the time, stable in time) and that it moves in a force field, described by a potential energy E_p, function of the coordinates x_i, y_i, and z_i. The function Ψ is a solution of Schrödinger's equation taking into account these conditions. It is

$$1/m_i\left(\partial^2\Psi/\partial x_i{}^2 + \partial^2\Psi/\partial y_i{}^2 + \partial^2\Psi/\partial z_i{}^2\right) + \left(8\pi^2/h^2\right)\left(E - E_p\right)\Psi = 0$$

where h is the Planck's constant and E the total energy of the particle. The function Ψ, of course, must satisfy some conditions because of the fact that it must describe a probability. It must, indeed, only possess one value, and be finished and continuous in the domain of changes of the coordinates of the system. It must be null at the outside of this domain. Let us notice, from the pure mathematical standpoint, that the expression just above is a differential (with partial derivatives) equation of order 2 and of first degree.

For a macroscopic system containing n particles, the corresponding Schrödinger's equation is

$$\sum_i 1/m_i\left(\partial^2\Psi/\partial x_i{}^2 + \partial^2\Psi/\partial y_i{}^2 + \partial^2\Psi/\partial z_i{}^2\right) + \left(8\pi^2/h^2\right)\left(E - E_p\right)\Psi = 0$$

where x_i, y_i, and z_i are the coordinates of each particle i and E and E_p the total and potential energies of the macroscopic system, the sum being calculated over the total number n of particles.

The equation remains of the same kind as the previous one, but extremely more complicated. Complications are due to the huge number of coordinates to consider. It is important, indeed, to highlight the phenomenal and even unappreciable difficulty that the resolution of Schrödinger's equation relative to 10^{20} molecules must show and this, after having admitted that it is possible to modelize the interactions between them from the mathematical viewpoint and, moreover, that Schrödinger's equation admits analytical solutions! Actually, it is quasi-never the case, even for very simple systems. Notably, let us only think of the time one should spend, in order to write the Hamiltonian operator of such a system!

Within the framework of this brief recall, let us also mention that the general principles of quantum mechanics entail the existence of the quantification of some physical quantities when and only when there is imposition of some conditions to the studied system, such as the occurrence of a finite volume of the system and that of a finite number of particles. This property is very important in the realm of statistical mechanics.

21.3 The Concept of Ensemble of Systems

An ensemble is simply a mental collection of a very great number ℵ of systems, each being supposed to be a replicate of the thermodynamic system under study (Fig. 21.1):

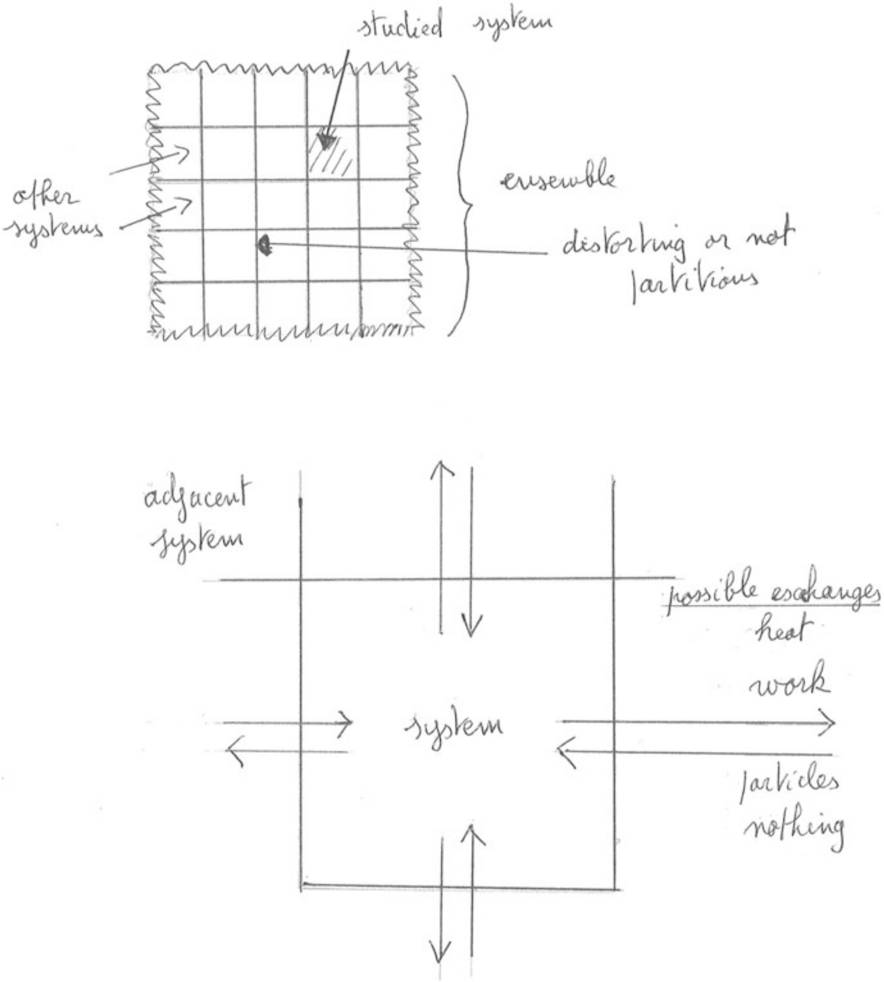

Fig. 21.1 Ensemble and systems

Let us suppose that the system possesses the volume V and contains N molecules of a component and that it is immerged in a very big heat bath at temperature T (it is the case of the canonical ensemble—see just below). The knowledge of N, V, and T is usually sufficient in order to determine the thermodynamic state of the system. The ensemble is constituted by a very large number $\aleph$ of these systems possessing the same *macroscopic* thermodynamic properties (N, V, T). Although they exhibit the same macroscopic properties, they are not similar to the molecular scale, since there exists an extremely important number of quantum states for the same set of values N, V, and T (quantum state signifying, here, *stationary energy state*). For example, in the case of pressure, there exist numerous such states. The average of the pressures of the ensemble is the average over the separated values of the pressures in each system, by giving the same weight to each system in order to perform the calculation. It is the same for each mechanical property.

Among the most important systems encountered in thermodynamics, let us mention the following:

- The *isolated system* defined in classical thermodynamics by the parameters N, V, and E, the replication of which constituting the *microcanonical ensemble*. (E is the symbol of internal energy. We are continuing to use it, as it is often the case in the literature devoted to statistical thermodynamics, although IUPAC recommends the symbol U.)
- The *closed isothermal system* defined by the parameters N, V, and T, the replication of which constitutes the *canonical ensemble*.
- The open isothermal system defined by the parameters μ, V, and T where μ is the chemical potential of the component. Its replication constitutes the grand canonical ensemble (or grand ensemble). Of course, these systems may be constituted of compounds labelized 1, 2, etc., the numbers of moles of which are N_1, N_2, etc. and the chemical potentials are μ_1, μ_2, etc. In this case, the system is defined in thermodynamics by the parameters μ_1, μ_2, V, and T (see later).

As we have just said, a system of an ensemble may or may not, according to its kind, exchange heat, work, particles, and even nothing with its neighbors (viz. Fig. 21.1).

21.4 Postulates

- First postulate: The value of the mechanical property M in the thermodynamic system under study is equal to its average over the ensemble of the systems, when $\aleph \rightarrow \infty$.
- Second postulate: In a representative ensemble ($\aleph \rightarrow \infty$) of an isolated system, the energy of which is constant, the systems are uniformly distributed, that is to say, they have the same probability of existence. This hypothesis of equiprobability is founded on the fact that each system of the ensemble does

possess the same internal energy. Thus, it seems to match the physical intuition which tends to say that two states of the same energy are equiprobable.

In any case, its consequences do not lead to results in contradistinction with experiments. This postulate constitutes the *ergodic* theory of matter.

Chapter 22
The Canonical Ensemble: Notion of Distribution

Abstract The goal of statistical thermodynamics is to permit to appreciate the significance of the thermodynamic functions in terms of molecular parameters. Firstly, this chapter illustrates this point with the aid of the study of the canonical ensemble. It deals with the obtaining of the probabilities of the systems constituting the canonical ensemble to be in some energy states. It provides a description of the canonical ensemble and describes the followed strategy to calculate the average of the mechanical properties such as the pressure and energy with the help of the reasoning based on the fact that the mechanical variables have well-definite values in a given quantum state. It leads to the notion of distribution of the systems in the ensemble. It is the set of the numbers of systems found in well-defined energy states exhibiting the same composition (in one or several compounds) and the same volume. There can exist several distributions. Calculations, exemplified in the chapter, permit to obtain the elementary and global probabilities that a system of the ensemble would be in a definite energetic state. Once the probabilities are obtained, it becomes possible to calculate the canonical partition function.

Keywords Mechanical properties • Partition function • Quantum state • Supersystem • Canonical partition function • Distribution • Maximum term method • Thermodynamic function

The goal of statistical thermodynamics is to permit to appreciate the significance of the thermodynamic functions in terms of molecular parameters. Firstly, we choose to illustrate this point with the aid of the study of the canonical ensemble.

Actually, this chapter is necessary to introduce this theory. It deals with the obtaining of the probabilities of the systems constituting the canonical ensemble to be in some energy states. Obtaining these probabilities is the first necessary condition in order to be able, later, to specify the significance of some thermodynamic quantities.

The problem of the obtention of the probabilities is essentially not different from that of the determination of the distribution of the systems constituting the ensemble in the different possible energetic states. (To aim at the same goal, later, we shall consider the handling of other ensembles.)

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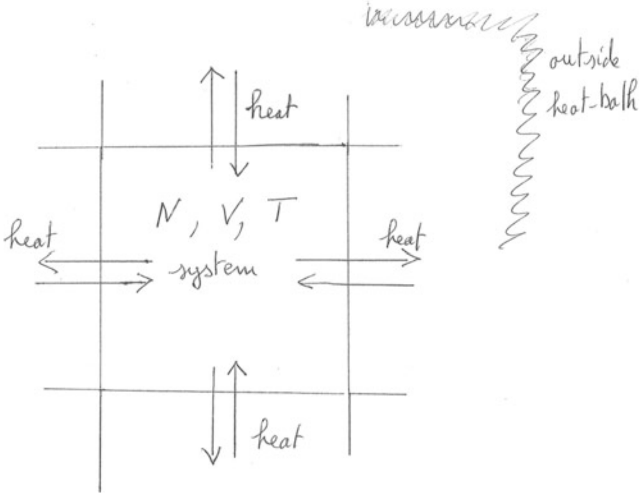

Fig. 22.1 Canonical ensemble

22.1 Description of the Canonical Ensemble (*N*, *V*, *T* Imposed)

The canonical ensemble is constituted by a very large number $\aleph$ ($\aleph \rightarrow \infty$) of systems replicating the thermodynamic system (under study) which, by definition, possesses the fixed volume *V*, the number of molecules *N* (there can be several types of molecules, the numbers of which N_1, N_2 … are then constant), and the temperature T uniform and constant (viz. Fig. 22.1). The partitions between the different systems are thermal conductors but do not allow the crossing of the particles through them. The ensemble is placed in a heat bath granting an equal temperature in the whole systems. The partitions of the systems are not distorting excluding, hence, no work exchange between them.

If one places an isolating membrane outside the ensemble and the whole device (ensemble + membrane) located outside the heat bath, the ensemble, now, constitutes an isolated system of volume $\aleph V$ and of number of molecules $\aleph N$ and with a total energy E_t. This isolated system is called a *supersystem*.

22.2 Strategy

Let us recall that, finally, the goal is to find the meaning of some quantities of classical thermodynamics with the help of a reasoning of statistical thermodynamics, the meaning of which being searched for in the conditions which prevail in the canonical ensemble (constant composition, temperature, volume). According to what is preceding, the problem is to calculate the average of the mechanical properties such as the pressure and the energy with the help of this reasoning. Let us notice, indeed, that since the thermodynamic system is not isolated (it is in contact with other systems of the same ensemble), its energy fluctuates.

The process entails to know the value of the quantity under study in each quantum state and to determine the number of systems of the ensemble exhibiting this quantum state. *The mechanical variables, indeed, have well-definite values in a given quantum state*. Hence, the problem is to determine the fraction of the systems of the ensemble possessing a given quantum state.

These considerations are equivalent to say that the probability P_j that a system of the ensemble is in the state of energy E_j must be known. Once known, the values of the energy $\overline{E}$ and of the pressure $\overline{p}$ can be calculated through the following expressions:

$$\overline{E} = \sum_j P_j E_j$$

$$\overline{p} = \sum_j P_j p_j$$

p_j is the pressure in the energetic state E_j; it is defined by the expression

$$p_j = -\left(\partial E_j / \partial V\right)_N$$

$-p_j\, dV = dE_j$ is the work that has to be done on the system (with a constant number of species N) in the energetic state E_j in order to increase its volume by dV. This expression is found by virtue of the quality of state function of E (viz. Appendix A). One can write, indeed,

$$dE = (\partial E / \partial V)_{N,T} dV + (\partial E / \partial T)_{N,\ V} dT$$

where by hypothesis $dT = 0$ (T imposed).

22.3 The Mathematical Problem

Let us, now, consider one system of the canonical ensemble. It is a system obeying quantum mechanics. Its characteristics depend on the values N and V which constitute the limits entailing the energy quantification (viz. quantum mechanics). As a result, there exists the collection of the following possible (authorized) energetic states written by order of increasing energy: E_1, E_2, …, E_j. We must not forget that they are the energy states of the whole system, that is to say of a great number of particles, and not the energy states of one species. Let us recall that, for different reasons (some of which being mathematical ones), it is not possible to calculate the energy states E_j

from the Schrödinger's equation for a very large number of particles. Nevertheless, for the following reasoning, we suppose that we know them.

22.3.1 The Notion of Distribution

Since all the systems of the canonical ensemble have the same composition N (in one or several compounds) and the same volume V, everyone does possess the same quantified levels of energy E_1, E_2, …, E_{j}. (It is a consequence of the principles of quantum mechanics.) Let us suppose that we can simultaneously observe the energetic state of each system and that we are able to count the number of systems in every energetic state E_1, …, E_j. Let n_1, n_2 … be the numbers of systems found in sates $E_1, E_2, \ldots$. The set of values $n_1, n_2 \ldots$ is a *distribution of the systems*. For each distribution, the following relations are obligatorily satisfied:

$$\sum_j n_{\mathrm{j}} = \aleph$$

$$\sum_j n_j E_j = E_t$$

where E_j is the energy of the considered system within the ensemble for the considered distribution. E_t is the energy of the ensemble (also named supersystem). (We shall see that it is not necessary to know the values $\aleph$ and E_t because they disappear during the calculations.)

Let us suppose, in order to simplify, that the ensemble possesses four systems labelized A, B, C, and D and that the possible energy states of each system are E_1, E_2, and E_3. Let us also suppose that the total energy (of the supersystem) is as follows:

$$E_t = E_1 + 2E_2 + E_3 \tag{22.1}$$

that is to say $n_1 = 1$, $n_2 = 2$, and $n_3 = 1$. These values (E_t, E_1, E_2, E_3, n_1, n_2, n_3) define the distribution.

22.3.2 The Notion of Sub-distribution

There are several possibilities of attribution of the energies E_1, E_2, and E_3 to the systems A, B, C, and D in order that the distribution defined by relation (22.1) exists. They are those mentioned in Table 22.1. We call them "sub-distributions" (personal terminology).

We notice that there are 12 sub-distributions corresponding to the same distribution, labelized k. This result is no more than the solution of the classical problem

Table 22.1 Sub-distributions corresponding to the distribution $n_1 = 1$, $n_2 = 2$, and $n_3 = 1$; $N = 4$, labelized systems A, B, C, and D

A	B	C	D
E_2	E_2	E_3	E_1
E_2	E_3	E_2	E_1
E_3	E_2	E_2	E_1
E_2	E_2	E_1	E_3
E_2	E_3	E_1	E_2
E_3	E_2	E_1	E_2
E_3	E_1	E_2	E_2
E_2	E_1	E_3	E_2
E_2	E_1	E_2	E_3
E_1	E_3	E_2	E_2
E_1	E_2	E_3	E_2
E_1	E_2	E_2	E_3

of combinatory analysis which, in this case, can be presented by giving the answer to the following question: How many (number Ω) possibilities to group 4 objects by groups of 2, 1, and 1 do exist? The answer is

$$\Omega = (2 + 1 + 1)!/(2\,!1\,!1\,!) = 12$$

From the general viewpoint, the number Ω of possibilities to group $(n_1 + n_2 + \ldots n_j)$ objects by groups of n_1, n_2, …, n_j objects is given by the relation

$$\Omega = \left(n_1 + n_2 + \ldots n_j\right)\,!\,/\,\left(n_1\,!\,n_2\,!\ldots n_j\,!\right) \tag{22.2}$$

Let us recall that all the sub-distributions have the same energy.

22.3.3 Case of Several Distributions

We must bear in mind that there are numerous distributions existing for the same set of parameters N, V, and T. For the same example as previously, let us suppose that it is the case for the distribution $n_1 = 2$, $n_2 = 0$, and $n_3 = 2$, that is to say

$$2E_1 + 0E_2 + 2E_3 = E_t$$

where the energy E_t is the same as that of the preceding distribution. This new distribution exists under $(2 + 0 + 2)\,!/(2\,!0\,!2\,!) = 6$ sub-distributions. Let us also suppose that only two distributions exist for the same total energy. Since they possess the same energy E_t, according to the second postulate, the sub-distributions of both distributions are equiprobable, whichever their origin.

What is being searched for is the probability to find a system of the ensemble in the energy state E_j, that is to say, remaining in the same example as previously, the

Table 22.2 Sub-distributions of the same total energy *E* and, hence, of the same probability stemming from two distributions (see text)

A	B	C	D
E_2	E_2	E_3	E_1
E_2	E_3	E_2	E_1
E_3	E_2	E_2	E_1
E_2	E_2	E_1	E_3
E_2	E_3	E_1	E_2
E_3	E_2	E_1	E_2 (1$^{\text{ère}}$ distribution)
E_3	E_1	E_2	E_2
E_2	E_1	E_3	E_2
E_2	E_1	E_2	E_3
E_1	E_3	E_2	E_2
E_1	E_2	E_3	E_2
E_1	E_2	E_2	E_2
E_1	E_1	E_3	E_3
E_1	E_3	E_1	E_3
E_3	E_1	E_3	E_1
E_3	E_1	E_1	E_3 (2$^{\text{ème}}$ distribution)
E_3	E_3	E_1	E_1
E_1	E_3	E_3	E_1

probability to find the system *A* or *B* or *C* or *D* with the energy E_1, E_2, or E_3. In this very simple example, the result can be found by a direct numbering by placing in the same table all the sub-distributions and by performing the numbering.

The direct numbering indicates that each system *A*, *B*, *C*, or *D* possesses 1/3 chance to possess the quantified energy levels E_1, E_2, and E_3. (The fact that all these probabilities are all equal (1/3) must not be generalized. It results solely from the chosen numerical values. It must be considered as a numerical accident (Table 22.2).)

The direct numbering is not, of course, envisageable in statistical thermodynamics, given the huge number of the existing distributions and sub-distributions. Fortunately, there exists a useful mathematical relation which generalizes what is preceding. It results from the following reasoning:

- The elementary probability prob_1 (1 because it concerns the first distribution) in order that one of the systems *A*, *B*, *C*, or *D* possesses the energy E_2 in the first distribution is 2/4 since $n_2 = 2$ and since there are four systems. The number of times that one of the systems in the first distribution is endowed with the energy E_2 is $12 \times 2/4 = 6$, that is to say by generalizing $\Omega_1 \bullet \text{prob}_1$.
- The elementary probability prob_2 in order that one of the systems possesses the energy E_2 in the distribution 2 is $6 \times 0/4 = 0$, that is to say $\Omega_2 \bullet \text{prob}_2$.
- The total number of possibilities that a system would be in an ordinary state of energy is this example $12 + 6 = 18$, that is, $\Omega_1 + \Omega_2$. The global probability (and not elementary) P_2 that a system would be in the energetic state E_2 is as follows:

$$P_2 = (12 \times 2/4 + 6 \times 0/4) \ / \ (12 + 6) = 1/\ 3$$

and by generalizing

$$P_j = \left(\sum_j \text{prob}_j \Omega_k \right) \Big/ \sum_k \Omega_k \tag{22.3}$$

where j marks the authorized state of energy of the system. prob_j is the elementary probability in order that in the distribution k, the energy be E_j.

- The probability P_2 can also be written (in a strictly equivalent manner) as

$$P_2 = (1/4)(2 \times 12 + 0 \times 6)/(12 + 6)$$

where 4 is the number of systems and 2 × 12 and 0 × 6 are the numbers of times that the state of energy E_2, respectively, appears in the first and second distribution.

The general relation (22.3) can also be written according to

$$P_j = (1/\aleph) \left(\sum_k n_j \Omega_k \right) \Big/ \sum_k \Omega_k \tag{22.4}$$

This expression is a generalization of the preceding which gave P_2.

22.4 Obtention of P_j

22.4.1 *Great Number of Distributions: Method of the Maximal Term*

The obtaining of P_j is performed in a mathematical way. It is based on the fact that there exist numerous possible distributions obeying the constraints of the problem. The latter ones are

- The number $\aleph$ of systems of the ensemble
- The temperature T
- The different possible energies E_j of every system. (They depend on the total number of particles N and of the volume V, according to the principles of quantum mechanics.)

Given the very large number $\aleph$, one demonstrates that one distribution weighs much more and even quasi-infinitely more than other ones. Therefore, one can make the assumption that it entails its repartition of the systems in the ensemble, and it is done as a function of the energies E_j. The hypothesis is entitled “method of the maximal term." From the mathematical standpoint, it consists in replacing the logarithm of a sum by the logarithm of the highest term of the sum, when the latter is constituted of very numerous terms. The expression giving the probability P_j to find a system of the ensemble in the energetic state E_j is constituted of very numerous terms. Taking only into account the largest term seems to be an approximation. It is the case, but it does not lead to any detectable error. (viz. Appendix A).

By applying the hypothesis, the relation (22.4) reduces to

$$P_j = n_j^* / \aleph$$

where n_j^* is the number of times that the quanto-energetic state E_j appears in the most probable distribution. Of course, there are as many n_j^* to calculate as quanto-energetic E_j levels do exist.

Hence, the most probable distribution must be found.

22.4.2 Calculations

The calculations are performed by starting from ln Ω rather than from Ω. It is easier to process in such a manner and it does not change anything concerning the result since ln x varies as x.

According to the expression (22.2), we obtain

$$\ln \Omega = \ln \left[\left(n_1 + n_2 + \ldots n_j \right)! \right] - \ln n_1 ! - \ln n_2 ! - \ldots \ln n_{\mathrm{j}}!$$

Then, they are performed by using Stirling's approximation which is written as

$$\ln y ! \approx y \ln y - y$$

The use of this approximation is all the more justified as y is a large number. This is the case here. With this approximation, ln Ω becomes

$$\begin{aligned} \ln \Omega = {} & \left(n_1 + n_2 + \ldots\ n_j \right) \ln \left(n_1 + n_2 + \ldots\ n_j \right) - \left(n_1 + n_2 + \ldots\ n_j \right) - n_1 \ln n_1 \\ & + n_1 - n_2 \ln n_2 + n_2 \ldots\ldots - n_j \ln n_j + n_j \end{aligned}$$

The mathematical process coming immediately in mind is to have to successively vanish the partial derivatives (∂ ln $\Omega/\partial n_1$), (∂ ln $\Omega/\partial n_2$) … (∂ ln $\Omega/\partial n_j$) and, from this process, to extract the values $n_1, n_2, \ldots, n_j$ leading to this result. But, there is a difficulty: the mathematical system is submitted to the following constraints:

$$\begin{aligned} & n_1 + n_2 + \ \ldots n_j = \aleph \\ & n_1 E_1 + n_2 E_2 + \ \ldots n_j E_j = E_t \end{aligned}$$

The smartest means permitting this process of maximalization taking into account these constraints is to use the method of Lagrange's multipliers (viz. Appendix A) which, in this case, translates itself into the successive vanishing of the partial derivatives with respect to $n_1, n_2, \ldots, n_j$ of function F, and no longer of function ln Ω:

$$F = \ln\Omega - \alpha\left(n_1 + n_2 + \ldots n_j\right) - \beta\left(n_1E_1 + n_2E_2 + \ldots n_jE_j\right)$$

where α and β are two constants, the physical meaning of which will appear in the following calculations.

When the calculation of the derivatives is performed, we obtain the following relations:

$$\begin{aligned} n_1 &= \aleph\, \mathrm{e}^{-\alpha-\beta E_1} \\ n_2 &= \aleph\, \mathrm{e}^{-\alpha-\beta E_2} \\ n_j &= \aleph\, \mathrm{e}^{-\alpha-\beta E_j} \end{aligned} \tag{22.5}$$

These relations are very important. We can deduce the following points from them:

- The signification of the constant e^{α}.

  Since $\Sigma_\mathrm{j}\, n_j = \aleph$, the addition of relations (22.5) leads to

$$\mathrm{e}^{\alpha} = \mathrm{e}^{-\beta E_1} + \mathrm{e}^{-\beta E_2} + \ldots \mathrm{e}^{-\beta E_j}$$

- The mean energy $\overline{E}$ of each system.

  Since $E_t = \aleph\, \overline{E}$,

$$\sum_j n_jE_j = \aleph\overline{E}$$

By replacing the n_j by their expressions (22.5) and $\mathrm{e}^{-\alpha}$ by the above expression, we obtain

$$\overline{E} = \sum_j E_j\mathrm{e}^{-\beta E_j} \Big/ \sum_j \mathrm{e}^{-\beta E_j} \tag{22.6}$$

It is important to notice that, according to the expression (22.6), the parameter β appears as being an implicit function of the mean energy $\overline{E}$ and also, therefore, of the composition N and of the volume V which govern the quantum levels E_j. It is the same for α which depends on the same parameters. But, actually, the studied ensemble is that defined by the macroscopic parameters N, V, and T and not by N, V, and $\overline{E}$. However, as we shall see, $\overline{E}$ depends on T. Let us anticipate what is following by mentioning that β is inversely proportional to the absolute temperature. More precisely, $\beta = 1/kT$ where k is Boltzmann's constant and T the absolute temperature.

- The expression giving the probability P_j to find a system of the ensemble in the energetic state E_j is constituted of very numerous terms. Taking only into account the largest term seems to be an approximation. It is the case, but it does not lead to any detectable error.

It is calculated by applying the general definition of a probability, through the relation

$$P_j = n_j/\aleph$$

By replacing n_j by its expression (22.5) and by introducing the above expression $\mathrm{e}^{-\alpha}$, we find

$$P_j = \mathrm{e}^{-\beta E_j}/\sum_i \mathrm{e}^{-\beta E_i} \tag{22.7}$$

We shall see in the following chapter that these expressions permit to grasp the meaning at the molecular scale of the great thermodynamic functions.

The expressions (22.6) and (22.7) call for the great importance of the sum $\Sigma_i \mathrm{e}^{-\beta E_i}$. Indeed, it will play a considerable part. In statistical thermodynamics, such a function is called *partition function*. As it happens here, it is the partition function of the canonical ensemble. It is symbolized by Q:

$$Q = \sum_i \mathrm{e}^{-\beta E_i}$$

Chapter 23

Thermodynamic Quantities Within the Framework of the Canonical Ensemble

Abstract The chapter describes the handling of the mathematical relations previously found within the framework of the canonical ensemble through the partition function in order to assimilate them to the expressions of classical thermodynamic functions. Concerning now the introduction of the nonmechanical functions such as the entropy and the temperature into the realm of statistical thermodynamics, the strategy consists in comparing the expressions concerning the mechanical quantities obtained (thanks to the theory of the canonical ensemble) and those stemming from classical thermodynamics. Therefore, the statistical expressions of internal energy, entropy, pressure, and chemical potential are obtained. Some of these functions are calculated with the aid of the characteristic function of the canonical function which spontaneously introduces itself into the calculations.

Keywords Thermodynamic quantities • Entropy • Enthalpy • Partition function • System • Quantum mechanics • Statistical analogues of classical thermodynamic functions • Boltzmann's constant • Characteristic functions • Canonical function • Closed system • Chemical potential • Characteristic function • Nonmechanical properties • Internal energy • Gibbs and Helmholtz energies

The theoretical handling of some ensembles throws some light, in terms of molecular parameters, on the deep significance of some thermodynamic quantities, among them, notably, the Gibbs energy from which are following the concepts of fugacity and of activity.

In this chapter, as a first example, we handle the mathematical relations previously found within the framework of the canonical ensemble.

In order to introduce the nonmechanical functions such as the entropy and the temperature into the realm of statistical thermodynamics, the strategy consists in comparing the expressions concerning the mechanical quantities obtained thanks to the theory of the canonical ensemble and those stemming from classical thermodynamics.

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23.1 Association Average Energy $\overline{E}$ and Internal Energy

According to the expressions (22.6) and (22.7) of the previous chapter

$$\overline{E} = \sum_j E_j \mathrm{e}^{-\beta E_j} \Big/ \sum_j \mathrm{e}^{-\beta E_j} \quad \text{(relation 6 } - \text{ previous chapter)}$$

$$P_j = \mathrm{e}^{-\beta E_j} \Big/ \sum_i \mathrm{e}^{-\beta E_i} \quad \text{(relation 7 } - \text{ previous chapter)}$$

we obtain

$$\overline{E} = \sum_j P_j E_j$$

or in differentials

$$d\overline{E} = \sum_j E_j \, dP_j + \sum_j P_j \, dE_j \tag{23.1}$$

The first term of the right member of (23.1) represents the energy change due to the variation of the probability P_j for a system being in the energy state E_j which does not vary during the process. This entails that there is no change in the volume of the system, i.e., there is no work done on the system or performed by it. Hence, this term represents an energy change of the system without the fact that a work would be involved. According to the first principle, it follows that the first term of the right member represents a heat exchange. A consideration of the fundamental postulates shows that a heat absorption by a system must be associated with the probability that a system of the ensemble does possess the (authorized) energy E_j. Hence, we can set up the correspondence:

$$dq \leftrightarrow \sum_j E_j \, dP_j$$

According to the algebraic formulation of the first principle, the second term of the right member of (23.1) must be identified to the work done on the system, whence

$$dw \leftrightarrow \sum_j P_j \, dE_j$$

Finally, we can set up the correspondence:

$$\overline{E} \leftrightarrow \text{internal energy}$$

23.2 Statistical Expression of the Entropy

From relation (23.7) of the preceding chapter

$$P_j = \mathrm{e}^{-\beta E_j} / \sum_i \mathrm{e}^{-\beta E_i} \quad \text{(relation 7 – preceding chapter)}$$

we deduce

$$E_j = -1/\beta \left(\ln P_j + \ln Q \right) \quad \text{with} \quad Q = \sum_j \mathrm{e}^{-\beta E_j} \tag{23.2}$$

whence, according to (23.1) and the just preceding considerations,

$$d\overline{E} = -1/\beta \sum_j \left(\ln P_j + \ln Q \right) dP_j + \sum_j P_j \, dE_j \tag{23.3}$$

Moreover, according to the expression of the total differential, we can write

$$dE_j = \left(\partial E_j / \partial V \right)_N dV + \left(\partial E_j / \partial N \right)_V dN$$

Since, according to the conditions prevailing to the canonical ensemble, the number of the particles of the system is constant, $dN = 0$, and

$$dE_j \; = \left(\partial E_j / \partial V \right)_N dV$$

Relation (23.3) becomes

$$d\overline{E} = -1/\beta \sum_j \left(\ln P_j + \ln Q \right) \, dP_j \; + \sum_j P_j \left(\partial E_j / \partial V \right)_N dV$$

and since $dV = 0$

$$d\overline{E} = -1/\beta \sum_j \left(\ln P_j \; + \; \ln Q \right) \, dP_j$$

From another standpoint

$$\sum_j P_j = 1 \quad \text{whence} \quad \sum_j dP_j = 0$$

we obtain

$$d\overline{E} = -1/\beta \sum_j \ln P_j \, dP_j$$

This relation can be transformed into another one, more general. The transformation is done in the following manner. Already, let us mention that this transformation leads to the notion of *statistical entropy*. Let us consider the function $\Sigma_{\mathrm{j}} P_j \ln P_j$. In differential writing, it gives

$$d\left(\sum_j P_j \ln P_j\right) = \sum_j \ln P_j \, dP_j + \sum_j P_j \, d\ln P_j$$

$$d\left(\sum_j P_j \ln P_j\right) = \sum_j \ln P_j \, dP_j + \sum_j P_j \, dP_j/P_j$$

$$d\left(\sum_j P_j \ln P_j\right) = \sum_j \ln P_j \, dP_j \quad \text{since} \quad \sum_j dP_j = 0$$

As a result

$$d\overline{E} = -1/\beta \, d\left(\sum_j P_j \ln P_j\right)$$

Let us compare this relation with that purely thermodynamic governing the internal energy change of a system during a reversible heat exchange, without any production of work:

$$dE = TdS$$

Let us make the association:

$$TdS \leftrightarrow -1/\beta \, d\left(\sum_j P_j \ln P_j\right)$$

whence

$$dS = (-1/\beta T) \, d\left(\sum_j P_j \ln P_j\right)$$

dS being an exact differential, the ratio $1/\beta T$ cannot be anything else than a constant. It is called Boltzmann's constant: symbol k. Its unity is the joule by kelvin J K^{-1}. Let us notice that we again find the fact that the ensemble is isothermal, condition of the study with the canonical ensemble. Therefore

$$dS = -k \, d\left(\sum_j P_j \ln P_j\right)$$

To sum up, by regarding these two first analogies: in a closed, isothermal, system (ensemble N, V, T):

- The probability for the system to be in the state of energy E_j, entailed by the composition N and the volume V (condition coming from the principles of quantum mechanics), is given by the expression

$$P_j(N,V,T) = \mathrm{e}^{-E_j\ (N,V)\ /\ kT} / \ Q(N,V,T) \tag{23.4}$$

where $Q(N,V,T) = \sum_j \mathrm{e}^{-E_j(N,V)/kT}$ is the partition function of the canonical ensemble. (Let us recall that the symbolism N is general and can mean that there is only one or several components with a constant number of moles, as well.)

- The entropy is given by the expression

$$S(N,V,T) = -k \sum_j P_j \ln P_j \tag{23.5}$$

where P_j is given by relation (23.4). It clearly appears that entropy is a statistic quantity.

23.3 The Characteristic Function of the Canonical Ensemble

As we shall see it, firstly in the case of the canonical ensemble and later in that of other ensembles, there exists a characteristic function of each ensemble. It is a function different from the *partition function* of the same ensemble, even if both are mathematically related to each other.

The characteristic function appears naturally in thermodynamics, but statistical thermodynamics permits to relate it, mathematically, to the corresponding partition function. Once known, the characteristic function permits to calculate all the other thermodynamic functions. We know, indeed, that to some thermodynamic functions, i.e., the internal energy, the Gibbs and Helmholtz energies, and the enthalpy, corresponds a set of independent variables for each of them, called their natural variables (viz. Chap. 4). These sets (defining the system) permit to immediately calculate all the other quantities of the system. For example, for the Gibbs energy, they are the pressure, volume, and numbers of moles of every component. They are the same variables than those which define the corresponding ensembles in statistical thermodynamics.

The characteristic function of the canonical ensemble is obtained as follows. Let us introduce the expression of P_j into that of entropy (given just above); we obtain, after having taken into account the relation (23.6) of the preceding chapter and since

$$\overline{E} = \sum\nolimits_j E_j \mathrm{e}^{-\beta E_j} / \sum\nolimits_j \mathrm{e}^{-\beta E_j}$$

$$S = \overline{E}/T + k \ \ln Q$$

By assimilating this expression of S to that of purely thermodynamic origin

$$S = E/T - A/T$$

where A is the Helmholtz energy, it comes to light the following meaning of the latter in statistical thermodynamics:

$$A(N, V, T) \leftrightarrow -kT \ \ln Q(N, V, T)$$

The function A is the characteristic function of the canonical ensemble defined by the parameters N, V, and T since, once it is known, it permits, as we shall see, to calculate the entropy, pressure, internal energy, and chemical potentials of the components.

23.4 Calculation of the Thermodynamic Functions by Starting from the Characteristic Function of the Canonical Ensemble

This kind of calculation is particularly important. It is the one which is practiced, notably in the statistical part of this book, for the calculation of the changes of the thermodynamic quantities and for obtaining the energy levels E_j. Analogous calculations, of course, are also performed by starting from partition functions of other ensembles.

Let us consider the following relation from purely thermodynamic origin by noticing that it contains the three variables defining the canonical system (T, V, n_k, or N):

$$dA = -\,SdT \ - p\,dV + \sum_k \mu_k dn_k \qquad (23.6)$$

$$(k \text{ index of the component the number of moles of which is } n_k)$$

and also from the expression of the total differential

$$dA = \ (\partial A/\partial T)_{V,\ nk} dT \ - \ (\partial A/\partial V)_{T,\ nk} dV + \sum_k (\partial A/\partial n_k)_{T,V,n_j} dn_k \quad (n_i \neq n_k)$$

By replacing $A(N, V, T)$ by the characteristic function $kT \ln Q(N, V, T)$, by operating the calculations of partial derivation on the characteristic function and by identifying with the corresponding elements of the relation (23.6), some very interesting results are obtained. Concerning:

23.4.1 The Entropy

Since $S = -(\partial A/\partial T)_{V,\ N}$ (dA exact total differential)

$$S = -[-\partial kT\ \ln\ Q(N, V, T)\ /\partial T]_{V,N}$$

As a result

$$S = kT(\partial \ln Q/\partial T)_{V,N} + k\ \ \ln\ Q \tag{23.7}$$

23.4.2 The Pressure

Since $p = -(\partial A/\partial V)_{T,\ N,}$ we obtain

$$p = kT(\partial \ln Q/\partial V)_{T,N} \tag{23.8}$$

23.4.3 The Internal Energy

Since $E = -T^2\ (\partial A/T/\partial T)_{V,\ N}$

$$U = kT^2(\partial \ln Q\ /\partial T)_{V,N} \tag{23.9}$$

23.4.4 The Chemical Potential

Even if the canonical ensemble is a closed system, its component(s) possess(es) a well-determined chemical potential, of course in the state of the system. It can also be calculated from the characteristic function. According to relation (23.6), we immediately obtain

$$\begin{aligned} \mu_k &= (\partial A/\partial N_k)_{T,V,N\ k\neq i} \\ \mu_k &= -kT(\partial \ln Q/\partial N_k)_{T,V,N\ k\neq i} \end{aligned} \tag{23.10}$$

23.5 Degenerated Energy States E_j and Energy Levels

For numerous applications or to tackle new problems, it is interesting to group all the energetic states of the same level E_j. Let Ω_i (N, V) be the number of states of the energy level E_i (N, V), i.e., in the listing of the possible states E_j, the same value E_i exists Ω_i times. Ω_i (N, V) is the degeneracy. As a result, the partition function which was

$$Q\ (N, V, T) = \sum_j \mathrm{e}^{-E_j(N,V)/kT}$$

becomes

$$Q(N, V, T) = \sum_i \Omega_i(N, V)\mathrm{e}^{-E_i\ (N,V)/kT} \tag{23.11}$$

where, this time, the sum is calculated on the energy levels, whereas before it was calculated on all the states, included those of the same energy.

Chapter 24
Other Ensembles

Abstract The chapter is a study of some other ensembles distinct from the canonical one and which are of some interest for the purpose of activity. The concerned ones are the grand ensemble, the microcanonical, and the isothermal-isobaric ones. Calculations analogous to those carried out in the case of the canonical ensemble permit to find the statistical analogues of classical thermodynamic functions. Partition and characteristic functions introduce themselves during these calculations. Overall, the famous Boltzmann's relation appears within the framework of the microcanonical ensemble.

Keywords Isothermal-isobaric ensemble • Grand ensemble partition function • Microcanonical ensemble partition function • Statistical analogues of classical thermodynamic functions • Absolute activity • Boltzmann's constant • Characteristic functions

In this chapter, we briefly study some other ensembles which are interesting for our purpose.

24.1 Grand Canonical Ensemble or Grand Ensemble

24.1.1 Generalities

The grand canonical ensemble may be imagined as being one ensemble of thermodynamic systems characterized by a constant volume. The ensemble itself is dipped into a giant heat-bath-marie which maintains it at a constant temperature. The systems can exchange the particles of their component(s) with their surroundings (the other systems of the ensemble). The exchanges evolve up to equality of their chemical potentials. Contrary to the case of the canonical ensemble, the systems are not closed. The partitions of each system of the ensemble permit the crossing of heat and matter through them. The ensemble is characterized by the thermodynamic quantities V, T, and μ (Fig. 24.1).

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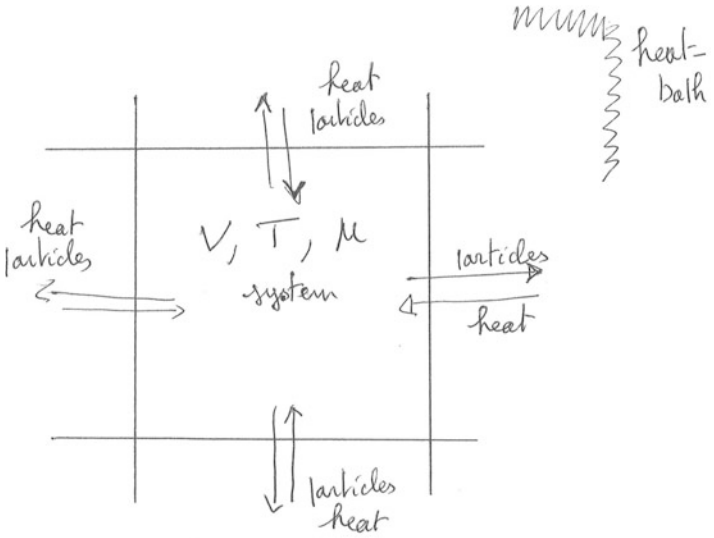

Fig. 24.1 Grand canonical ensemble

The strategy followed in order to study these systems from the statistical standpoint is analogous to that followed for the study of the canonical ensemble. However, here, there exists a great difference with the preceding case. According to the principles of quantum mechanics, the stationary energetic states E_j are function of V which remains constant as previously but are also function of N which is, now, variable. As in the case of the canonical ensemble, each system may possess several components.

Again, as before, one makes out several distributions and sub-distributions among which one seeks the most probable ones. The research is performed through a derivative calculation taking into account the Lagrange's multipliers. From this calculation, one deduces the probability $P_j(N)$ that a system of the ensemble would be in the energetic state $E_j\ (N, V)$ with the number of moles N of the component(s). The energetic states $E_j\ (N, V)$, of course, are different from each other as a function of N and, also, since they are dependent on V. As an example, in Table 24.1, we mention an example of distribution. In this table, j is the number of particles in the volume V. For the same volume V, there exist several levels of energy for the same number j, for example: $E_1(1, V)$–$E_2(1, V)$–$E_3(1, V)$ … and so f….

The constraints for the determination of the most probable distribution are the following:

- The total number (imposed) $\aleph$ of the systems of the ensemble

$$n_1(1) + n_1(2) + n_1(3) + n_2(1) + n_2(2) + n_2(3) + n_3(1) + n_3(2) + n_3(3) = \aleph$$

or generally

Table 24.1 Example of a distribution in the grand ensemble

$E_1(1, V)$	$E_1(2, V)$	$E_1(3, V)$	$E_2(1, V)$	$E_2(2, V)$	$E_2(3, V)$	$E_3(1, V)$	$E_3(2, V)$	$E_3(3, V)$
$n_1(1)$	$n_1(2)$	$n_1(3)$	$n_2(1)$	$n_2(2)$	$n_2(3)$	$n_3(1)$	$n_3(2)$	$n_3(3)$

The possible energetic states are $E_1(1, V)$, ..., $E_3(3, V)$. The $n_i(j)$ are the number of systems exhibiting the energy $E_i(j, V)$

$$\sum_j \sum_N n_j(N) = \aleph$$

- The total energy (imposed) E_t of the ensemble

$$n_1(1)E_1(1,V) + n_1(2)E_1(2,V) + n_1(3)E_1(3,V) + n_2(1)\,E_2(1,V) + \ldots$$
$$n_3(1)E_3(1,V) + \ldots = E_t$$

or

$$\sum_j \sum_N n_j(N)\,E_j(N,V) = E_t$$

- The total (constant) number N_t of the components in the ensemble

$$n_1(1).\,1 + n_1(2).2 + \ldots\ldots..n_3(3).3 = N_t$$

This latter expression is generalized as

$$\sum_j \sum_N n_j(N)N = N_t$$

The number of the possible quantum states of the supersystem Ω_t is given by the relation

$$\Omega_t = \left[\sum_j \sum_N n_j(N)\right]\,!\,/\prod_{j,N} n_j(N)! \qquad (24.1)$$

By developing the calculations as in the case of the canonical ensemble, one obtains

$$n_j^*(N) = \aleph e^{-a} e^{-\beta E_j(N,V)} e^{-\gamma N}$$

for the most probable distribution. α, β, and γ are the three Lagrange's multipliers, the using of which is induced by the presence of three constraints. By operating as previously, we find

$$\mathrm{e}^{\alpha} = \sum_{j}\sum_{N} \mathrm{e}^{-\beta E_j(N,V)}\mathrm{e}^{-\gamma N}$$

The probability $P_j(N)$ that a randomly chosen system in the grand ensemble does contain N molecules and would be in the energy state $E_j(N, V)$ is given by the relation

$$P_j(N) = \mathrm{e}^{-\beta E_j(N,V)}\mathrm{e}^{-\gamma N} / \sum_{i}\sum_{N} \mathrm{e}^{-\beta E_i(N,V)}\mathrm{e}^{-\gamma N'} \tag{24.2}$$

According to the first postulate, we can proceed to the following associations in order to define the mechanical variables in statistical thermodynamics:

$$\text{Internal energy} \leftrightarrow \overline{E}(= E_t/\aleph) = \sum_{j}\sum_{N} P_j(N)E_j(N,V) \tag{24.3}$$

$$N \leftrightarrow \overline{N}\,(= \nu_t/\aleph) = \sum_{j}\sum_{N} P_j(N)N \tag{24.4}$$

$$p \leftrightarrow \overline{p} = \sum_{j}\sum_{N} P_j(N)\left(-\left[\partial E_j(N,V)\,/\partial V\right]N\right) \tag{24.5}$$

where ν_t is the total number of particles in the ensemble. In order to introduce the nonmechanical variables and in order to evaluate the parameters β and γ, we use the expression (24.3) of $\overline{E}$ that is written in differentials:

$$d\overline{E} = \sum_{j}\sum_{N} E_j(N,V)\,dP_j(N) + \sum_{j}\sum_{N} P_j(N)\,dE_j(N,V) \tag{24.6}$$

The first term of the right member shows the change in the energy related to that of the probabilities $P_j(N)$ when the energy levels $E_j(N, V)$ are constant. It clearly corresponds to an energy change of the system without any work having been performed. Hence, it must be identified to the heat exchanged by the system. On the contrary, the second term of the right member must be identified as being the work exchanged by the system. By replacing the first term in the right member of $E_j(N,V)$ by its expression stemming from (24.2), we find

$$\begin{aligned} d\overline{E} = {} & -1/\beta \sum_{j}\sum_{N}\left[\gamma N + \ln P_j(N) + \ln \Xi\right] dP_j(N) \\ & + \sum_{j}\sum_{N} P_j(N)\left[\partial E_j(N,V)\,/\partial V\right]dV \end{aligned}$$

where

$$\Xi = \sum_j \sum_N \mathrm{e}^{-\beta E_j(N,V)} \mathrm{e}^{-\gamma N}$$

The second term of the right number is obtained, as in the case of the canonical ensemble, by taking into account the fact that dE is an exact total differential and by expressing it as a function of the two independent variables T and V. We obtain

$$d\overline{E} = -(1/\beta) \sum_j \sum_N \left[\gamma N + \ln P_j(N) + \ln \Xi\right] dP_j(N) - \overline{p} dV$$

Let us develop the first term of the right member. Let us, firstly, notice that the differential writing of (24.4) leads to

$$d\overline{N} = \sum_j \sum_N N dP_j(N)$$

Taking into account this result on the one hand and the fact that $\Sigma_j \, \Sigma_N \, dP_j(N) = 0$ on the other, we obtain

$$d\overline{E} = -\gamma/\beta \, d\overline{N} - \overline{p} dV - (1/\beta) \sum_j \sum_N \ln P_j(N) dP_j(N)$$

For the same reason as for the canonical ensemble,

$$\sum_j \sum_N \ln \, P_j(N) dP_j(N) = d \left[\sum_j \sum_N P_j(N) \ln \, P_j(N) \right]$$

As a result, the preceding expression can be written as

$$-(1/\beta) \, d \left[\sum_j \sum_N P_j(N) \ln \, P_j(N) \right] = d\overline{E} + \overline{p} dV + \gamma/\beta d\overline{N}$$

that must be compared to the following expression which is of purely thermodynamic origin:

$$TdS = dE + pdV - \mu dN$$

where μ is the chemical potential of the component and E its internal energy. As a result, the following assimilations may be made:

$$\mu \leftrightarrow -\gamma/\beta$$
$$S \leftrightarrow -k\sum_j\sum_N P_j(N)\ \ln\ P_j(N)$$
$$\mu\ /kT \leftrightarrow -\gamma$$

with

$$\beta = 1/kT$$

Therefore, for an open, isothermal system defined by the thermodynamic parameters V, T, and μ, the probability that it possesses N molecules and that it is in the energy state $E_j(N, V)$ is

$$P_j(N\ ; V, T, \mu)\ = \mathrm{e}^{-\ E_j(N,V)/kT} \bullet P_j(N; V, T, \mu)\ \mathrm{e}^{N\mu/kT}/\Xi(V, T, \mu)$$
$$\text{avec}\ \Xi(V, T, \mu)\ = \sum_j\sum_N \mathrm{e}^{-\ E_j(N,V)/kT}\mathrm{e}^{N\mu/kT}$$

The function Ξ is called the grand partition function. (In the symbolism $P_j(N; V, T, \mu)$, N has the status of a particular writing because, as j, it is a summation index, whereas V, T, and μ are true thermodynamic variables.)

It is very important to notice that Ξ may also be written as follows:

$$\begin{aligned}\Xi(V, T, \mu)\ &=\ \Xi_N\left[\mathrm{e}^{N\mu/kT}\sum_j \mathrm{e}^{-\ E_j(N,V)/kT}\right]\\ \Xi(V, T, \mu)\ &=\ \textstyle\sum_N Q(N, V, T)\ \mathrm{e}^{N\mu/kT}\end{aligned} \tag{24.7}$$

Hence, the function grand partition appears as being a collection of functions of partition of canonical ensembles. This property is very often used in this part of the book.

The probability that the system possesses N molecules, whatever its energetic state is, is given by the expression

$$\begin{aligned}P(N;\ V,\ T,\ \mu)\ &= \sum_j P_j(N)\\ &=\ Q(N, V, T)\ \mathrm{e}^{N\mu/kT}/\Xi(V, T, \mu)\end{aligned} \tag{24.8}$$

As a consequence, the mean number of molecules is given by the expression

$$\overline{N}(V, T, \mu)\ = \sum_N N\ Q(N, V, T)\ \ \mathrm{e}^{N\mu/kT}/\Xi(V, T, \mu)$$

By a reasoning similar to that followed in the case of the canonical ensemble, by linking the results obtained through statistical thermodynamics to the thermodynamic function ST $= E - N\mu + pV$, one finds that the function pV is characteristic of the grand canonical ensemble (viz. Appendix V). It is given by the expression

$$pV = kT \ln \Xi(V, T, \mu)$$

Once known, it permits to calculate S, N, and p with the help of a reasoning analogous to that followed for the canonical ensemble. The found expressions are

$$S = kT\,(\partial \ln \Xi / \partial T)_{V,\mu} + k \ln \Xi$$

$$N = kT\,(\partial \ln \Xi / \partial \mu)_{V,T}$$

$$p = kT\,(\partial \ln \Xi / \partial V)_{\mu,T} = kT\,(\ln \Xi)$$

24.1.2 Grand Ensemble and Absolute Activity

In some cases, the grand ensemble is easier to handle than the canonical ensemble. It is notably the case when we have to study systems containing numerous particles. It is the case of chemical systems. With this ensemble, the challenge amounts to the study of a system of one component, of a system of two components and so forth. Relation (24.7), indeed, can also be written, equivalently, under the form of the following series development:

$$\Xi(V, T, \mu) = Q(0, V, T) + Q(1, V, T)\lambda^1 + Q(2, V, T)\lambda^2 + \cdots$$

with

$$\lambda = \mathrm{e}^{\mu/kT}$$

λ is called the absolute activity of the component. Hence, the relation (24.7) can also be written as

$$\Xi(V, T, \mu) = \sum_N [Q(N, V, T)\lambda]^N / N! \tag{24.9}$$

We again find the fact that the function grand partition Ξ is a collection of canonical functions $Q(N, V, T)$. It is through the handling of this relation that, for example, the significance in molecular terms of the activity and of the fugacity of an imperfect gas is grasped (viz. Chap. 34).

24.1.3 The Case of Several Components (Grand Ensemble)

The preceding considerations spread to the cases where there are several components. Let us envisage the case where there are two components, numbered 1 and 2. Therefore, we are facing with a system at constant temperature and volume and in which the components 1 and 2 exhibit the chemical potentials μ_1 and μ_2. Let us recall that it can freely exchange the compounds 1 and 2 with the other systems. In this study, we also make the hypothesis that there is no interaction between the molecules.

The first point to consider is that the possible quanto-energetic levels E_j depend on the volume V and on the number of moles N_1 and N_2.

The study of the system is analogous to the preceding one. The existing constraints prevailing over the system are

$$\sum_j \sum_{N_1} \sum_{N_2} n_j(N_1, N_2) = \aleph$$

$$\sum_j \sum_{N_1} \sum_{N_2} n_j(N_1, N_2)\, E_j(V, N_1, N_2) = E_t$$

$$\sum_j \sum_{N_1} \sum_{N_2} n_j(N_1, N_2)\, N_2 = \mathcal{N}_2$$

$$\sum_j \sum_{N_2} \sum_{N_1} n_j(N_2, N_1)\, N_1 = \mathcal{N}_1$$

where N_1 and N_2 are the numbers of moles of compounds 1 and 2. The number of possible quantum states of the "supersystem" Ω_t is given by the relation (analogy with the relation (24.1))

$$\Omega_t = \left[\sum_j \sum_{N_1} \sum_{N_2} n_j(N_1, N_2)\right]! \,/\Pi_{j,N_1,N_2} n_j(N_1,\ N_2)!$$

Successively cancelling the partial derivatives Ω_t with respect to the terms n_j (N_1, N_2) by taking into account the preceding constraints permits to obtain the dominant sub-distribution.

The probability $P_j(N_1,\ N_2;\ V,\ T,\ \mu_1,\ \mu_2)$ for the system to be in the quanto-energetic state E_j (N_1, N_2, V) is given by the expression

$$P_j(N_1, N_2; V, T, \mu_1, \mu_2) = \mathrm{e}^{-E_j(N_1,N_2,V)/kT}\, \mathrm{e}^{N_1\mu_1/kT}\, \mathrm{e}^{N_2\mu_2/kT} / \Xi(V, T, \mu_1, \mu_2)$$

with

$$\Xi = \sum_j \sum_{N_1} \sum_{N_2} \mathrm{e}^{-E_j(N_1\ ,N_2,\ V)} \mathrm{e}^{\ N_1\mu_1/kT} \mathrm{e}^{\ N_2\mu_2/kT}$$

Ξ can also be written as

$$\Xi = \sum_{N_1} \sum_{N_2} \left\{ \mathrm{e}^{N_1\mu_1/kT} \mathrm{e}^{N_2\mu_2/kT} \sum_j \mathrm{e}^{-\ E_{\mathrm{j}}(N_1,N_2,V)/kT} \right\}$$

By writing

$$Q(N_1,N_2,\ V,T)\ = \sum_j \mathrm{e}^{-\ E_j(N_1,N_2,V)/kT}$$

$$\lambda_1 =\ \mathrm{e}^{\mu_1\ /kT} \text{ and } \lambda_2 = \mathrm{e}^{\mu_2/kT}$$

we obtain

$$P_j(N_1,N_2\ ;V,T,\mu_1,\mu_2)\ =\ \mathrm{e}^{-\ E_j(N_1,N_2,V)/kT} {\lambda_1}^{N_1} {\lambda_2}^{N_2} / \Xi(V,T,\mu_1,\mu_2)$$

with

$$\Xi = \sum_{N_1} \sum_{N_2} Q(N_1,N_2,\ V,T) {\lambda_1}^{N_1} {\lambda_2}^{N_2}$$

24.2 Microcanonical Ensemble: Boltzmann's relation

The microcanonical ensemble permits to study the properties of an isolated system characterized by the following thermodynamic variables: E, V, and N. Its energy, volume, and composition are constants since the system is isolated. That means that there are no heat, no matter, and no work exchanges with the surroundings (Fig. 24.2).

The characteristic function of such an ensemble can be obtained, among different ways, by starting from the properties of the canonical ensemble. Let us consider a canonical ensemble and suppose that we only choose the systems possessing the energy E, among all the systems it contains. Now, let us suppose that these systems are picked out from the canonical ensemble. Therefore, we obtain a collection of isolated systems which, all, possess the same energy, composition, and volume V. Another equivalent manner to describe the system is to consider that the only accessible quanto-energetic state is that of energy E. In the initial canonical state, the probability P for a system to possess the energy E was proportional to $\mathrm{e}^{-E/kT}$. E is the same for the systems of the new ensemble. Therefore, their probability P in

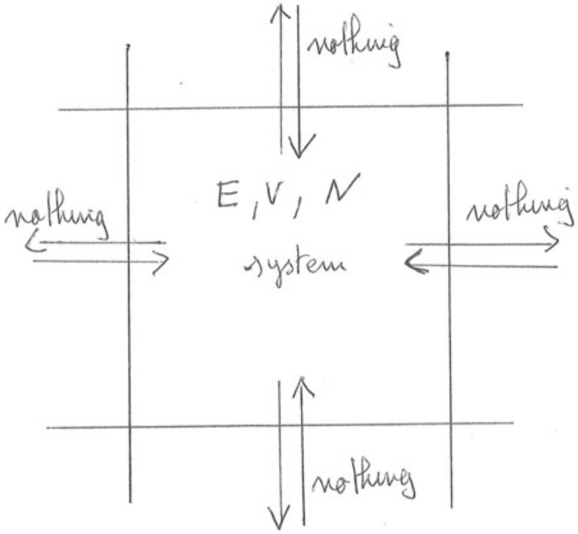

Fig. 24.2 Microcanonical ensemble

the canonical initial ensemble was the same. Let Ω(N, V, E) be the number of these states. Within the microcanonical system, we can write

$$P = 1/\Omega \quad \text{since} \quad \sum \mathrm{P} = 1.$$

The entropy being a mean statistical quantity over all the systems of the initial canonical ensemble and their number ℵ being very large, every system of the new ensemble (called the degenerated state) possesses the same entropy since they have the same energy. Hence, we can use the following relation concerning the canonical ensemble:

$$S(N, V, T) = -k\sum_j P_j \ln P_j$$

For the present new ensemble, it can be written as

$$S(N, V, E) = -k\sum_j P_j \ln P_j \tag{24.10}$$

In order to find the relation being searched for, it is only sufficient to replace P_j by 1/Ω into these expressions of S, since P_j is the same for all Ω quantum states and moreover since $\sum_j P_j = 1$:

$$P_j = 1/\Omega$$

As a result

$$\begin{aligned} S &= -k\Omega(\,1/\Omega \ln 1/\Omega) \\ S &= k \ln \Omega(N, V, E) \end{aligned} \tag{24.11}$$

This is the very famous Boltzmann's relation which, the first, has given a "probabilistic" meaning to the function entropy.

Expression (24.11) is the characteristic function of the microcanonic ensemble. Once known, as in the cases of the other ensembles, it permits to calculate all the other thermodynamic functions, by comparison with the relation from purely thermodynamic origin:

$$dS = (1/T)\,dE + (p/T)\,dV - \sum_k (\mu_k/T)\,dN_k$$

where k is the index marking the different components.

24.3 Isothermal-Isobaric Ensemble

Now, we are considering a closed system in thermal and mechanical equilibrium with the surroundings. It can be regarded as an ensemble of systems analogous to those encountered in the canonical ensemble but where their volumes vary by adoption of supple partitions for each of them to be in mechanical equilibrium with its neighbor. Then, the volume of each system fluctuates. The studied system is defined by the independent variables T, p, and N (Fig. 24.3).

By analogous processes to those already considered that the probability P_V for a system to possess a volume V is given by the relation

$$P_V = \mathrm{e}^{-\,pV/kT} Q(T, V, N)\;/\Delta$$

where Δ is the partition function of the ensemble. We must remark that this expression is of the same type (24.8). In addition, it is obtained in an analogous manner. The isothermal-isobaric partition function is given by the expression

$$\Delta(T, \mathbf{p}, N) = \sum_V Q(N, V, T)\,\mathrm{e}^{-\,pV/kT}$$

The sum is calculated over all the possible volumes. We remark that it appears as a collection of canonical functions. In classical mechanics, where the volume varies continuously, it is written as

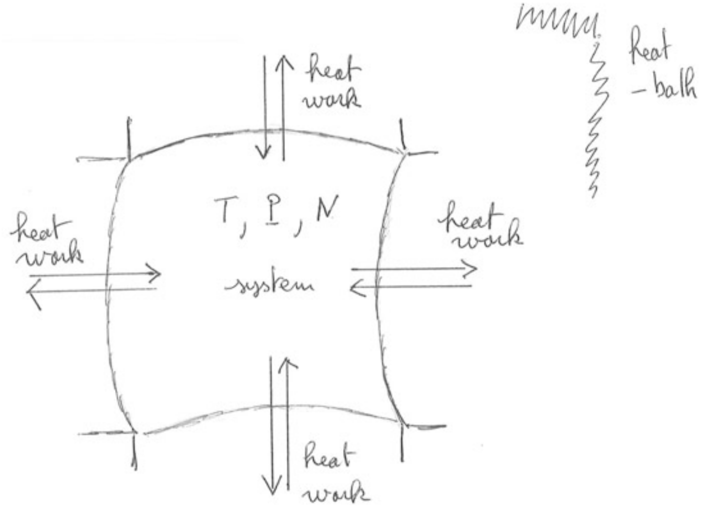

Fig. 24.3 Isothermal-isobaric ensemble

$$\Delta(T, \mathbf{p}, N) = C \int_{0}^{\infty} dV \, Q(N, V, T) \, \mathrm{e}^{-pV/kT}$$

where C is a constant having the dimension of the inverse of a volume. The function characteristic of the ensemble is the Gibbs energy:

$$G(T, p, N) = -kT \quad \ln \Delta(T, p, N)$$

It permits to calculate the chemical potential μ_{i} (T, p, N) of the component(s), the entropy S (T, p, N) of the system, and the mean value of the volume of the system $\overline{V_i}$ which is equally function of T, p, and N.

Chapter 25
Systems of Molecules or Subsystems: Independent, Distinguishable, and “Indistinguishable”

Abstract In this chapter are given some general principles permitting the study of systems composed of atoms, molecules, groups of molecules, and independent “subsystems,” with the aid of statistical thermodynamics. “Subsystems” are defined as, for example, the different degrees of freedom in the same molecule (such as translational, rotational a.s.f.). They can also be the molecules adsorbed on independent adsorption sites located on a solid surface . . . a.s.f.

The meaning of independent being specified, the cases of the molecules or “subsystems” distinguishable and “indistinguishable” are studied. The invoked calculations in this chapter are based on the handling of the canonical partition function. Such calculations induce the introduction of a new kind of a partition function, the molecular partition one.

Keywords Adsorption sites • Subsystems • Distinguishable and indistinguishable systems and subsystems • Degrees of freedom • Maxwell–Boltzmann statistics • Molecular partition function • Translational, rotational quanto-energetic states

In this chapter, we recall some general principles permitting the study of systems composed of atoms, molecules, groups of molecules, and independent “subsystems,” with the aid of statistical thermodynamics. For example, we call “subsystem” the different degrees of freedom in the same molecule (such as translational, rotational, a.s.f.). It can also be the molecules adsorbed on independent adsorption sites located on a solid surface . . . a.s.f.

After having specified what we mean by independent, we successively envisage the cases of the molecules or “subsystems” distinguishable and “indistinguishable.” This chapter is based, in the different cases, on the structure of the partition function.

25.1 Meaning of the Independence of the Molecules and “Subsystems”

One can consider that the particles, present in the same container, are independent from each other when their displacement is not influenced by that of another. Each particle exhibits a purely random displacement in the container. The lack of

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independence of atoms, molecules constituting the system, may be due to physical interactions between the components or to some restrictions of symmetry regarding the wave functions describing the system. The latter case is not envisaged here.

Actually, the strict independence of the components of the system cannot enter within the framework of this study, since in such a case, the studied system cannot reach the internal state of equilibrium. The statistical study of such systems becomes, then, very difficult, if not impossible. Let us specify this point by, for example, briefly, considering the case of perfect gases. Their density in the container must be sufficiently weak so that the intermolecular forces do not play a part in the properties of the gases. However, the internal equilibrium (entailing that the perfect gas law is satisfied) must be still reached by the collisions between the molecules out by the collisions between the latter with the partitions of the container in order that the thermodynamic properties of such systems do exist.

25.2 Calculation of the Partition Function of Independent and Distinguishable Molecules or Subsystems

Since the thermodynamic properties of a system may be obtained from its partition function, the latter must be calculated.

25.2.1 *Definition of the System*

Let us regard the case of one container of volume V, only containing two molecules of different natures. Let ε_0, ε_1, ε_2, and so forth be the quantified energies of the first molecule, and $\varepsilon_0{}'$, $\varepsilon_1{}'\varepsilon_2{}'$ and so forth those of the second molecule. (These possible energies are obtained by resolution of the Schrödinger's equation related to each kind of molecule.)

- The independence of the particles is expressed by the fact that, since by hypothesis both molecules do not exhibit noticeable interactions between them, the energy of the system constituted by both kinds of molecules in the volume V is the sum of the energies of the individual molecules, which are those they possess when they are alone in the volume V.
- Clearly, in the previous reasoning, the particles are distinguishable. That is shown by the fact that the possible energies ε_i, $\varepsilon_i{}'$ are distinctly marked.

25.2.2 Calculation of the Partition Function

In the above example, it is evident that, since the molecules are independent, when one is in the state of energy ε_i, the other may be found in every authorized other one $\varepsilon_j{}'$. As a result, the partition function Q of the whole system is given by the expression

$$\begin{aligned} Q = {} & \mathrm{e}^{-(\varepsilon_0+\varepsilon_0{}')/kT} + \mathrm{e}^{-(\varepsilon_0+\varepsilon_1{}')/kT} + \mathrm{e}^{-(\varepsilon_0+\varepsilon_2{}')/kT} \\ & + \mathrm{e}^{-(\varepsilon_1+\varepsilon_0{}')/kT} + \mathrm{e}^{-(\varepsilon_1+\varepsilon_1{}')/kT} + \mathrm{e}^{-(\varepsilon_1+\varepsilon_2{}')/kT} \\ & + \mathrm{e}^{-(\varepsilon_2+\varepsilon_0{}')/kT} + \text{asf} \ldots . \end{aligned}$$

That is,

$$Q = \sum_i \mathrm{e}^{-\varepsilon_i/kT} \left(\sum_j \mathrm{e}^{-\varepsilon_j/kT} \right)$$

When the energy states ε_i are degenerated ω_i times and those $\varepsilon_j{}'\omega_j{}'$ times, the partition function Q is given by the relation (viz. Chap. 22)

$$Q = \left(\sum_i \omega_i \mathrm{e}^{-\varepsilon_i/kT} \right) \left(\sum_j \omega_j{}' \ \mathrm{e}^{-\varepsilon_i{}'/kT} \right)$$

The functions $\left(\sum_i \mathrm{e}^{-\varepsilon_i/kT}, \sum_j \mathrm{e}^{-\varepsilon_j/kT} \right)$, $\sum_i \omega_i \mathrm{e}^{-\varepsilon_i/kT}$, and $\sum_j \omega_j{}' \mathrm{e}^{-\varepsilon_j{}'/kT}$ are called molecular partition functions. They must not be confused with the partition function of the whole system Q. The former are symbolized by q.

Generalizing the foregoing example, we can deduce that in the case of systems constituted by molecules or subsystems independent and distinguishable, the partition function of the system Q is given by the relation

$$Q = q_1 q_2 \mathrm{q}_3 \ldots . \quad \text{(independent and distinguishable particles)} \tag{25.1}$$

where $q_1, q_2, q_3 \ldots$ are the molecular partition functions of the molecules 1, 2, 3 … or of the subsystems 1, 2, 3, and so forth.

25.3 Independent and "Indistinguishable" Molecules or Subsystems

It is the case for example in which the molecules are identical and, hence, "indistinguishable," while not being in interactions by hypothesis, i.e., still independent from each other.

The calculation of the partition function stems from the following reasoning. Relation (1), if it was legitimate, would be in this case

$$Q = q^N$$

where the molecular partition function q is the same for each molecule (or each subsystem) since the molecules are identical and are contained in the same volume V.

Actually, this relation is not exact. So, we adopt the same reasoning as in the example above concerning both kinds of molecules; it appears, for example, that the state energy of the previous system $\varepsilon_0 + \varepsilon_1{}'$ of the foregoing example is, now, equal to the energy of the state $\varepsilon_0{}' + \varepsilon_1$ of the former example, since in this new case $\varepsilon_\mathrm{i}{}' = \varepsilon_i$. It is the same thing for all the states where $i \neq j$. As a result, in this case where there are two molecules, these "crossed" terms appear two times with the preceding numeration system. It is clear that they must be counted only once in the calculation of the partition function of the system. The generalization of this result leads to the fact that for a system constituted by N identical molecules, the crossed terms would appear $N!$ times. The adopted solution in order to calculate Q is to use the relation

$$Q = q^N/N! \quad \text{(independent and “indistinguishable” particules)} \tag{25.2}$$

However, by calculating in such a way, we are making an error since we also divide the "non-crossed" terms of energy $\varepsilon_i + \varepsilon_i$ by $N!$ the "non-crossed" terms of energy $\varepsilon_i + \varepsilon_i$ which do appear only once during the preceding numeration. But, this error may be qualified justifiably as being perfectly negligible since, given the number of molecules N excessively large (of the order of 10^{20}), the number of "crossed terms" is incomparably larger than that of the "non-crossed" ones and as a result the latter ones are negligible in the sum Q.

Let us mention the important following point :the relation (25.2) *is legitimate if only the number of quanto-energetic states is by far larger than the number N. In these conditions, it proves to be correct that all the terms bringing an important contribution to the partition function Q correspond to the fact that each molecule is in a different quanto-energetic state. It is said, then, that the kind of statistics which is obeyed is that of Maxwell–Boltzmann.*

Chapter 26
Perfect Gases

Abstract This chapter is an example of calculation of the thermodynamic properties of compounds through reasonings of statistical thermodynamics. It gives the demonstration of the perfect gas law by considerations of statistical thermodynamics. Finally, some thermodynamic quantities relative to the perfect gases are mentioned in terms of molecular parameters.

The demonstration is performed by handling the grand ensemble. In the case of perfect monoatomic gases, the resolution of the Schrödinger's equation is possible. The internal energy of each individual atom is then equal to the sum of its energies of rotation, vibration, and electronic. The internal energy of the atom does not depend on its position in space. As a result, the molecular partition function corresponds to the whole internal and translation properties of the atom. Given these facts, the classical thermodynamic functions, such as the Gibbs energy, the chemical potential, and even the standard chemical potential of the gas (which is a quantity somewhat mysterious in classical thermodynamics) can be expressed in terms of molecular parameters as it is shown.

Keywords Perfect gas law • Schrödinger's equation • Standard chemical potential • Perfect gas • Standard chemical potential • de Broglie's thermal wavelength • Perfect gas internal energy • Perfect gas Gibbs energy • Helmholtz energy • Translational energy • Vibrational energy • Electronic energy • Molecular partition function

Although the activity notion is principally applied to the case of liquid solutions, it seems to us judicious, in introduction to their study, to consider the behavior of gases and particularly to begin by that of perfect gases. A valuable reason to proceed in such a manner is that the theoretical study of gases is by far more advanced than that of liquids. Moreover, it is well known that the model of perfect gases has proved to be particularly fruitful for the study of thermodynamics. Noteworthy especially, it is very interesting for the study of the chemical potential and, through the latter, for that of the activity notion.

We begin with the definition of a perfect gas. Then, we give a demonstration of the perfect gas law by starting from considerations of statistical thermodynamics. Finally, with the help of the same considerations, we explicit some thermodynamic quantities relative to the perfect gases in terms of molecular parameters.

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26.1 Definitions

There exists some haziness concerning the definition of a perfect gas.

- For some authors, a gas is called perfect or ideal if it obeys the state equation:

$$p\,V\ =\ n\,R\,T$$

where p is the pressure of the gas, V the total volume it occupies, n its number of moles, T its absolute temperature, and R the perfect gas constant. R is a universal constant. It is equal to the product of the Avogadro's number N_{A} and the Boltzmann's constant, $k = 1{,}3807 \times 10^{-23}\mathrm{J\,K^{-1}}$:

$$R = k\,N_{\mathrm{A}}$$
$$R = 8{,}3145 \times 10\ \mathrm{J\,K^{-1}mol^{-1}}$$

For other authors, a supplementary condition must be added to the preceding one: the internal energy E of a perfect gas must be only a function of the temperature. It is not a function of the volume in which it is contained nor it is a function of its pressure, i.e.,

$$(\partial E/\partial V)_T = 0 \quad \text{and} \quad (\partial E/\partial p)_T = 0$$

- Finally, a latter group of authors defines a perfect gas by the following expression of its chemical potential μ in the considered thermodynamic state where it is at the pressure p and at the temperature T:

$$\mu\ = \mu^{\circ}\ +\ RT\ln\,p/p^{\circ}$$

In this expression, μ° is its chemical potential in the standard state where its pressure is $\mathbf{p}^{\circ}$. The temperature is equal to T, identical to the previous one.

This latter definition is strictly equivalent to the first one. Later, we shall confine ourselves to the first definition.

26.2 A Brief Discussion of These Definitions

A perfect gas is an abstraction that the real gases may approach more or less according to their nature and the conditions where they are. From the molecular standpoint, a perfect gas is composed of molecules (or atoms), the interactions between them being fully negligible and the volume they occupy being also fully negligible with respect to that of their container. There is no release nor heat absorption during the expansion of a perfect gas, provided that there is no work arising during the process. The result is the occurrence of the two relations both involving partial derivatives, already encountered in the statement of the second definition. Actually, it seems that the state equation entails these two relations.

26.3 Types of Perfect Gases: The Case of Mixtures

Let us recall that every gas, whatever its molecular type is (monoatomic, diatomic, polyatomic), including mixtures of different gases, tends toward the perfect behavior. The sine qua non condition of existence of such a behavior is that every gas (and even every molecule or atom of these gases) exhibits no interaction with the others.

26.4 The State Equation in Statistical Thermodynamics

The state equation in statistical thermodynamics is (viz. later Chap. 27)

$$\mathbf{p}V = N\,k\,T$$

or

$$\mathbf{p} = \rho kT$$

N is the number of molecules (and not the number of moles), k the Boltzmann's constant, and $\rho = N/V$ the density number of the gas.

This equation may be obtained in different manners. We mention one, here. We shall give another one, later, in Chap. 27.

We are considering the case of an ensemble of identical particles of a monoatomic gas, without any mutual interactions and being "indistinguishable." For the perfect diatomic and polyatomic gases, we confine ourselves to recalling some results. But, previously, we show that the perfect gas law can be obtained by using the theory of the grand ensemble.

26.5 Obtaining the Perfect Gas Law Using an Ensemble of Identical Molecules Without Mutual Interactions and Being "Indistinguishable"

The demonstration is performed by handling the grand ensemble. The corresponding partition function Ξ can be written (viz. Chap. 24) as

$$\Xi = \sum_N Q(N, V, T)\lambda^N \quad N \geq 0$$

At this point of the demonstration, it must be noticed that within the framework of the hypothesis of no interaction between the particles, the canonical partition function intervening in Ξ does not contain a term involving any potential energy of interaction. This fact is evidenced by a reasoning involving classical statistical mechanics (viz. Chap. 27).

In this case, this relation can also be written as follows:

$$\Xi = \sum_N [q(N, V, T)\lambda]^N / N!$$

That is, more explicitly

$$\Xi = 1 + q(1, V, T)\lambda + [q(2, V, T)\lambda]^2/2! + [q(3, V, T)\lambda]^3/3! + \text{and so f}\ldots.$$

(This relation comes from the fact that the particles are independent and "indistinguishable." See Sect. 26.6.4).

Let us notice the value $q(0,V,T) = 1$. The empty system has only one state, that of null energy.

The previous expression of Ξ is nothing different from the expansion in series of the expression

$$\Xi = e^{q\lambda} \tag{26.1}$$

From another standpoint, we know (viz. Chap. 24) that the characteristic function of the grand ensemble is the function $pV = kT \ln \Xi$, i.e.,

$$\Xi = e^{pV/kT}$$

The obtaining of the perfect gas equation results from the following equality. It is evident according to the last two relations found above:

$$Q\lambda = pV/kT$$

It remains to demonstrate that $Q\lambda = N$ is the number of particles of the system.

The starting point of the demonstration is the relation

$$\overline{N} = kT(\partial \ln \Xi / \partial \mu)v, t \tag{26.2}$$

stemming from the great ensemble theory.

According to (26.1)

$$\ln \Xi = q\lambda \quad \text{or} \quad q = \ln \Xi/\lambda \tag{26.3}$$

$$d\ln \Xi = q\,d\lambda \quad \text{whence}$$

$$d\ln \Xi/d\lambda = q \tag{26.4}$$

By eliminating q between relations (26.3) and (26.4), we obtain

$$\ln \Xi = \lambda(d\ln \Xi/d\lambda) \quad \text{or} \quad \ln \Xi = d\ln \Xi/(d\lambda/\lambda)$$
$$\text{i.e. } \ln \Xi = (d\ln \Xi/d\ln \lambda)$$

or, since $\lambda = \mathrm{e}^{\mu/KT}$ (k being the Boltzmann's constant)

$$\ln \lambda = \mu/kT$$
$$\ln \Xi = kT\,(\partial \ln \Xi/\partial \mu)_{V,T}$$

and $\ln \Xi = \overline{N}$ according to (26.2)

since

$\ln \Xi = q\lambda$ according to (26.3)

and

$\ln \Xi = \overline{N}$ according to (26.2)

we obtain

$$q\lambda = \overline{N}$$

and

$$\overline{N}kT = \mathbf{p}V \quad \text{(perfect gas law)}$$

Since we have worked within the framework of the grand ensemble, the value N is a mean value, whence the symbolism $\overline{N}$ is derived. One demonstrates that its fluctuations are very weak.

From the viewpoint of the pure scientific rigor, it is exceedingly satisfactory to again find the perfect gas law, by starting from the principles of quantum mechanics and by using statistical thermodynamics.

26.6 A Study of Perfect Monoatomic Gases

26.6.1 Translation Energy and Internal Energy

In the case of the perfect monoatomic gases, the resolution of the Schrödinger's equation is possible, at least as regards the translation motion of the atoms. *The* *internal energy* of each individual molecule $\varepsilon^{\mathrm{int}}$ is equal to the sum of its energies of rotation $\varepsilon^{\mathrm{rot}}$, vibration $\varepsilon^{\mathrm{vib}}$, and electronic $\varepsilon^{\mathrm{elec}}$, i.e.,

$$\varepsilon^{\mathrm{int}} = \varepsilon^{\mathrm{rot}} + \varepsilon^{\mathrm{vib}} + \varepsilon^{\mathrm{elec}}$$

The internal energy of the atom does not depend on its position in space. As a result, the energy of an atom ε may be considered as being the sum of a translation energy $\varepsilon^{\mathrm{tr}}$ and of an internal energy. Hence, one can write

$$\varepsilon = \varepsilon^{\mathrm{tr}} + \varepsilon^{\mathrm{int}}$$

In the canonical system, the molecular partition function is

$$q = \sum_i \mathrm{e}^{-\varepsilon i/kT}$$

where q is the partition function which corresponds to the whole internal and translation properties of the atom. By virtue of the "separability" of ε, we can write

$$q = \sum_i \mathrm{e}^{-\varepsilon i\,\mathrm{tr}\,/\,kT} \sum_i \mathrm{e}^{-\varepsilon i\,\mathrm{int}\,/\,\mathrm{kT}}$$

$$q = q^{\mathrm{tr}} q^{\mathrm{int}}$$

Regarding, now, the internal partition function q^{int}, calculations show that its value can be taken to be equal to the unity for the majority of monoatomic gases. Consequently, all the following results only stem from the translation of the atoms.

26.6.2 Expression of the Molecular Partition Function of Translation q^{tr}

Calculations show (viz. Chap. 27) that the molecular partition function of translation is

$$q^{\mathrm{tr}} = \left(2\pi mkT/h^2\right)^{3/2} V \tag{26.5}$$

where m is the mass of each particle, k the Boltzmann's constant, h the Planck's constant, and V the volume of the container.

26.6.3 de Broglie's Thermal Wavelength

It is convenient to introduce the parameter Λ into the varied relations. It is called de Broglie's thermal wavelength (viz. Chap. 27) such as

$$\Lambda = h/(2\pi mkT)^{1/2}$$

The molecular partition function of translation is now

$$q^{\mathrm{tr}} = V/\Lambda^3 \tag{26.6}$$

26.6.4 Expression of ln **Q** as a Function of the Atomic Parameters

Setting up this expression proved to be particularly fruitful because it actually constitutes a kind of hub because it permits the quasi-immediate calculation of the thermodynamic quantities of these gases as a function of their molecular parameters, owing to the general relations stemming from the theory of the varied ensembles.

Let us regard the canonical ensemble. Given the high dilution of the gas in the volume V, the gas molecules are independent from each other and are not distinguishable. In these conditions, the canonical partition function can be written according to

$$Q = (1/N!)q^N$$

with the principle $q = q^{\mathrm{tr}}q^{\mathrm{int}}$, but since $q^{\mathrm{int}} \approx 1$,

$$Q = (1/N!)\,q^{\mathrm{tr}N} \tag{26.7}$$

By introducing (26.5) into (26.7) and by using Stirling's approximation, we obtain

$$\ln Q = N \ln \left[\left(2\pi mkT/h^2\right)^{3/2} (Ve/N) \right]$$

where e is the basis of the Napierian logarithms.

26.6.5 Helmholtz Energy A

Since

$A\,(N, V, T) = -kT \ \ln Q$ (viz. Chap. 23) we immediately obtain

$$A = -NkT\ln\left[\left(2\pi mkT/h^2\right)^{3/2}(Ve/N)\right]$$

We notice that A is an extensive property, since it is proportional to N. However, the ratio A/N is an intensive quantity since it only depends on intensive quantities themselves T and V/N. It is the Helmholtz energy.

26.6.6 *Pressure*

Since (viz. Chap. 23)

$$p = kT(\partial \ln Q/\partial V)_{T,\ N} \tag{26.8}$$

by introducing the relations (26.5) and (26.7), we again find the perfect gas law.

26.6.7 *Internal Energy* E

It is calculated by using the relation (26.9) (Chap. 23):

$$E = kT^2(\partial \ln Q\ /\partial T)_{V\ ,N}$$

That is,

$$E = (3/2)NkT$$

The sample containing n moles of gas, one can also write

$$E = (3/2)nRT$$

since $n = N/N_A$. The origin of this energy is entirely kinetic since, by hypothesis, the potential energy is null. Indeed, we assumed that there exists no interaction between the species. The expression above is equally found by starting from purely kinetic considerations and it obeys the principle of energy equipartition. (Actually, this principle is not general.)

26.6.8 Entropy

The entropy can be calculated from the relation

$$S = (E - A)/T$$

E and A are already expressed above. As a result:

- In terms of volume:

$$S = Nk \ \ln \left[\left(2\pi mkT/h^2\right)^{3/2} \left(V \mathrm{e}^{5/2}/N\right) \right]$$

- In terms of pressure:

$$S = Nk \ \ln \left[\left(2\pi mkT/h^2\right)^{3/2} \left(kT \ \mathrm{e}^{5/2}/p\right) \right]$$

26.6.9 Gibbs Energy G

The Gibbs energy being defined in thermodynamics by the relation

$$G = A + pV$$

we obtain the following relations after the replacing of A and p by their expressions above:

- In terms of volume:

$$G = -N\,kT \ \ln \left[\left(2\pi mkT/h^2\right)^{3/2} V/N \right]$$

- In terms of pressure:

$$G = -N \ kT \ \ln \left[\left(2\pi mkT/h^2\right)^{3/2} kT/p \right]$$

or

$$G = -NkT \ \ln \left(kT \ /p\Lambda^3 \right)$$

26.6.10 Chemical Potential μ

We know (viz. Chap. 23) that the chemical potential can be calculated through the relation

$$\mu = -\,kT\;(\partial \ln Q\;/\partial N)_{T,V}$$

Given relation (26.6), we obtain

$$\mu = -\,kT\;\ln(q\;/N)$$
$$\mu = -\,kT\;\ln\left[\left(2\pi mkT/h^2\right)^{3/2} V/N\right]$$

or

$$\mu\;=-\,kT\;\ln\left[\left(2\pi mkT/h^2\right)^{3/2}\,kT/p\right] \tag{26.9}$$

26.6.11 Standard Chemical Potential of a Perfect Gas

The relation (26.9) is particularly interesting since it permits to obtain one expression of the standard potential of a perfect gas in terms of molecular parameters. The standard chemical potential, as it is introduced in thermodynamics, appears indeed to be very mysterious because of two reasons. The first one, of course, is the fact it is an integration constant. The second is that it may vary according to arbitrary conventions.

In thermodynamics, we know that in the case of a perfect gas, the chemical potential of a perfect gas is given by the expression

$$\mu(p,T) = \mu^\circ(T)\;+\;kT\;\ln p\;/p^\circ \tag{26.10}$$

where $\mu^\circ(T)$ is the chemical potential in the standard state of the gas and p° is the chosen standard pressure (for example $p^\circ = 1$ bar). The standard state itself (chosen at temperature T of the system and at pressure p°) is particularly interesting. By using relations (26.9) and (26.10), its chemical potential is given by the relation

$$\mu^\circ(T,\mathbf{p}^\circ)\;=\;-\;kT\;\ln\left[\left(2\pi mkT/h^2\right)^{3/2}\,kT/p^\circ\right] \tag{26.11}$$

It is quite interesting to notice that the term below, between square brackets

$$\left[\left(2\pi mkT/h^2\right)^{3/2}kT\right]$$

has the dimension of a pressure. As a result, the argument of the logarithm of relation (26.11) is truly dimensionless, as it must be the case from the mathematical standpoint.

26.7 Binary Mixture of Two Perfect Monoatomic Gases

It seems interesting for us to study the case of the binary mixture of two perfect monoatomic gases. In this case, the canonical partition function is simply the product of the two canonical partition functions of each gas. Their behaviors are different from each other. Hence, we can set up

$$Q = \left(q_1^{N_1}/\, N_1!\right)\left(q_2^{N_2}/N_2!\right)$$

where

$$q_1 = V/\Lambda_1^3 \quad \text{and} \quad q_2 = V/\Lambda_2^3$$

Λ_1 and Λ_2 are only different from each other through their masses m_1 and m_2. The expressions of the Helmholtz energy and of the entropy are found by starting from the general expressions (viz. Chap. 23):

$$A = -\, kT\ \ln Q$$
$$S = k\ \ln Q + \ kT(\partial \ln Q/\partial T)_{N,V}$$

whence

$$S = N_1 k\ \ln\left(V\mathrm{e}^{5/2}/{\Lambda_1}^3 N_1\right)\ +\ N_2 k\ \ln\left(V\mathrm{e}^{5/2}/{\Lambda_2}^3 N_2\right)$$

Likewise, starting from the general equations governing the canonical ensemble, we immediately find

$$pV = \ (N_1 +\ N_2)kT$$

and

$$E = 3/2\ (N_1 +\ N_2)kT$$

26.8 The Perfect Gas Law from Other Ensembles

Let us mention the fact, without stressing it, that it is possible to also find the perfect gas law by reasoning with other types of ensembles.

26.9 Perfect Polyatomic Gases

Perfect polyatomic gases may obey the state law. Here, we just recall a general formulation of their chemical potential.

- Obeying the state equation, as previously, entails that the molecules should be independent, that is to say without interactions between them. They must also be indistinguishable. In the present case, the respect of the law also entails to consider the independence of the degrees of freedom in a molecule itself. The latter condition constitutes an approximation which seems to be rather satisfactory.

  According to the theory of the canonical ensemble

$$Q = 1 \,/\, N! \, q^N$$

The difference between the cases of the polyatomic and monoatomic gases is that in the former case, the molecular partition function q is more complex than in the second. With the terminology of paragraph 2, we must also, at least in the reasoning, take into account the internal molecular partition function q^{int} which is no longer equal to unity. The molecular partition function is of the type

$$q = \sum_j \mathrm{e}^{-\ \varepsilon j/kT}$$

One can admit that, *here is the approximation of the independence of the degrees of freedom,* each level of energy ε of the molecule is the sum of the energy levels of translation, vibration, rotation, and electronic, i.e.,

$$\varepsilon = \varepsilon^{\mathrm{t}} + \varepsilon^{\mathrm{r}} + \varepsilon^{\mathrm{v}} + \varepsilon^{\mathrm{el}}$$

ε^{t}, ε^{r}, ε^{v}, and $\varepsilon^{\mathrm{el}}$ are, respectively, the energy levels of translation, rotation, vibration, and electronic. It is at this point that the approximation of the independence of the degrees of freedom is present. The latter relation is valid for a diatomic molecule, because of the existence of a vibration energy. For a polyatomic molecule, eventually, one must also take into account the energy involved in the rotation of some atoms or groups of atoms around a simple bond.

The independence of the levels of energy permits to the Hamiltonian of the molecule to be separable into Hamiltonians of translation, rotation, vibration, etc. Then, the Schrödinger equations with each Hamiltonian can be solved and one can obtain the corresponding molecular partition functions q^{t}, q^{r}, q^{v}, q^{el} …. The global molecular partition function is therefore

$$q \;=\; q^{\mathrm{t}}q^{\mathrm{r}}q^{\mathrm{v}}q^{\mathrm{el}}$$

and the canonical partition function

$$Q \;=\; \left(q^{\mathrm{t}}q^{\mathrm{r}}q^{\mathrm{v}}q^{\mathrm{el}}\right)^N / \, N\,! \tag{26.12}$$

Calculations show that the molecular partition functions q^{r}, q^{v}, and q^{el} are only functions of the temperature (and of course of the nature of the molecule). However, the partition function q^{t} is a function of the volume of the container. For example, for a diatomic molecule, its expression is

$$q^t = \left[2\pi kT(m_1 + m_2)/h^2\right]^{3/2} V \tag{26.13}$$

where m_1 and m_2 are the masses of both atoms. For a polyatomic molecule, it is

$$q^t = \left[2\pi kT\left(\sum_i m_i\right)/h^2\right]^{3/2} V$$

where $\Sigma_i m_{\mathrm{i}}$ is the sum of the masses of the atoms of the molecule. According to the properties of the canonical ensemble, the pressure is given by the relation

$$p = kT(\partial \ln Q / \partial V)_{T,N}$$

Replacing Q in the latter relation by its expression (26.12) directly leads to the expression

$$p = NkT(\partial \ln q^t / \partial V)_T$$

i.e.,

$$p = NkT \,/\, V$$

the equation of state.

Finally, this result found by considering the case of a diatomic molecule is the same as that which would be obtained in the same manner in the case of a polyatomic molecule.

- Concerning now the expression of the chemical potential of these gases, it is obtained by using the relation

$$\mu = A\,/\,N + \mathbf{p}V\,/N \tag{26.14}$$

stemming from chemical thermodynamics. A is the Helmholtz function (viz. Chap. 23). The division by the number N of molecules stands out since A and **p**V are extensive quantities whereas the chemical potential is an intensive quantity (molar quantity). The reasoning is close to the preceding. A is given by the expression stemming from the canonical system:

$$A = -\,kT\;\ln\;Q(N, V, T)$$

Replacing Q by the expression (26.12), we obtain

$$A = -kT\ln\left[\left(q^{\mathrm{t}}q^{\mathrm{r}}q^{\mathrm{v}}q^{\mathrm{el}}\right)^{\mathrm{N}}/\,N!\right]$$
$$A = -kT\left[\ln q^{\mathrm{t}N}/N! + \ln q^{\mathrm{r}N} + \ln q^{\mathrm{v}\,N} + \ln q^{\mathrm{el}\,N}\right]$$

or

$$A = A^{\mathrm{t}} + A^{\mathrm{r}} + A^{\mathrm{v}} + A^{\mathrm{el}}$$

A^{t}, A^{r}, A^{v}, A^{el} are the Helmholtz energies of translation, etc.

Remembering that for a diatomic molecule relation (26.13)

$$q^{\mathrm{t}} = \left[2\pi kT(m_1 + m_2)\,/\,h^2)\right]^{3/2}V$$

one immediately finds by using Stirling's approximation

$$A^{\mathrm{t}} = -NkT\;\ln\left(\mathrm{e}\;q^{\mathrm{t}}/\,N\right)$$

(*e* base of Napierian logarithms).

Moreover,

$$A^{\mathrm{r}} = -NkT\;\ln\;q^{\mathrm{r}}$$
$$A^{\mathrm{v}} = -NkT\;\ln\;q^{\mathrm{v}}\quad \text{and s.f.}$$

The introduction of these relations into the expression (26.14) permits to calculate the chemical potential μ of the gas in some conditions.

Chapter 27
Classical Statistical Mechanics, Configuration, and Classical Canonical Partition Function

Abstract To deeply grasp the physical significance of an activity, statistical thermodynamics must be considered and, in particular, it is the case of the notions of configuration of a system and of the classical canonical partition function.

Firstly, the chapter presents a definition of the configuration of a system. Secondly, the chapter is a presentation of the classical canonical partition function and of some relations stemming from it. It may be viewed as being an extension, in some definite conditions, of the canonical partition function occurring in quantum mechanics. All the mathematical terms constituting the function are presented. This is especially the case of the hamiltonian of the system. In some conditions, Hamilton's function is nothing more or less than the energy of the system. It entails the kinetic energy of the whole particles constituting the system and their mutual interacting potential energy. A simple example of its handling, concerning perfect gases, is given at the end of the chapter.

The partition function, indeed, is the most used partition function in the field of applications of statistical thermodynamics to chemistry. The function will be quasi-systematically used until the end of the book. It is a physical parameter of first importance in the grasping of the significance of an activity.

Keywords System • Stirling's approximation • System configuration • Classical statistical mechanics • Configurational partition function • Classical and quantum mechanics • Classical canonical partition function • Hamiltonian

In order to grasp the physical significance of an activity more deeply than before, we must turn ourselves toward statistical thermodynamics and especially, at the beginning, toward the notion of partition function, notion which also exists in the realm of classical statistical mechanics.

In this chapter, we present the classical canonical partition function and we mention some relations stemming from it. It may be viewed as being an extension of the canonical partition function occurring in quantum mechanics in some definite conditions. This is the standpoint we adopt here.

The canonical partition function, indeed, is the most used partition function in the field of applications of statistical thermodynamics to chemistry. We give an example of its handling with the case of perfect gases at the end of this chapter.

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27.1 Classical and Quantum Mechanics

In the classical mechanics, we consider that the state of a system is defined, at any instant, by the values of its coordinates and of its momenta.

In quantum mechanics, the state of the system at any instant is defined by a probability amplitude permitting to only know the probability of occurrence of some values of its coordinates and its momenta.

In either case, there are some situations in which the theoretical treatments just above evoked are not possible. In these cases, one no longer studies a sole system but a collection (one ensemble) of several systems, each of them duplicating the one studied. This is the essence of statistical methods.

27.2 Quantum and Classical Mechanics in Statistical Thermodynamics

It is true that, in some definite conditions, the results following from quantum-mechanical arguments tend toward those obtained from classical mechanics ones. This is the case, for instance, when the quantum numbers involved in a process take high numerical values. Thus, in the quantum-mechanical canonical ensemble partition function, the terms corresponding to the higher quantum numbers make more and more important contributions to the sum constituting it as the temperature increases. Owing to the importance of the canonical partition function for our purpose, it is of great interest for us to know the classical canonical partition function.

According to the preceding example, one may prejudge that the quantum-mechanical canonical function must tend toward the classical one.

Hence, one can infer that the quantum-mechanical canonical partition function $[Q(T,V,N)]_{\text{quant}} = \sum_i \exp[-\beta E_i(N,V)]$ (viz. Chap. 23) must go over asymptotically into the corresponding classical function in the limit of large quantum numbers,

$$Q(T,V,N)_{\text{quant}}(\text{large quantum numbers}) \rightarrow Q_{\text{class}} = ?$$

The principal goal of this chapter is to express the function Q_{class}.

According to the very foundations of classical mechanics, the energy of a moving body, for instance, varies continuously. Hence, one may already infer from this observation that Q_{class} is a continuous function of energy instead of Q_{quant} which is a discrete function.

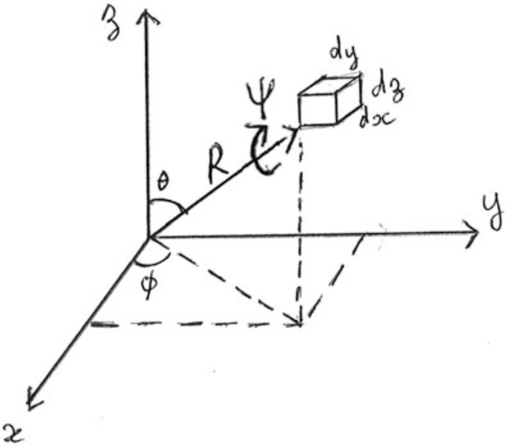

Fig. 27.1 Symbolism used to describe the configuration of a molecule

27.3 Cartesian Coordinates of a Specific Particle in a System

The locations of the centers of the molecules are often denoted in rectangular coordinates x, y, z. It is the same as to locate it at the extremity of the vector $\mathbf{R}$ defined by its components x, y, z. Thus, the center of the molecule i is defined by the vector $\mathbf{R}_i$ (Fig. 27.1).

For simple particles such as hard spheres (which do not actually exist although, however, argon atoms look closely like them), vectors $\mathbf{R}_i$, $\mathbf{R}_j$, ... are sufficient to describe one configuration of the system (constituted by the N particles $i, j\ldots$). This means that, in this case, the sole location of their centers is sufficient to describe the configuration of the system symbolized by $\mathbf{R}^N$. It is symbolically written:

$$\mathbf{R}^N = \mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \ldots \mathbf{R}_N$$

The symbol $\mathbf{R}^N$ means that the location of the centers of *all* the particles constituting the system is known through the knowledge of vectors $\mathbf{R}_{i.}$ They are, of course, defined by the three components x_i, y_i, and z_i.

27.4 Configuration of a System

More generally, the description of the configuration of a molecule may necessitate to know both its location and its orientation $\mathbf{X}_i$. This was not the case of the preceding spherical particles having no internal structure. For a rigid nonspherical molecule i (such as water for example), its orientation, defined by the parameter $\boldsymbol{\Omega}_i$, must also be taken into account. $\boldsymbol{\Omega}_i$ is given by the relation (viz. Fig. 27.1):

$$d\mathbf{\Omega}_i = d\phi_i \sin\theta_i d\theta_i \, d\psi_i$$

The whole configuration of such a molecule is symbolized by $\mathbf{X}_i$. The vector $\mathbf{X}_i$ is related to vectors $\mathbf{R}_i$ and $\mathbf{\Omega}_i$ by:

$$\mathbf{X}_i = \mathbf{R}_i\mathbf{\Omega}_i$$

The configuration of the system is given by the relation:

$$\mathbf{X}^N = \mathbf{X}_1, \mathbf{X}_2, \ldots \mathbf{X}_N$$

and the infinitesimal element of a single molecule i is given by:

$$d\mathbf{X}_i = d\mathbf{R}_i d\mathbf{\Omega}_i$$

Vector $\mathbf{X}_i$ is a six-dimensional $(x_i, y_i, z_i, \phi_i, \theta_i, \psi_i)$ vector (the definitions of these six variables are given in Fig. 27.1). The integration over $\mathbf{\Omega}_i$ takes into account all the orientations of the molecule. It is represented by the expression:

$$\int d\mathbf{\Omega}_i = \int_0^{2\pi} d\phi_i \int_0^{\pi} \sin\theta_i d\theta_i \int_0^{2\pi} d\psi_i$$

that is to say:

$$\int d\mathbf{\Omega}_i = 8\pi^2$$

and

$$\mathbf{X}_i = 8\pi^2\mathbf{R}_i$$

Remark: For nonrigid molecules, a supplementary parameter describing their internal rotations may be needed. This is the case, for example, of n-butane. It is not treated further in this book.

27.5 Spherical Coordinates ϕ, θ, r of a Particle

An infinitesimal element of volume located at the extremity of the vector $\mathbf{R}$ is equally denoted dV, dR or $dx\,dy\,dz$ (viz. Fig. 27.1). The change of the cartesian to the spherical coordinates systems is done by using the expression:

$$d\mathbf{R}_i = dx_i\, dy_i\, dz_i = r^2 \sin\theta\, d\theta\, d\phi\, dr$$

where r is the radius of the studied sphere.

27.6 Classical Analogue of the Quantum-Mechanical Canonical Partition Function

Let E_i be the energy of a molecule i in a system of N simple, "indistinguishable," in mutual interactions but for which it is unnecessary to specify their orientations. It is equal to the sum of its potential and kinetic energies U and E_k.[1] Its potential energy U depends on its proper coordinates x_i, y_i, z_i but also on those of other molecules in mutual interactions with it. These interactions, indeed, depend on the intermolecular distances. The kinetic energy of i depends on the components p_{xi}, p_{yi}, p_{zi} of its momentum **p**. Therefore, one can write:

$$E_i = U(x_i, y_i, z_i) + E_k\left(p_{xi}, p_{yi}, p_{zi}\right) \quad i = 1 \ldots N$$

The whole energy E of the system is equal to the sum of the individual energies E_i.

It is demonstrated that the classical canonical partition function of a N spherical particles system, without an internal structure, is given by the relation (for an approach of it, viz. Appendix F and the supplement one):

$$\begin{aligned} Q(N,T,V) = \left[1/N!h^{3N}\right) \times \int_{-\infty\cdots}^{+\infty} \int \exp\left[-H\left(x_1, y_1, z_1 \ldots x_N y_N z_N;\, p_{x1}, p_{y1}, p_{z1} \cdots p_{xN}\, p_{yN}\, p_{zN}\right)\right] \\ \times /kT \times dx_1, dy_1, dz_1 \ldots dx_N, dy_N, dz_N \ldots dp_{x1}, dp_{y1}, dp_{z1} \ldots dp_{xN}, dp_{yN}, dp_{zN} \end{aligned} \tag{27.1}$$

H is Hamilton's function involved in Lagrange's mechanics. The terms in brackets, $x_1, y_1, z_1 \ldots x_N\, y_N\, z_N;\, p_{x1}, p_{y1}, p_{z1} \ldots p_{xN}\, p_{yN}\, p_{zN}$ are the variables on which depend H. It is sufficient for our purpose to know that Hamilton's function is usually expressed in terms of generalized coordinates q and p, but in the present case, using cartesian coordinates and momenta is equivalent to the use of the generalized ones. h is Planck's constant $\left(h = 6.626 \times 10^{-34}\,\mathrm{J\,s}\right)$ and k Boltzmann's constant $\left(k = 1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}}\right)$. T is the thermodynamic temperature.

For this kind of system, Hamilton's function is nothing more or less than the energy of the system, hence:

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[1] We are continuing to symbolize the potential energy, which is an energy of interaction between molecules, by U. According to IUPAC, U is, usually, the symbol of the internal energy and E_p is the potential energy.

$$H = \sum_i (1/2m)\left(p_{x1}^2 + \cdots p_{zN}^2 + U(x_1, \ldots, z_N)\right. \tag{27.2}$$

m is the molecular mass of each particle. In equation (27.1), all the summations are over the whole coordinates from $-\infty$ to $+\infty$.

The fact that equation (27.1) contains the factor $N!$ must be noticed. Its presence is for the same reason as in the analogous quantum-mechanical partition function. That is to say: particles are "indistinguishable" and the interactions between two of them must not be taken into account several times. Surprisingly, also, equation (27.1) contains Planck's constant h which is a reminiscence of quantum mechanics. It is introduced as an integration constant in the mathematical developments devoted to the classical partition function. Its introduction is necessary since, without it, calculations performed through the classical partition function fail to provide correct values of the entropy and of other thermodynamic quantities of the system.

Relation (27.1) is by no means surprising. We can, indeed, notice the similarity:

$$\sum \mathrm{e}^{-\mathrm{energy}/kT} \Leftrightarrow \int_{\ldots}\int e^{-\mathrm{energy}\,/kT} dx_1 \ldots dz_N$$

Let us recall that the sum Σ goes over all the quantum states. Here, one again finds the pathway between quantum and classical functions and, from a strict mathematical standpoint, the fact that an integral is a sum of infinitely small quantities over an infinitely large number of them. Relation (27.1) is not surprising for a second reason. Quite evidently, $Q(N, T, V)$ is a continuous function. (This point is somewhat detailed in Appendix F).

Equation (27.1) is often written equivalently as:

$$Q(N,T,V) = \left[1/N!h^{3N})\right]\int_{-\infty\cdots}^{+\infty}\int \exp[-H/kT]d\mathbf{R}^N d\mathbf{p}^N \tag{27.3}$$

with:

$$H = H\left(\mathbf{p}^N, \mathbf{R}^N\right)$$

and more precisely:

$$H\left(\mathbf{p}^N, \mathbf{R}^N\right) = \mathrm{U}_N\left(\mathbf{R}^N\right) + \sum_{i=1}^{N}\left(\mathbf{p}_i^2/2m\right) \tag{27.4}$$

where $\mathbf{p}^N$ and $\mathbf{R}^N$ recalls the dependence of Hamilton's function on momenta and on the configuration.

With more complex molecules, the classical canonical partition function is:

$$Q(N,T,V) = \left[q^N/8\pi^2\right)^N \Lambda^{3N} N!)\Big] \int_{-\infty\cdot\cdot}^{+\propto} \int \exp\left[-\beta H\left(\mathbf{X}^N\right)\right] d\mathbf{X}^N d\mathbf{p}^N \tag{27.5}$$

$$H = \sum_{i=1} \left(\mathbf{p}_i^2/2m\right) + U_N\left(\mathbf{X}^N\right)$$

and

$$\beta = 1/kT$$

The symbol $U_N(\mathbf{X}^N)$ means the total potential energy of interaction of the system in the configuration $\mathbf{X}^N$. Note the use of $(\mathbf{X}^N)$ in place of $(\mathbf{R}^N)$ (with respect to the preceding case) in agreement with the working hypothesis.

In the relation (27.5), there exist also some supplementary terms. Let us recall that Λ is the thermal de Broglie wavelength, q is the *molecular* partition function of the species constituting the system. q takes into account the proper partition functions of translation, electronic, of vibration, of rotation, and nuclear of the species (viz. Chap. 26). For example, for most monoatomic gases: $q = 1$. (The product of electronic, nuclear, vibration, and rotation partition functions is called internal partition function.) The factor $8\pi^2$ lying in the denominator is introduced in order not to count the volume twice in the integration. The integration over $d\mathbf{R}$ amounts, indeed, to obtain the volume in a first time and, in a second one, the integration over the three angles also leads to the volume (viz. preceding paragraph):

$$\int d\mathbf{\Omega}_i = 8\pi^2$$

27.7 Condition Required for the Applicability of the Partition Functions (27.1) and (27.3)

Partition functions (27.1) and (27.3) and those deriving from them cannot be used for all kinds of systems. Their handling is legitimate when the following condition is satisfied:

$$\Lambda^3 N/V \ll 1$$

where Λ is the thermal de Broglie wavelength of the particle defined by:

$$\Lambda = h/(2\pi mkT)^{1/2}$$

We see that the condition is satisfied when its density number N/V is small and the mass of the particle and temperature are large. Both conditions are frequently satisfied.

27.8 Some Examples of Handling of Classical Partition Functions: The Case of Perfect Gases

A gas is considered as being perfect when there exist no intermolecular forces between its particles. The mathematical counterpart of this definition is:

$$U_N\left(\mathbf{X}^N\right) = 0$$

whichever the configuration $\mathbf{X}^N$ is.

When the gas is monoatomic and is not endowed with internal structure, the classical partition function reduces to:

$$Q(N, T, V) = \left[1/N!h^{3N})\right]\int_{-\infty\cdots}\int \exp\left[-\beta H\left(\mathbf{p}^N\right)\right] d\mathbf{R}^N d\mathbf{p}^N \qquad (27.6)$$

Since the potential energy does not exist, the expression of $H(\mathbf{p}^N)$ is:

$$H\left(\mathbf{p}^N\right) = \sum_{i=1} 1/2m\left(p_{x1}^2 + \cdots + p_{zN}^2\right)$$

Integrations over $d\mathbf{R}^N$ and $d\mathbf{p}^N$ give:

$$Q(T, V, N) = V^N/\Lambda^{3N}N! \qquad (27.7)$$

since:

- The integration over $d\mathbf{R}^N$ is immediate, because it is carried out on a cube of length unity:

  $$\int d\mathbf{R}_i = \int_0^1 dx_i \int_0^1 dy_i \int_0^1 dz_i$$

  and because there are N particles;
- The integration over the momenta $d\mathbf{p}^N$ is carried out, firstly, by setting up the following equality:

$$h^{-3N}\int_{-\infty\cdots}^{+\infty}\int \exp\left[-\beta\left(\mathbf{p}_i^2/2m\right)\right]d\mathbf{p}^N$$
$$= \left[h^{-1}\int_{-\infty}^{+\infty}\exp\left[-\beta p^2/2m\right]\mathrm{d}p\right]^{3N}$$

The right side of the last equality is justified by the fact that the particles are identical and by the fact that there are $3N$ variables of integration (so that $d\mathbf{p}_i = dp_i^3$ and $d\mathbf{p}_i = d\mathbf{p}_j$). The remaining integral is easily calculated by starting from the standard integral value:

$$\int_0^\infty \exp\left[-ax^2\right]dx = 1/2(\pi/a)^{1/2}$$

It is very interesting to notice that the equality (27.7) is equivalent to the following one:

$$\mu = kT\ln\Lambda^3 + kT\ln N/V \tag{27.8}$$

or:

$$\mu = kT\ln\Lambda^3 + kT\ln\rho$$

(27.8) is obtained from the equality (27.7) and from the general relationship (viz. Chap. 23)

$$\mu = -kT(\partial\ln Q/\partial N)_{T,V}$$

after use of Stirling's approximation. Relation (27.8) is already very interesting. It is sufficient to compare it to the following one (viz. Chap. 6)

$$\mu = \mu^\circ + RT\ln x$$

to be convinced.

- A polyatomic gas may exhibit a perfect behavior, but because it is polyatomic, it does possess an internal structure. Its molecular partition function q is no longer equal to 1 as in the monoatomic case. Of course, since by hypothesis, there exist no mutual interactions between molecules

  $$U\left(\mathbf{X}^N\right) = 0$$

  The knowledge of the whole coordinates $\mathbf{R}^N$ is no longer sufficient to describe the system. The whole ensemble coordinates $\mathbf{X}^N$ must be used. As a result, the canonical partition function is:

$$Q(N,T,V) = \left\{q^N / \left[\left(8\pi^2\right)^N \Lambda^{3N} N!\right]\right\} \int v \ldots \int d\mathbf{X}^N$$

The limits of integration are noticed in the following relation (v means that the integration of **R** is carried out over a cube of length unity) (see before):

$$Q(N,T,V) = \left\{q^N / \left[\left(8\pi^2\right)^N \Lambda^{3N} N!\right]\right\} \left[\int_v d\mathbf{R} \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\psi\right]^N$$

Finally:

$$Q(N,T,V) = q^N V^N / \Lambda^{3N} N!$$

Chapter 28
The Configurational Partition Function: Molecular Distribution Functions

Abstract The chapter introduces the very important notions of configurational partition function and of molecular distribution functions. They are at the basis of the notion of radial distribution function which, in turn, is at the cornerstone of our purpose (which is to get some insight about the significance of an activity). The radial distribution function enters, indeed, in the theoretical expressions of thermodynamic quantities, among which the chemical potential.

The chapter is essentially devoted to definitions. The first given one is that of the configuration integral. Other defined functions are the basic density distribution function, the molecular distribution functions (both the specific and the generic ones), the pair molecular distribution functions, and the pair correlation function with the radial distribution function. The chapter mentions only one theoretical study. It concerns the molecular distribution functions of monoatomic fluids. Some aspects of the theoretical study of the radial distribution function are postponed to the following chapter.

Most of the theoretical considerations mentioned in this chapter are developed within the framework of the canonical ensemble and, only, the case of pure liquids is investigated.

Keywords Configuration integral • Basic distribution function • Average of a quantity • Molecular distribution function • Specific and generic distribution functions • Pair correlation function • Radial distribution functions

This chapter introduces the very important notions of *configurational partition function* and of *molecular distribution functions*. It will be seen later that they are at the basis of the notion of *radial distribution function* which, in turn, is at the cornerstone of our purpose which is to get some insight about the significance of an activity. The radial distribution function enters, indeed, in the theoretical expressions of thermodynamic quantities, among which the chemical potential. The latter is of utmost importance.

The chapter is essentially devoted to definitions. It mentions only one theoretical study. It concerns the molecular distribution functions of monoatomic fluids. Some aspects of the theoretical study of the radial distribution function are postponed to the following chapter.

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28.1 The Configuration Integral Z_N

In order to express the thermodynamic quantities starting from classical mechanics considerations (and also in order to calculate them), the notion of configuration integrals Z_N has been introduced. They are also named *configurational partition functions*.

Their expressions come from those of classical canonical partition functions, such as the following one already encountered:

$$Q(N,T,V) = \left[1/\left(N!\,h^{3N}\right)\right]\int_{-\infty\cdots}\int \exp[-H/kT]d\mathbf{R}^N d\mathbf{p}^N \tag{28.1}$$

where H is the Hamilton's function of the system:

$$H = (1/2m)\left(p_{x1}^2 + \cdots p_{zN}^2\right) + U_N(x_1, \ldots, z_N)$$

It is known (see Chap. 26) that:

$$\begin{aligned}
&\int_{-\infty\cdots}^{+\infty}\int \exp\left[-H/KT\right]d\mathbf{R}^N d\mathbf{p}^N \\
&\quad = \int_{-\infty\cdots}^{+\infty}\int \exp\left[-(1/2m)\left(p_{x1}^2 + \cdots p_{zN}^2\right)/kT\right]dp_1\ldots dp_N \\
&\quad \times \int_{-\infty\cdots}^{+\infty}\int \exp\left[-U_N(x_1,\ldots,z_N)/kT\right]dx_1\ldots dz_N
\end{aligned} \tag{28.2}$$

The first group of multiple integrals of the right side can be immediately evaluated. It is not possible to do that with the second since the analytical function linking U_N to variables $x_1\ldots z_N$ is unknown. The term which virtually results from the evaluation of this second group is named the *configuration integral*.

Hence, the configuration integral is defined by the expression:

$$Z_N = \int_{V\ldots}\int \exp\left[-\beta U\left(\mathbf{R}^N\right)\right]d\mathbf{R}^N \tag{28.3}$$

or with a more explicit symbolism:

$$Z_N = \int_{V\cdots}\int \exp[-\beta U_N(x_1 \ldots z_N)]dx_1 \ldots dz_N \tag{28.4}$$

N is the number of particles of the system and the limit v means that integrations are evaluated over the three space coordinates from $-\infty$ to $+\infty$.

The first point to notice is that Z_N depends on (and even characterizes) a given configuration as it is evidenced by the occurrence of the term $U(\mathbf{R}^N)$ in its expression.

Another important point for our purpose must be already stressed. In connection with the study of the activity of gases (viz. Chap. 34), we shall see that the configuration integral is related to the corresponding canonical partition function Q_N through the equality:

$$Z_N = N!\left(Q_N V^N / Q_1^N\right) \tag{28.5}$$

In (28.5), V is the volume of the system and Q_1 is the canonical partition function of the system when it is constituted by only *one* molecule.

As an example, the expression of the canonical partition function $Q(N, T, V)$ in which the configuration integral for only one molecule (without any internal structure but being in interaction with other molecules of the system) is incorporated is:

$$Q(N,T,V) = \left[1/\left(N!\Lambda^{3N}\right)\right]Z_N$$

Note, also, that according to expressions (28.3) and (28.4), when the interactions between molecules do not exist ($U = 0$):

$$Z_N = V^N$$

[This result may be directly found from the equality (28.7) of the preceding chapter.]

One can already conceive the important part played by the configuration integral in the grasping of the significance of activity. It has, indeed, been already mentioned (viz. Chap. 6) that an activity takes into account the interactions between particles whichever the state of matter where they are is, and it is a well-established fact that these interactions are at the origin of the potential energy U. Let us briefly anticipate what Chap. 33 contains in saying that the potential energy of the system is the energy coming from the mutual interactions between its molecules.

It is not surprising that the evaluation of the configuration integral is endowed with insuperable computational difficulties, given the fact that the function $U(\mathbf{R}^N)$ is unknown, and, even if its evaluation was possible, it would be untractable given the huge number of particles constituting the system.

28.2 Basic Distribution Function

Let us consider the simple case where the studied system is constituted by N monoatomic particles at temperature T and in a container of volume V. The function, which can be called the basic one of all the other molecular distribution functions which are defined below, is the basic density distribution function $P(\mathbf{R}^N)$. It is expressed by the relation:

$$P(\mathbf{R}^N) = \exp[-\beta U_N(\mathbf{R}^N)] \Big/ \int\!\!\underset{\ldots}{}\!\!\int d\mathbf{R}^N \exp[-\beta U_N(\mathbf{R}^N)] \tag{28.6}$$

$U_N(\mathbf{R}^N)$ is the total potential energy of the system with the configuration $\mathbf{R}^N$. Let us recall that the symbolism $\mathbf{R}^N$ means that particle 1 is in $\mathbf{R}_1$, 2 in $\mathbf{R}_2$. . .N in $\mathbf{R}_N$, that is to say in formal writing:

$$\mathbf{R}^N = \mathbf{R}_1\mathbf{R}_2 \ldots \mathbf{R}_N$$

In the expression (28.6), the denominator $\int\!\!\underset{\ldots}{}\!\!\int d\mathbf{R}^N \exp[-\beta U_N(\mathbf{R}^N)]$ is the configurational partition Z_N. Hence, the basic density distribution function can also be expressed by:

$$P(\mathbf{R}^N) = \exp[-\beta U_N(\mathbf{R}^N)]/Z_N \tag{28.7}$$

The meaning of $P(\mathbf{R}^N)$ is the following one: it is the probability density for observing the configuration $\mathbf{R}^N$. It is clear that, behind these considerations and notably behind relation (28.6), there are the notions of continuous random variables and of probability density (viz. Appendix F).

28.3 Average of Any Quantity $F(\mathbf{R}^N)$

In the canonical (T, V, N) ensemble, the average of any quantity $F(\mathbf{R}^N)$ dependent on configuration $\mathbf{R}^N$ is given by the relation:

$$\langle F(\mathbf{R}^N) \rangle = \int\!\!\underset{\ldots}{}\!\!\int d\mathbf{R}^N P(\mathbf{R}^N) F(\mathbf{R}^N) \tag{28.8}$$

Of course, the quantity, the average of which is required, must be dependent on the configuration $\mathbf{R}^N$ of the system.

The expression (28.8) is a generalization of the relation giving the average or the expected value $E(X)$ of the random variable X (viz. Appendix F and just below):

$$E(X) = \sum_{i=1} p_i x_i \quad (1 \leq i \leq N)$$

28.4 Molecular Distribution Functions

Let us define now a series of functions named *molecular distribution functions*.

Before doing that, we give the meaning of the term $P(\mathbf{R}^N)\, d\mathbf{R}_1\, d\mathbf{R}_2 \ldots d\mathbf{R}_N$.

Let us suppose that we are observing the configuration $\mathbf{R}^N$ of the system of N particles, the total potential energy of which is $U_N\,(\mathbf{R}^N)$. Since $P(\mathbf{R}^N)$ is the probability density function of the existence of the configuration $\mathbf{R}^N$, the probability to find particle 1 in the element of volume $d\mathbf{R}_1$ $(dx_1 dy_1 dz_1)$, particle 2 in the element $d\mathbf{R}_2$…particle N in $d\mathbf{R}_N$ is, according to the preceding considerations:

$$P\left(\mathbf{R}^N\right)\, d\mathbf{R}_1 d\mathbf{R}_2 \ldots d\mathbf{R}_{\mathrm{N}} \quad \text{or} \quad P\left(\mathbf{R}^N\right) d\mathbf{R}^N \tag{28.9}$$

which can be explicited according to:

$$P\left(\mathbf{R}^N\right) d\mathbf{R}^N = \left\{ \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right] \Big/ \int_{\cdots} \int d\mathbf{R}^N \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right] \right\} d\mathbf{R}_1 \ldots d\mathbf{R}_N \tag{28.10}$$

or, according to the definition (28.3) of Z_N:

$$P\left(\mathbf{R}^N\right) d\mathbf{R}^N = \left\{ \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right] / Z_N \right\} d\mathbf{R}_1 \ldots d\mathbf{R}_N$$

Hence, the term $P(\boldsymbol{R}^N)\, d\boldsymbol{R}^N$ does have the meaning of a probability while $P(\boldsymbol{R}^N)$ is a probability density.

The term $P(\mathbf{R}^N) d\mathbf{R}^N$ turns out to be the limit of the relation coming from quantum considerations expressing the probability $P_j(N, V, T)$ that the system should be in the state of energy $E_j(N, V)$ (viz. Chap. 23). The pure formal correspondence is:

$$\underbrace{d\mathbf{R}^N \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right]}_{\text{classical mechanics}} \Big/ \int_{\cdots} \int d\mathbf{R}^N \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right]$$

$$\Leftrightarrow \underbrace{\exp\left[-E_j(N, V)/kT\right]}_{\text{quantum mechanics}} \Big/ \sum_j \exp\left[-E_j(N, V)/kT\right]$$

is evident.

Molecular distribution functions are defined according to their order n and according to the fact they are specific or generic.

28.4.1 Specific Distribution Functions

The probability $P^{(n)}(\mathbf{R}_1 \ldots .\mathbf{R}_n) d\mathbf{R}_1 \ldots d\mathbf{R}_n$ that particle 1 could be in $d\mathbf{R}_1$ at $\mathbf{R}_1$, particle 2 in $d\mathbf{R}_2$ at $\mathbf{R}_2$. . ..and particle n $(n < N)$ in $d\mathbf{R}_n$ at $\mathbf{R}_n$, whichever the configurations of the $(N-n)$ remaining molecules are, is the sum of all the probabilities (28.9), once the configurations assignated to the molecules 1 to n have been taken into account, that is to say:

$$P^{(n)}(\mathbf{R}_1 \ldots .\mathbf{R}_n) = \int_V \int \left\{\exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right]/Z_N\right\} d\mathbf{R}_{n+1} \ldots d\mathbf{R}_N \tag{28.11}$$

$P^{(n)}(\mathbf{R}_1 \ldots \mathbf{R}_n)$ is the specific molecular distribution function of the system of order n. It must be noted that the integration is performed over the variables $\mathbf{R}_{n+1} \ldots \mathbf{R}_N$, while the integrand involves all of them, from $\mathbf{R}_1$ to $\mathbf{R}_N$.

28.4.2 Generic Distribution Functions

One defines generic distribution functions $\rho^{(n)}$ of order n such as:

$$\begin{aligned} \rho^{(n)}(\mathbf{R}_1 \ldots \mathbf{R}_n) &= [N!/(N-n)!]P^{(n)}(\mathbf{R}_1 \ldots .\mathbf{R}_n) \\ &\times \rho^{(n)}(\mathbf{R}_1 \ldots \mathbf{R}_n) = [N\,!/(N-n)!] \\ &\times \int_v \int \left\{\exp\left[-\beta U_N\left(\mathbf{R}^N\right)/Z_N\right\} d\mathbf{R}_{\mathrm{n}+1} \ldots d\mathbf{R}_N \end{aligned} \tag{28.12}$$

It must be noted that they are defined in terms of the preceding specific functions. $\rho^{(n)}(\mathbf{R}_1 \ldots \mathbf{R}_n) d\mathbf{R}_1 \ldots d\mathbf{R}_n$ is the probability that a molecule (not necessarily molecule 1) will be found in the element of volume $d\mathbf{R}_1$ at $\mathbf{R}_1$, a second in $d\mathbf{R}_2$ at $\mathbf{R}_2$ . . .and another in $d\mathbf{R}_n$ at $\mathbf{R}_n$ when the configuration of the system of N molecules is observed.. It appears, therefore, that $\rho^{(n)}(\mathbf{R}_1 \ldots \mathbf{R}_n)$ is a probability density.

28.4.3 Examples

The most practical functions are those of orders (28.1) and (28.2) because they are the best known ones from the theoretical standpoint. Among both kinds of molecular distribution functions, those which are the most useful are the generic ones.

- Functions of order (28.1)
  According to the preceding definition of generic function, it is evident that:

$$\rho^{(1)} = NP^{(1)}$$

$\rho^{(1)}$ is not only a probability density but it is also an average particles number. More precisely, $\rho^{(1)}(\mathbf{R}')$ is the average particles number or the average local density of the particles in the element of volume $d\mathbf{R}'$. According to the definition of the specific function $P^{(1)}$, the probability to find the particle 1 in $d\mathbf{R}_1$ is the certitude. As a result:

$$\int_v P^{(1)}(\mathbf{R}')d\mathbf{R}' = 1$$

For the same reason:

$$\int_V \rho^{(1)}(\mathbf{R}')d\mathbf{R}' = N$$

An important property of function $\rho^{(1)}$ is such that, in a homogeneous and isotropic fluid, the local particles density in $\mathbf{R}'\rho^{(1)}(\mathbf{R}')$ is equal to the density ρ ($\rho = N/V$) of the particles in the bulk of the solution. ρ is also named *number of density*. It is clear that ρ is related to the molar concentration, that is to say:

$$\rho^{(1)}(\mathbf{R}') = \rho \tag{28.13}$$

This result was foreseeable given the meaning of the different terms and given, also, the fact that the system is a homogeneous fluid.

- Pair molecular distribution functions
  The specific pair molecular distribution function in the ensemble T, V, N is defined as being the probability density function $P^{(2)}(\mathbf{R}', \mathbf{R}'')$ to find particle 1 in the element of volume $d\mathbf{R}'$ and particle 2 in $d\mathbf{R}''$ ($d\mathbf{R}'$ and $d\mathbf{R}''$ are actually $d\mathbf{R_1}$ and $d\mathbf{R_2}$ or any other pair of elements of volume. It is proved that from the standpoint of the readability, it is interesting to use both kinds of symbols, according to the circumstances). This specific pair distribution function is expressed from the basic probability function $P(\mathbf{R}^N)$—viz. relation (28.9):

$$P^{(2)}\left(\mathbf{R}', \mathbf{R}''\right) = \int_{V\cdots}\int d\mathbf{R}_3 \ldots d\mathbf{R}_N P(\mathbf{R}_N)$$

or

$$P^{(2)}\left(\mathbf{R}', \mathbf{R}''\right) = \int_{V\cdots}\int d\mathbf{R}_3 \ldots d\mathbf{R}_N P\left(\mathbf{R}', \mathbf{R}'', \mathbf{R}_3 \ldots \mathbf{R}_N\right) \tag{28.14}$$

in which the dependence on the variables is clarified. $P^{(2)}(\mathbf{R}', \mathbf{R}'')d\mathbf{R}'d\mathbf{R}''$ is the probability to find particle 1 in $d\mathbf{R}'$ at $\mathbf{R}'$ and particle 2 in $d\mathbf{R}''$ at $\mathbf{R}''$. These considerations apply to any possible pair of particles. The probabilities of the events: particle i in $d\mathbf{R}'$, particle j in $d\mathbf{R}''$… is the same, that is to say $P^{(2)}$ $(\mathbf{R}', \mathbf{R}'')d\mathbf{R}'d\mathbf{R}''$. For example, the integration over $d\mathbf{R}'d\mathbf{R}''$ of $\rho^{(2)}(\mathbf{R}', \mathbf{R}'')$—*see immediately below the meaning of this function*—can be that of $\rho^{(2)}(\mathbf{R_1}, \mathbf{R_2})$ over $d\mathbf{R}_1$ and $d\mathbf{R}_2$ as it can also be that of $\rho^{(2)}(\mathbf{R}_3, \mathbf{R_7})$ over $d\mathbf{R}_3$ and $d\mathbf{R}_7$.

The *generic* pair molecular distribution function $\rho^{(2)}(\mathbf{R}',\mathbf{R}'')$ is defined by the expression:

$$\rho^{(2)}\left(\mathbf{R}',\mathbf{R}''\right) = N(N-1)P^{(2)}\left(\mathbf{R}',\mathbf{R}''\right) \tag{28.15}$$

The term $\rho^{(2)}(\mathbf{R}', \mathbf{R}'')d\mathbf{R}'d\mathbf{R}''$ is the probability to find any one molecule in $d\mathbf{R}'$ at $\mathbf{R}'$ and any other one in $d\mathbf{R}''$ at $\mathbf{R}''$. It can be demonstrated that it is the average number of pairs of particles in elements $d\mathbf{R}'$ and $d\mathbf{R}''$.

28.5 Pair Correlation Function and Radial Distribution Function

This paragraph is an introduction to the notion of radial distribution function which is studied in the next chapter. The radial distribution function is, indeed, a pair correlation function.

It is known that two events are claimed to be independent when the probability of their intersection (in other terms, the probability of the occurrence of the whole event) is equal to the product of their probabilities. The event of interest here is:

$$\text{one particule in } d\mathbf{R}' \text{ and another one in } d\mathbf{R}''$$

Usually, both events are not disjoint. The occurrence of one influences that of the other. For example, if the separation between $\mathbf{R}'$ and $\mathbf{R}''$ is small compared to the diameter of the particles, the occupancy of $d\mathbf{R}'$ greatly influences that of $d\mathbf{R}''$ and inversely.

The problem of the intersection of two events may be tackled as it follows.

Since $\rho^{(2)}(\mathbf{R}', \mathbf{R}'')d\mathbf{R}'d\mathbf{R}''$ is the probability to find a particle in $d\mathbf{R}'$ and another in $d\mathbf{R}''$ while $\rho^{(1)}(\mathbf{R}')d\mathbf{R}'$ is that to find one in the element $d\mathbf{R}'$, the question to know if the following equality is satisfied is open:

$$\rho^{(2)}\left(\mathbf{R}',\mathbf{R}''\right)d\mathbf{R}'d\mathbf{R}'' = \rho^{(1)}(\mathbf{R}')d\mathbf{R}' \cdot \rho^{(1)}\left(\mathbf{R}''\right)d\mathbf{R}''?$$

Intuitively, it may be conceivable that if the separation of the two elements is very large, both events are independent. Hence, it is possible to set up the equality:

$$\rho^{(2)}\left(\mathbf{R}',\mathbf{R}''\right)d\mathbf{R}'d\mathbf{R}'' = \underset{\text{(volume elements very far from each other)}}{\rho^{(1)}(\mathbf{R}')d\mathbf{R}'\cdot\rho^{(1)}\left(\mathbf{R}''\right)d\mathbf{R}''} \tag{28.16}$$

or:

$$\rho^{(2)}\left(\mathbf{R}',\mathbf{R}''\right) = \rho^{(1)}(\mathbf{R}')\rho^{(1)}\left(\mathbf{R}''\right) \tag{28.17}$$

and given what is preceding:

$$\rho^{(2)}\left(\mathbf{R}',\mathbf{R}''\right) = \rho^2 \tag{28.18}$$

This last equality is satisfied when the separation is very large and, moreover, when the fluid is isotropic.

For any finite separation, relations (28.16), (28.17), and (28.18) are no longer satisfied. Relations (28.16) and (28.17) must be replaced by:

$$\rho^{(2)}\left(\mathbf{R}',\mathbf{R}''\right) = \rho^{(1)}(\mathbf{R}')\rho^{(1)}\left(\mathbf{R}''\right)g\left(\mathbf{R}',\mathbf{R}''\right) \tag{28.19}$$

$g(\mathbf{R}',\mathbf{R}'')$ is the pair correlation function. It plays the part of a corrective function. For an isotropic fluid, for any finite distance between volume elements, (28.18) becomes:

$$\rho^{(2)}\left(\mathbf{R}',\mathbf{R}''\right) = \rho^2\, g\left(\mathbf{R}',\mathbf{R}''\right) \tag{28.20}$$

Chapter 29
Radial Distribution Function

Abstract In the chapter, the concept of radial distribution function is introduced. After that, two definitions of it have been recalled. Its physical meaning is given, together with the link relating it to the potential of average force, under the influence of which the studied particle is when it is surrounded by the whole particles of the system. Studies of radial distributions of some simple systems are then recalled. They are the cases of perfect gazes and also that of a gas of a moderate low density. Finally, the general form of a radial distribution function is shown.

The radial distribution function permits the calculation of some thermodynamic quantities of a fluid such as, especially, the chemical potential of its components. Here is its major interest for the purpose of the study of the activities. Hence, it can be easily conceived that the study of liquids at the molecular level with this function should help the understanding of the activity notion. The concept of radial distribution function is very useful because its value can be evaluated either experimentally or theoretically. In the chapter, the study is limited to the case of a sole homogenous and isotropic liquid.

Keywords Radial distribution function (definition) • Physical meaning • Another expression • Ion central curve • Radial distribution functions of some systems

In this chapter, we introduce the concept of radial distribution function. We give its physical meaning and we also mention the link that relates it to the potential of average force under the influence of which is a chosen particle when it is surrounded by the whole particles of the system.

The radial distribution function permits the calculation of some thermodynamic quantities of a fluid such as, especially, the chemical potentials of its components. Here is its major interest for our purpose. Hence, we can conceive that the study of liquids at the molecular level with this function should help the understanding of the activity notion. The concept of radial distribution function is very useful because its value can be evaluated either experimentally or theoretically. In this chapter, we limit ourselves to the study of a sole homogenous and isotropic liquid.

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29.1 Definition of the Radial Distribution Function

In the preceding chapter, we defined the pair correlation function $g(\mathbf{R}', \mathbf{R}'')$ by the following expression:

$$\rho^{(2)}\left(\mathbf{R}', \mathbf{R}''\right) = \rho^{(1)}(\mathbf{R}')\rho^{(1)}\left(\mathbf{R}''\right)g\left(\mathbf{R}', \mathbf{R}''\right) \tag{29.1}$$

where $\rho^{(1)}(\boldsymbol{R}')$ and $\rho^{(1)}(\boldsymbol{R}'')$ are the generic molecular distribution functions of order 1 with respect to the presence of one molecule in the volume element $d\mathbf{R}'$ and to that of another one in the other element $d\mathbf{R}''$. $\rho^{(2)}(\mathbf{R}', \mathbf{R}'')$ is the generic pair distribution function with respect to the simultaneous presence of both particles in the elements $d\mathbf{R}'$ and $d\mathbf{R}''$. This definition applies to the case for which the configurations of the particles of the system depend only on their localization as it is notified by the use of the symbolism $\mathbf{R}'$, $\mathbf{R}''$. Starting from these definitions, one demonstrates that the pair correlation function, in the particular case where the system is constituted by simple and spherical particles, writes, according to the relations (28.14) and (28.15) of the preceding chapter, as follows:

$$\begin{aligned} g\left(\mathbf{R}',\mathbf{R}''\right) = \; & [N(N-2)/\rho^2]\int\ldots\int d\mathbf{R}_3\ldots d\mathbf{R}_N \exp\left[-\beta U_N\left(\mathbf{R}',\mathbf{R}'',\mathbf{R}',\mathbf{R}_3,\ldots\mathbf{R}_N\right)\right] \\ & /\int_{V\ldots}\int d\mathbf{R}_1\ldots d\mathbf{R}_N \exp\left[-\beta U_N\left(\mathbf{R}',\mathbf{R}'',\mathbf{R}_3,\ldots\mathbf{R}_N\right)\right] \end{aligned} \tag{29.2}$$

Let us recall the following equality satisfied by every homogenous and isotropic fluid (viz. Chap. 28).

$$\rho^{(2)}\left(\mathbf{R}', \mathbf{R}''\right) = \rho^2 g\left(\mathbf{R}', \mathbf{R}''\right) \tag{29.3}$$

In this chapter, we are only interested in this kind of fluid. Hence, the function $g(\mathbf{R}', \mathbf{R}'')$ depends only on the scalar distance $R = |\mathbf{R}' - \mathbf{R}''|$. For example, owing to the isotropic character of the medium, $\mathbf{R}'$ may be chosen as origin, that is to say $\mathbf{R}' = \mathbf{0}$. Then, R remains the only variable. As a result, the pair correlation function $g(\mathbf{R}', \mathbf{R}'')$ may be written $g(R)$. $g(R)$ is the *radial distribution function*. Because of the spherical symmetry, implicitly involved by the kind of studied particles, the local density of particles exhibits the same value at every point of a sphere of radius R, the center of which being at $\mathbf{R}'$. Hence, it is judicious to consider an infinitesimal spherical volume element of thickness dR located at the distance R of $\mathbf{R}'$. The average particles number in this volume element is: $\rho g(R) 4\pi R^2 dR$. In the framework of this spherical symmetry and for a homogenous and isotropic fluid, equation (29.2) can be written now:

$$\rho^{(2)}(R) = \rho^2 g(R) \tag{29.4}$$

29.2 Physical Meaning of the Radial Distribution Function

Consider a fluid at temperature T and with number density ρ. Imagine that an observer is stationed on a particular particle in the solution, named central particle, and that he counts the number of particles located at the distance R from him. Since the system is a fluid, the distribution of the particles around the central one is symmetrical and spherical. (Let us recall, indeed, that a fluid is characterized by the homogeneity of its composition in all the directions of space.)

It is clear that the number of particles present in the volume element $d\tau$ located at the distance R from it is not equal to the product $\rho d\tau$ and that it changes with the distance R.

The presence of a particle, indeed, disturbs the distribution of others. The average number of particles located into $d\tau$ takes the value $\rho g(R)d\tau$, because of this influence.

The average number of charged particles observed in the volume $d\tau$ is:

$$\rho g(R)d\tau$$

Hence, $g(R)$ is the factor by which the mean "local density" $\rho g(R)$ at distance R deviates from the bulk density ρ.

$$\rho g(R) \neq \rho$$

29.3 Another Expression of the Radial Distribution Function

The function $g(\mathbf{R}', \mathbf{R}'')$ can be developed according to the following power series:

$$g\left(\mathbf{R}',\mathbf{R}''\right) = \left\{\exp\left[-\beta U\left(\mathbf{R}',\mathbf{R}''\right)\right]\right\}\left[1 + B\left(\mathbf{R}',\mathbf{R}''\right)\rho + C\left(\mathbf{R}',\mathbf{R}''\right)\rho^{2} + \cdots\right] \tag{29.5}$$

In turn, the coefficients $B(\mathbf{R}', \mathbf{R}'')$, $C(\mathbf{R}', \mathbf{R}'')$, etc. can be expressed in terms of Mayer's f-functions $f(\mathbf{R}', \mathbf{R}'')$, where:

$$f(\mathbf{R},\mathbf{R}') = \exp\left[-\beta U\left(\mathbf{R}',\mathbf{R}''\right)\right] - 1$$

For example:

$$B\left(\mathbf{R}',\mathbf{R}''\right) = \int_V f\left(\mathbf{R}',\mathbf{R}''\right)f\left(\mathbf{R}'',\mathbf{R}_3\right)d\mathbf{R}_3$$

These functions will be again encountered, but briefly, later. They are in connection with the virial development and with activity coefficients of gases.

29.4 The Curve *g*(*R*)/*R*

By truncating the development (29.5), the equation of the curve $g(R)/R$ becomes:

$$g(R) = \exp[-U(R)]$$

$g(R)$ is a complicated function of R since $U(R)$ is itself a complicated function of R (viz. Chap. 6). But, it can be already seen that:

$$g(R) \to 0 \quad \text{where} \quad R \to 0$$

This is because the "central" molecule does possess a finite radius and, as a result, other particles cannot approach its center for a distance lower than it. It becomes, then, a kind of "hard sphere."

Yet, we know that:

$$g(R) \to 1 \quad \text{where} \quad R \to \infty$$

as we have already seen it.

The radial distribution function depends on temperature, density number ρ and R. Hence, it is sometimes written $g(R, T, \rho)$.

Figure 29.1 shows a typical radial distribution curve for a liquid.

Figure 29.2 shows the radial distribution curves for liquid and gaseous argon.

It is interesting to notice that the liquid argon curve exhibits secondary peaks that already existed for solid argon. In both cases, they are located at the same distances. That means that the liquid state keeps a certain amount of short-range order which existed in the crystal. For the sake of comparison, gaseous radial distribution curves do not exhibit secondary peaks.

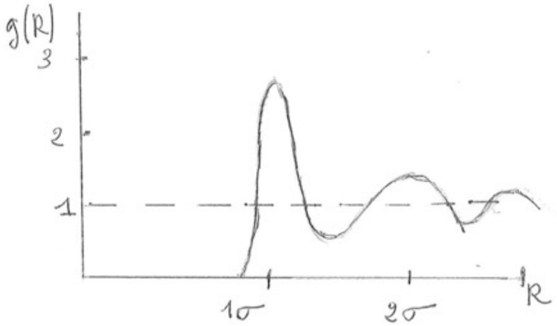

Fig. 29.1 Typical radial distribution function for a liquid. (In the picture, σ is the van der Waals diameter of the order of the few angstroms)

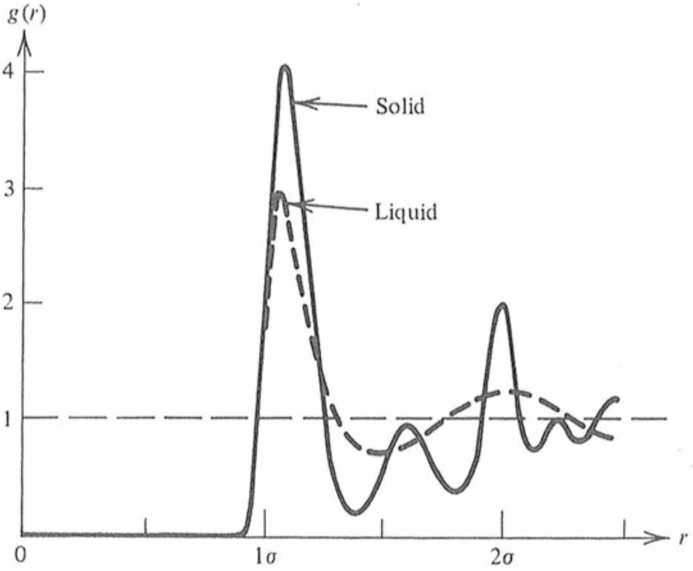

Fig. 29.2 Radial distribution functions for liquid and gaseous argon (σ: atom diameter)

29.5 Radial Distribution Functions of Some Systems

Here, we give the expressions of the radial distribution functions of spherical particles in some simple cases.

29.5.1 *Perfect Gas*

Since the Gas is perfect, the total potential energy is null:

$$U = 0$$

Then, expression (29.2) becomes:

$$g\left(\mathbf{R}', \mathbf{R}''\right) = \left[N(N-1)/\rho^2\right] \int \ldots \int d\mathbf{R}_3 \ldots d\mathbf{R}_N / \int_V \ldots \int d\mathbf{R}_1 \ldots d\mathbf{R}_N$$

and since:

$$\int_V d\mathbf{R}_1 = \int_V d\mathbf{R}_2 = V$$

one obtains:

$$g\left(\mathbf{R}', \mathbf{R}''\right) = N(N-1)/\rho^2 V^2$$

Since $\rho = N/V$

$$g\left(\mathbf{R}', \mathbf{R}''\right) = 1 - 1/N$$

and

$$g(R) = 1 - 1/N$$

29.5.2 Radial Distribution Function of a Gas with a Low Density Number

In this case, the expression of the radial distribution function is obtained as follows. There exist, by definition, some interactions between particles but, since the density number is low, the hypothesis on which the reasoning is based is that only interactions between two particles occur. In other words, the system may be considered as consisting of two particles only. Then, the general relation (29.5) becomes:

$$g(R) = \left(2/\rho^2\right)\exp[-\beta U(R)]/Z_2$$

(since the potential energy of the system is $U(\mathbf{R}', \mathbf{R}'')$, introducing the differentialized $d\mathbf{R}_3 \ldots d\mathbf{R}_N$ is devoid of any meaning). In this expression, Z_2 is the configuration integral when there only exists two particles and $U(R)$ is the potential energy related to a particles pair. Given the fact that $R \to \infty$ when $g(\infty) = 1$ the function becomes:

$$g(R) = 2/\left(\rho^2 Z_2\right) \quad R \to \infty$$

The ratio $g(R)/g(\infty)$ is equal to $\exp[-\beta U(R)]$. Then, setting also up $g(\infty) = 1$, we obtain the relation being searched for:

$$g(R) = \exp[-\beta U(R)]$$

This result must be noticed, since it implies that the distribution of the particles system is of the Boltzmann's type. Let us anticipate what is studied in Chap. 46 by saying that ***Debye and Hückel*** *have adopted this kind of distribution when they have formulated their famous theory.*

Analogous, but more complex, reasoning than the preceding ones may be followed for the cases of more complicated systems than the preceding ones.

29.6 Determination of the Radial Distribution Function

We have already mentioned that the radial distributions can be determined. We confine ourselves in saying that this can be done:

- Experimentally by measurements of X-ray and neutron diffraction of the studied liquid,
- Theoretical calculations,
- By simulations which consist in comparing experimental data to theoretical calculations (viz. Chap. 47).

Chapter 30

Radial Distribution Function and Thermodynamic Quantities: Calculation of the Internal Energy and of the Pressure of the System

Abstract This chapter is devoted to the establishment of mathematical relations between some thermodynamic quantities exhibited by a system and its radial distribution function. The study is limited to establishment of the relations concerning the energy and the pressure of the system. The setting up of the relations between the radial distribution function and the compressibility factor on one hand and with the chemical potential on the other are postponed in the two following chapters. Given the fact that radial distribution functions can be experimentally accessible, the interest of all these relations is evident.

The relations are obtained by putting the "pairwise additivity" hypothesis into practice. The latter is briefly recalled at the beginning of the chapter. Then, the general reasoning carried out in order to obtain the different relations being searched for is described.

The considerations mentioned here are developed with respect to the simple system formed by spherical particles. They can be generalized to more complicated ones at the cost of some modifications of the mathematical relations figuring the configurations.

Keywords Compressibility factor • Internal energy calculation • Pressure calculation • Pairwise additivity hypothesis • State equation of a perfect gas • Radial distribution function (specific or generic)

This chapter is devoted to the establishment of mathematical relations between some thermodynamic quantities exhibited by a system and the radial distribution function. We limit ourself to establish the relations concerning the energy and the pressure of the system. Establishments of the relations between the radial distribution function and the compressibility factor on one hand and the chemical potential on the other are postponed in the two following chapters. We have already mentioned the fact that radial distribution functions can be experimentally accessible, hence, the evident interest of all these relations.

The relations are obtained by putting the "pairwise additivity" hypothesis into practice. The latter is briefly recalled at the beginning of the chapter. Then, the general reasoning carried out, in order to obtain the different relations being searched for, is described.

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The considerations mentioned here are developed with respect to the simple system formed by spherical particles. They can be generalized to more complicated ones at the cost of some modifications of the mathematical relations figuring the configurations.

30.1 The “Pairwise Additivity” Hypothesis

We have already highlighted the fact that the evaluation of the configuration integral creates insuperable difficulties. It is because the potential energy of the system $U(\mathbf{R}^N)$ is present in its expression. As a result, the main points about the subject we presently know come from hypothesis, the most fruitful of them being, probably, that of the “pairwise additivity”.

Let us consider the quantity $F(\mathbf{R}^N)$. The hypothesis amounts to saying that the following equality is satisfied:

$$F\left(\mathbf{R}^N\right) = \sum_{i,j} f\left(\mathbf{R}_i, \mathbf{R}_j\right) \quad (i \neq j) \tag{30.1}$$

the sum being evaluated by considering the whole of the possible pairs of particles. It is calculated such as $1 \leq i < j \leq N$. This hypothesis is, of course, an approximation since the interactions between two particles are not the only ones that exist. For the best, it is only an approximation. Nevertheless, it proved to be very interesting.

30.2 Gaining the Relations Being Searched for: Principle

In the canonical ensemble (T, V, N), the mean value $\langle F \rangle$ of $F(\mathbf{R}^N)$ is given by the relation (viz. Chap. 28)

$$\langle F \rangle = \int \ldots \int d\mathbf{R}^N P\left(\mathbf{R}^N\right) F\left(\mathbf{R}^N\right) \tag{30.2}$$

where $P(\mathbf{R}^N)$ is the probability density to observe the configuration $\mathbf{R}^N$. It is given by the relation:

$$P\left(\mathbf{R}^N\right) = \exp\left[- \beta U_N\left(\mathbf{R}^N\right) / Z_N\right.$$

Substitution of (30.1) into (30.2) gives:

$$\langle F\rangle = \int \dots \int d\mathbf{R}^N P\left(\mathbf{R}^N\right) \sum_{i,j} f\left(\mathbf{R}_i, \mathbf{R}_j\right)$$

All the particles being equivalent, the value of the quantity $f(\mathbf{R}_i, \mathbf{R}_j)$ is the same for each pair. Hence, one can invert the sign sum and the symbol sigma, that is to say, we set up the expression:

$$\langle F\rangle = \sum_{i,j} \int \dots \int d\mathbf{R}^N P\left(\mathbf{R}^N\right) f\left(\mathbf{R}_i, \mathbf{R}_j\right)$$

Each sum in i and j has the same value whichever i and j are. Hence, it is possible to arbitrarily choose a particular pair, for example, the pair $\mathbf{R}_1$, $\mathbf{R}_2$ and since there exist $N(N–1)$ pairs by distinguishing the pairs i –j from the pairs j–i, one can write:

$$\langle F\rangle = N(N-1) \int \dots \int d\mathbf{R}^N P\left(\mathbf{R}^N\right) f(\mathbf{R}_1, \mathbf{R}_2)$$

The multiple integral can be split up remembering that the quantity $f(\mathbf{R}_1, \mathbf{R}_2)$ depends only on coordinates $\mathbf{R}_1$ and $\mathbf{R}_2$ and not on $\mathbf{R}_3 \dots \mathbf{R}_N$. The preceding relation can, hence, be transformed into a product of several integrals:

$$\langle F\rangle = N(N-1) \iint d\mathbf{R}_1 d\mathbf{R}_2 f(\mathbf{R}_1, \mathbf{R}_2) \cdot \left[\int \dots \int d\mathbf{R}_3 \dots d\mathbf{R}_N P\left(\mathbf{R}^N\right)\right]$$

As a result, the integrals can be successively evaluated. Moreover, we already know that (see Chap. 28):

$$N(N-1) \int \dots \int d\mathbf{R}_3 \dots d\mathbf{R}_N P\left(\mathbf{R}^N\right) = \rho^{(2)}(\mathbf{R}_1, \mathbf{R}_2)$$

Hence, we obtain the relation:

$$\langle F\rangle = \iint d\mathrm{R}_1 d\mathrm{R}_2 f(\mathbf{R}_1, \mathbf{R}_2) \rho^{(2)}(\mathbf{R}_1, \mathbf{R}_2) \tag{30.3}$$

If one wants to rid oneself of the arbitrary character of the pair $\mathbf{R}_1$, $\mathbf{R}_2$, relation (30.3) can be written as

$$\langle F\rangle = \iint dR' dR'' f\left(\mathbf{R}', \mathbf{R}''\right) \rho^{(2)}\left(\mathbf{R}', \mathbf{R}''\right) \tag{30.4}$$

A particularly interesting case is that in which the quantity $f(\mathbf{R}', \mathbf{R}'')$ does depend only on $\mathbf{R}'$ together with the separation $R'' - R' = R$ between the two points (R is a scalar). Then, the integration over R leads to a result which is independent on the localization of $\mathbf{R}'$. $\rho^{(2)}(\mathbf{R}', \mathbf{R}'')$ depends only on R. The relation (30.4) can then be modified. In order to perform this transformation, we proceed to the following coordinates change:

$$\overline{\mathbf{R}} = \mathbf{R}' \quad \text{and} \quad R = \mathbf{R}'' - \mathbf{R}'$$

by locating the central particle in $\mathbf{R}'$, whence:

$$\langle F\rangle = \int d\overline{\mathbf{R}} \int d\mathbf{R} f(\mathbf{R})\rho^{(2)}(\mathbf{R})$$

and after integration over $\overline{\mathbf{R}}$

$$\langle F\rangle = V \int d\mathbf{R} f(\mathbf{R})\rho^{(2)}(\mathbf{R})$$

according to relation (30.12) (viz. Chap. 28). Owing to the spherical symmetry and since $\mathbf{R}$ becomes the scalar R, it is more convenient to reason with spherical coordinates (viz. Chap. 27):

$$d\mathbf{R} = dx\, dy\, dz$$
$$d\mathbf{R} = R^2 \sin\theta d\theta\, d\phi\, dR$$

After integration over all the orientations (θ varying from 0 to π and ϕ from 0 to 2π) while R varies from 0 to ∞, we get:

$$\langle F\rangle = V \int_0^\infty f(R)\rho^{(2)}(R) 4\pi R^2 dR \tag{30.5}$$

and, finally, since:

$$\rho^{(2)}(R) = \rho^2 g(R)$$

the definitive relation is:

$$\langle F\rangle = \rho^2 V \int_0^\infty f(R)\, g(R) 4\pi R^2 dR \tag{30.6}$$

Thus, the very fact to know the "additivity function" $f(R)$ together with that of radial distribution $g(R)$ permits the calculation of the average value of ‹F›, at least within the framework of the "pairwise additivity" hypothesis. It is at this point that the pair correlation functions and, hence, the radial distribution one begins to play a part.

30.3 Radial Distribution Function and Internal Energy of a System

The starting points of the reasoning leading to the research for relation are the two following relations. They issue from the general theory of the canonical ensemble (viz. Chaps. 23 and 28).

$$E = kT^2(\partial \ln Q)/\partial T)_{V,N} \tag{30.7}$$

$$Q \; = q^N Z_N / N! \tag{30.8}$$

After adoption of the "pairwise additivity" hypothesis at this point by setting up the equality:

$$U_N\left(\mathbf{R}^N\right) = 1/2 \sum_{ij} U\left(\mathbf{R}_i, \mathbf{R}_j\right) \quad (i \neq j)$$

(The factor 1/2 avoids counting the energy of two pairs two times when the pair *i*–*j* is identical to the pair *j*–*i*), and following a simple mathematical reasoning applied to spherical particles with no rigid structure (whence the symbolism **R**), we obtain (viz. Appendix G):

$$E = (3/2)NkT + \int \ldots \int d\mathbf{R}^N \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right]\left[U_N\left(\mathbf{R}^N\right)\right] / Z_N \tag{30.9}$$

(3/2)*NkT* is the average kinetic energy ‹*K*› of the system. The ratio $\exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right] / Z_N$ is the probability density $P(\mathbf{R}^N)$ to observe the event $\mathbf{R}^N$. As a result:

$$\int \ldots \int d\mathbf{R}^N \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right]\left[U_N\left(\mathbf{R}^N\right)\right] / Z_N \;=\; \int \ldots \int d\mathbf{R}^N \, P\left(\mathbf{R}^N\right)\right]\left[U_N\left(\mathbf{R}^N\right)\right]$$

The term $\int \ldots \int d\mathbf{R}^N \, P\left(\mathbf{R}^N\right)\right]\left[U_N\left(\mathbf{R}^N\right)\right.$ is the average energy of interactions between particles ‹U_N›. The internal energy of the system is given by:

$$E = \; \langle K \rangle \; + \langle U_N \rangle \tag{30.10}$$

we obtain:

$$E = \langle \mathrm{K} \rangle \; + \; 1/2 \iint d\mathbf{R}' d\mathbf{R}'' f\left(\mathbf{R}', \mathbf{R}''\right) \rho^{(2)}\left(\mathbf{R}', \mathbf{R}''\right) \tag{30.11}$$

In the conditions described at the end of paragraph 2, that is to say when the pairs functions *f*(**R**′, **R**″) depend only on *R* (the distance between both particles):

$$E = \langle K \rangle \ + 1/2\rho^2 V \int_0^\infty U(R) g(R) 4\pi R^2 dR \tag{30.12}$$

relation in which:

$$U(R) \ = f\left(\mathbf{R}', \mathbf{R}''\right)$$

It is interesting to somewhat explore the physical meaning of the average potential energy term in the expression (30.12). Let us begin by recalling that it can be also written as:

$$1/2\rho N \int_0^\infty U(R) \ g(R) 4\pi R^2 dR$$

since in the conditions in which it is obtained, $\rho = N/V$. Let us consider a particle and calculate its total interaction with the remainder of the system. Since the local density of particles located at the distance R of the chosen molecule is $\rho g(R)$, the average number of particles in the volume element $4\pi R^2 dR$ is $\rho g(R) 4\pi R^2 dR$. Thus, the average interaction of the particle with the remainder of the system is given by the expression:

$$\int_0^\infty U(R) \rho g(R) 4\pi R^2 dR$$

In order to obtain the total interaction, that is to say that involving the N particles, we must multiply the previous expression by N and also by the factor 1/2 to avoid counting the interaction between two particles, twice.

30.4 Radial Distribution Function and Pressure of the System. Equation of State of a Perfect Gas

Let us recall that in the framework of the canonical ensemble, in quantum mechanics, the pressure is given by the relation (viz. Chap. 23)

$$p = \ kT\left(\partial \ln Q_{\text{quant}}/\partial V\right)_{T,N}$$

In classical mechanics, it is given by:

$$p = kT(\partial \ln Q_{\text{class}}/\partial V)_{T,N}$$

We know (viz. Chap. 28) that:

$$Q_{\text{class}} = Z_N/\left(N!\Lambda^{3N}\right)$$

Finally, since N and T are kept constant during the derivation operation, the pressure is given by the relation:

$$p = \ kT(\partial \ln Z_N/\partial V)_{T,N} \tag{30.13}$$

This is the starting relation of the mathematical calculation.

The followed reasoning followed to obtain the relation being searched for is mentioned in Appendix H. It is:

$$p = kT\rho - \left(\rho^2/6\right)\int_0^\infty R\ (\partial U(R)/\partial R)\ g(R)4\pi R^2 dR \tag{30.14}$$

It can be applied for a system of spherical particles obeying to the "pairwise additivity" hypothesis with respect to the total potential energy. It is interesting to notice that the first term of the right member of this equation is that corresponding to that of a perfect gas. Thus, relation (30.14) may be considered as being an approach to the equation of state of natural gas.

It is very interesting for our purpose. Within the framework of the previous hypothesis, it explicitly exhibits a term which, at least theoretically, permits to evaluate the deflections of behavior with respect to perfect gases. It is a term which must be in mathematical relation with the corresponding activity and activity coefficient. It is the right term of the right member of equation (30.14). It is sufficient to compare the latter to the equation of state of a perfect gas to be convinced.

Chapter 31
The Radial Distribution Function and the Isothermal Compressibility Coefficient of a System

Abstract The setting up of relations between the radial distribution function and some thermodynamic quantities is continued in this chapter. That of interest, here, is the isothermal compressibility coefficient. During the course of the reasoning mentioned in this chapter, a new function is introduced. It is the function G which, in turn, is itself a function of the radial distribution function $\overline{g}(R)$. The name of G is spatial pair correlation function or Kirkwood–Buff's integral. Another relation, which relates the fluctuations of the numbers of molecules to the isothermal compressibility factor, is also set up. All these quantities are linked together. These relations are, actually, the starting theoretical basis of Kirkwood–Buff's theory which is very interesting for the study of activities.

Another very important quantity for our purpose is the chemical potential, given its links with the activity. It can be related to the radial distribution function. Actually, the chemical potential is related to the function G. This point is studied in the next chapter.

All these evoked reasonings are set up in the realm of the grand ensemble. This is the reason why considering the generic molecular distribution function in the grand ensemble is mentioned firstly in the chapter.

Keywords Radial distribution function • Isothermal compressibility coefficient of a system • Spatial pair correlation • Kirkwood–Buff's integral • Kirkwood–Buff's theory • Generic molecular distribution function in the grand ensemble • Compressibility coefficient of a fluid

In this chapter, we are continuing to set up relations between the radial distribution function and some thermodynamic quantities. That of interest, here, is the isothermal compressibility coefficient. During the course of the reasoning mentioned in this chapter, a new function is introduced. It is the function G which, in turn, is itself a function of the radial distribution function $\overline{g}(R)$. Another relation, which relates the fluctuations of the numbers of molecules to the isothermal compressibility factor, is also established. All these quantities are linked together. These relations are, actually, the starting theoretical basis of Kirkwood–Buff's theory (viz. Chap. 42) which is very interesting for our purpose.

Another very important quantity for our purpose is the chemical potential, given its links with the activity (viz. Chap. 5 and the following ones). It can be related to

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the radial distribution function. Actually, the chemical potential is related to the function G. This point is studied in the next chapter.

All these evoked reasonings are set up in the realm of the grand ensemble (T, V, μ, ensemble). This is the reason why we begin them by considering the generic molecular distribution function in the grand ensemble.

31.1 The Generic Molecular Distribution Function in the Grand Ensemble

In the T, V, μ, ensemble, the probability $P(N)$ of finding a system with exactly N particles is (viz. Chap. 24):

$$P(N) = Q(T, V, N)[\exp(\beta\mu N)]/\Xi(T, V, \mu) \tag{31.1}$$

Let us recall that in the grand ensemble, the system number of particles is variable, $Q(T, V, N)$ is the canonical partition function, and $\Xi(T, V, \mu)$ the grand canonical one.

When one of the canonical ensembles constituting the grand ensemble contains exactly N particles, relations (31.1) and (31.2) apply (viz. Chap. 23):

$$P^{(n)}(\mathbf{R}_1, \mathbf{R}_2 \ldots \mathbf{R}_n) = \int v \ldots \int d\mathbf{R}_{n+1} \ldots d\mathbf{R}_N P(\mathbf{R}_1, \mathbf{R}_2 \ldots \mathbf{R}_N) \tag{31.2}$$

$P^{(n)}(\mathbf{R}_1, \mathbf{R}_2 \ldots \mathbf{R}_n) d\mathbf{R}_1 d\mathbf{R}_2 \ldots d\mathbf{R}_n$ is the probability of a well-specified molecule 1 being in $d\mathbf{R}_1$ at $\mathbf{R}_1$, a (well-specified) molecule 2 being in $d\mathbf{R}_2$… a last one n being in $d\mathbf{R}_n$ whichever the configurations of the $N-n$ remaining particles, $P(\mathbf{R}_1, \mathbf{R}_2 \ldots \mathbf{R}_N)$ being the probability density function for observing the configuration $\mathbf{R}^N$.

$\rho^{(n)}$, for its part, is the generic molecular distribution function of order (n) of the configuration $\mathbf{R}^N$. For instance, the term $\rho^{(2)}(\mathbf{R}', \mathbf{R}'') d\mathbf{R}' d\mathbf{R}''$ is the probability of a particle in $d\mathbf{R}'$ and another in $d\mathbf{R}''$. $\rho^{(n)}$ is related to $P^{(n)}$ by the expression:

$$\rho^{(n)} = [N!/(N-n)!]P^{(n)} \tag{31.3}$$

In the grand canonical ensemble, the average generic molecular distribution function $\overline{\rho^{(n)}}\left(\mathbf{R}^N\right)$ is given by the expression:

$$\overline{\rho^{(n)}}\left(\mathbf{R}^N\right) = \sum_N P(N) \rho^{(n)}\left(\mathbf{R}^N/N\right) \quad (N > n)$$

where $P(N)$ is defined by (31.1). *(One must note the used symbolism in this last relation $\rho^{(n)}(\mathbf{R}^N/N)$. It expresses the fact that it is a conditional probability.*

After the development of the expression according to (31.1), one obtains *(in the writing below, the limits of integration are not mentioned in order to lighten it. The integrals are evaluated from 0 to + ∞)*:

$$\begin{aligned}\overline{\rho^{(n)}}\left(\mathbf{R}^N\right) &= (1/\Xi)\Big\{\sum_{\mathrm{N}} [N!/(N-n)!] \\ &\times Q(T,V,N)[\exp(\beta\mu N)] \int\ldots\int d\mathbf{R}_{n+1}\ldots d\mathbf{R}_N \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right]/Z_N\Big\}\end{aligned} \tag{31.4}$$

For each value N, i.e., for each canonical ensemble constituting the grand ensemble, we know that:

$$\rho^{(n)}\left(\mathbf{R}^N\right) = [N!/(N-n)!]\int v\,..\int d\mathbf{R}_{n+1}\ldots d\mathbf{R}_N \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right]/Z_N$$

according to the properties of the canonical ensemble.

Let us integrate the left-hand side member of this equality over the differentials $d\mathbf{R}_1\ldots d\mathbf{R}_n$. We obtain the following result for the canonical ensemble containing N particles:

$$\int v\,..\int \rho^{(n)}(\mathbf{R}^n) d\mathbf{R}_1\ldots d\mathbf{R}_n = [N!/(N-n)!]$$

The result is the same for each of the canonical ensembles involved in the grand ensemble, i.e., for each value N. The explanation of this relation is as follows: the integration from $d\mathbf{R}_1$ up to $d\mathbf{R}_n$ completes that from $d\mathbf{R}_{n+1}$ up to $d\mathbf{R}_N$. As a result:

$$\int v\,..\int d\mathbf{R}_1\ldots d\mathbf{R}_n, d\mathbf{R}_{n+1}\ldots d\mathbf{R}_N \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right]/Z_N = 1$$

Thus, the numerator of the left-hand member is purely and simply equal to Z_N by definition of the latter.

Let us carry out the same operation for each value of N. Integrate the right-hand member of (31.4) over the same differentials and according to the same limits. According to (31.1), we obtain the equality (31.5):

$$\begin{aligned}\int\ldots\int d\mathbf{R}^n \overline{\rho^{(n)}}\left(\mathbf{R}^N\right) &= \sum_N P(N)\,[N!/(N-n)!] \\ \int\ldots\int d\mathbf{R}^n \overline{\rho^{(n)}}\left(\mathbf{R}^N\right) &= \langle N!/(N-n)!\rangle\end{aligned} \tag{31.5}$$

for the generic molecular distribution function in the grand ensemble. Quite evidently, it is an average value.

$\sum_N P(N)[N!/(N-n)!]$ is the average value $\langle N!/(N-n)!\rangle$ of how many ways one particle (not obligatory that labeled 1) is located at $\mathbf{R}_1$, a second at $\mathbf{R}_2$, and so forth up to the particle n at $\mathbf{R}_n$ The average is calculated over all the possible values N.

This relation is of utmost importance. We can, already, say that the Kirkwood–Buff's theory which provides us with a great insight into the meaning of an activity (viz. Chap. 42) is based on it.

As a consequence of relation (31.5), one finds that:

– for $n = 1$,

$$\int d\mathbf{R}_1 \overline{\rho^{(1)}}(\mathbf{R}_1) = \langle N \rangle \tag{31.6}$$

– For $n = 2$:

$$\begin{aligned} \iint d\mathbf{R}_1 d\mathbf{R}_2 \overline{\rho^{(2)}}(\mathbf{R}_1\mathbf{R}_2) &= \langle N(N-1)\rangle \\ \iint d\mathbf{R}_1 d\mathbf{R}_2 \overline{\rho^{(2)}}(\mathbf{R}_1\mathbf{R}_2) &= \left\langle N^2 \right\rangle - \langle N \rangle \end{aligned} \tag{31.7}$$

Finally, starting from (31.6) and by integration, one demonstrates that for a homogeneous and isotropic system:

$$\begin{aligned} \overline{\rho^{(1)}}(\mathbf{R}_1) &= \langle N \rangle / V \\ \overline{\rho^{(1)}}(\mathbf{R}_1) &= \rho \end{aligned} \tag{31.8}$$

(All the terms located between ‹ › are average values). From a different standpoint, one defines the pair correlation function $\overline{g}(\mathbf{R}_1, \mathbf{R}_2)$ for the grand ensemble by the expression:

$$\overline{\rho^{(2)}}(\mathbf{R}_1, \mathbf{R}_2) \;=\; \overline{\rho^{(1)}}(\mathbf{R}_1)\overline{\rho^{(1)}}(\mathbf{R}_1)\overline{g}(\mathbf{R}_1, \mathbf{R}_2) \tag{31.9}$$

31.2 Radial Distribution Function and Isothermal Compressibility Coefficient of the System

The compressibility coefficient of a fluid κ_T is defined by the expression:

$$\kappa_T \;= -(1\,/\,V)\;(\partial V\,/\partial p)_{V,T}$$

where V and T are the volume and the temperature.

The reasoning is carried out according to the theory of the grand ensemble. We have just set up the relations (31.6) and (31.7) above. Starting from them and also from (31.9), it is possible to demonstrate (viz.: the end of this paragraph) that, in the case of spherical particles and when $\overline{g}(\mathbf{R}_1, \mathbf{R}_2)$ only depends on the separation distance $R = |\mathbf{R}' - \mathbf{R}''|$, κ_T is given by the relation:

$$\kappa_{\mathrm{T}} = 1/kT\rho + 1/kT\int_0^{\infty} [\overline{g}(R) - 1]4\pi R^2 dR \tag{31.10}$$

and, after having set up:

$$G = \int_0^{\infty} [\overline{g}(R) \ - 1]4\pi R^2 dR \tag{31.11}$$

$$kT\rho\kappa_T \ = \ 1 \ + \ \rho G \tag{31.12}$$

The name of the G functions (such functions can be of several kinds according to the number of components of the system—viz.: Chap. 42) is the spatial pair correlation function or Kirkwood–Buff's integral. Let us notice that the first term on the right of (31.10) is the compressibility coefficient of a perfect gas. The second one is the contribution brought to the compressibility by the interactions between particles, that are expressed by the radial distribution function $\overline{g}(R)$. It is noteworthy that in the reasoning leading to relation (31.12), in no case, it is a question of a hypothesis concerning the total potential energy of the system ("pairwise additivity hypothesis"). Moreover, the last relation applies whichever the kind of particles is.

The relation (31.10) is obtained as follows. It is set up by starting from the two following relations which are just below, which must be demonstrated:

$$1 + \rho\int_0^{\infty} dR\left[g(R) - 1\right]4\pi R^2 dR = \left(\left\langle N^2\right\rangle \ - \langle N\rangle^2\right) / \langle N\rangle \tag{31.13}$$

$$\left\langle N^2\right\rangle \ - \langle N\rangle^2 \ = kTV\rho^2\kappa_{\mathrm{T}} \tag{31.14}$$

Actually, after injection of (31.14) into (31.13), one obtains (31.10).

- *Obtention of relation (31.13)*
  Let us consider a homogeneous and isotropic fluid, square (31.6) and subtract the latter from (31.7). We obtain:

$$\begin{aligned}&\iint d\mathbf{R}_1 d\mathbf{R}_2\overline{\rho^{(2)}}(\mathbf{R}_1\mathbf{R}_2) \ - \ \int d\mathbf{R}_1\overline{\rho^{(1)}}(\mathbf{R}_1)\int d\mathbf{R}_2\overline{\rho^{(1)}}(\mathbf{R}_2)\\ &= \left\langle N^2\right\rangle - \langle N\rangle^2 - \langle N\rangle\end{aligned}$$

or

$$\iint d\mathbf{R}_1 d\mathbf{R}_2\left[\overline{\rho^{(2)}}(\mathbf{R}_1\mathbf{R}_2) - \ \overline{\rho^{(1)}}(\mathbf{R}_1)\overline{\rho^{(1)}}(\mathbf{R}_2)\right] = \left\langle N^2\right\rangle \ - \langle N\rangle^2 - \langle N\rangle$$

By expressing $\overline{\rho^{(2)}}(\boldsymbol{R}_1\boldsymbol{R}_2)$ from the relation) (31.9), we obtain:

$$\iint d\mathbf{R}_1 d\mathbf{R}_2 \overline{\rho^{(1)}}(\mathbf{R}_1)\overline{\rho^{(1)}}(\mathbf{R}_2)[g(\mathbf{R}_1\mathbf{R}_2)-1] \;=\; \left\langle N^2\right\rangle - \langle N\rangle^2 - \langle N\rangle$$

and according to (31.8):

$$\rho(N/V)\iint d\mathbf{R}_1 d\mathbf{R}_2[g(\mathbf{R}_1\mathbf{R}_2)-1] = \left\langle N^2\right\rangle - \langle N\rangle^2 - \langle N\rangle$$

Since $\overline{g}(\boldsymbol{R}_1,\boldsymbol{R}_2)$ *only depends on the separation distance R (a scalar quantity) such as* $R=/\boldsymbol{R}_1-\boldsymbol{R}_2/$ *(viz.: Chap. 30), we obtain the relation:*

$$\rho(N/V)\int d\mathbf{R}_1\int dR[g(R)-1] = \left\langle N^2\right\rangle - \langle N\rangle^2 - \langle N\rangle$$

$$\rho N\int dR[g(R)-1] = \left\langle N^2\right\rangle - \langle N\rangle^2 - \langle N\rangle$$

Choosing polar coordinates (given the spherical symmetry) gives the following relation:

$$\rho N\int dR[g(R)-1]4\pi R^2 dR = \left\langle N^2\right\rangle - \langle N\rangle^2 - \langle N\rangle$$

or

$$1+\rho\int_0^\infty dR[g(R)-1]4\pi R^2 dR = \left(\left\langle N^2\right\rangle - \langle N\rangle^2\right)/\langle N\rangle \tag{31.13}$$

- *Relation (31.14)*
  In the grand ensemble theory, the fluctuation of the number N of particles for a one-component system is (viz. Appendix I):

$$\left\langle\left(N-\langle N\rangle^2\right)\right\rangle \;=\; \left\langle N^2\right\rangle - \langle N\rangle^2$$

It is given by the expression (viz. Appendix J):

$$\left\langle N^2\right\rangle - \langle N\rangle^2 \;=\; kT(\partial\langle N\rangle/\partial\mu)_{T,V}$$

$$\left\langle N^2\right\rangle - \langle N\rangle^2 = kTV(\partial\rho/\partial\mu)_T$$

The problem is, now, to obtain the partial derivative $(\partial\rho/\partial\mu)_{T.}$ *It is obtained through this other partial derivative* $(\partial P/\partial\mu)_T$*.*

Let us start from Gibbs–Duhem's relation (there is only one component):

$$-SdT + Vd\mathbf{p} \;=\; Nd\mu$$

or

$$(\partial \mathbf{p}/\partial \mu)_T = N/V \quad (dT = 0)$$

$$(\partial \mathbf{p}/\partial \mu)_{\mathrm{T}} = \rho \tag{31.15}$$

$$(\partial \rho/\partial \mu)_T = (\partial \rho/\partial \mathbf{p})_T (\partial \mathbf{p}/\partial \mu)_T \tag{31.16}$$

Finally, in order to accede to $(\partial \rho/\partial \mu)_T$*, it remains to explicit the quantity* $(\partial \rho/\partial \boldsymbol{p})_T$*. This last partial derivative is obtained as follows. Since:*

$$V = N/\rho$$

$$d\rho \;=\; -\left(N/V^2\right)dV \quad (dN = 0)$$

$$(d\rho/\partial p)_T = -\left(N/V^2\right)(\partial V/\partial p)_{T,N}$$

and by taking into account the expression of κ_T*, we obtain the relation being searched for:*

$$\left\langle N^2 \right\rangle - \langle N \rangle^2 = kTV\rho^2\kappa_{\mathrm{T}} \tag{31.14}$$

Chapter 32
The Chemical Potential and the Radial Distribution Function: General Formal Introduction of the Activity and of the Activity Coefficient

Abstract The chemical potential μ plays a central part in the realms of physics, chemistry, and even biochemistry. It is related to the activity a of the species that it characterizes through a mathematical logarithmic relation. The latter can be formally written under only one kind of mathematical expression, whichever the type of activity is considered.

It is a well-known fact that, while relating the chemical potential of a perfect gas to molecular parameters to its number density is not endowed with any problem, it is not the case as soon as there exist interactions between the particles. In this case, the problem becomes, even, immensely complicated to solve exactly. This chapter mentions the setting up of general, but approximate, expressions, of the chemical potential of the components of a system, when such interactions exist. The first one links a decreasing exponential of the studied chemical potential to the difference of two other exponentials involving Helmholtz' energies of the system. It is obtained within the framework of the canonical ensemble. The second relation is obtained from the previous one through the using of the pairwise additivity hypothesis. It is very interesting since it takes the form of the relation expressing the chemical potential of a perfect gas, but does possess a supplementary term. The latter only takes into account the mutual interactions of the particles and, hence, must be related to an activity coefficient. Finally, the chapter also mentions the setting up of theoretical relations between the chemical potential and the radial distribution function.

Keywords Radial distribution function • Activity (general formal introduction) • Activity coefficient • Chemical potential (formal expression when interactions occur) • Helmholtz energy change • Chemical potential (formal expression within the framework of the pairwise additivity hypothesis) • Other general expression of the activity coefficient

The chemical potential μ plays a central part in the realms of physics, chemistry, and even biochemistry. We also know (viz. Chap. 6) that it is related to the activity a of the species that it characterizes through a mathematical logarithmic relation. We also know that the latter can be formally written under only one kind of expression, whichever the type of activity is considered.

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It is a well-known fact that, while relating the chemical potential of a perfect gas to molecular parameters to its number density is not endowed with any problem, it is not the case as soon as there exist interactions between the particles. In this case, the problem becomes, even, immensely complicated. In this chapter, we give a general expression of the chemical potential of the components of a system, when such interactions exist. We also establish theoretical relations between the chemical potential and the radial distribution function. The latter is experimentally accessible.

32.1 General Relations

We know with the aid of statistical theory that, in the framework of the canonical ensemble for instance, the chemical potential μ of a species is given by the relation (viz. Chap. 23):

$$\mu = -kT(\partial \ln Q/\partial N)_{T,V} \tag{32.1}$$

The canonical partition function Q is given by the relation (viz. Chap. 27)

$$Q(N,T,V) = \left[q^N/\left(8\pi^2\right)^N \Lambda^{3N} N!)\right] \int_{-\infty}^{+\propto} .. \int \exp\left[-\beta H\left(\mathbf{X}^N\right)\right] d\mathbf{X}^N d\mathbf{p}^N \tag{32.2}$$

with

$$\beta = 1/kT$$

Hamilton's function H of the system is given by the expression:

$$H = \sum \left(\mathbf{p}_i^2, \mathbf{X}^N\right) + U_N\left(\mathbf{X}^N\right) \quad i = 1 \ldots N$$

The occurrence of the symbol X is the mark that, here, we are considering the case in which the component does possess an internal structure (with the occurrence of the quantity $q \neq 1$). When this is not the case, the canonical partition function is:

$$Q(N,T,V) = \left[1/\left(N!\Lambda^{3N}\right)\right] \int_{-\infty}^{+\propto} .. \int \exp[-H/kT]\, d\mathbf{R}^N d\mathbf{p}^N \tag{32.3}$$

with

$$\begin{gathered} H = H\left(\mathbf{p}^N, \mathbf{R}^N\right) \\ H\left(\mathbf{p}^N, \mathbf{R}^N\right) = \sum \left(\mathbf{p}_i^2/2m\right) + U_N\left(\mathbf{R}^N\right) \quad i = 1 \ldots N \end{gathered} \tag{32.4}$$

32.2 The Case of a Perfect Gas

The gas being perfect, there is by definition the lack of any intermolecular force between the particles, whence in (32.2)::

$$\mathrm{U}_N\left(\mathbf{X}^N\right) = 0$$

Then, (32.2) becomes:

$$Q(N,T,V) = \left[q^N/\left(8\pi^2\right)^N \Lambda^{3\mathrm{N}} N!\right)\Big] \int_{-\infty}^{+\infty} .. \int dX^N$$

or (viz.: Chap. 27):

$$Q(N,T,V) = q^N/\left(8\pi^2\right)^N \Lambda^{3N} N!\Big) \left[\int_v d\mathbf{R} \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta \int_0^{2\pi} d\psi\right]^N$$

that is to say

$$Q(N,T,V) = q^N V^N/\Lambda^{3N} N! \tag{32.5}$$

If the particles are simple and spherical ($q = 1$), the canonical partition function reduces to:

$$Q(N,T,V) = V^N/\Lambda^{3N} N! \tag{32.6}$$

Applying relation (32.1) to (32.5) leads to (32.7) after derivation and use of Stirling's approximation:

$$\mu = kT \ln\left(\Lambda^3 q^{-1}\right) + kT \ln\rho \tag{32.7}$$

where $\rho = N/V$ is the number density (more simpler the density) of the gas (m^{-3}). It is a kind of "concentration" of the gas. Relation (32.7) can also be written:

$$\mu = \mu^{\circ \mathrm{g}}(T) + kT \ln\rho \tag{32.8}$$

$\mu^{\circ \mathrm{g}}(T)$ is, by definition, the standard chemical potential of the particle in the gaseous state. The factor $kT\ln(\Lambda^3 q^{-1})$, quite evidently, takes molecular characteristics of the gas into account.

From the standpoint of the scientific accuracy, it is very satisfying to find the usual expression of the chemical potential of a gas, again. This is an argument in favor of the hypothesis constituting a basis of statistical thermodynamics, even if it is an indirect one.

Let us notice in passing, without considering this point further, that relations (32.7) and (32.8) written as they stand, are not fully satisfactory since, in them, intervene logarithms of dimensional quantities.

(It may seem curious to express the chemical potential of a species in a liquid phase as a function of its standard chemical potential in the gaseous phase. This must not be the case because of the fact the choice of that state is purely arbitrary, as we have already seen that. Moreover, at equilibrium, the chemical potential of the solute is the same in both phases. Hence, the choice of the standard state does not matter, but, then, activity values differ according to it).

32.3 A General Formal Expression of the Chemical Potential When There Exist Interactions Between the Particles of the System

Let us assume that the particles constituting the system are simple. That is to say, their configuration is only defined by the vector **R** (monoatomic particles without internal structure, $q = 1$).

In the N, T, V ensemble, the chemical potential is defined by the relation (viz. Chap. 23)

$$\mu = (\partial A/\partial N)_{T,V} \tag{32.9}$$

where A is the Helmholtz energy. We can also write:

$$\mu = A(T, V, N+1) - A(T, V, N) \tag{32.10}$$

or:

$$\mu/kT = [A(T, V, N+1) - A(T, V, N)]/kT$$

The chemical potential, indeed, is equal to the change in the Helmholtz energy dA when an infinitesimal amount dn mole of the species M is added, at constant temperature and pressure, to the system already containing a finite amount of M itself and of solvent. A "thought" equivalent process is to add 1 molecule M to a very great amount of this solution. This is true because A is an extensive quantity (Fig. 32.1).

Obtaining the general formal expression of the chemical potential when there are interactions between the particles is as follows. According to what is aforementioned, the change in the Helmholtz energy due to the addition of one particle to the system (in very great quantity) must be firstly expressed. Starting from (32.9) and (32.10), we obtain:

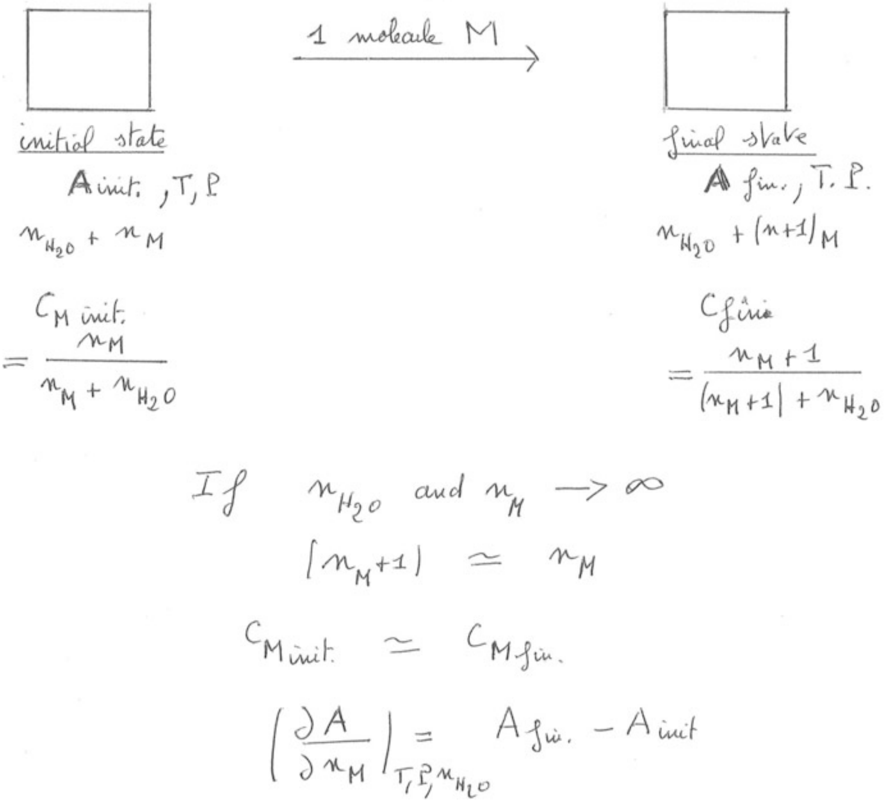

Fig. 32.1 One way to define to define the chemical potential

$$\exp(-\mu/kT) = \exp\{-[A(T,V,N+1) - A(T,V,N)](1/kT)\}$$

Handling the general relation, characteristic of the canonical ensemble (viz. Chap. 23):

$$A(T,V,N) = -kT\ln Q(T,V,N)$$

we obtain, according to relation (32.5):

$$\begin{aligned}\exp(-\mu/kT) = \quad & \left[q^{N+1}/\Lambda^{3(N+1)}(N+1)!\right]\int v\ldots\int \exp(-\beta U_{N+1}) \\ & \times d\mathbf{R}_0\ldots d\mathbf{R}_\mathrm{N}/q^N/\Lambda^{3N}N!\int v\ldots\int \exp(-\beta U_N)d\mathbf{R}_1\ldots d\mathbf{R}_N\end{aligned} \tag{32.11}$$

In the following sentences, the subscript 0 is the label of the added particle.

The general formal expression of the chemical potential when there exist interactions between particles is obtained as it follows. According to what is previously said, we must calculate the Helmholtz energy change when one molecule is added to the system. Starting from relations (32.9) and (32.10), we obtain:

$$\exp\left(-\mu/kT\right) = \exp\{-[A(T,V,N+1) - A(T,V,N)](1/kT)\}$$

This relation expresses the chemical potential of the species in the conditions of the canonical ensemble (N, T, V) for the kind of investigated particle. Quite evidently, it takes into account the total potential energies $\mathrm{U}_N(\mathbf{R}^N)$ and $\mathrm{U}_{N+1}(\mathbf{R}^{N+1})$ for the configurations $\mathbf{R}^N$ and $\mathbf{R}^{N+1}$.

Relation (32.11) is the expression being searched for of the chemical potential. It is general but formal. It turns out to be of great usefulness for the study of the concept of activity coefficient. This study is valid for every fluid.

32.4 A General Expression of the Chemical Potential in the Framework of the "Pairwise Additivity" Hypothesis

Another expression of the chemical potential can be obtained from relation (32.11) by using the "pairwise additivity" hypothesis. It consists in setting up the equality:

$$U_{N+1}(\mathbf{R}_\mathrm{o}\ldots\mathbf{R}_N) = U_N(\mathbf{R}_1\ldots\mathbf{R}_N) + \sum_j U\left(\mathbf{R}_\mathrm{o},\mathbf{R}_j\right) = U_N(\mathbf{R}_1\ldots\mathbf{R}_N) + B(\mathbf{R}_\mathrm{o}\ldots\mathbf{R}_N) \quad j=1\ldots N \tag{32.12}$$

$\mathrm{U}_N(\mathbf{R}_1\ldots\mathbf{R}_N)$ is the sum of potential energies, the origins of which are the interactions between particles 1 to N in configurations $\mathbf{R}_1$ to $\mathbf{R}_N$.

The term $B(\mathbf{R}_\mathrm{o}\ldots\mathbf{R}_N)$ is the sum of all the interactions between particle 0 and others, in the same configurations.

The substitution of (32.12) into (32.11) leads to the expression (32.13):

$$\exp(-\mu/kT) = q/\left[\Lambda^3(N+1)\right] \cdot \int v..\int dR_\mathrm{o}\ldots dR_N \exp(-\beta U_N) \exp\left(-\beta B(\mathbf{R}_\mathrm{O}\ldots\mathbf{R}_N)\right/\int v..\int d\mathbf{R}_1\ldots d\mathbf{R}_N \exp(-\beta U_N) \tag{32.13}$$

where

$$\exp(-\beta U_N)/\int v..\int d\mathbf{R}_1\ldots d\mathbf{R}_N\exp(-\beta U_N) = P(\mathbf{R}_1\ldots\mathbf{R}_N)$$

$P(\mathbf{R}_1\ldots\mathbf{R}_N)$ is the basic distribution function or density probability function to observe the configuration $\mathbf{R}_1\ldots\mathbf{R}_N$ (viz. Chap. 28).

The relation (32.12) can also be written:

$$\exp(-\mu/kT) = q/\left[\Lambda^3(N+1)\right]\cdot\int v\int d\mathbf{R}_\text{o}\ldots d\mathbf{R}_N P(\mathbf{R}_1\ldots\mathbf{R}_N)\exp[-\beta B(\mathbf{R}_\text{O}\ldots\mathbf{R}_N)] \tag{32.14}$$

At this point of the reasoning, we must remark that the term $\exp(-\beta B(\mathbf{R}_0\ldots\mathbf{R}_N)$ which quantifies the interactions between the added particle "0" and the other ones "1 to N" does not depend on the configuration $\mathbf{R}_1\ldots\mathbf{R}_N$ [the probability of which is $P(\mathbf{R}_1\ldots\mathbf{R}_N)$] but is on the dependence of the configuration $\mathbf{R}_\text{O}\ldots\mathbf{R}_N$. However, we can adopt a system of relative coordinates defined by the general expression:

$$\mathbf{R}'_i = \mathbf{R}_i - \mathbf{R}_0 \quad (\text{with } i \text{ from 1 to } N)$$

Then, the term $B(\mathbf{R}_\text{O}\ldots\mathbf{R}_N)$ becomes a function of the relative coordinates $\mathbf{R}_i{}'$, that is to say can be symbolized $B(\mathbf{R}_1{}'\ldots\mathbf{R}_N{}')$. Hence, one can write:

$$\exp(-\mu/kT) = q/\left[\Lambda^3(N+1)\right]\cdot\int d\mathbf{R}_\text{o}\int\ldots\int \mathrm{d}\mathbf{R}'_1\ldots d\mathbf{R}'_N P\left(\mathbf{R}'_1\ldots\mathbf{R}'_N\right)\exp\left[-\beta\left(\mathbf{R}'_1\ldots\mathbf{R}'_N\right)\right] \tag{32.15}$$

Then, after this transformation, one can take out $\mathbf{R}_0$ and integrate over. The integration gives V.

Given the fact that the integrand is the product of the exponential taking into account the sum B (of all the interactions between the added particle and those constituting the initial system) and of the basic distribution $P(\mathbf{R}'_N)$, it appears that the internal energy of the right-member of relation (32.14) is the average of the quantity $\exp[-\beta B(\mathbf{R}'_1\ldots\mathbf{R}'_N)]$ in the (T, V, N) ensemble. Hence, we obtain:

$$\exp(-\mu/kT) = \left[q\,V/\Lambda^3(N+1)\right]\left\langle\exp\left((-B/kT)\right)\right\rangle$$

After the replacement of $(N+1)/V$ by N/V since $N+1\approx N$ and by introduction of:

$$\rho = N/V$$

we obtain:

$$\exp(-\mu/kT) = \left[q/\Lambda^3\rho\right]\langle\exp(-B/kT)\rangle$$

When all is done:

$$\mu = kT\ln\rho\Lambda^3/q - kT\ln\langle\exp(-B/kT)\rangle \qquad (32.16)$$

or

$$\mu = kT\ln\Lambda^3/q + kT\ln\rho \ - kT\ln\langle\exp(-B/kT)\rangle \qquad (32.17)$$

It is interesting to notice that the right member of (32.17) is the chemical potential of every gas, even if the studied fluid here, is a liquid. To be convinced, it is sufficient to consider its "mathematical structure." When the behavior of the fluid is actually ideal, there is no interaction and $B = 0$. Then the relation (32.17) becomes:

$$\mu \ = kT\ln\Lambda^3/q + kT\ln\rho$$

This expression is identical to that giving the chemical potential of a perfect gas.

$$\mu \ = \mu^{0\mathrm{g}} + kT\ln\rho \qquad (32.18)$$

According to (32.17), the chemical potential of a real gas can be expressed by the relation:

$$\mu = \mu^{0\mathrm{g}} + kT\ln\rho \ - kT\ln\langle\exp(-B/kT)\rangle \qquad (32.19)$$

32.5 A General Meaning of the Activity Coefficient

Hence, the last term of the right member (32.19) is the contribution to the value of the chemical potential of the interactions between molecules. B is actually the interaction energy of the added particle with all others at the location $\mathbf{R}_1\ldots\mathbf{R}_N$ of the system.

When we compare the relation (32.18) with the relation (32.19) below:

$$\mu = \mu^{0\mathrm{g}} + kT\ln\rho + kT\ln\gamma \qquad (32.20)$$

where γ is the activity coefficient empirically introduced by Lewis in order to take into account the interactions between the particles, it appears that:

$$\gamma \equiv 1/\langle \exp(-B/kT) \rangle \tag{32.21}$$

Relation (32.19) is very important. It is the basis of the affirmation that activity coefficients take into account the particle interactions in the system. It provides a general expression of an activity a, in terms of statistical thermodynamics:

$$a = \rho/\langle \exp(-B/kT) \rangle$$

Moreover, by itself, relation (32.21) is a general expression of activity coefficients. However, these expressions cannot be considered as anything else than an approach to an activity because they are grounded in an approximation which is the "pairwise additivity" hypothesis.

32.6 The Chemical Potential and the Radial Distribution Function

Here, we mention one relation between the chemical potential and the radial distribution function. (Obtaining it is given in Appendix K). It is:

$$\mu = kT\ln\left(\rho \Lambda^3 q^{-1}\right) + \rho \int_0^1 d\xi \int_0^\infty U(R) g(R,\xi) 4\pi R^2 dR \tag{32.22}$$

It has been set up by Kirkwood. From a general standpoint, it is based on the "pairwise additivity" hypothesis applied to the global potential energy. More precisely, it is founded on the virtual process consisting in coupling a particle with others bit by bit, all along the addition. It involves the presence of the coupling parameter ξ which can vary from 0 up to 1. When $\xi = 0$, the added particle is not coupled to others, but the latter ones are coupled between themselves. When $\xi = 1$, it is fully coupled with others. For the intermediary values, $0 < \xi < 1$, the added particle is only partly coupled with others.

Hence, the term $\rho \int_0^1 d\xi \int_0^\infty U(R) g(R,\xi) 4\pi R^2 dR$ is the work which has to be done in order the interactions of the particle with the others constituting the system to be effective. Let us symbolize the particle by A and the work by $W(A|A)$. The left-hand A figures the particle A which is coupled. The right-hand one figures the kind of particles with which the previous one is coupled. In the occurrence, it is A itself:

$$W\left(A\middle|A\right) = \rho \int_0^1 d\xi \int_0^\infty U(R) g(R,\xi) 4\pi R^2 dR$$

Let us, already, notice that this relation is interesting because it directly leads to another expression of the activity coefficient of a gas. Actually,

$$kT\ln\left(\rho\Lambda^3 q^{-1}\right) = kT\ln\left(\Lambda^3 q^{-1}\right) + kT\ln\rho$$

By definition, the term $kT\ln(\Lambda^3 q^{-1})$ is the standard potential in the gaseous phase:

$$kT\ln\left(\Lambda^3 q^{-1}\right) = \mu^\circ\mathrm{g}$$

Relation (32.21) can also be written:

$$\mu = \mu^{\circ\mathrm{g}} + kT\ln\rho - \rho\int_0^1 d\xi \int_0^\infty U(R\,)g(R,\xi)4\pi R^2 dR$$

By comparison with the classical expression:

$$\mu = \mu^{\circ\mathrm{g}} + kT\ln\rho + kT\ln\gamma^{\mathrm{g}}$$

where γ^{g} is the activity coefficient of the gas.

Hence, the term $\rho\int_0^1 d\xi\int_0^\infty U(R)g\,(R,\xi)4\pi R^2 dR$ is an expression of the activity coefficient.

Relation (32.22) proves to be very interesting for a study of activity coefficients.

32.7 Relation Between the Chemical Potential and the Function *G*

We have already introduced the function G (cf. Chap. 31). It involves the radial distribution function. It is given by the relation:

$$G = \int_0^\infty \left[g\left(\overline{R}\right) - 1\right]4\pi R^2 dR$$

It results from the theory of grand ensemble.

It is also possible to express the chemical potential μ starting from G with the help of the relation which we establish below. It involves the isothermal compressibility coefficient of the system. The expression which links both quantities is:

$$\mu(\rho) = \int kT\left[d\rho/\left(\rho + \rho^2 G\right)\right] + \text{constant} \tag{32.23}$$

Therefore, once the change in G as a function of the density number ρ is known, one can conceive that the chemical potential can be obtained, the fact that G is accessible through $g(R)$ being well understood. Evidently, the relation (32.23) is one integral solution of the expression (32.24):

$$(\partial\mu/\partial\rho)_T = kT/\left(\rho + \rho^2 G\right) \tag{32.24}$$

The way followed to obtain the latter is postponed to the end of this paragraph. Relation (32.23) can also be equivalently written according to (32.25). Hence, the integration can be done from it:

$$\mu(\rho) = kT\int dr\,[1/\rho - G/(1+\rho G)] \quad + \text{ constant} \tag{32.25}$$

During the integration, the following mathematical difficulty happens: when $\rho = 0$, the chemical potential does not exhibit a finite value. The trick used to overcome it is as follows. Let us consider a solution of very low density ρ_0 ($\rho_0 \to 0$). In these conditions, the interactions between molecules are negligible. Then, the chemical potential $\mu(\rho_0)$ is expressed according to a relation which is of the same type as that which is encountered with the perfect gases:

$$\mu(\rho_0) = kT\ln\left(\rho_0 \Lambda^3 q^{-1}\right)$$

$$\mu(\rho_0) = kT\ln\left(\Lambda^3 q^{-1}\right) + kT\ln\rho_0$$

The first term of the right member is nothing else than the chemical standard potential $\mu^{\circ g}$ of the liquid when it is in the gaseous state, as its mathematical structure shows it. As a result,

$$\mu(\rho_0) = \mu^{\circ g} + kT\ln\rho_0$$

Hence, one can integrate from the lower limit ρ_0 (and not from 0) up the limit ρ, given the expression:

$$kT\int_0^{\rho} d\rho'[1/\rho' - G/(1+\rho' G)] = \mu^{\circ g} + kT\ln\rho_0 + \; kT\int \rho_0^{\rho}[1/\rho' - G/(1+\;\rho' G)]d\rho'$$

whence:

$$\mu(\rho) = \mu^{\circ g} + kT\ln\rho - kT\int_0^{\rho}[G/(1+\rho' G)]d\rho' \tag{32.26}$$

A relation between the function G and the activity coefficient must now be found.

Evidently, it can be done through the integration of the latter expression. According to what is preceding, we know that:

$$kT\ln\langle\exp(-B/kT)\rangle \;=\; kT\int_o^{\rho}[G/(1+\rho' G)]d\rho'$$

Hence, we can deduce that the work of coupling of a molecule with all the others is equal to the necessary work to increase the system density from 0 up to the final one ρ. Hence, the relation (32.26) permits to find another expression of the activity coefficients, which is:

$$\ln\gamma = -\int_o^{\rho}[G/(1+\rho' G)]d\rho' \tag{32.27}$$

As a result, thanks to this expression, it is possible to link the activity coefficient to the radial distribution function $g(R)$ through the function G.

The relation (32.26) will be generalized to systems consisting in fluid mixtures. This possibility is demonstrated by the Kirkwood–Buff's theory (viz. Chaps. 42 and 44).

- *Obtention de la relation (32.24)*

The demonstration is given in Chap. 31. Let us only recall that it involves the isothermal compressibility coefficient k_T and that it involves the following equalities already demonstrated:

$$(\partial\rho/\partial\mu)_T = (\partial\rho/\partial p)_T(\partial p/\partial\mu)_T$$

$$(\partial\rho/\partial p)_T \;=\; \rho\kappa_T$$

$$(\partial p/\partial\mu)_T \;=\; \rho$$

$$(\partial\mu/\partial p)_T \;= 1/\,\rho^2\kappa_T$$

$$kT\rho\kappa_T \;=\; 1+\rho G$$

Chapter 33
Virial Coefficients in Terms of Interaction Potential Energies: Mayer's Theory

Abstract It is proved that the experimental coefficients of the virial expansion are related to some parameters coming from the theory of statistical thermodynamics. This is a very important point since it permits to link theoretical results (coming from statistical thermodynamics) with experimental ones. Above all, it permits to attribute a physical origin to each virial coefficient, that is to say to attribute interactions between well-known numbers of particles to every coefficient of the virial expansion. The theory, mentioned in this chapter, leads to mathematical expressions relating parameters stemming from the statistical theory to purely thermodynamic quantities and inversely. The demonstration is done within the framework of the great ensemble. It is based on some series developments. Intervene in it some parameters such the absolute activity λ of the compound, canonical partition functions, configuration integrals, and also, of course, the virial coefficients $B(n)$. The expression of the latter involve an integral, which is also introduced from another starting viewpoint, i.e., within the framework of the Kirkwood–Buff's theory, which has a different nature than that studied in this chapter and which will be considered later.

Keywords Virial coefficient • Mayer's theory • Absolute activity • Kirkwood–Buff's theory • Perfect and imperfect gases (in terms of canonical partition function) • Virial expansion • Virial coefficients and statistical parameters • Grand canonical ensemble • Physical significance of the virial coefficients in statistical mechanics (monoatomic gas)

It is proved that the experimental coefficients of the virial expansion are related to some parameters coming from the theory of statistical thermodynamics. This is a very important point since it permits to link theoretical results with experimental ones. Above all, it permits to attribute a physical origin to each virial coefficient, that is to say to attribute interactions between well-known numbers of particles to every coefficient of the virial expansion. The theory, given just below, leads to interesting mathematical expressions relating parameters stemming from the statistical theory to purely thermodynamic quantities and inversely. One of them involves an integral, which is also introduced from another starting viewpoint, i.e., within the framework of the Kirkwood–Buff's theory, which has a different nature from that studied in this chapter. It will be considered later.

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33.1 Difference Between Perfect and Imperfect Gases

Let us recall that, according to considerations of classical mechanics, the canonical partition function of a system consisting in only one component but possessing an internal structure is given by the expression (relation (33.5)—Chap. 27):

$$Q(N,T,V) = \left[q^N/\left(8\pi^2\right)^N \Lambda^{3N} N!\right)\Big] \int_{-\infty}^{+\infty} .. \int \exp\left[-\beta H\left(\mathbf{X}^N\right)\right] d\mathbf{X}^N d\mathbf{p}^N \quad \text{(relation (5)—Chap. 27)}$$

$$H = \sum_{i=1}^{N} \left(\mathbf{p}_i{}^2/2m\right) + U_N\left(\mathbf{X}^N\right)$$

with:

$$\beta = 1/kT$$

This general expression applies to every system consisting in an imperfect gas. We know that the term $\mathrm{U}_N(\mathbf{X}^N)$ is the total potential energy due to interactions between the molecules of the gas in the configuration $\mathbf{X}^N$.

The fact that a gas is perfect is a consequence of the absence of intermolecular forces between its molecules. This results in the equality:

$$\mathrm{U}_N\left(\mathbf{X}^N\right) = 0$$

in the expression of the canonical partition function, whatever the configuration $\mathbf{X}^N$ is.

33.2 The Virial Expansion

Let us also recall that for a sufficiently dilute gas so that it exhibits a perfect behavior, the state equation (which is a universal law) is written as follows:

$$p = \rho/kT$$

where ρ is the density number of the gas ($\rho = N/V$, N being the number of moles of the gas, V the container volume), k the Boltzmann's constant, and T the temperature of the system. For a greater density, the gas is no longer perfect. Its state equation is given by the virial expression:

$$p/kT = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \cdots \tag{33.1}$$

The coefficients $B_n(T)$ are called virial coefficients. As a general rule, they differ with each gas and their values depend on the intermolecular forces. The series (33.1) is convergent up to a given value ρ when the temperature is lower than the critical temperature. When the temperature is higher, the series is convergent for every density number ρ.

Expression (33.1) can be also written:

$$p/\rho kT = 1 + B_2(T)\rho + B_3(T)\rho^2 + \cdots \tag{33.2}$$

Let us remark, in passing, that when the gas is sufficiently dilute, the virial expression reduces to the state equation of perfect gases.

Expanding in series the function $p/\rho kT$ as a function of ρ according to Taylor's development leads to the expression:

$$p/\rho kT = 1 + [\partial(p/\rho kT)/\partial\rho]_{T,\rho=0}\rho + 1/2!\left[\partial^2(p/\rho kT)/\partial\rho^2\right]_{T,\rho=0}\rho^2 + \cdots \tag{33.3}$$

The comparison of Equations (33.2) and (33.3) leads to the identities:

$$B_n(T) = [1/(n-1)!]\left[\partial^{n-1}(p/\rho kT)/\partial\rho^{n-1}\right]_{T,\rho=0} \tag{33.4}$$

The virial coefficients are obtained from the slopes of the experimental curves. For example, for the coefficient $B_2(T)$, the slope of the curve $(\beta\mathbf{p} - \rho)/\rho$ with respect to ρ permits to obtain the coefficient when ρ tends toward 0. The reasoning stems evidently from the relation:

$$\beta\mathbf{p} = \rho + B_2(T)\rho^2$$

Remark: Let us also notice that the virial expansion is also written in the literature under the form:

$$\mathbf{p}V = RT\left(1 + B/V_\mathrm{m} + C/{V_\mathrm{m}}^2 + \cdots\right)$$

where $B, C \ldots$ are constants depending on temperature and on the nature of the gas. V_m is the molar volume of the gas. It is also written under other forms close to the previous ones.

33.3 Virial Coefficients and Parameters Coming from Statistical Thermodynamics

We shall show that the virial coefficients $B_n(T)$, experimentally accessible, are related to statistical parameters, especially to canonical partition functions.

The demonstration is performed in several steps which are:

- The establishment of a relation between λ and $\overline{\rho}$, respectively, the absolute activity and the average density number of the particle. The average is calculated over the canonical partition functions which constitute the corresponding grand canonical partition function
- The comparison of the classical expression of the virial and the relation between λ and $\overline{\rho}$

Let us consider a gas, mono or polyatomic but constituted by only one component. It is simpler to reason in this case with the partition function of the great ensemble Ξ (viz.: Chap. 24).

33.3.1 Setting Up the Relation Between λ and $\overline{\rho}$

This relation is:

$$\overline{\rho} = (Q_1/V)\lambda + \left[2\left(Q_2 - 1/2Q1^2\right)/V\right]\lambda^2 + \cdots \tag{33.5}$$

The Q_N are the canonical partition functions. Relation (33.5) is itself set up by starting from two other relations which must be demonstrated:

- The first one is the relation (33.6) relating the average density number $\overline{\rho}$ to the absolute activity λ. No canonical partition functions still intervene in this relation:

$$\rho = \lambda(\partial \mathbf{p}/kT)/\partial\lambda \tag{33.6}$$

- The second one is the following relation (33.7):

$$\mathbf{p}V/kT = \ln\left[1 + \sum_{N\geq 1} Q_N(V,T)\lambda^N\right] \tag{33.7}$$

Both relations stem from properties of the grand canonical ensemble. They are based on the definition of the absolute activity of a species $\left(\lambda = \mathrm{e}^{\mu/kT}\right)$ and on its characteristic function $(pV = kT\ln\Xi)$—viz. Chap. 24 and Appendix V.

1. Setting up of the relation (33.6)
   The mean density ρ is defined by the expression:

$$\overline{\rho} = \overline{N}/V$$

In the grand ensemble theory (viz. Chap. 24), the average number of molecules is given by the relation:

$$\overline{N} = kT(\partial \ln \Xi / \partial \mu) v, T$$

Let us express $\overline{N}$. We know that:

$$\ln \Xi = \mathbf{p} V / kT$$

whence:

$$\overline{\rho} = kT[\partial(\mathbf{p}V/kT)/\partial\mu]_{v,T}(1/v)$$

and:

$$\overline{\rho} = (\partial \mathbf{p}/\partial\mu)_{v,T}$$

From another side:

$$\begin{aligned} \ln\lambda &= \mu/kT \\ d\ln\lambda &= (1/kT)d\mu \\ d\mu &= kT\, d\ln\lambda \\ \overline{\rho} &= \partial(\mathbf{p}/kT)/\partial\ln\lambda \\ \overline{\rho} &= \lambda\partial(\mathbf{p}/kT)/\partial\lambda \end{aligned} \tag{33.6}$$

2. Setting up the relation (33.7)
   The starting relation is:

$$\Xi(\lambda, V, T) = e^{pV/kT} \tag{33.8}$$

We also know that (viz.: Chap. 24):

$$\Xi(\lambda, V, T) = 1 + \sum_{N \geq 1} Q_N(V, T)\lambda^N \tag{33.9}$$

where we used the symbolism:

$$Q_N(V, T) = Q(N, V, T)$$

$Q_N(V, T)$ is the canonical partition function relative to the number of particles N. (This function enters into the grand canonical partition function—viz. Chap. 24). Equation (33.9) is the series expansion of Ξ as a function of λ. It is interesting to notice in passing that:

$$Q_o = 1$$

When $N = 0$, the empty system does possess only one state, that of null energy, whence the value $Q_o = 1$.

From (33.8) and (33.9), one immediately obtains (33.7).

3. Obtaining of the relation (33.5)

   Let us expand in series the right member of relation (33.7) and limit it to its first terms, according to the relation:

$$\ln(1 + x) = x - x^2/2 + \cdots$$

We obtain:

$$\mathbf{p}V/kT = Q_1\lambda + \left[\left(Q_2 - 1/2Q_1{}^2\right)/V\right]\lambda^2 + \cdots \tag{33.10}$$

We can relate ρ to the canonical functions Q_1, Q_2 by using relations (33.6) and (33.10). In order to do that, we derive expression (33.10) term by term with regard to λ, divide by V and multiply by λ. We obtain:

$$\overline{\rho} = (Q_1/\mathbf{V})\lambda + \left[2\left(Q_2 - 1/2Q_1{}^2\right)/V\right]\lambda^2 + \cdots \tag{33.5}$$

33.3.2 Expressions of the Virial Parameters $\mathbf{B_n(T)}$ Containing the Canonical Partition Functions

As it has been already said, we operate by comparison.

We begin by expressing λ as a function of $\overline{\rho}$ through a relation involving the partition functions Q_1, Q_2, etc. Hence, we set up as a rule:

$$\lambda = a_o + a_1\overline{\rho} + a_2\overline{\rho}^2 + \cdots$$

and we determine a_o, a_1, a_2, etc. by replacing λ by this expression into (33.8) and by identifying. Once all the calculations have been done, we obtain:

$$a_o \equiv 0, \quad a_1 \equiv V/Q_1, \quad a_2 \equiv -2\left(Q_2 - 1/2Q_1{}^2\right)V^2/Q_1{}^3, \ldots$$

and as a result:

$$\mathbf{p}/kT = \overline{\rho} - \left(V/Q_1{}^2\right)\left(Q_2 - 1/2Q_1{}^2\right)\overline{\rho}^2 + \cdots \tag{33.11}$$

The comparison of (33.11) and (33.1) permits, for example, to find the coefficient of order two of the virial. It is:

$$B_2(T) = -a_2/2$$

that is to say:

$$B_2(T) = -\left(V/{Q_1}^2\right)\left(Q_2 - 1/2{Q_1}^2\right)$$

The terms of higher orders are obtained likewise. The parameter $B_2(T)$ taken as an example is very important. It is the most useful virial coefficient (viz. just below).

Hence, we can express the virial coefficients as being a function of different canonical partition functions Q_N playing a part in the description of the system through the use of the grand ensemble.

33.4 Physical Significance of the Virial Coefficients of a Monoatomic Gas in Statistical Mechanics

It is interesting to explicit the virial coefficients in terms of potential energies of molecular interactions. The study of a particular case, that is to say, that of a monoatomic gas, the intermolecular potential energy of which obeying the pairwise-additivity hypothesis, permits to do it.

In this chapter, we confine ourselves to only giving the mathematical expression relating the configuration integrals Z_1, Z_2 and the virial coefficient $B_2(T)$ and also, the corresponding expression of the coefficient $B_3(T)$, though it is, by far, less interesting than the previous ones.

Let us recall firstly that the configuration integrals Z_N are given by the expressions (viz. Chap. 28):

$$Z_N = \int_V \mathrm{e}^{-UN(x1\ldots zN)} dx_1 \ldots dz_N$$

(We have already seen and we shall again see in the next chapter that they are related to canonical partition functions Q_1, Q_N by the expressions:

$$Z_N(V,T)/N! = Q_N(V,T)V^N/Q_1(V,T)^N$$

One demonstrates that the relation between $B_2(T)$ and the configuration integrals Z_1 and Z_2 is the following one (viz. Chap. 34):

$$B_2(T) = -(1/2V)\left(Z_2 - {Z_1}^2\right)$$

Equivalently, it can be written as follows:

$$B_2(T) = -(1/2V)\left[\int_V\int \exp[-U(\mathbf{r}_1, \mathbf{r}_2)/kT] d\mathbf{r}_1 d\mathbf{r}_2 - V^2\right]$$

where $U(\mathbf{r}_1, \mathbf{r}_2)$ is the intermolecular potential energy between particles 1 and 2 of the system. It depends on their coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ ($x_1 \ldots z_2$). It can also be written:

$$B_2(T) = -(1/2)\int_0^\infty \exp[-U(r)kT - 1]4\pi r^2 dr \tag{33.12}$$

This expression is often given in literature under the form:

$$B_2(T) = -(1/2)\int_0^\infty f(r_{12})4\pi {r_{12}}^2\, dr$$

$f(r_{12})$ is called the Mayer's *f*-function. Generally, Mayer's *f*-functions are defined by the expression:

$$f\left(\mathbf{X}_i, \mathbf{X}_j\right) = \exp\left[-\beta U\left(\mathbf{X}_i, \mathbf{X}_j\right)\right] - 1$$

or

$$f\left(\mathbf{X}_i, \mathbf{X}_j\right) = x_{i,j} - 1$$

It appears the function G in the integrand of relation (33.12). It has been already defined within the framework of the great ensemble (viz.: Chap. 31):

$$G = \int_0^\infty \left[\overline{g}(R) - 1\right]4\pi R^2 dR$$

In the latter expression, R is a scalar and, hence, no longer a vector as were $\mathbf{r}_1$ and $\mathbf{r}_2$. R is the distance between the particles 1 and 2 (viz.: Chap. 42).

Owing to the importance of integrals G (viz.: Chap. 42 devoted to Kirkwood–Buff theory), it is interesting to represent the curve $[\overline{g}(R) - 1]$ as a function of R and more precisely its relationship with the electrostatic on which it is dependent through the function $g(R)$ (Fig. 33.1).

We notice that $f(R)$ tends towards 0 when R tends toward ∞.

Supposing that the pairwise-additivity hypothesis is validated, the configuration integral Z_3 can be written:

$$Z_3 = \iiint\limits_V \exp\{-[U(\mathbf{r}_1, \mathbf{r}_2) + U(\mathbf{r}_1, \mathbf{r}_3) + U(\mathbf{r}_2, \mathbf{r}_3)]\}\, d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3$$

and $B_3(T)$ is given by the expression:

$$B_3(T) = -(1/3V)\iiint\limits_V (x_{12} - 1)(x_{13} - 1)(x_{23} - 1)d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3$$

Hence, we notice that statistical thermodynamics provide explicit expressions of the virial coefficients B_k *in terms of molecular interactions energies which occur in a group of k particles. This is one of the most fundamental results it leads to.*

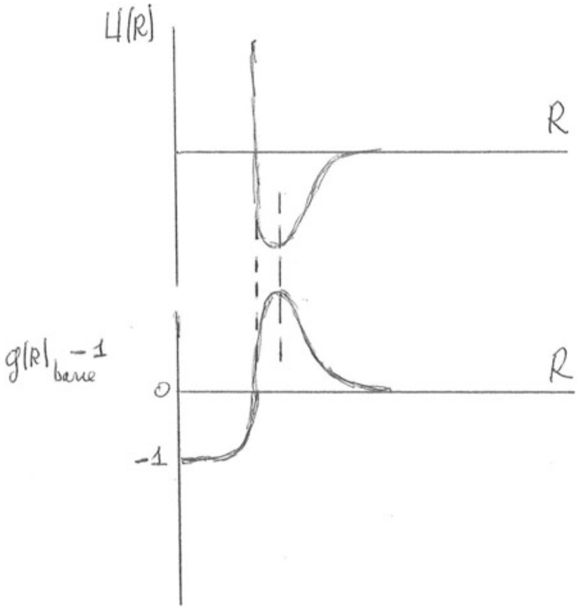

Fig. 33.1 Comparison between electrostatic potential $U(R)$ and function $f(R) = [\overline{g}(R) - 1]$ curves

One can say that, because of the handling of the varied canonical functions Q_N*, this theory amounts implicitly to considering the studied particle as being located in the average electrostatic field developed by all the remaining particles of the system, whereas the Kirkwood–Buff theory does only consider pairs interactions* (cf. Chap. 42).

We shall see (viz. Chaps. 39 and 40) that this is also true for some cases of solutions. More precisely, the virial coefficients make due allowance for the fact that, according to their order, they result from successive corrections (with respect to the ideal behavior of gases) taking into account the interactions between pairs, triplets, quadruplets of particles, and so forth. One result, among the most remarkable ones, is that the coefficient B_k depends on the properties of the system exactly containing k particles. For example, the coefficient B_2 can be calculated for a system containing two particles.

Chapter 34
A Statistical Expression of the Activity of a Species: A Relation Between It and the Corresponding Concentration in the Case of an Imperfect Gas

Abstract This chapter brings some elements of answer to one of the most significant questions regarding the notion of activity, i.e., how are, mathematically related to each other, the value of an activity and that of the corresponding "concentration" of a species when the latter, no longer, tends toward zero? Recall, indeed, that G.N. Lewis, when he introduced it, defined the notion of activity by the following sentence:

> a quantity which is "an active density number which bears the same relation to the chemical potential μ at any density that N/V does as $N \rightarrow 0$."

The results mentioned in this chapter constitute a first mark of the fact that statistical thermodynamics permits, at least in part, to answer the question. The content of this chapter shows that the setting up of the expression relating the activity of a gas to its corresponding concentration stems from a reasoning which, at the onset, requires the definition of the activity in terms of statistical parameters. It also shows that the obtained relation involves terms which are related to the virial coefficients. According to the theory, an activity z of a compound can be identified to the product of its absolute activity λ and of the second canonical function of the grand ensemble $Q_1(N, V, T)$ (that is to say that corresponding to the presence of only one particle in the system), product divided by the volume V of the system. The relation also shows that z exhibits all the properties of Lewis' activity. It has the form of a series development of z in density ρ, the coefficients of which can be, in principle, calculated from the experimental values of the virial relation.

Keywords Statistical expression of the activity of a species • Activity–concentration relation of an imperfect gas • Lewis' definition of an activity • Statistical analogue of the activity • Configuration integral • Activity and concentration relation • Grand ensemble • Series development • Density number • Activity and virial coefficient relation • Fugacity in statistical thermodynamics • Virial coefficients and configuration integrals

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> a quantity which is "an active density number which bears the same relation to the chemical potential μ at any density that N/V does as $N \rightarrow 0$."

The results mentioned in this chapter constitute a first mark of the fact that statistical thermodynamics permits, at least in part, to answer the question.

We shall see that the obtaining of the expression relating the activity of a gas to its corresponding concentration stems from a reasoning which, at the onset, requires the definition of the activity in terms of statistical parameters. We shall also see that the obtained relation involve terms which are related to the virial coefficients which can be experimentally obtained.

34.1 The Followed Reasoning

Let us recall the fact that the handling of the activity coefficient (and of that of fugacity) finds all its interest when there are interactions between the particles constituting the system. We know indeed (viz. Chap. 32) that, that in the framework of the "pairwise additivity" hypothesis, the expression of the chemical potential of the component is:

$$\mu = \mu^{0\mathrm{g}} + kT\ln\rho - kT\ln\langle\exp(-B/kT)\rangle$$

It contains the term $-kT\ln\langle\exp(-B/kT)\rangle$ which takes into account the interactions between the particles.

The reasoning followed in order to obtain the relation being searched for consists in:

- In a first step, arbitrarily defining a parameter z which exhibits the behavior of the activity as it has been introduced by Lewis, i.e., that $z \rightarrow \rho$ when $\rho \rightarrow 0$. We can call this quantity *the statistical analog* of the activity, symbolized by z.
- In a second one, setting up the mathematical relation activity–concentration being searched for. It requires the crossing through the configuration integrals Z_N.
- In a third step, then, to set up the relations between the parameters playing a part in the preceding relations and the virial coefficients applying to the real gases (for which, actually, there exist interactions between the different particles).

At this point of the reasoning, we justify the calculations and the validity of the statistical definition adopted for the activity. Then, we demonstrate that one of the parameters involved in the preceding calculations is actually equal to a configuration integral. Then, we shall perform a brief analysis of the physical meaning of the activity of a gas and give a statistical definition of its fugacity. Finally, we shall give the expression of the virial coefficients as a function of the configuration integrals.

34.2 Introduction of the Activity

Let us consider a mono or polyatomic gas. Let us reason within the framework of the grand ensemble. We know that the partition function can be written (viz. Chap. 24):

$$\Xi(\lambda, V, T) = \mathrm{e}^{pV/kT} \tag{34.1}$$

the term **p**V/kT representing the thermodynamic function characteristic of the grand ensemble (viz. Appendix V). We also know that (viz. relation (33.9)—previous chapter):

$$\Xi(\lambda, V, T) \;=\; 1 + \sum_{N \geq 1} Q_N(V, T)\lambda^N \tag{34.2}$$

where

$$Q_N(V, T) = Q(N, V, T) \quad \text{and} \quad \lambda = \mathrm{e}^{\mu/kT}$$

$Q_N(V, T)$ is the canonical partition function entailing the constant number N of particles which, with other canonical functions taking into account different numbers, enters into the grand canonical partition function. Equation (34.2) is the expansion in series of Ξ in λ. The parameter λ has already been introduced and is, in the occurrence, called the absolute activity of the gas (viz. Chap. 24).

According to what is preceding:

$$\mathbf{p}V/kT = \ln\left[1 + \sum_{N \geq 1} Q_N(V, T)\lambda^N\right] \tag{34.3}$$

Let us develop the logarithm in series. By only retaining the first terms, we obtain:

$$\ln\left[1 + \sum_{N \geq 1} Q_N \lambda^N\right] = \left[Q_1\lambda + Q_2\lambda^2 + Q_3\lambda^3 + \cdots\right] \\ - \left[Q_1\lambda + Q_2\lambda^2 + Q_3\lambda^3 + \cdots\right]^2/2 + \ldots \tag{34.4}$$

i.e.:

$$\ln\left[1+\sum_{N\geq 1} Q_N\lambda^N\right] \approx Q_1\lambda \tag{34.5}$$

according to the relation:

$$\ln(1+x) = x - 1/2x^2 + 1/3x^3 - 1/4x^4 + \cdots \quad (-1 < x \leq 1)$$

$$\ln\Xi \approx Q_1\lambda \tag{34.6}$$

The equivalent expressions (34.5) and (34.6) induce the introduction of the parameter z defined by the following expression:

$$z = Q_1\lambda/V \tag{34.7}$$

The interest to adopt this definition is to show that, actually:

$$z \rightarrow \rho \quad \text{when} \quad \rho \rightarrow 0$$

The property of z to tend toward ρ is only true if all the other terms of the development are lower than that kept.

As we shall see below, z exhibits the properties of Lewis' activity. z is called *a statistical analogue of the activity*.[1] With this choice, according to relation (34.1) we can write:

$$PV/kT = Q_1\lambda \tag{34.8}$$

A beginning of proof of the identity of the Lewis' activity and of z is provided by demonstrating that $z \rightarrow \rho$ when $\rho \rightarrow 0$ which, indeed, is the definition of Lewis, originating in thermodynamics.

The identification of z to the Lewis' activity firstly entails to set up a relation between the density number ρ and z. We immediately do that in two steps. In the first step, we show that z tends toward ρ when the latter tends toward zero. In the second step, we set up the relation being searched for.

34.3 Analogy of the Behaviors of z and of ρ When ρ Tends Toward Zero

Since we are reasoning by using the grand ensemble, the density number is given by the relation:

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[1] Within the framework of statistical thermodynamics, we use the symbol z instead of a in order to mark the fact than z is introduced by the statistical way.

$$\rho = \overline{N}/V \tag{34.9}$$

The number of particles cannot be anything else than an average number given the use of the grand ensemble. We have seen (viz. Chap. 33) that:

$$\overline{N} = \lambda(\partial \ln \Xi / \partial \lambda)_{V,T} \tag{34.10}$$

According to (34.9) and (34.10), the condition:

$$\rho \rightarrow 0$$

entails that:

$$\overline{N} \rightarrow 0 \quad \text{and} \quad \lambda \rightarrow 0$$

According to the statistical definition of the activity (adopted above), the relation (34.7) is evidently satisfied lorsque $\lambda \rightarrow 0$, $z \rightarrow 0$. Consequently:

$$z \rightarrow \rho \quad \text{when} \quad \rho \rightarrow 0$$

The quantity $z = Q_1\lambda/V$, from purely statistical origin, exhibits the same behavior as the Lewis activity, at least when $\rho \rightarrow 0$.

34.4 Relation Between the Number of Density ρ and Activity z

We have seen that, within the framework of the hypothesis of the truncation of the series development of the grand partition function Ξ as a function of λ, the activity z tends toward the density number of the gas ρ when the latter tends toward zero. It is no longer the case when the latter does not tend toward zero.

Now, we set up a more general relation between z and ρ than that constituting the Lewis' definition.

Let us replace λ by z into (34.3) through:

$$\lambda = zV/Q_1$$

We obtain:

$$\Xi = 1 + \sum_{N \geq 1} (Q_N V^N / Q_1^N) z^N \tag{34.11}$$

Let us introduce the term Z_N' by the relation:

$$Z'_N = N!\left[Q_N/Q_1^N\right]V^N \tag{34.12}$$

As we have already mentioned it in Chap. 28 and as we demonstrate it (viz. paragraph 8), Z_N is nothing else than the configuration integral $Z_{N.}$ Expression (34.11) can be, now, written by already assimilating Z'_N to Z_N. Therefore:

$$\Xi = 1 + \sum_{N\geq 1} (Z_N/N!)z^N \tag{34.13}$$

Let us take the logarithm of both members of this equality, i.e.:

$$\ln\Xi = \ln\left[1 + \sum_{N\geq 1} (Z_N/N\,!)\; z^N\right] \tag{34.14}$$

or, taking into account (34.1):

$$pV/kT = \ln\left[1 + \sum_{N\geq 1} (Z_N/N!)\; z^N\right] \tag{34.15}$$

Let us divide the above equation by V and expand in series the logarithm. We can easily forecast that we shall obtain one relation of the type:

$$p/kT = b_1 z^1 + b_2 z^2 + b_3 z^3 + \cdots \tag{34.16}$$

or equivalently:

$$p/kT = \sum_{j\geq 1} b_j z^j \tag{34.17}$$

Or

$$pV/kT = V\sum_{j\geq 1} b_j z^j \tag{34.18}$$

or

$$\ln\Xi = V\sum_{j\geq 1} b_j z^j \tag{34.19}$$

$b_1, b_{2,}$ . . .. depend on temperature owing to the fact that we are reasoning within the framework of the great ensemble.

The simple fact to identify the terms of same degree in z of both members of relation (34.19), after having expanded in series the logarithm of the kind ln $(1 + x)$

of relation (34.15) by using the symbol $x = \sum_{N \geq 1} (Z_N/N!)\, z^N$, permits to immediately find:

$$\begin{gathered} Vb_1 \equiv Z_1 \quad \text{i.e.} \quad b_1 = 1 \\ Vb_2 \equiv \left(Z_2 - Z_1^2\right)/2 \\ Vb_3 \equiv \left(Z_3 - 3Z_1Z_2 + Z_1^2\right)/3! \\ \vdots \end{gathered} \tag{34.20}$$

Hence, coefficients b_1, b_2, b_3... can be expressed as a function of the configuration integrals. By limiting ourselves to the term of order 3, we obtain:

$$\begin{aligned} p/kT = [(Z_1/V)]z^1 + \left[(1/2V)\left(Z_2 - \ Z_1^2\right)\right]z^2 \\ + \left[(1/6V)\left(\left(Z_3 - 3Z_1Z_2 + 2Z_1^3\right)z^3 + \cdots\right.\right. \end{aligned} \tag{34.21}$$

At this point of the reasoning, we notice that the function p/kT, which is a remnant of the perfect gas law, can be written under a series development as a function of the statistical analogue z of the activity.

The relation being searched for between ρ, z, and the coefficients b_i is found as it follows. According to (34.10):

$$\overline{N} = \lambda(\partial \ln \Xi / \partial \lambda)_{V,T} \tag{34.22}$$

Since:

$$\lambda = (V/Q_1)z$$

i.e.:

$$d\lambda = (V/Q_1)dz$$

As a result:

$$\overline{N} = z(\partial \ln \Xi / \partial z)_{V,T}$$

According to (34.1),

$$\begin{gathered} \overline{N} = z[\partial(pV/kT)/\partial z]_{V,T} \\ \overline{N}/V = \rho = z[\partial(p/kT)/\partial z]_T \end{gathered} \tag{34.23}$$

and according to (34.17):

$$\begin{aligned}[\partial(p/kT)/\partial z]_T &= \sum_{j\geq 1} jb_j(T)z^{j-1} \\ \rho &= \sum_{j\geq 1} jb_j(T)z^j\end{aligned} \tag{34.24}$$

The relation (34.24) between the density number ρ and the activity of the component z is that which is being searched for. It depends on the configuration integrals Z_N, parameters stemming from statistical thermodynamics through the coefficients b_j.

Another interesting relation is its reciprocal one, i.e., that relating the activity z to the density number ρ. Let us assume that it is of the following analytical type:

$$z = a_1\rho + a_2\rho^2 + a_3\rho^3 + \cdots \tag{34.25}$$

At once, one can remark that a_1 is set up equal to 1 in agreement with what is preceding. In order to find the other coefficients a_n, it is sufficient to replace z by its development (34.25) into its expression (34.24) and to identify the terms of the same degree in ρ. Hence, by limiting ourselves to the terms of degree 2, we obtain:

$$\begin{aligned}\rho &= b_1(\rho + a_2\rho^2) + 2b_2(\rho + a_2\rho^2)^2 + \cdots \\ \rho &= b_1\rho + b_1a_2\rho^2 + 2b_2\left(\rho^2 + 2a_2\rho^3 + a_2^2\rho^4\right) + \cdots \\ \rho &= b_1\rho + (b_1a_2 + 2b_2)\rho^2 + \text{terms of superior degrees}\end{aligned}$$

We deduce that, since $b_1 = 1$, the terms of superior degrees must be null, i.e.,

$$a_2 = -2b_2$$

Likewise, we would find:

$$\begin{aligned}a_3 &= -3b_3 - 4a_2b_2 \\ a_3 &= -3b_3 + 8b_2^2 \ \text{etc} \ldots\end{aligned}$$

Such is the relation (34.25) between the activity z and the density number, whatever the value of the latter is. Its coefficients a_1, a_2 … are accessible by starting from experimental data. Actually, from the practical standpoint, it is more interesting than the relation (34.24). The density numbers being, indeed, data which are immediately at our disposal, it is possible to reach the value of the activity which is a thermodynamic data very important, as we have already said it. In principle, the calculation can be done whatever the value of ρ is.

34.5 Discussion Around the Relation Between the Activity and the Corresponding Concentration of the Imperfect Gas

The relation (34.25) is at the core of our purpose. It can also be written:

$$z = \rho - 2b_2\rho^2 + \left(-3b_3 + 8b_2^2\right)\rho^3 + \cdots \tag{34.25}$$

with the coefficients $b_2, b_3, \ldots$ which are function of the configuration integrals and which are related to the virial coefficients (viz. the following paragraph).

We notice that:

- When ρ tends toward zero, z tends toward ρ
- z varies with ρ
- According to the Lewis' definition of the activity, for every "concentration" ρ, the chemical potential of the species must obey the relation:

$$\mu = \mu_0 + RT\ln z$$

As a result, z appears as being a *pseudo-concentration* which would confer the same value to the chemical potential of the species as actually its concentration ρ does, whatever its value, *during an ideal behavior*.

Unfortunately, in our current state of calculations, the expression (34.25) cannot be anything else than a formal one, although as a rule, it permits the calculation of the activity for every "concentration," provided the values of the virial coefficients are known after experimental measurements. The number of the virial coefficients to know may be huge, owing to the recurrence of the calculation of the coefficients b_i and a_i (about 10^{20} coefficients!).

34.6 Relations Between the Density Number of the Gas, Its Activity, and the Virial Coefficients

It is possible to obtain the numerical values of the coefficients b_j and a_n from those of the virial coefficients which are the experimental ones. Let us, indeed, compare the virial relation:

$$p/kT = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \cdots$$

and

$$p/kT = b_1 z^1 + b_2 z^2 + b_3 z^3 + \cdots \tag{34.16}$$

Let us replace the activities z by the development (34.25) into (34.16). We obtain by writing only until the term of degree 2:

$$p/kT = b_1\left(\rho + a_2\rho^2\right) + b_2\left(\rho + a_2\rho^2\right)^2 + \cdots$$

whence:

$$p/kT = b_1\rho + (a_2 b_1 + b_2)\rho^2 + \cdots \tag{34.26}$$

By comparing (34.26) and the virial relation and by taking into account the a_n expressions as a function of b_j previously obtained, we find:

$$\begin{aligned} &B_2(T) = -b_2 \\ &B_3(T) = 4b_2^2 - 2b_3 \\ &\vdots \end{aligned}$$

Therefore, the coefficients b_j and a_n (the latter ones through the reciprocal relation) can be expressed as a function of the virial coefficients.

Moreover, it appears that the coefficients a_n do not depend on the coefficients b_j when $j > n$. For example, a_2 only depends on b_2 and on b_1, i.e., only on the configuration integrals Z_1 and Z_2. It is the same thing for a_n and b_n which only depend on the configuration integrals $Z_1 \ldots Z_n$. This point is very important. It means that these coefficients together with those of the virial, take into account:

- When b_2, a_2, $B_2(T)$ are concerned, only the interactions between two particles
- When b_3, a_3, $B_3(T)$ are concerned, only the interactions between three particles
- When b_n, a_n, $B_n(T)$ are concerned, only those between n particles.

In other words, $B_2(T)$ only depends on the interactions between two particles, etc.

34.7 Justification of the Preceding Calculations. Validity of the Statistical Definition of the Activity

The problem, now, is to justify the validity of relation (34.16).

A first point to notice before the justification is the characteristic of the reasoning followed up to now. It is the embedding and the interdependence of the different calculations. Consequently, if the legitimacy of expression (34.19) can be demonstrated, all the inferences stemming from it become legitimate.

From the pure mathematical standpoint, the difficulty lays in the fact that, at this point of the reasoning, it is not sure at all that the expansion in series, stemming from (34.15), can be truncated as it has been done.

The justificatory reasoning given below can be qualified of "upside down reasoning." We start from the expression (34.16) set up, postulated as being a priori perfectly legitimate, and we demonstrate that we come back to expression (34.15).

According to (34.16), we have:

$$\mathrm{e}^{pV/kT} = \exp\left[V\sum_{j\geq 1} b_j z^j\right]$$

Because of the properties of the exponential function:

$$\exp\left[V\sum_{j\geq 1} b_j z^j\right] = \exp\left(Vb_1z^1\right)\cdot\exp\left(Vb_2z^2\right)\cdot\exp\left(Vb_3z^3\right)\cdots \tag{34.27}$$

Let us develop in series the exponentials of the right member of this expression and let us perform the products. Let us explicit the product of the two series developments (limited to the third degree) of the first two exponentials. This product is:

$$\begin{aligned}\exp(Vb_1z^1)\cdot\exp(Vb_2z^2) = \big[1 &+ (Vb_1)^1z^{11} + 1/2!(Vb_1)^2z^{12}\\ &+ 1/3!(Vb_1)^3z^{13} + \cdots\big]\\ \bullet\big[1 + (Vb_2)^1z^{21} &+ 1/2!(Vb_2)^2z^{22} + 1/3!(Vb_2)^3z^{23} + \cdots\big]\end{aligned}$$

(Notice the use of both indices qualifying the activities, the first one permitting the mark of the coefficient $b_{j,}$ the second being the exponent). The calculation performed by multiplying the previous product by the series development of the third exponential $\exp(Vb_3z^3)$ leads to a series development as a function of z the coefficients of the increasing powers of which are:

for z^1 $\quad z^2 \quad (Vb_1/1)$

for z^2 $\quad z^2 \quad ½(Vb_1)^2 + (Vb_2/1)$

for z^3 $\quad z^3 \quad 1/3!(Vb_1)^3 + (Vb/1)(Vb_2/1) + (Vb_3/1)$

⋮

Equalizing the coefficients Z_N of equation (34.13) and those of equation (34.27), we obtain the equalities:

$$(Vb_1/1) = Z_1$$

$$½(Vb_1)^2 + (Vb_2/1) = 1/2Z_2$$

$$1/3!(Vb_1)^3 + (Vb_1/1)(Vb_2/1) + (Vb_3/1) = 1/6Z_3$$

In brief, we again find expression (34.13). It is the result that we wanted to demonstrate.

34.8 Identity of Z'_N and of the Integral of Configuration in Classical Statistical Thermodynamics Z_N

We have already mentioned in the paragraph 4 that the parameter Z'_N introduced in the preceding calculations and defined by the expression:

$$Z'_N(V,T) = N!\left[Q_N/Q1^N\right]V^N \tag{34.12}$$

is identical to the corresponding configuration integral Z_N in classical statistical thermodynamics, defined by the expression (viz. Chap. 28):

$$Q_{\text{class}} = Z_N/N\,!\Lambda^{3N} \tag{34.28}$$

Hence, we must demonstrate that:

$$Z'_N \equiv Z_N$$

When the gas is very weakly concentrated, it exhibits a perfect behavior. It is obviously the case when there is only one molecule in the system, to which corresponds the partition function Q_1 by definition. Since the gas behaves ideally, the following expression is justified (viz. Chap. 26):

$$Q = (1/N!)q^N$$

and therefore for $N = 1$:

with:

$$q = V/\Lambda^3$$

where q is the molecular partition function of the system—viz. Chap. 27. As a result:

$$Q_1 = V/\Lambda^3$$

Replacing Q_1 into (34.12) by the latter expression immediately leads to the identity being searched for.

34.9 Physical Meaning of the Activity of a Gas

In this paragraph, we briefly comment on the results which we have obtained just above.

- Let us begin by saying that relations (34.24) and (34.25) show distinctly how the activity and the density numbers differ from each other. The relation (34.25), for example, shows that the difference between both is expressed by terms containing the density number itself at degrees larger than 2. As a result, one can conceive that the more dense the gas is, the larger the difference between both quantities may be. This conclusion can also be found when the notion of activity coefficient is regarded (viz. Chap. 37).
- Let us consider the relation (34.7) defining the activity:

$$z = Q_1\lambda/V \tag{34.7}$$

  Clearly, the activity takes its roots in classical thermodynamics through the absolute activity λ. Certainly, the absolute activity is a quantity which is introduced in statistical thermodynamics at the level of the grand ensemble, but its definition:

$$\lambda = e^{\mu/kT}$$

involves the concept of chemical potential of purely thermodynamic origin. Clearly, we notice that, by its sole definition, the activity of a substance is linked to its chemical potential.

- Still more significant than the last argument is the occurrence of the canonical partition function Q_1 in the definition of the activity. It is a characteristic of the system which possesses one particle only in the system V. No interaction with other particles, of course, can exist. Here, we again find the meaning which was attributed to an activity by Lewis himself: i.e., to characterize a species as it would have no interaction with other ones. (In passing let us recall that, according to the general principles of quantum mechanics, Q_1 depends on the volume V and on the fact that there is one molecule in the system).

34.10 Definition of the Fugacity

Incidentally, in this paragraph, we are interested in the meaning of the fugacity in statistical thermodynamics. According to Lewis, the fugacity is defined as being the quantity which tends toward the pressure p of a gas when the latter tends toward zero (viz. Chap. 7), i.e.,

$$\lim_{p\to 0} f = p$$

According to relation (34.24), it is evident that:

$$p/kT \to b_1 z^1 \quad \text{when} \quad p \to 0$$

Since $b_1 = 1$, and since $f \to p$ when $p \to 0, f$ must be defined by the expression:

$$f = kTz \quad f/kT = z \tag{34.29}$$

i.e.,

$$f = (kT/V)Q_1\lambda \tag{34.30}$$

34.11 Virial Coefficients and Configuration Integrals

We have mentioned in the preceding chapter that the virial coefficient of order 2, $B_2(T)$ can be expressed as a function of the configuration integrals Z_2 and Z_1.

$$B_2(T) = -(1/2V)\left(Z_2 - Z_1^2\right)$$

It can also be written according to:

$$B_2(T) = -(1/2V)\left\{\int_V\int \exp[-U(\mathbf{r}_1,\mathbf{r}_2)/kT]d\mathbf{r}_1 d\mathbf{r}_2 - V^2\right\}$$

where $U(\mathbf{r}_1, \mathbf{r}_2)$ is the intermolecular potential energy between the two particles of the system of coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ $(x_1\ldots z_2)$. It can also be written:

$$B_2(T) = -(1/2)\int_0^\infty \exp[-U(r)/kT - 1]4\pi r^2 dr$$

In the latter expression, r is a scalar. It is the distance which separates particles 1 and 2, particle 1 being supposed fixed.

Let us recall that in this special case, the configuration integral is given by the following expression:

$$Z_N = \int_V \cdots \int \exp[-U_N(x_1, \ldots z_N)/kT] dr_1 \cdots dr_N$$
$$\text{with} \quad d\mathbf{r}_1 = dx_1 dy_1 dz_1 \cdots$$

- For the calculation of Z_1, evidently $U(x_1, \ldots z_N) = 0$, since there is only one particle. Consequently:

$$Z_1 = \textstyle\int_V d\mathbf{r}_1$$
$$Z_1 = V$$

- Z_2 is given by the expression:

$$Z_2 = \int_V \int \exp[-U(\mathbf{r}_1, \mathbf{r}_2)/kT] d\mathbf{r}_1 d\mathbf{r}_2$$

$U(\mathbf{r}_1,\ \mathbf{r}_2)$ is the intermolecular potential energy between the two particles, depending on the coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ ($x_1 \ldots . z_2$). In order to relate $B_2(T)$ to the intermolecular potential energy between both particles, we use the equalities, already demonstrated above, in which the configuration integrals intervene:

$$B_2(T) \ = \ -b_2$$

and

$$Vb_2 \ = \ Z_2 - Z_1^2$$

whence:

$$B_2(T) = -(1/2V)\left(Z_2 - {Z_1}^2\right)$$
$$B_2(T) = -(1/2V)\left[\int_V \int \exp[-U(\mathbf{r}_1, \mathbf{r}_2)/kT] d\mathbf{r}_1 d\mathbf{r}_2 - V^2\right]$$
$$B_2(T) = -(1/2V)\int_V \int \exp[-U(\mathbf{r}_1, \mathbf{r}_2)/kT] d\mathbf{r}_1 d\mathbf{r}_2 + V/2$$
$$B_2(T) = -(1/2V)\int_V \int \exp[-U(\mathbf{r}_1, \mathbf{r}_2)/kT] d\mathbf{r}_1 d\mathbf{r}_2 + 1/2 \textstyle\int d\mathbf{r}_1$$
$$B_2(T) = -(1/2V)\int_V \int \exp[-U(\mathbf{r}_1, \mathbf{r}_2)/kT] d\mathbf{r}_1 d\mathbf{r}_2 + 1/2V \textstyle\int d\mathbf{r}_1 \int d\mathbf{r}_2$$
$$B_2(T) = -(1/2V)\int_V \int \exp[-U(\mathbf{r}_{1v}, \mathbf{r}_2)/kT - 1] d\mathbf{r}_1 d\mathbf{r}_2$$

By changing the variables, i.e., by using the variables d$\mathbf{r}_1$ and $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$ (which is the location of particle 2 with respect to particle 1 regarded as being at the origin), we obtain:

$$B_2(T) = -(1/2V) \int_V \int \exp[-U(\mathbf{r}_{12})/kT - 1] d\mathbf{r}_{12}$$

and adopting the polar coordinates:

$$d\mathbf{r}_{12} = 4\pi r^2 dr$$
$$B_2(T) = -(1/2) \int_0^\infty \exp[-U(r)/kT - 1]\, 4\pi r^2 dr$$

or, according to what is preceding:

$$B_2(T) = -1/2 \int (x_{12} - 1) dr_{12}$$

- By supposing the hypothesis of the "pairwise additivity" validated (besides, it is only at this term that it can be applied for the first time), the configuration integral Z_3 can be written:

$$Z_3 = \iiint_V \exp[-U(\mathbf{r}_1, \mathbf{r}_2) - U(\mathbf{r}_1, \mathbf{r}_3) - U(\mathbf{r}_2, \mathbf{r}_3)] d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3$$

By adopting a reasoning analogous to the preceding and by using the same symbolism, we obtain the following relation for $B_3(T)$:

$$B_3(T) = -(1/3V) \iiint_V v(x_{12} - 1)(x_{13} - 1)(x_{23} - 1) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3$$

Analogous expressions would be found for the superior coefficients.

Chapter 35
Activities of Gases in a Mixture of Imperfect Gases

Abstract The chapter is a simple generalization of a previous one. It is devoted to the study of a binary mixture. The case is studied with the aid of the grand ensemble and the activities of each gas are defined as for a sole imperfect one. In their definition intervene their absolute activities, the volume of the solute and the canonical partition functions when one molecule of each gas is present without any molecule of the other.

Relations linking the chemical potential of each gas to its partial pressure through statistical parameters are also mentioned.

Keywords Statistical gas activities in a mixture of perfect gases • Partial pressure • Grand ensemble • Configuration integrals • Chemical potentials of the gases

This chapter is a simple generalization of the previous one. We confine ourselves to the study of a binary mixture.

35.1 Activity of Both Gases

We have seen that, in the case of a fluid constituted by a binary mixture (viz. Chap. 24), the grand partition function is:

$$\Xi(\lambda_1, \lambda_2, V, T) = \sum_{N1 \geq 0} \sum_{N2 \geq 0} Q_{N1N2}(V, T) \lambda_1^{N1} \lambda_2^{N2}$$

or, with a slightly simplified writing:

$$\Xi(\lambda_1, \lambda_2, V, T) = \sum_{N1, N2 \geq 0} Q_{N1N2}(V, T) \lambda_1^{N1} \lambda_2^{N2}$$

Q_{N1N2} is the canonical partition function of the system for the number of particles N_1 and N_2, and λ_1, λ_2 the absolute activities:

J.-L. Burgot, *The Notion of Activity in Chemistry*,
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$$\lambda_1 = e^{\mu 1/kT} \quad \lambda_2 = e^{\mu 2/kT}$$

The function Ξ can be also written as:

$$\Xi(\lambda_1, \lambda_2, V, T) = 1 + \sum_{N1, N2 \geq 1} Q_{N1N2}(V,T)\lambda_1^{N1}\lambda_2^{N2}$$

(This writing is strictly equivalent to the previous one). By expanding in series with respect to λ_1 and λ_2, it becomes:

$$\Xi = 1 + Q_{10}\lambda_1^1 + Q_{01}\lambda_2^1 + Q_{20}\lambda_1^2 + Q_{10}Q_{01}\lambda_1^1\lambda_2^1 + Q_{02}\lambda_2^2 + \cdots \tag{35.1}$$

Symbols Q_{10}, Q_{01}, respectively, represent the canonical partition functions of the systems made up by only one molecule 1 and by zero molecule 2 on one hand and by zero molecule 1 and by one molecule of 2 on the other.

As previously, one defines the activities z_1 and z_2 of species 1 and 2 by the expressions:

$$z_1 = Q_{10}\lambda_1/V \quad \text{and} \quad z_2 = Q_{01}\lambda_2/V \tag{35.2}$$

As in the case of only one gas, z_1 and z_2 tend toward ρ_1 and ρ_2 when the latter ones tend toward zero. This assertion is justified by the series development in series of ln Ξ where Ξ is given by expression (35.1).

Let us replace λ_1 and λ_2 by their expressions in z_1 and z_2 (35.2), we obtain:

$$\begin{aligned}\Xi = 1\ &+\ Q_{10}(V/Q_{10})z_1\ + Q_{01}(V/Q_{01})\,z_2\ +\ Q_{20}(V/Q_{10})^2 z_1^2\\ &+ Q_{10}Q_{01}(V/Q_{10})(V/Q_{01})\,z_1z_2\ +\ Q_{02}(V/Q_{01})^2 z_2^2\ + \cdots\end{aligned}$$

Let us set up the general expression:

$$Q_{N1N2}V^{N1+N2}\ /Q_{10}^{N1}Q_{01}^{N2} = Z_{N1N2}/N_1\ !N_2! \tag{35.3}$$

The Z_{NIN2} are the configuration integrals.

We obtain:

$$\Xi = 1 + Vz_1 + Vz_2 + ½Z_{20}z_1^2 + Z_{11}z_1z_2 + ½\,Z_{02}z_2^2 + \cdots \tag{35.4}$$

It appears the numeral 2 in the denominator of some terms. Its presence results from the definition of Z_{NIN2}.

For the whole system,

$$\ln\Xi = pV/kT$$

By expanding in series ln Ξ stemming from (35.4), we obtain:

$$pV/kT = \left(Vz_1 + Vz_2 + ½\,Z_{20}z_1^2 + Z_{11}z_1z_2 + ½\,Z_{02}z_2^2 + \cdots\right) \\ - \left(Vz_1 + Vz_2 + ½\,Z_{20}z_1^2 + Z_{11}z_1z_2 + ½\,Z_{02}z_2^2 + \cdots\right)^2/2$$

and by truncating the development by limiting it to the terms up to the degree two:

$$pV/kT = Vz_1 + Vz_2 + 1/2Z_{20}\,z_1^2 - \left(V^2/2\right)z_1^2 + (Z_{11}/V)\,z_1z_2 - V^2z_1z_2 \\ + 1/2Z_{02}z_2^2 - \left(V^2/2\right)z_2^2$$

whence:

$$p/kT = z_1 + z_2 + (Z_{20}/2V - V/2)\,z_1^2 + (Z_{11}/V - V)\,z_1z_2 \\ + (Z_{02}/2V - V/2)\,z_2^2\cdots \tag{35.5}$$

which can be written after introduction of the intermediary coefficients b_{ij}:

$$p/kT = z_1 + z_2 + b_{20}(T)z_1^2 + b_{11}(T)z_1z_2 + b_{02}(T)\,z_2^2 + \cdots \tag{35.6}$$

This expression is analogous to the relation (34.16) of the preceding chapter. The comparison of (35.5) and (35.6) permits to express the b_{ij} coefficients as a function of the configuration integrals Z_{ij}.

As previously, it is possible to relate the virial coefficients to the configuration integrals and to the different parameters after derivation.

In this case, the virial equation is:

$$p/kT = \rho_1 + \rho_2 + B_{20}(T)\rho_1^2 + B_{11}(T)\rho_1\rho_2 + B_{02}\rho_2^2 + \cdots$$

The reasoning which leads to this relation is the same as previously. It consists in, successively, expressing ρ_1 and ρ_2 as a function of z_1 and z_2 through the coefficients b_{ij} and b_{ji}, then, in expressing z_1 and z_2 as a function of ρ_1 and ρ_2 and, finally, in setting up an expression of p/kT as a function of the found relations and in comparing it to the virial equation.

The relation:

$$\overline{N_1} = \lambda_1(\partial \ln\Xi/\partial\lambda_1)$$

remains valid. Given the definition of the activity z_1, we obtain:

$$\overline{N_1} = (V/Q_{10})z_1[\partial \ln\Xi/(V/Q_{10})\partial z_1]_{V,T,z2}$$

$$\overline{N_1} = z_1(\partial \ln\Xi/\partial z_1)_{V,T,z2}$$

The reasoning leading to the expression (34.23) of the preceding chapter remains also valid. As a result $\left(\text{with } \overline{\rho_1} = \overline{N_1}/V \text{ i.e. } = \overline{\rho_1}\right)$:

$$\rho_1 = z_1[\partial(p/kT)/\partial z_1]_{T,V,z2}$$

According to (35.5):

$$[\partial(p/kT)/\partial z_1]_{T,V,z2} = 1 + 2(Z_{20}/2V - V/2)z_1 + (Z_{11}/V - V)z_2 + \cdots$$
$$[\partial(p/kT)/\partial z_1]_{T,V,z2} = 1 + 2\,b_{20}z_1 + b_{11}z_2 + \cdots$$

and

$$\rho_1 = z_1 + 2b_{20}z_1^2 + b_{11}z_1z_2 + \cdots$$
$$\rho_2 = z_2 + 2b_{02}z_2^2 + b_{11}z_1z_2 + \cdots$$

The expressions z_1 as a function of ρ_1 and z_2 as a function of ρ_2 are found by putting down:

$$z_1 = \rho_1 + a_{10}\rho_1^2 + \cdots$$
$$z_2 = \rho_2 + a_{01}\rho_2^2 + \cdots$$

By injecting the two latter expressions into the two preceding ones and by identifying the coefficients of the terms in ρ_1 and ρ_2 of the same degree, we find:

$$z_1 = \rho_1 - 2b_{20}\rho_1^2 - b_{11}\rho_1\rho_2 + \cdots$$
$$z_2 = \rho_2 - 2b_{02}\rho_2^2 - b_{11}\rho_1\rho_2 + \cdots$$

These two relations immediately provide us with the expressions of the corresponding activity coefficients $\gamma_1 = z_1/\rho_1$ and $\gamma_2 = z_2/\rho_2$.

From another standpoint, by putting back these expressions of z_1 and z_2 into (35.6) and by comparing the obtained expression with that of the virial, we obtain the "statistical" expressions of the coefficients of the latter. Hence, we obtain:

$$B_{20} = -b_{20} \quad B_{11} = -b_{11} \quad B_{02} = -b_{02}$$

It is significant to notice that the coefficients B_{20} and B_{02} are purely and simply the second order coefficients of the virial expansion of each of the pure gas. However, the coefficient B_{11} is new. It depends on the properties of the two different particles in the same volume V. It is given by the expression:

$$B_{11} = -1/V\left(Z_{11} - V^2\right)$$
$$B_{11} = -\int_0^\infty \exp[-U_{11}(r)/kT - 1]4\pi r^2 dr$$

U_{11} is the intermolecular potential between a molecule of each type.

In the particular case in which there is a mixture of two gases constituted by spherical particles (gases without any internal structure), the term Z_{N1N2} present in the expression below:

$$Q_{N1N2} = Z_{N1N2} / \left(N_1! N_2! \Lambda_1^{3N1} \Lambda_2^{3N2} \right)$$

is one of the configuration integrals of the system, defined by the expression:

$$Z_{N1N2} = \int_V \exp[-\, U_{N1N2}/kT] d\{N_1\} d\{N_2\}$$

where $d\{N_1\}$ means $d\mathbf{r}_1 \ldots d\mathbf{r}_{N1}$ and so forth …. so that we can write in an equivalent manner:

$$Z_{N1N2} = \int_V \exp[-U_{N1N2}/kT] d\{\mathbf{R}_1\} d\{\mathbf{R}_2\}$$

35.2 Chemical Potentials of Both Components as a Function of Their Partial Pressure

It is interesting to express the chemical potential of each of the two components of the mixture. Besides, these expressions will be handled in the case of diluted solutions (viz. Chap. 38). Let us only reason on the compound 1 (the reasoning is quite identical for the compound 2). According to relations (35.2), we can write:

$$\rho_I = Q_{I0} \lambda_I / V$$

since for a very weak density number ρ_1 tends toward z_1. Hence, we can write:

$$N_I / V \ = Q_{I0} \lambda_I / V$$

Owing to the perfect gas law (applied at the molecular level), obligatorily satisfied, once we have admitted the equivalence activity–concentration, we can write:

$$pV = N_I kT$$
$$p/kT \ = \ Q_{I0} \lambda_I / V$$

where k is the Boltzmann's constant. From another standpoint, according to the properties of the grand ensemble (viz. Chap. 24),

$$\lambda_I = \mathrm{e}^{\mu I/kT}$$

As a result, after the handling of the last two relations:

$$(V/Q_{10})\,(p/kT) = \mathrm{e}^{\mu 1/kT}$$

$$\mu_1 \;=\; kT\ln\left[V/(kTQ_{10})\right] \;+\; kT\ln p_1 \tag{35.7}$$

In the same manner, we would find:

$$\mu_2 \;=\; kT\ln[V/(kTQ_{01})] \;+\; kT\ln p_2 \tag{35.8}$$

The factors $kT\ln[V/(kTQ_{10})]$ or $kT\ln[V/(kTQ_{01})]$ represent the corresponding standard potentials according to the meaning of classical thermodynamics. These expressions of standard potentials are only accurate in the eventuality of the species concentrations being indirectly expressed in terms of pressures. It is significant to recall that when the latter ones are expressed in terms of density numbers, these quantities do not exhibit the same value.

Besides, the following reasoning permits to calculate the standard potential of a species according to the adopted type of "concentration" and that by starting from another kind of "concentration."

Let us, for example, reason with compound 2. According to relation (35.8), the chemical potential μ_2 may be written:

$$\mu_2 \;=\; -kT\ln kT + kT\ \ln V/Q_{01} + \; kT\ln p_2$$

From another standpoint, we can explicit the chemical potential as a function of the activity. Now, let us take the example of compound 1. We know (viz. paragraph 2) that $\rho_1 = Q_{10}\lambda_1/V$. In very dilute solution, we can assimilate ρ_1 and z_1, and by expressing λ_1, we obtain:

$$\mu_1 = kT\ln V/Q_{01} \;+\; kT\ln z_1$$

and likewise:

$$\mu_2 = kT\ln V/Q_{02} \;+\; kT\ln z_2$$

In this case, the standard potential becomes:

$$\mu_2^0(z) \;=\; kT\ln(V/Q_{01})$$

The chemical potential μ_2 being obligatory the same, we can deduce from the preceding result that:

$$\mu_2^0(p) \;=\; \mu_2^0(z) \;-\; kT\ln kT \tag{35.9}$$

Besides, this result may be directly found by using the perfect gas law, i.e.:

$$pV = NkT$$

$$p = \rho kT$$

$$\ln p = \ln kT + \ln \rho$$

In sufficiently dilute solution $z \rightarrow \rho$, whence:

$$\ln p = \ln kT + \ln z$$

Chapter 36

Chemical Equilibrium Between Gases and Statistical Thermodynamics

Abstract The chapter mentions an overview of the study of the chemical equilibrium from the standpoint of statistical thermodynamics. This subject is quite evidently of importance since equilibrium constants between gases (and also between species in solutions) are expressed in activity or fugacity terms once they do not exhibit an ideal behavior.

After a brief recall of the equilibrium condition in classical thermodynamics, several examples of chemical equilibria are examined from the viewpoint of statistical thermodynamics. Finally, the case of equilibria between imperfect gases is dealt with. It is in this context that activities and fugacities play an important part. From the developments of the chapter, it appears that the thermodynamic equilibrium constants are only function of the partition functions of the species involved in the equilibrium together with the stoichiometry of the reaction. The described theory is carried out within the framework of the canonical ensemble.

Keywords Chemical equilibria between gases and statistical thermodynamics • Partition function • Equilibrium constants and molecular partition functions • Absolute activities • Equilibrium constants and partition functions • Equilibrium constants expressed in activities and in concentrations

In this chapter, we give an overview of the study of the chemical equilibrium from the standpoint of statistical thermodynamics. This subject is quite evidently of importance since equilibrium constants between gases (and also between species in solutions) are expressed in activity or fugacity terms once they do not exhibit an ideal behavior.

After a brief recall of the equilibrium condition in classical thermodynamics, we study several examples of chemical equilibria from the viewpoint of statistical thermodynamics. Finally, we deal with the case of equilibria between imperfect gases. It is in this case that activities and fugacities play their part.

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36.1 Some Recalls: Chemical Equilibria and Classical Thermodynamics

Let us recall (viz. Chap. 6) that, for example, for a reaction of the kind:

$$\nu_A \mathrm{A} + \nu_B \mathrm{B} \rightleftharpoons \nu_C \mathrm{C} \tag{36.1}$$

evolving in a closed system at constant pressure and temperature, the equilibrium condition from the standpoint of classical thermodynamics is given by the following expression, which must be satisfied:

$$\nu_A \mu_A + \nu_B \mu_B = \nu_C \mu_C \tag{36.2}$$

where the ν_i are the stoichiometric coefficients and the μ_i the chemical potentials, once the chemical equilibrium is reached. Let us also recall that this condition is general. Not only does it apply to ideal (or not) gases but also it applies to all types of chemical equilibria whether they occur between gases or not. It is a consequence of the second principle of thermodynamics.

36.2 Equilibrium Constants and Molecular Partition Functions of the Reactants and Products: Case of a Mixture of Ideal Gases

Let us consider the case of the reaction (36.1) in which the reactants and products A, B, and C are perfect gases. In order to treat the problem of this equilibrium from the statistical standpoint, we must relate the chemical potentials appearing in relation (36.2) to the partition function Q of the whole system and, through it, to the molecular partition functions q of every reactant and product participating to the equilibrium (viz. Chap. 26).

The first point we must take into account is that since the gases are perfect, their behaviors are independent from each other. They are as if they were alone in the container. This point is very important. Let us anticipate that is following by asserting that this property differentiates them from imperfect gases. More specifically, in the case of perfect gases, it is not fruitful to introduce the notions of activity and fugacity in order to express the equilibrium constants.

(At this point of the reasoning, the ability to express the equilibrium constants as a function of the activities and fugacities under an analogous form as in the case of equilibria between perfect gases probably constitutes the major practical interest of the introduction of the notions of activity and of fugacity.)

We know that when the gas (monoatomic, diatomic, or polyatomic) is *alone*, the partition function of the system Q can be written (q being the molecular partition function and N the number of molecules) (viz. Chap. 26):

$$Q(N,V,T) = q(V,T)^N/N!$$

Let us also recall that according to the fact the gas is monoatomic or polyatomic, q may be (or not) a composite function. For a mixture of two perfect gases 1 and 2 (and hence independent), the canonical partition function of the system is given by the general relation:

$$Q(N_1,N_2,V,T) = \left[q_1(V,T)^{N1}/N_1!\right]\left[q_2(V,T)^{N2}/N_2!\right] \tag{36.3}$$

N_1 and N_2 are the numbers of moles of 1 and 2. The product of the molecular partition functions must be considered because each of all the levels of energy of molecule 2 can be associated with every level of molecule 1, since the gases are independent. Let us insist on the fact that the partition function $Q(N_1,N_2,V,T)$ is that of the system composed by N_1 molecules of 1 and by N_2 molecules of 2.

The relation between the chemical potentials of the species participating to the equilibrium and the system partition function is that very general already seen (viz. Chap. 26):

$$\mu_i = -kT\left(\partial \ln Q\left(N_i,N_j,T,V\right)/\partial N_i\right)_{T,V,Nj} \quad (j \neq i) \tag{36.4}$$

The calculation of μ_1 and μ_2 by starting from (36.3) by taking into account (36.4) easily leads to the following expressions (after the use of the Stirling's approximation):

$$\mu_1 = -kT\ln[q_1(V,T)/N_1] \quad \text{and} \quad \mu_2 = -kT\ln[q_2(V,T)/N_2] \tag{36.5}$$

Hence, we deduce that the chemical potential of each of the gas is the same as it would be alone, provided, of course, that the mixture behaves "ideally."

Let us apply to the reaction (36.1) the equilibrium condition (36.2) while taking into account expressions (36.5) permitting the calculation of the different chemical potentials, taking granted the fact that the canonical partition function of the system $Q(N_\text{A},N_\text{B},N_\text{C},T,V)$ is then given by the following expression:

$$Q(N_\text{A},N_\text{B},N_\text{C},T,V) = \left[q_\text{A}(T,V)^{N\text{A}}/N_\text{A}!\right]\left[q_\text{B}(T,V)^{N\text{B}}/N_\text{B}!\right] x \left[q_\text{C}(T,V)^{N\text{C}}/N_\text{C}!\right]$$

We obtain:

$$N_\text{C}^{v\text{C}}/N_\text{A}^{v\text{A}} \cdot N_\text{B}^{v\text{B}} = q_\text{C}^{v\text{C}}/q_\text{A}^{v\text{A}} q_\text{B}^{v\text{B}} \tag{36.6}$$

N_C, N_A, and N_B are the numbers of molecules of C, A, and B at equilibrium.

The expression (36.6) can be differently written by introducing the density numbers ρ of the species. It is an easy task since the number of density is defined as being the ratio of a number of molecules of a species and of the volume V of the system:

$$\rho_i = N_i/V$$

By dividing all the terms of expression (36.6) by V brought to the corresponding power, we obtain:

$$\rho_C^{\nu C}/\rho_A^{\nu A} \cdot \rho_B^{\nu B} = (q_C/V)^{\nu C}/(q_A/V)^{\nu A} \cdot (q_B/V)^{\nu B} \tag{36.7}$$

An important point to highlight is that the molecular partition functions q are equal to the volume V of the system multiplied by a function which only depends on the temperature, since they are of the type $q = V \bullet f(T)$. We have seen, indeed, (viz. Chap. 26) that:

$$q(V,T) = V\left(2\pi mkT/h^2\right)^{3/2} \quad \text{(perfect gas monoatomic gas)}$$

$$q(V,T) = V\left[2\pi(m_1 + m_2)kT/h^2\right]^{3/2} \quad \text{(perfect diatomic gas)}$$

$$q(V,T) = V\left[2\pi\left(\sum_i m_i\right)/kT/h^2\right]^{3/2} \quad \text{(perfect polyatomic gas)}$$

As a result, whatever the gas (monoatomic or polyatomic) is, the right member of the expression (36.7) only depends on the temperature. Hence, we can write:

$$\rho_C^{\nu C}/\rho_A^{\nu A} \cdot \rho_B^{\nu B} = K(T) \tag{36.8}$$

Therefore, the mass action law is confirmed on the bases of statistical thermodynamics.

36.3 A Simple Example: A Dimerization Equilibrium

As an example, let us consider the following equilibrium of dimerization at constant volume and temperature:

$$A \rightleftharpoons 2B$$

Contrary to the preceding problem in which we wanted to relate the equilibrium constant value to those of the numbers moles existing at equilibrium, our present goal, here, is to obtain the numbers of moles of A and B once the equilibrium is reached, with the constraint that the initial matter must be conserved.

This constraint is explicited by the equality:

$$2N_{\mathrm{A}} + N_{\mathrm{B}} = N \quad (N : \mathrm{constant})$$

Let $N_{\mathrm{A}}^{\mathrm{o}}$ and $N_{\mathrm{B}}^{\mathrm{o}}$ be the number of molecules A and B initially present in a container of volume V at the temperature T. From the experimental viewpoint, the obtaining of the equilibrium at constant volume and temperature can be obtained, for example, by addition of a catalysor, whereas, initially, the mixture was frozen to the number of moles $N_{\mathrm{A}}^{\mathrm{o}}$ and $N_{\mathrm{B}}^{\mathrm{o}}$ such as:

$$2N_{\mathrm{A}}^{\mathrm{o}} + N_{\mathrm{B}}^{\mathrm{o}} = N$$

The partition function of the system in the initial state $Q(N_{\mathrm{A}}^{\mathrm{o}}, N_{\mathrm{B}}^{\mathrm{o}}, V, T)$ is given, as we have seen it previously, by the expression:

$$Q\left(N_{\mathrm{A}}^{\mathrm{o}}, N_{\mathrm{B}}^{\mathrm{o}}, V, T\right) = q_{\mathrm{A}}^{N\mathrm{A}\circ}/N_{\mathrm{A}}^{\circ}! \quad q_{\mathrm{B}}^{N\mathrm{B}\circ}/N_{\mathrm{B}}^{\circ}! \tag{36.9}$$

According to considerations of thermodynamics, we know that the equilibrium is reached when the Helmholtz energy $A = -kT\ln Q$ of the whole system is minimized, i.e., when the function Q is maximal. Hence, the problem is to search for the number of moles N_{A}^{*} maximizing Q, the following constraint:

$$2N_{\mathrm{A}}^{*} + N_{\mathrm{B}}^{*} = N$$

being obligatorily satisfied. It is quite evident that it is not necessary to separately search for the value N_{B}^{*} since the mole numbers N_{A}^{*} and N_{B}^{*} are related to by the preceding expression. Hence, to solve the problem, it is sufficient to set up:

$$(\partial \ln Q/\partial N_A)_{N,V,T} = 0$$

It is a “mathematical fact” that the function Q is then maximal. We obtain:

$$N_{\mathrm{B}}^{*2}/N_{\mathrm{A}}^{*} = q_{\mathrm{B}}^{2}/q_{\mathrm{A}}$$

This result is perfectly analogous to that previously obtained. The equilibrium constant is given by the expression:

$$K(T) = \rho_{\mathrm{B}}^{2}/\rho_{\mathrm{A}}$$

Let us highlight the fact that the value of the canonical partition function regarded in this example $Q(N_{\mathrm{Ao}}, N_{\mathrm{Bo}}, V, T)$ is imposed by the number of moles of species A and through it by that of B. Recall, indeed (viz. Chap. 21), that the different energetic states allowed by quantum mechanics are a function of the volume V and of the number of moles of the system. In the present case, the study is performed with the number of moles $N_{\mathrm{A}}{}^{\circ}, N_{\mathrm{B}}{}^{\circ}$, and N which are certainly arbitrary but fixed numbers.

36.4 Chemical Equilibrium Between Imperfect Gases

When one studies the equilibria between imperfect gases, the mass action law, as we shall see it now, is expressed in terms of activities and, no longer, in terms of density numbers. In order to study such a case, let us again consider the case of a dimerization equilibrium:

$$\mathrm{A} \rightleftharpoons 2\mathrm{B}$$

The equilibrium condition remains:

$$\mu_{\mathrm{A}} = 2\mu_{\mathrm{B}}$$

or, in terms of absolute activities:

$$\lambda_{\mathrm{A}} = \lambda_{\mathrm{B}}^2 \tag{36.10}$$

since the chemical potential of a species is related to its absolute activity through the relation $\lambda = \mathrm{e}^{\mu/kT}$. We know that when the density numbers are sufficiently weak, the behavior of the species tends to be ideal and we have seen that (viz. the above paragraph) the equilibrium constant expresses as a function of them:

$$K(T) = \rho_{\mathrm{B}}^2/\rho_{\mathrm{A}}$$

with:

$$K(T) = (Q_{01}/V)^2/(Q_{10}/V)$$

the indices 01 and 10, respectively, being referred to compounds B and A. Symbols Q_{10} and Q_{01}, respectively, are related to the canonical partition functions of systems of only 1 molecule of 1 and of 0 molecule 2 on one hand and of 0 molecule of 1 and of 1 molecule of 2 on the other.

When the behavior is no longer perfect, the chemical potential must be expressed as a function of the activity of the species and not as a function of the density number as before in order to keep its significance of the tendency of the species to change its thermodynamic state. Finally, *the chemical potential when it is related to the activity of a species, quantifies its tendency to react according to physical or chemical transformations while taking into account its interactions with the other species of the medium.*

The equilibrium constant is expressed as a function of the activities with the help of the following reasoning. The equilibrium condition (36.10) expressed as a function of the absolute activities remains valid. From another standpoint, by definition of the activity z in statistical thermodynamics:

$$\lambda_{\mathrm{A}} = Vz_{\mathrm{A}}/Q_{10} \quad \text{and} \quad \lambda_{\mathrm{B}} = Vz_{\mathrm{B}}/Q_{01}$$

By applying relation (36.10), we immediately obtain:

$$z_{\mathrm{B}}^2 V^2/Q_{01}^2 = z_{\mathrm{A}} V/Q_{10}$$

and since the ratios *Q*/*V* are only function of temperature:

$$K(T) = z_{\mathrm{B}}^2/z_{\mathrm{A}}$$

It can also be written, by taking into account the activity coefficients γ_{B} and γ_{A} (viz. the following chapter):

$$K(T) = \rho_{\mathrm{B}}^2 \gamma_{\mathrm{B}}^2/\rho_{\mathrm{A}}\gamma_{\mathrm{A}}$$

They are given by the expressions (viz. the preceding chapter):

$$z_{\mathrm{A}} = \rho_{\mathrm{A}} - 2b_{02}\rho_{\mathrm{A}}^2 - b_{11}\rho_{\mathrm{B}}\rho_{\mathrm{A}} + \cdots$$

As a result:

$$K(T) = \left(\rho_{\mathrm{B}}^2/\rho_{\mathrm{A}}\right)[1 + (b_{11} - 4b_{20})\rho_{\mathrm{B}} + \cdots]$$

The term in square brackets expresses the deflection with respect to the “ideality.” Actually, we notice that:

$$K(T) = \left(\rho_{\mathrm{B}}^2/\rho_{\mathrm{A}}\right)$$

when ρ_{B} and ρ_{A} tend toward zero.

The definition of the formal, or conditional constant $K'(T)$ used, once the behaviors are no longer ideal, by the expression:

$$K'(T) = \left(\rho_{\mathrm{B}}^2/\rho_{\mathrm{A}}\right)$$

differs from the thermodynamic constant $K(T)$ by the term located between the square brackets. It varies with ρ_{B} and ρ_{A}.

Chapter 37
Activity Coefficients of Gases

Abstract It is evident that the notion of activity coefficient is of utmost importance, because of the fact that expressed in general terms, the activity of a species is equal to its concentration multiplied by its activity coefficient. Given the link between activities and activity coefficients, it clearly happens that a thorough study of the latter ones may lead to a better knowledge of the activities, but, of course, indirectly.

Reasonings mentioned in the chapter show that the activity coefficient of a gas can be expressed in terms of the virial coefficients, parameters which are, in principle, experimentally accessible. They are based on the fact that there exists a well-defined series development linking the activity of a compound and its density (concentration). As a result of this fact, a mathematical expression of the corresponding activity is immediately found.

Keywords Activity coefficients of gases • Activity coefficient on the molecular level • Activity coefficient of a real gas • Gibbs–Duhem relation

It is evident that the notion of activity coefficient is of utmost importance for our purpose, because of the fact that expressed in general terms, the activity of a species is equal to its concentration multiplied by its activity coefficient. A direct study of the activity with the help of considerations of statistical thermodynamics has already been mentioned, here, in the case of the gases. Given the link between activities and activity coefficients, it clearly happens that a thorough study of the latter ones may provide us with a better knowledge of the activities, but this time, of course, indirectly.

We shall see that the activity coefficient of a gas may be expressed in terms of virial coefficients, parameters which are, in principle, experimentally accessible.

37.1 The Activity Coefficient at the Molecular Level

We have already mentioned that two theories somewhat explicit the general significance of an activity coefficient. It seems interesting for us to briefly recall the conclusions they lead to.

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- A first expression of the chemical potential of the component of a system, in statistical thermodynamics, is the relation (37.1) (viz. Chap. 32):

$$\begin{aligned}\exp(-\mu/kT) = \; & \left[q^{N+1}/\Lambda^{3(N+1)}(N+1)!\right] \int v \ldots \int \exp(-\beta U_{N+1}) \\ & \times d\mathbf{R}_0 \ldots d\mathbf{R}_N / q^N / \Lambda^{3N} N! \int v \ldots \int \exp(-\beta U_N) d\mathbf{R}_1 \ldots d\mathbf{R}_N\end{aligned} \tag{37.1}$$

where the zero indice index concerns only one particle added into a very great quantity (in principle an infinity) of other molecules of the system, a process which permits to define the chemical potential. This relation expresses the chemical potential of the compound within the framework of the canonical ensemble (N, T, V). Let us recall that given the symbolism of this expression, the gas chosen in this example possesses an internal structure (occurrence of the parameter q in the expression) and, moreover, that its configuration only needs the knowledge of the location of each particle (vectors $\mathbf{R}$) in order to be specified.

Relation (37.1) is an expression of the chemical potential. It is proved of great use for the study of the activity coefficient notion. It is important to notice that it applies to every fluid.

We have seen that by adopting the hypothesis of the "pairwise additivity", expression (37.1) becomes:

$$\exp(-\mu/kT) = \left[qV/\Lambda^3 N\right] \langle \exp(-B/kT) \rangle \tag{37.2}$$

whence:

$$\mu = kT \ln \rho \Lambda^3 / q - kT \ln \langle \exp(-B/kT) \rangle \tag{37.3}$$

B is given by the expression:

$$B = \sum_j U(\mathbf{R}_0, \mathbf{R}_j) \quad 1 \leq j \leq N$$

B is the sum of interaction energies, from one particle to the other one, between the added particle (particle zero) and all the other constituting the initial system. The factor $\langle \exp(-B/kT) \rangle$ is the average value of the quantity $\exp[-\beta B]$ with ($\beta = 1/kT$).

We have seen that the second term of the right member of (37.3) represents the contribution to the value of the chemical potential of the interactions between molecules and where γ is the activity coefficient, empirically introduced by Lewis in order to take into account the interactions between molecules, is related to the factor B by

$$\gamma \equiv 1/\langle \exp(-B/kT) \rangle \tag{37.4}$$

The relation (37.3) is, like relation (37.1), very significant. It is important to notice that it also applies to every fluid.

- A second expression stemming from Kirkwood's theory (viz. Chap. 32) provides us with an algebraic expression in which intervenes the function $g(R,\xi)$ permitting the calculation of γ:

$$\mu = kT\ln\left(\rho\Lambda^3 q^{-1}\right) - \rho\int_0^1 d\xi\int_0^\infty U(R)g(R,\xi)4\pi R^2 dR$$

The comparison of the latter with (37.3), indeed, leads to:

$$kT\ln\gamma = \rho\int_1^1 d\xi\int_0^\infty U(R)g(R,\xi)4\pi R^2 dR \tag{37.5}$$

The latter relation seems to attribute a meaning to the activity coefficient which is different from that coming from the previous one. Actually, this is not the case since the Kirkwood's theory involves the coupling of a particle with the other ones of the system, i.e., takes into account their mutual interactions.

Both theories stemming from statistical thermodynamics demonstrate that the activity coefficients permit to take into account the interactions between the particles of a system, i.e., finally, the differences of behavior with "ideality." Although these considerations have been developed in Chap. 32 in the case of gases, they are also valid for liquids and solutions.

We shall see (Chaps. 42, 43 and 44) that the Kirkwood–Buff's theory brings some further details concerning the meaning of activity coefficients in the case of mixtures and solutions.

37.2 Expression of the Activity Coefficient of a Real Gas

The relation (34.25) of Chap. 34:

$$z = \rho\ + a_2\rho^2 + a_3\rho^3 + \cdots(\text{relation (34.25)} - \text{Chap. 34})$$

permits to immediately get an expression of the activity coefficient of the gas since $\gamma = z/\rho$, i.e.:[1]

$$\gamma = 1 + a_2\rho + a_3\rho^2\ + \cdots \tag{37.6}$$

According to the study mentioned in Chap. 34, it is evident that the activity coefficient takes into account the interactions between the different molecules of

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[1] The letter γ is used here as being a general symbol of an activity coefficient.

gas *through* the coefficients a_2, $a_3 \ldots a_n$, given the relations existing between the a_n and the coefficients b_j on one hand and those existing between the b_j and the configuration integrals Z_N on the other hand and, finally, owing to the meaning of the latter ones.

We notice that when the density number tends toward zero, the activity coefficient tends toward 1 and the activity value tends toward the corresponding value ρ. It is a familiar result in thermodynamics. However, the form of relation (37.6) is not. It is usual within the framework of thermodynamics, indeed, to handle the activity coefficient under the form of its logarithm, in relation with the chemical potential of the species. The logarithmic expression is found by starting from the two relations just below, of definition of the activity:

$$z = Q_1 \lambda / V \quad \text{and} \quad \gamma \rho = z$$

By identifying both values of z and replacing in the obtained equality the absolute activity by its definition and, finally, taking its logarithm, we obtain:

$$\mu = kT \ln \rho \ + kT \ln \gamma + kT \ln (V/Q_1) \tag{37.7}$$

the following writing of which:

$$\mu = kT \ln (V/Q_1) + kT \ln \gamma \rho$$

is very often encountered in pure thermodynamics.

γ is a function of ρ and of the temperature since the coefficients a_n of the expression (37.6) depend on the configuration integrals. The term V/Q_1, as for it, is only function of the temperature since Q_1 depends on the temperature and is proportional to the volume V.

Evidently, it is interesting to relate the activity coefficient γ to the coefficients B_n of the virial which are parameters in principle experimentally accessible. In order to set up this relation, let us start from the purely thermodynamic one:

$$d(\mu / kT) = v(dp / kT) \tag{37.8}$$

where v is the volume occupied by one molecule of gas. It is convenient to report the volume of one mole into this expression since the chemical potential is a molar property. Relation (37.8) results from:

$$d\mu = v dp$$

This equality, itself, stems from the Gibbs–Duhem's relation:

$$SdT - VdP + \sum_i n_i d\mu_i = 0$$

applying to the case of only one component at constant temperature. V is the molar volume. N_1/V is the density number ρ since $v = 1/\rho$ and by using the mathematical identity:

$$(dp/kT) = [\partial(p/kT)/\partial\rho]dp$$

we obtain:

$$v(dp/kT) = 1/\rho[\partial(p/kT)/\partial\rho]dp \tag{37.9}$$

Therefore:

$$d(\mu/kT) = 1/\rho[\partial(p/kT)/\partial\rho]d\rho \tag{37.10}$$

Using relation (37.10) and the expression of the virial:

$$p/kT = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \cdots \tag{37.11}$$

it is easy to express the function μ/kT. We obtain:

$$d(\mu/kT) = 1/\rho + 2B_2(T) + 3B_3(T)\rho + \cdots$$

i.e.:

$$\mu/kT = \text{integration constant } + \ln\rho + 2B_2\rho \ + 3/2B_3\rho^2 + \cdots \tag{37.12}$$

The comparison of the expressions (37.7) and (37.12) for $\rho \to 0$ shows that the integration constant is:

$$\text{integration constant} = \ln(V/Q_1)$$

and that:

$$\ln\gamma = 2B_2\rho \ + 3/2B_3\rho^2 + \cdots$$

or, equivalently, by using a recurrence formula (where k is an indice):

$$\ln\gamma = -\sum_{k\geq 1}\beta_k(T)\rho^k \tag{37.13}$$

β_k is an intermediary parameter defined by:

$$\beta_k = -[(k+1)\ /k]B_{k+1} \tag{37.14}$$

In principle, ln γ can be, therefore, expressed and calculated through the expansion in series (37.14), as a function of the virial coefficients B_{k+1}.

Chapter 38
Activities and Concentrations of Nonelectrolytes in Dilute Liquid Solutions Study of the Osmotic Pressure

Abstract The chapter mentions the study of the osmotic pressure of dilute liquid solutions of nonelectrolytes. The study is performed within the framework of the grand ensemble. Through a reasoning analogous to that followed for the study of the activities of gases, a mathematical relation between the activity of the solute and its density number is set up in the case of a binary solution solute–solvent. It is valid for dilute solutions. In its expression intervene parameters related to the virial coefficients, so-called coefficients of the osmotic pressure virial. The theory is due to McMillan–Mayer. It entails the introduction of a new activity coefficient. The developments constituting the theory take into account not only the interactions solute–solute but also the solute–solvent ones and those exerting between solvent molecules.

The reasoning developed here constitutes a model for that followed later devoted to the study of solutions at constant temperature and pressure.

Keywords Activities and concentrations (nonelectrolytes dilute solutions) • Osmotic pressure • Solute activity • McMillan–Mayer's theory • Osmotic activity coefficient • Osmotic equilibrium • Osmotic pressure (new activity type) • Fundamental aspects of McMillan–Mayer's theory • Grand ensemble

Here, we study the osmotic pressure of dilute liquid solutions of nonelectrolytes. This study is performed within the framework of the grand ensemble. Through a reasoning analogous to that followed for the study of the activities of gases, we set up a mathematical relation between the activity of the solute and its density number in the case of a binary solution solute–solvent. It is valid for dilute solutions. In its expression intervene parameters related to the virial coefficients so-called coefficients of the osmotic pressure virial. The theory is due to McMillan–Mayer. It entails the introduction of a new activity coefficient. The developments constituting the theory take into account not only the interactions solute–solute but also the solute–solvent ones and those exerting between solvent molecules.

The reasoning developed here constitutes a model for that followed later devoted to the study of solutions at constant temperature and pressure.

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38.1 The Main Difference Between the Cases of a Mixture of Real Gases and of Solutions

It is evident that even in the extremal case of a highly dilute solution, the interactions between the solute and the solvent still remain. It is not the case for a mixture of real gases, the density numbers of which are very weak. In this case, there remains no longer interactions between the gas particles. Then, their chemical potential only depends on their density number and on the temperature. Gases are, then, ideal.

In the present case, even when the solution is very dilute, three types of interactions must be still considered, the interactions solute–solute (which tend to vanish, when the solutions are all the more diluted), the solute–solvent and the solvent–solvent ones.

38.2 Osmotic Equilibrium

Figure 8.3 (viz. Chap. 8) shows the studied osmotic equilibrium. The compartment called the "outside compartment" contains the pure solvent 1 the chemical potential of which is μ_1 and its temperature is T. The values μ_1 and T fix its pressure p. The "inside compartment" is also at the temperature T. Initially, before any addition of solute, it is at the same pressure p as the "outside compartment" and the chemical potential of the solvent is also μ_1. Both compartments are separated by a membrane through which the solvent (and only the solvent) can permeate. We know that the addition of the solute 2 into the "inside compartment" increases its pressure which takes the value $p+\pi$, π varying with the concentration of the solute in the compartment. π is the osmotic pressure of the solution. Actually, adding solute 2 changes the chemical potential of solvent 1 in the "inside compartment." However, at the equilibrium concerning the solvent, its chemical potential must be the same in both compartments since it can freely move between both phases. The equilibrium is restored by a change of the pressure exerting on the "inside compartment." In order to reach it, an extra pressure, equal to the osmotic pressure, must be applied on it.

38.3 Some Results Stemming from the McMillan–Mayer's Theory

In brief, the McMillan–Mayer's theory leads to the following results:

- The expression just below which gives the osmotic pressure of a binary solution (solute–solvent) is:

$$\pi/kT = \rho_2 + B_2{*}(T, \lambda_1)\rho_2{}^2 + B_3{*}(T, \lambda_1)\rho_2{}^3 + \cdots \tag{38.1}$$

π is the osmotic pressure, λ_1 the absolute activity of the solvent, ρ_2 the number density of the solute, $B_2{}^*(T,\ \lambda_1)$, $B_3{}^*(T,\ \lambda_1)$, … the coefficients of the series development called the virial coefficients of the virial of the osmotic pressure. Hence, the McMillan–Mayer's theory expresses the osmotic pressure as a function of the density number ρ_2 of the solute.

Expression (38.1) shows a great formal analogy with the series development expressing the pressure of a real gas:

$$p/kT = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \cdots$$

However, there exists a very significant difference between the coefficients B_j^* $(T,\ \lambda_1)$ and $B_j(T)$. The former ones depend on both temperature and absolute activity absolute of the solvent, whereas the latter ones only depend on temperature.

- The theory also leads to the definition of a new type of activity δ_2. It is related to the density number ρ_2 by a relation of the type:

$$\delta_2 = \rho_2 + m_2\rho_2{}^2 + m_3\rho_2{}^3 + \cdots \tag{38.2}$$

This relation only applies to the sufficiently dilute solutions. It is analogous to that obtained in the case of the activity of a gas (viz. Chap. 34):

$$z = a_1\rho + a_2\rho^2 + a_3\rho^3 + \cdots$$

In the expression (38.2), the coefficients m_2, m_3 are given by the expressions:

$$m_2 \equiv -2b_2, \quad m_3 \equiv 8b^2 - 3b_3, \quad \ldots$$

where the b_i are related to the coefficients B_j of the virial. We must notice that the coefficients m_2, m_3, …m_j.… depend only on the coefficients b_i where i cannot be larger than j. Hence, we find:

$$\delta_2 = \rho_2 + (-2b_2)\rho_2{}^2 + (8b_2 - 3b_3)\rho_2{}^3 + \cdots$$

The obtained expressions permit to explicit the activity coefficients and, hence, the activities in terms of statistical thermodynamics.

38.4 Fundamental Aspects of the McMillan–Mayer's

The McMillan–Mayer's theory shows that as in the case of the coefficients $B_j(T)$ of real gases, those $B_j^*(T, \lambda_1)$ exhibit the interactions between each other of j particles of solute (immersed in the solvent). For the successive values (2, 3, …) of the indices j of the coefficients $B_j^{\,*}(T, \lambda_1)$, they respectively are the interactions between $2, 3, j, \ldots$ particles of solute.

Another essential feature characterizing the McMillan–Mayer's theory is that the solvent 1 is considered as being a continuous medium of absolute activity λ_1. Regarding the solvent as being a continuous medium of constant absolute activity constitutes an approximate consideration of the interactions solvent–solvent. Owing to this fact, this theory is considered as being a theory of solutions at the first level. (Another example of theory of the first same level is that of Debye–Hückel—viz. Chap. 46. There exist more elaborate theories than the latter ones which take into account more realistic models of the interactions solvent–solvent.)

38.5 Some Features of the McMillan–Mayer' Theory

- The species which are considered in the study can be monoatomic or polyatomic ones as well. The reasoning at the base of the theory is analogous to that treating the case of real gases. It is described in the Appendices L, M, and N.
- It is founded on the handling of the grand canonical partition function. *In order to obtain the relation being searched for, we proceed to a series expansion of the partition function as a function of the solute activity*. The handled partition function is given by the expression (viz. Chap. 35):

$$\Xi(T, V, \lambda_1, \lambda_2) = \sum_{N1 \geq 0} \sum_{N2 \geq 0} Q(T, V, N_1, N_2) \lambda_1^{N1} \lambda_1^{N2} \tag{38.3}$$

where $Q(T, V, N_1, N_2)$ are the canonical partition functions corresponding to all the possible arrangements of the number of solvent molecules N_1 and of solute N_2, evidently variable since the study is located within the framework of the grand ensemble.

- The osmotic pressure π is introduced through the relation characteristic of the great ensemble:

  $$\Xi = \mathrm{e}^{PV/kT}$$

  P and V being the pressure and the volume of the system. In this expression, P is the total pressure exerting on the inside compartment, once the osmotic equilibrium is reached:

  $$P = p + \pi$$

p being the pressure over the outside compartment. Moreover let us recall that this equality is valid only for the solutions sufficiently dilute (viz. Chaps. 8, 13 and 14). This entails that this theory only applies to this type of solutions.

- The reasoning leading to the relations being searched for, notably, introduces the following ratio Ψ_1/Ψ_o. Ψ_1 and Ψ_o are canonical partition functions constituting (with others) the grand canonical ensemble. They are the starting-points of the theory (see Appendices L and M). As we shall see (see Appendix L), the ratio Ψ_1/Ψ_o appears as being the mark of the interaction energy of one solute molecule with the pure solvent. The occurrence of the ratio Ψ_1/Ψ_o in the calculations below permits to specify the physical meaning of the new kind of activity δ_2 (see below).
- The reasoning also uses the statistical activities z_1 and z_2 of the solute and the solvent as in the case of gases. From the standpoint of their definitions, they exactly correspond to the general one introduced by Lewis which is from purely thermodynamic origin, i.e.:

$$z_1 \rightarrow \rho_1 \quad \text{where} \quad \rho_1 \rightarrow 0 \tag{38.4}$$

$$z_2 \rightarrow \rho_2 \quad \rho_2 \rightarrow 0 \tag{38.5}$$

In statistical thermodynamics, they are expressed by the relations (38.6):

$$z_1 = Q_{10}\lambda_1/V \quad \text{and} \quad z_2 = Q_{01}\lambda_2/V \tag{38.6}$$

Q_{10} Q_{01} are the canonical partition functions of the system only containing respectively one molecule of solvent and no molecule of solute on one hand and the converse on the other. λ_1 and λ_2 are the absolute activities of both components and V is the volume of the system.

- Performing it according to the same process as that followed in the case of real gases, however, entails the introduction of new parameters. One of them δ_2 proves to be a new kind of activity and another, $\gamma_2{}^{\circ}$, to be a new activity coefficient.

*The activity of a new type δ_2 of the solute has the properties to be proportional to z_2 and to tend toward ρ_2 when ρ_2 tends toward zero, since μ_1 and T are fixed in the bulk solution by the conditions of the osmotic equilibrium. Hence, the activity δ_2 is defined as follows:

$$\delta_2 \propto z_2 \quad \text{and} \quad \delta_2 \rightarrow \rho_2 \quad \text{where} \quad \rho_2 \rightarrow 0 \tag{38.7}$$

The part played by the new activity δ_2 is to take into account the interaction between a molecule of solute and the whole of solvent molecules (viz. Fig. 38.1).

The theory also introduces the term $\gamma_2{}^0$, which has the meaning of an activity coefficient. Actually, z_2 does not tend toward ρ_2 when ρ_2 tends toward zero as in the case of a real gas, but toward the value of the term $\gamma_2{}^0\rho_2$. This is due to the fact that, in this case, the activity z_2 must take into account the *interaction solute–solvent* when $\rho_2 \rightarrow 0$. This possibility, of course, does not exist in the case of gases. We can symbolize this behavior by:

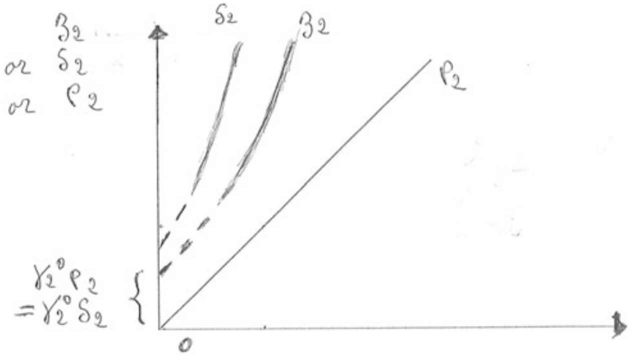

Fig. 38.1 Relations between the activities z_2, δ_2, and ρ_2

$$z_2 \rightarrow \gamma_2{}^0\rho_2 \quad \rho_2 \rightarrow 0 \tag{38.8}$$

We have mentioned that, according to the manner through which it has been introduced, $\delta_2 \rightarrow \rho_2$ when $\rho_2 \rightarrow 0$, as the Lewis' definition of an activity demands it. Hence, this property is sufficient to attribute the meaning of an activity to $\delta_{2,}$ at least in part..

Since by virtue of (38.7) $\delta_2 \rightarrow \rho_2$ when $\rho_2 \rightarrow 0$, it is judicious to immediately assert that:

$$z_2 \rightarrow \gamma_2{}^0\delta_2 \quad \rho_2 \rightarrow 0 \tag{38.9}$$

where $\gamma_2{}^0$ is a constant at a given temperature. According to what is described previously concerning the activity coefficients, we can already anticipate the fact that $\gamma_2{}^\circ$ is the limit value (obtained for an infinite dilution of the solute) of its activity coefficient γ_2, defined as every activity coefficient by the expression:

$$z_2 = \gamma_2\rho_2 \tag{38.10}$$

According to the relations (38.6) and (38.9), we obtain:

$$Q_{01}\lambda_2/V = \gamma_2{}^\circ\delta_2 \tag{38.11}$$

In the Appendix O, we mention that the activity δ_2 may also be defined by the following expression, equivalent to the preceding:

$$\delta_2 = \lambda_2\Psi_1/\Psi_{\mathrm{o}}V$$

This definition permits to introduce the constant $\gamma_2{}^\circ$ in terms of the statistical functions Ψ_1 *and* Ψ_{o}. According to (38.11) and the latter definition, one, indeed, deduces:

$$\gamma_2{}^{\circ} = Q_{01}\Psi_{\mathrm{o}}/\Psi_1$$

According to the meaning of the functions Ψ_{o} and Ψ_1 (see Appendix N), not only $\gamma_2{}^{\circ}$ characterizes the solute, but also depends on the chemical potential of the solvent μ_1 which is constant in the case of the osmotic equilibrium. Moreover, $\gamma_2{}^0$ does possess a finite value. $\gamma_2{}^{\circ}$ depends on the properties of one molecule of solute in vacuum *through* Q_{01}.$\gamma_2{}^{\circ}$ also depends on the nature of the interaction between the molecule and the solvent.

According to the relation (38.11), we find:

$$\delta_2 = Q_{01}\lambda_2/\gamma_2{}^{\circ}V \tag{38.12}$$

The comparison of the expressions (38.6) of z_2 and (38.12) of δ_2 permits to better grasp the meaning of these quantities. Let us recall that Q_{01} defines the behavior of the compound 2 in vacuum, because of its statistical definition. The ratio $Q_{01}/\gamma_2{}^{\circ}$ may be defined as describing the behavior of 2 in the solvent 1. *It plays the part of an actual partition function for one molecule 2 in the volume V filled by the solvent 1, the chemical potential of which is* μ_1 *at the temperature T*. Therefore, we may regard δ_2 as playing the part of an activity z_2 adapted to the experimental conditions under study.

- Another thermodynamic meaning of the constant $\gamma_2{}^0$
  The constant $\gamma_2{}^0$ is also endowed with another thermodynamic meaning, different from that mentioned above, at first glance. The term 1 /$\gamma_2{}^0$, indeed, is nothing else than the constant of the following equilibrium:

$$\text{solute in a gas} \rightleftharpoons \text{solute in solution}$$

This result is obtained by considering the ratio:

density number of the compound in infinite dilute solution/density number of the compound in gaseous infinite dilute phase

It is simply the ratio δ_2/z_2 since, in these dilution conditions, the activities are equal to the density numbers. By replacing δ_2 and z_2 by their expressions (38.12) and (38.5), we obtain:

$$\delta_2/z_2 = \left(Q_{01}\lambda_2/V\gamma_2{}^0\right)/Q_{01}\lambda_2/V$$

i.e.:

$$\delta_2/z_2 = \left(Q_{01}/V\gamma_2{}^0\right)/Q_{01}/V$$

Let us symbolize this ratio by *K*. Hence, we have:

$$K = 1/\gamma_2{}^0$$

K is the constant of the above equilibrium. The numerical value $\gamma_2{}^0$ depends on the affinity of one solute molecule for those of the solvent. This is in agreement with the preceding result which proved that the numerical value $\gamma_2{}^0$ depends on the affinity of one molecule of solute for those of solvent.

38.6 Obtaining the Relations (38.1) and (38.2)

The problem is to express the osmotic pressure as a function of the number density ρ_2 of the solute. The obtained expression permits to clarify the meaning of the activity coefficients and hence the activities in terms of statistical thermodynamics. As we have already mentioned it, the followed reasoning is analogous to that applied to the case of imperfect gases.

The starting point of the reasoning is the partition function of the grand ensemble $\Xi(T, V, \lambda_1, \lambda_2)$. It is given by the expression (viz. Chap. 35):

$$\Xi(T,V,\lambda_1,\lambda_2) = \sum_{N1\geq 0}\sum_{N2\geq 0} Q(T,V,N_1,N_2)\lambda_1{}^{N1}\lambda_2{}^{N2} \tag{38.13}$$

where $Q(T, V, N_1, N_2)$ are the canonical partition functions corresponding to all the possible arrangements of the numbers of moles N_1 and N_2, evidently changing, since the study is performed within the framework of the grand ensemble. Given the very general fact that,

$$\Xi(T,V,\lambda_1,\lambda_2) \;=\; \mathrm{e}^{PV/kT} \tag{38.14}$$

p and V being the pressure and the volume of the system, the general process is the following. It consists in:

- Introducing the pressure (including or not the osmotic one) present on the system into the exponential of the right term of the relation (38.14).
- Expanding in series the partition function Ξ as a function of the solute activity
- Equalizing both members

  Proceeding in such away permits to (somewhat arbitrarily) distinguish two steps.
- The first step consists in obtaining the relation:

$$\exp(\pi V/kT) = \;1\; + \sum_{N\geq 1}\left[Z_N{}^*(\mu_1,V,T)/N!\right]\delta_2{}^N \tag{38.15}$$

where π is the osmotic pressure. The analogy with the following relation concerning an imperfect gas is quasi-perfect (viz. Chap. 34).

- The second step consists in expanding in series the right member of (38.15) after having set it up under the logarithmic form. The course of the process is quite analogous to that followed in the case of real gases (viz. Chap. 34). We obtain, by limiting ourselves to the term of order 2:

$$\Pi/kT = \left(Z_1{}^*/V\right)\delta_2 + 1/2V\left(Z_2{}^* - Z_1{}^{*2}\right)\delta_2{}^2 + \cdots$$

Setting up:

$$b_1 = Z_1{}^*/V, \ \ b_2 = 1/2V\left(Z_2{}^* - Z_1{}^*\right), \quad \ldots$$

we obtain:

$$\Pi/kT = \sum_{j\geq 1} b_j \delta_2^j \tag{38.16}$$

Let us notice that the coefficients b_j depend on μ_1 and T.

Concerning the obtaining of the expression relating the osmotic pressure π to the density number ρ_2 entails to express ρ_2 as a function of δ_2. Such a function is obtained by using the following relation resulting from the properties of the grand canonical ensemble:

$$\overline{N_2} = kT(\partial \ln \Xi / \partial \mu_2)_{v,T}$$

Chapter 39
Relation(s) Activity: Concentration of Nonelectrolytes in Dilute Liquid Solutions at Constant Pressure and Temperature

Abstract This chapter remains devoted to the study of dilute solutions of nonelectrolytes. It is limited to the study of binary solutions. It exhibits very great analogies with the previous one. What is mentioned here regards solutions at constant temperature and pressure in which the changing composition of the solute is expressed in molalities. The molality scale is that which is the most often used in physical chemistry in order to express the "concentration" of a solute. The goal of the study is to obtain a relation between the molality of the solute and its activity. The mentioned developments are based on a new ensemble, the Γ one depending on the independent variables which are the density number of the solvent, the pressure, the temperature, and the chemical potential of the solute. The activity of the solute is now defined in terms of its absolute activity and also in terms of two characteristic functions of the isothermal isobaric ensemble. These functions take into account the interactions between the solute and the solvent. The so-defined activity exhibits the same properties as the Lewis' one. It is linked to its molality by a well-defined series development.

Keywords Activities and concentrations of nonelectrolytes (dilute solutions at constant temperature and pressure) • Molalities scale • Gamma ensemble • Isothermal isobaric ensemble • Statistical definition of an activity (at constant temperature and pressure) • Activities molalities relations

This chapter is also devoted to the study of dilute solutions of nonelectrolytes. We confine ourselves to the study of binary solutions. It shows very great analogies with the previous one. What is mentioned here regards solutions at constant temperature and pressure in which the changing composition of the solute is expressed in molalities. The molality scale is that which is the most often used in physical chemistry in order to express the "concentration" of a solute. The goal of the study is to obtain a relation between the molality of the solute and its activity.

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39.1 The Studied Physical Process

The study of the dilute solutions at constant pressure and temperature differs from the preceding one by the fact that the pressure is constant whereas it was not in the preceding case. The consequence was the advent of the osmotic pressure. In the present case, the initial state is constituted by the pure solvent (N_1 molecules) at constant temperature and pressure.

N_2 molecules of solute are then added to the solution while keeping constant these values. As a result, for the equilibrium to be maintained, the chemical potential of the solvent μ_1 varies with the number of solute molecules added.

39.2 Study

In this chapter we follow the theory of T.L. Hill (viz. bibliography).

39.2.1 Formalism

From the statistical thermodynamics standpoint, the most appropriate ensemble for the study of this problem is the ensemble Γ depending on the independent variables N_1, p, T, μ_2 defined by the expression:

$$-\ln\Gamma(N_1, p, T, \mu_2) = N_1\mu_1/kT \tag{39.1}$$

of which the characteristic function is $N_1\mu_1/kT$ or G_1. G_1 is the Gibbs energy of the component 1 (solvent) in the system. Γ is given by the expression:

$$\Gamma(N_1, p, T, \mu_2) = \sum_{N2\geq 0} \Delta N_2(N_1, p, T)\exp[N_2\mu_2/kT] \tag{39.2}$$

where

$$\Delta N_2 = \sum_V Q(N_1, N_2, V, T)\mathrm{e}^{-pV\ /kT} \tag{39.3}$$

The function ΔN_2 is the function $\Delta(p, T, N)$ already encountered (cf. Chap. 24). Its expression is:

$$
\begin{aligned}
\Delta N_2 = & \, Q(N_1, 0, V_1, T)\mathrm{e}^{-pV1/kT} \quad (N_2 = 0) \\
& + Q(N_1, 0, V_2, T)\mathrm{e}^{-pV2/kT} \quad (N_2 = 0) \\
& + \cdots \\
& + Q(N_1, 1, V_1, T)\mathrm{e}^{-pV1/kT} \quad (N_2 = 1) \\
& + Q(N_1, 1, V_2, T)\mathrm{e}^{-pV2/kT} \quad (N_2 = 1) \\
& + \cdots
\end{aligned}
$$

i.e., by setting up for:

$$
\begin{array}{ll}
N_2 = 0 & \sum_V Q(N_1, 0, V, T) = \Delta_0 \\
N_2 = 1 & \sum_V Q(N_1, 1, V, T) = \Delta_1 \\
\cdots & \cdots
\end{array}
\tag{39.4}
$$

and since $\lambda_2 = \mathrm{e}^{-pV/kT}$, we obtain:

$$
\Gamma = \Delta_0 + \Delta_1\lambda_2 + \Delta_2\lambda_2^2 + \Delta_3\lambda_2^3 + \cdots \tag{39.5}
$$

39.2.2 Definition of the Activity

Let us define the activity a_2 of the solute as being related to its absolute activity λ_2 by the expression (39.6). (Notice that the symbolism is no longer z but a. In principle, according to IUPAC, the accurate symbolism should be a_m in order to express the fact that the activity is related to the molality through Henry's law):

$$
a_2 = \lambda_2(\Delta_1/\Delta_0 N_1) \tag{39.6}
$$

Let us notice that the term $\Delta_1/\Delta_0 N_1$ takes into account the interactions between one solute molecule with the N_1 molecules of solvent.

By definition, according to Lewis, the activity a_2 tends toward the molality m_2 when the latter tends toward zero:

$$
a_2 \to m_2 \quad \text{when} \quad m_2 \to 0 \tag{39.7}
$$

Let us recall (cf. Chap. 1) that the molality m_2 is related to the number of moles N_2 by the expression:

$$
m_2 = N_2 1000/N_1 M_1
$$

where M_1 is the molar mass of the solvent expressed in g mol^{-1}. The system being open to the compound 2, we must consider the average number of moles of compound 2, i.e., $\overline{N_2}$, and write:

$$m_2 = \overline{N_2}\,1000/N_1M_1$$

For the sake of simplifying the above writing, let us assert that from now on:

$$m_2 = \overline{N_2}/N_1$$

being understood that this is true although the proportionality constant 1000/M_1 is neglected. The accuracy of the reasoning, however, is not affected by this simplification. It is already interesting to notice that with this convention on the molality, the latter slightly differs from the molar fraction x_2:

$$m_2 \approx x_2$$

because only dilute solutions are considered here and then:

$$N_2 \ll N_1$$

39.2.3 Calculations

Let us replace the absolute activity λ_2 by the relative one a_2 in (39.5). We obtain:

$$\Gamma = \Delta_0 + \Delta_1(\Delta_0N_1/\Delta_1)a_2 + \Delta_2(\Delta_0N_1/\Delta_1)^2a_2^2 + \Delta_3(\Delta_0N_1/\Delta_1)^3a_2^3 \quad \cdots$$

or after rearrangement:

$$\Gamma/\Delta_0 = 1 + \Delta_1(N_1/\Delta_1)a_2 + \Delta_2(N_1/\Delta_1)^2\Delta_0a_2^2 + \Delta_3(N_1/\Delta_1)^3\Delta_0^2a_2^3 \quad \cdots \tag{39.8}$$

Inserting the intermediary variable X_N such as:

$$X_N = \Delta_NN_1^N\Delta_0^{N-1}N!/\Delta_1^N$$

The expression (39.8) becomes:

$$\Gamma/\Delta_0 = 1 + \sum_{N\geq1}(X_N/N!)a_2^N \tag{39.9}$$

Let us remark in passing that:

$$X_1 = N_1$$

The relation (39.9) exhibits a very great similarity with, respectively, the relations (34.13) and (38.18) of the Chaps. 34 and 38. This justifies the great similarity of the theoretical treatments according to the respective cases.

What is differing slightly from the two other cases is the following change of variable. In order to find the relation between the molality of the solute and its activity in these conditions, let us begin by noticing that according to relations (39.1) and (39.4), we find:

$$N_1\mu_1(p, T, 0) = -kT\ln\Delta_0$$

$\mu_1(p, T, 0)$ being the chemical potential of the pure solvent. It is interesting, as it is proved by the following reasoning, to relate the chemical potential of the solvent, which changes by addition of the solute 2 and which is expressed in terms of molalities, to the activity a_2 of the latter. Let us set up the relation (39.10) by introducing the Gibbs energy $\mu_1{}'(T, \mathbf{p}, m_2)$:

$$\mu_1{}'(T,\ \mathbf{p},\ m_2) = \mu_1(\mathbf{p}, T, m_2) - \mu_1(p, T, 0) \tag{39.10}$$

$\mu_1{}'(T, \mathbf{p}, m_2)$ is the change in the Gibbs energy of the solvent accompanying the addition of the solute 2 at the molality m_2 to itself, pure. The introduction of the factor $\mu_1{}'$ facilitates the handling of the expressions. The value of the chemical potential of a species, of course, does not depend on the fact that it is expressed as a function of its activity or of its molality, molarity and so forth. The relation (39.10) can also be written:

$$\mu_1{}'(T, \mathbf{p}, a_2) = \mu_1(\mathbf{p}, T, a_2) + (kT/N_1)\ln\Delta_0$$

and since:

$$\Gamma(N_1, p, T, \mu_2) = \mathrm{e}^{-N1\mu1/kT}$$

$$\mu_1/kT = -\ln\Gamma/N_1$$

we deduce from that:

$$-\mu_1{}'(T, \mathbf{p}, a_2)/kT = (1/N_1)\ln(\Gamma/\Delta_0) \tag{39.11}$$

From the standpoint of the pure reasoning, the significant point is that we can handle the relation (39.9) exactly as we have already done in the case of relations (34.13) and (34.14) of Chap. 34.

$$\overline{N} = \lambda(\partial \mathrm{In}\, \Xi/\partial\lambda)_{V,T} \quad \text{(relation (34.22) Chap. 34)}$$

$$\Xi = 1 + \sum_{N\geq 1}(Z_N/N!)z^N \quad \text{(relation (34.13) Chap. 34)}$$

$$\ln \Xi = \ln\left[1 + \sum_{N\geq 1}(Z_N/N!)z^N\right] \quad \text{(relation (34.14) Chap. 34)}$$

which applied to the case of imperfect gases and as we have done with the relation (38.15) of the Chap. 38 devoted to the osmotic pressure:

$$\exp(\pi V/kT) = 1 + \sum_{N\geq 1}\left[Z_N^*(\mu_1, V, T)/N!\right]\delta_2^N \quad \text{(relation (38.15), Chap. 38)}$$

Taking into account relations (39.9) and (39.11), we obtain:

$$\ln(\Gamma/\Delta_0) = \ln\left[1 + X_1 a_2 + (X_2/2\,!)a_2^2 + (X_3/3\,!)a_2^3 + \cdots\right]$$

and by expanding in series the logarithm, there comes the relation:

$$\begin{aligned}\ln(\Gamma/\Delta_0) = {} & \big[X_1 a_2 + (X_2/2!)a_2^2 + (X_3/3!)a_2^3 + \cdots \\ & - 1/2\big[X_1 a_2 + (X_2/2!)a_2^2 + (X_3/3!)a_2^3 + \cdots\big]^2\end{aligned} \tag{39.12}$$

Let us set up:

$$-\mu_1{}'(T, \mathbf{p}, a_2)/kT = \sum_{j\geq 1}\vartheta_j(\mathbf{p}, T)a_2^j \tag{39.13}$$

The identification of the expansion in series (39.12) with (39.13) leads to the identities:

$$\begin{aligned}&N_1\vartheta_1 = X_1 = N_1 \qquad (\vartheta_1 = 1)\\ &2!N_1\vartheta_2 = X_2 - X_1^2\\ &3!N_1\vartheta_3 = X_3 - 3X_1X_2 + 2X_1^3\\ &\cdots\end{aligned}$$

The relations between the molality m_2 and the activity a_2 is found with the aid of the Gibbs–Duhem relation applied at constant temperature and pressure.

We must, now, successively relate the molality m_2 to the activity a_2 and then, inversely, to relate the activity a_2 to the molality m_2. According to the Gibbs–Duhem relation at constant temperature and pressure:

$$N_1 d\mu_1 + \overline{N_2}\, d\mu_2 \ = \ 0$$

According to (39.10):

$$d\mu_1{}' \ = \ d\mu_1$$

Since the term $(kT/N_1)\ln \Delta_0$ is constant, hence:

$$\begin{aligned}
&N_1 d\mu_1{}' + \overline{N_2} d\mu_2 = 0 \\
&d\mu_1{}' + \left(\overline{N_2}/N_1\right) d\mu_2 = 0 \\
&d\mu_1{}' + m_2 d\mu_2 = 0 \\
&-d\mu_1{}' = m_2 d\mu_2 \\
&-\partial\mu_1{}'/\partial a_2 = m_2(\partial\mu_2/\partial a_2)
\end{aligned} \tag{39.14}$$

and, since very generally

$$\mu_2 \ = \ \mu_2{}^\circ \ + \ kT\ln a_2$$

whence:

$$\begin{aligned}
d\mu_2/da_2 \ &= \ kT(d\ln a_2/da_2) \\
d\mu_2/da_2 \ &= \ kT/a_2
\end{aligned}$$

We obtain:

$$a_2[\partial(-\mu_1{}'/kT)/\partial a_2]_{T,p} \ = \ m_2$$

Finally, according to (39.13) and the latter relation:

$$m_2(p, T, a_2) = \sum_{j\geq 1} j\vartheta_j(p, T)\, a_2^j$$

In order to determine the relation a_2 as a function of m_2, let us set up:

$$a_2 \ = \ r_0 m_2 \ + r_1 m_2^2 + r_2 m_2^3 + \cdots$$

39.3 Relation Being Searched for

Let us identify the two latter relations. We find, given the fact that $\vartheta_1 = 1$,

$$r_0 \equiv 1, \quad r_2 \equiv -2\vartheta_2, \quad r_3 \equiv \left(8\vartheta_2^2 - 3\vartheta_3\right)$$

and

$$a_2 = m_2 - 2\vartheta_2 m_2^2 + \left(8\vartheta_2^2 - 3\vartheta_3\right)m_2^3 \ldots$$

This is the relation between the solute activity and its molality being searched for. Let us recall that it is established for constant temperature and pressure and that the molality appearing in this expression is not equal to the usual molality. There is a multiplicative term between them. As a result, the adopted standard state in this case is not the usual one.

Remark: One also demonstrates (viz. Appendix O) that the logarithm of the ratio $\Delta_N {\Delta_0}^{N-1}/{\Delta_1}^N$ intervening in the term X_N does possess the physical meaning of the Gibbs energy change accompanying the following process:

$$\begin{aligned} &N\,\text{systems}\ \ (N_1, N_2 = 1, p, T) \rightarrow 1\,\text{system}\ \ (N_1, N_2 = N, p, T) \\ &\quad + (N-1)\ \ \text{systems}\ \ (N_1, N_2 = 0, p, T) \end{aligned}$$

the $N-1$ systems being constituted by the pure solvent.

Chapter 40
Activity Coefficient of a Solute

Abstract The chapter mentions the relations which on one hand link the activity and the concentration of the solute in the conditions in which an osmotic pressure is developing and, on the other one, when the solution is maintained at constant temperature and pressure. In other words, the activity coefficients are focused. It is known that the activity coefficients of the imperfect gases can be theoretically related to the virial coefficients (changing with the nature of the gas) which are purely experimental parameters. For very weak density numbers of the gases, this result is very interesting since it permits, at least in principle, to forecast the changes in the value of the activity coefficient and therefore in the changes of the activity when the density number vary, while, however, keeping a weak value.

Given the fact that the preceding theories, devoted to the osmotic pressure and to the solutions at constant pressure and temperatures, are very close to that applied to the real gases, it is not surprising that it is possible to theoretically relate the activity coefficients of the nonelectrolyte solutes to some experimental parameters. The reasonings involve the introduction of a new kind of activity applying to the osmotic equilibrium. The chapter mentions these relations and their setting up.

Keywords Activity coefficient (solute) • Osmotic pressure • Osmotic equilibrium • New kind of activity coefficient of a solute (when osmotic pressure is developing) • Activity coefficients in relation with the concentrations and the virial coefficients • Relations between activities and molalities

In this chapter, we give the relations between activity and concentration of the solute, on one hand, in the conditions in which an osmotic pressure is developing and, on the other one, when the solution is maintained at constant temperature and pressure. In other words, we focus ourselves on the activity coefficients. We know that the activity coefficients of the imperfect gases can be theoretically related to the virial coefficients (changing with the nature of the gas) which are purely experimental parameters. For very weak density numbers, this result is very interesting since it permits to forecast the changes in the value of the activity coefficient and therefore in the changes of the activity when the density number vary, while, however, keeping a weak value.

Given the fact that the preceding theories, devoted to the osmotic pressure and to the solutions at constant pressure and temperatures, are very close to that applied to

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the real gases, it is not surprising that it is possible to theoretically relate the activity coefficients of the nonelectrolyte solutes to some experimental parameters. It is the goal of this chapter to give these relations.

40.1 Expression of the Activity Coefficient of the Solute in Terms of Experimental Parameters When an Osmotic Pressure is Developing

Let us recall (viz. Chap. 38) that it is judicious to introduce the new type of activity δ_2 in this case. We have demonstrated that it is related to the density number ρ_2 by the following relation:

$$\delta_2 = \rho_2 + m_2\rho_2^2 + m_3\rho_2^3 + \cdots \tag{40.1}$$

The coefficients m_2, m_3 are given by the expressions:

$$m_2 \equiv -2b_2, m_3 \equiv 8b^2 - 3b_3, \quad \ldots$$

It must be noticed that the coefficients m_2, m_3, …, m_j…only depend on the coefficients b_i where i cannot be larger than j. Hence, we find:

$$\delta_2 = \rho_2 + (-2b_2)\rho_2^2 + (8b_2 - 3b_3)\rho_2^3 + \cdots$$

The coefficients b_i themselves are related to the configuration integrals Z_N^{*}· adapted to the studied case. The latter ones, here in the case where N molecules of solute are dissolved in the solvent, play the same formal part as the one played by the integrals Z_N in the case of N molecules of gas in vacuum (Appendix N). The coefficients b_j, here, are related to the integrals Z_N^{*}·by the same expressions as those found in the case of an imperfect gas (viz. Chap. 34).

It is evident that relation (40.1) is an expression of the activity coefficient γ_2 defined by the relation $\gamma_2 = \delta_2/\rho_2$.[1]

Using two thermodynamic relations, one classical and the other statistical, permits to explicit this expression of the activity coefficient of the solute.

The first results from the Gibbs–Duhem's relation. It permits to obtain a first expression of the chemical potential of the solute. The second expression permits to express the same chemical potential by starting from its absolute activity. The comparison of both expressions leads to the relation being searched for.

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[1] In order to be as general as possible, we symbolize an activity coefficient by γ without deserving any attention, for the moment, to the unity to which the solute concentration is related.

- The Gibbs–Duhem's relation can be written for a binary solution (viz. Chap. 5):

$$n_1 d\mu_1 + n_2 d\mu_2 = -SdT + Vd\mathbf{p}$$

where S is the entropy of the system and P its total pressure ($P = p + \pi$). In the present case of the osmotic equilibrium, i.e., at constant $\mu_{1,}$ p, and T, it becomes:

$$n_2 d\mu_2 = Vd\pi$$

Let us divide both members of this equality by the product kT in order to later introduce the series expansion of the function π/kT into the following calculations. We obtain:

$$\begin{aligned} n_2 d\mu_2/kT &= Vd\pi/kT \\ d\mu_2/kT &= (V/n_2)d\pi/kT \\ d\mu_{2./}kT &= (1/\rho_2)d\pi/kT \end{aligned} \tag{40.2}$$

By incorporating the expression (40.4) of statistical nature (viz. Appendix N) into the relation (40.2):

$$\pi/kT = \rho_2 + \sum_n B_n^* \rho_2^n \quad (n \geq 2) \quad \text{(relation (N.4) − Appendix N)}$$

(where the coefficients B_n^* are the virial coefficients of the osmotic pressure by differentiating (π et ρ_2 being the variables), dividing by ρ_2 and, finally, by integrating, we obtain:

$$\mu_2/kT = \text{constant} + \sum_{k \geq 1} (k + 1/k) B_{k+1} \rho_2^k + \ln\rho_2 \tag{40.3}$$

- From another view point, we know that:

$$z_2 = Q_{01}\lambda_2/V$$

i.e.:

$$z_2 = Q_{01}\exp[(\mu_2/kT)/V]$$

and moreover:

$$z_2 = \gamma_2\rho_2$$

From the latter two relations, we deduce that:

$$V\gamma_2\rho_2/Q_{01} = \exp(\mu_2/kT)$$

i.e.:

$$\mu_2/kT = \ln V/Q_{01} + \ln\gamma_2 + \ln\rho_2 \tag{40.4}$$

relation that we must compare with (40.3). The knowledge of the expression of γ_2 (being searched for) imposes to know the integration constant present in relation (40.3). Let us identify (40.3) and (40.4). We obtain:

$$\text{constant} + \sum_{k\geq 1} (k + 1/k)B_{k+1}\rho_2^k = \ln V/Q_{01} + \ln\gamma_2 \tag{40.5}$$

In very dilute solution, $\gamma_2 \rightarrow \gamma_2^0$ and according to (40.5):

$$\text{constant} = \ln V/Q_{01} + \ln{\gamma_2}^\circ - \sum_{k\geq 1} (k + 1/k)B_{k+1}\rho_2^k \tag{40.6}$$

Let us inject the expression (40.6) into (40.3) and identify to (40.4). The result is the relation being searched for, i.e.:

$$\ln\gamma_2 = \ln{\gamma_2}^\circ - \sum_{k\geq 1} (k + 1/k)B_{k+1}\rho_2^k \tag{40.7}$$

expression being searched for. It relates the activity coefficient to those of the virial of the osmotic pressure.

40.2 A New Type of Activity Coefficient Applying to the Osmotic Equilibrium

Relation (40.7) induces the introduction of a new thermodynamic parameter $\overline{\gamma_2}$, by setting up:

$$\ln\overline{\gamma_2} = -\sum_{k\geq 1} (k + 1/k)B_{k+1}\rho_2^k \tag{40.8}$$

One demonstrates that $\overline{\gamma_2}$ has the meaning of an activity coefficient. It is given by the following relation (40.9).

$$\overline{\gamma_2}\rho_2 = \delta_2 \tag{40.9}$$

The starting point of the reasoning leading to it is the relation below, stemming from relations (40.4), (40.7), and (40.8):

$$\mu_2/kT = \ln V\gamma_2^0/Q_{01} + \ln\rho_2 + \ln\overline{\gamma_2}$$

We know (viz. Chap. 38 and Appendix N) that:

$$\gamma_2^0 = Q_{01}\Psi_0/\Psi_1$$

whence:

$$\mu_2/kT = \ln V\Psi_0/\Psi_1 + \ln\rho_2 + \ln\overline{\gamma_2}$$

It can be equivalently written:

$$\exp(\mu_2/kT) = V(\Psi_0/\Psi_1)\rho_2\overline{\gamma_2}$$

Let us compare this latter expression with the following relation (viz. Chap. 30)

$$\delta_2 = \lambda_2 Q_{01}/\gamma_2{}^\circ V$$

in which λ_2 is replaced by $\exp(\mu_2/kT)$, i.e.:

$$\exp(\mu_2/kT) = \gamma_2^0\delta_2 V/Q_{01}$$

As a result:

$$V(\Psi_0/\Psi_1)\rho_2\overline{\gamma_2} = \gamma_2^0\delta_2 V/Q_{01}$$

and since:

$$\gamma_2^0 = Q_{01}\Psi_0/\Psi_1$$

we obtain:

$$V(\Psi_0/\Psi_1)\rho_2\overline{\gamma_2} = (Q_{01}\Psi_0/\Psi_1)(\delta_2 V/Q_{01})$$

and finally (40.9). $\overline{\gamma_2}$ has really the meaning of an activity coefficient. Let us also notice that, as a true activity coefficient, it tends toward 1 when $\rho_2 \to 0$ since, then $\delta_2 \to \rho_2$.

Another approach of the meaning of $\overline{\gamma_2}$ is as follows. According to the two relations already encountered:

$$z_2 = \gamma_2\rho_2$$
$$z_2 = \gamma_2^0\delta_2$$

we obtain:

$$z_2 = \gamma_2^0\overline{\gamma_2}\,\rho_2$$

with the aid of relation (40.9). Whence:

$$\begin{aligned}\gamma_2\rho_2 &= \gamma_2^0\overline{\gamma_2}\,\rho_2\\ \overline{\gamma_2} &= \gamma_2/\gamma_2^0\end{aligned}$$

Hence, $\overline{\gamma_2}$ is the ratio (changing with the concentration) between the normal activity coefficient γ_2 and the limit value of the latter γ_2^0 when the density number of the solute ρ_2 tends toward zero. This value is not null, as it has been already said.

40.3 Activity Coefficient in the Case of a Binary Mixture at Constant Temperature and Pressure

We have already seen (viz. Chap. 39) that the solute activity a_2 is a function of its molality m_2 according to the expression:

$$a_2 = m_2 - 2\theta_2 m_2^2 + \left(8\theta_2^2 - 3\theta_3\right)m_2^3\cdots \tag{40.10}$$

Let us recall that the parameter θ is defined by the expression :

$$-{\mu_1}'(T, \mathbf{p}, a_2)/kT = \sum_{j\geq 1}\vartheta_j(\mathbf{p}, T)a_2^j \tag{40.11}$$

where ${\mu_1}'(T$, $\mathbf{p}$, $a_2)/kT$ is the change in the Gibbs energy of the solvent accompanying the addition of the solute 2 up to the molality m_2 to the pure solvent. The molality m_2 (at constant temperature and pressure and at the activity a_2) is related to the parameter θ and at the activity a_2 by the relation:

$$m_2(p, T, a_2) = \sum_{j\geq 1} j\vartheta_j(p, T)a_2^j$$

The parameters θ are related to the intermediary variables X_N which, in the present case, play the part of the configuration integrals of the preceding cases. For example, N_1 being the number of molecules of pure solvent, we find:

$$\begin{aligned}N_1\vartheta_1 &= X_1 \quad (\vartheta_1 = 1)\\ 2!N_1\vartheta_2 &= X_2 - X_1^2\\ 3!N_1\vartheta_3 &= X_3 - 3X_1X_2 + 2X_1^3\end{aligned}$$

Let us also recall that these relations are only legitimate in the case of very dilute solutions in which the solute molality is proportional to its number of molecules.

The activity coefficient γ'_2 defined by the relation

$$\gamma'_2 = a_2/m_2$$

can be, hence, written as the function of m_2:

$$\gamma'_2 = 1 - 2\vartheta_2 m_2 + \left(8\vartheta_2^2 - 3\vartheta_3\right)m_2^2\cdots \tag{40.12}$$

$$\ln\gamma'_2 = \ln\left[1 - 2\vartheta_2 m_2 + \left(8\vartheta_2^2 - 3\vartheta_3\right)m_2^2\cdots\right] \tag{40.13}$$

Let us introduce the intermediary variable Y, given by the relation

$$Y = -2\vartheta_2 m_2 + \left(8\vartheta_2^2 - 3\vartheta_3\right)m_2^2$$

and expand ln $(1 + Y)$ in series:

$$\ln(1 + Y) = Y/1 - Y^2/2 + \cdots$$

We obtain:

$$\ln\gamma'_2 = -2\vartheta_2 m_2 + \left(6\vartheta_2^2 - 3\vartheta_3\right)m_2^2\cdots$$

that can be written under a more condensed form:

$$\ln\gamma'_2 = -\sum_{k\geq 1}\delta_k m_2^k \tag{40.14}$$

with

$$\delta_1 = 2\vartheta_2, \quad \delta_2 = 3\vartheta_2 - 6\vartheta_2^2$$

One can verify that, as it must be the case:

$$\gamma'_2 \to 1 \quad a_2 \to m_2 \quad \text{when} \quad m_2 \to 0$$

Such are the expressions of the solute activity coefficient as a function of its molality.

Let us notice that the preceding results permit to express the “corrected from the solvent chemical potential” in sufficiently dilute solution, by replacing a_2 by m_2 in (40.11). Then, we obtain:

$$-\mu_1{}'(T, \mathbf{p}, m_2)/kT = m_2 + \sum_n C_n m_2^n \quad (n \geq 2) \tag{40.15}$$

where

$$C_n = -[(n-1)/n]\delta_{n-1}$$

Chapter 41
Molecular Distribution Functions in Binary Mixtures

Abstract In this chapter, the generalization of the notion of molecular distribution functions to the cases of mixtures and solutions is described. It is based on the "pairwise additivity" hypothesis. Here, are only studied binary solutions. (The terms of mixtures and of solutions are endowed with the same general meaning for the purpose of this book, but that of solution is rather devoted to the case in which one substance, the solute, the quantity of which is the weakest one. It is dissolved in the other one, named the solvent).

Intervene in the evoked reasonings, some molecular distribution functions such as the pair distribution functions and the pair correlation function. It also appears the notion of conditional distribution function.

Keywords Molecular distribution functions (binary mixtures) • Pairwise additivity hypothesis • Pair distribution functions • Pair correlation functions • Conditional distribution function • Pairwise additivity hypothesis in the cases of mixtures • Density of base probability in the canonical ensemble

In this chapter, we generalize the notion of molecular distribution functions to the cases of mixtures and solutions. The generalization is based on the hypothesis of the "pairwise additivity". Here, we only study binary solutions. The terms of mixtures and of solutions are endowed with the same general meaning for our purpose, but the term solution is rather devoted to the case in which one substance, the solute, the quantity of which is the weakest one. It is dissolved in the other one, named the solvent.

41.1 The Notion of "Pairwise Additivity" in the Case of Mixtures

As in the case of pure liquids, the knowledge of fundamental molecular quantities imposes to determine the interactions between the different particles constituting the mixture. Again, the "pairwise additivity" hypothesis proves to be of great aid, although it remains a simplification, as before. A function F subscribing to this hypothesis obeys the following relation:

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$$\begin{aligned} F\left(\mathbf{R}^{\mathrm{NA+NB}}\right) = {} & \sum_{ij} f_{\mathrm{AA}}\left(\mathbf{R}_i, \mathbf{R}_j\right)\ (i \neq j) \ + \sum_{ij} f_{\mathrm{BB}}\left(\mathbf{R}_i, \mathbf{R}_j\right)\ (i \neq j) \\ & + \sum_i \sum_j f_{\mathrm{AB}}\left(\mathbf{R}_i, \mathbf{R}_j\right)\ (1 \leq i \leq N_{\mathrm{A}}; 1 \leq j \leq N_{\mathrm{B}}) \\ & + \sum_i \sum_j f_{\mathrm{BA}}\left(\mathbf{R}_i, \mathbf{R}_j\right)\ \ (1 \leq i \leq N_{\mathrm{B}};\ 1 \leq j \leq N_{\mathrm{A}}) \end{aligned} \tag{41.1}$$

$\mathbf{R}^{\mathrm{NA\,+\,NB}}$ is the configuration of the whole N_{A} and N_{B} particles of the system. f_{AA}, $f_{\mathrm{BB}}, f_{\mathrm{BA}}, f_{\mathrm{AB}}$ are the pair potential energy functions into which is the function F is decomposed. We must remark that in (41.1) the indices i and j are not related to the same operations whether they address to the "symmetrical" f_{AA} and f_{BB} or to the "crossed" ones f_{BA} and f_{AB}. In the first case, i and j apply to the same type of molecules. In the second, i apply to the particles A and j to the particles B, exclusively.

Let us explicit the relation (41.1) with the example of the interaction potential energy. Let $U\left(\mathbf{R}^{\mathrm{NA+NB}}\right)$ be the total potential energy of the mixture of N_{A} and N_{B} molecules of A and B in the well-specified $\mathbf{R}^{\mathrm{NA}}$, $\mathbf{R}^{\mathrm{NB}}$. The "pairwise additivity" hypothesis permits to write:

$$\begin{aligned} U\left(\mathbf{R}^{\mathrm{NA\,+\,NB}}\right) \ = {} & 1/2\sum_{ij} U_{\mathrm{AA}}\left(\mathbf{R}_i, \mathbf{R}_j\right) \ + 1/2\sum_{ij} U_{\mathrm{BB}}\left(\mathbf{R}_i, \mathbf{R}_j\right) \\ & + \sum_i \sum_j U_{\mathrm{AB}}\ \left(\mathbf{R}_i, \mathbf{R}_j\right) \quad 1 \leq i \leq N_{\mathrm{A}} \quad \text{and} \ \ 1 \leq j \leq N_{\mathrm{B}} \end{aligned}$$

The double sum of the last line takes into account the equality $U_{\mathrm{AB}} = U_{\mathrm{BA}}$. In the first line, $\mathbf{R}_i$ and $\mathbf{R}_j$ are the configurations of the i^{eme} and of the j^{eme} particle of A or of B. In the second, $\mathbf{R}_i$ is the configuration of the particle i of A and $\mathbf{R}_j$ that of particle j of B.

41.2 Density of Base Probability in the Canonical System

The density of base probability $P\left(\mathbf{R}^{\mathrm{NA\,+\,NB}}\right)$ is given in the present case by the expression:

$$P\left(\mathbf{R}^{\mathrm{NA\,+\,NB}}\right) = \ \exp\left[-\beta U\left(\mathbf{R}^{\mathrm{NA}}, \mathbf{R}^{\mathrm{NB}}\right)\right] \Big/ \int\int d\mathbf{R}^{\mathrm{NA}} d\mathbf{R}^{\mathrm{NB}} \exp\left[-\beta U\left(\mathbf{R}^{\mathrm{NA}}, \mathbf{R}^{\mathrm{NB}}\right)\right]$$

In the numerator, the symbolism $\mathbf{R}^{\mathrm{NA}}$, $\mathbf{R}^{\mathrm{NB}}$ represents the case in which we regard the total configuration of the well-specified system $\mathbf{R}^{\mathrm{NA}}$, $\mathbf{R}^{\mathrm{NB}}$ whereas the integrals of the denominator take into account all the possible configurations of the system.

41.3 Molecular Distribution Functions

They are defined, absolutely as in the case of a pure fluid (viz. Chap. 28). Notably, one can distinguish:

- The functions ${\rho_\mathrm{A}}^{(1)}(\mathbf{R}')$ and ${\rho_\mathrm{B}}^{(1)}(\mathbf{R}')$ are the densities of A and B in the configuration $\mathbf{R}'$. As previously, in a homogeneous and isotropic fluid, the following relations are verified:

$$\begin{aligned} {\rho_\mathrm{A}}^{(1)}(\mathbf{R}') &= N_\mathrm{A}/V &= \rho_\mathrm{A} \\ {\rho_\mathrm{B}}^{(1)}(\mathbf{R}') &= N_\mathrm{B}/V &= \rho_\mathrm{B} \end{aligned}$$

- The pair distribution functions

In the case of a binary mixture, several pairs are possible, i.e., AA, AB, BA, BB. For the "symmetrical pairs," one defines the functions $\rho^{(2)}{}_\mathrm{AA}(\mathbf{R}', \mathbf{R}'')$, $\rho^{(2)}{}_\mathrm{BB}(\mathbf{R}', \mathbf{R}'')$ and for the "crossed ones" the functions are $\rho^{(2)}{}_\mathrm{AB}(\mathbf{R}', \mathbf{R}'')$et $\rho^{(2)}{}_\mathrm{BA}(\mathbf{R}', \mathbf{R}'')$.

Let us recall that in the case of one type of particles:

$$\rho^{(2)}\left(\mathbf{R}', \mathbf{R}''\right) d\mathbf{R}' d\mathbf{R}''$$

is the probability to find one particle in d$\mathbf{R}'$ in $\mathbf{R}'$ and another in d$\mathbf{R}''$ in $\mathbf{R}''$. It is also the average number of pairs occupying d$\mathbf{R}'$ and d$\mathbf{R}''$. The generalization is immediate in the case of the binary mixture.

- Pair correlation functions

Several pair correlation functions are defined. They obey the general symbolism according to (where α and β equally symbolize A or B):

$$\rho^{(2)}{}_{\alpha\beta}\left(\mathbf{R}', \mathbf{R}''\right) = \rho^{(1)}{}_{\alpha}(\mathbf{R}')\rho^{(1)}{}_{\beta}\left(\mathbf{R}''\right) g_{\alpha\beta}\left(\mathbf{R}', \mathbf{R}''\right)$$

The function $g_{\alpha\beta}(\mathbf{R}', \mathbf{R}'')$ only depends on the distance $R = \left|\mathbf{R}' - \mathbf{R}''\right|$. R is a scalar. From that, we can deduce that:

$$g_\mathrm{AB}\left(\mathbf{R}', \mathbf{R}''\right) = g_\mathrm{BA}\left(\mathbf{R}', \mathbf{R}''\right)$$

- Conditional distribution function

Let us first recall that the definition of the conditional probability to see a particle in the configuration element d$\mathbf{X}''$ in $\mathbf{X}''$, another particle being located in the element d$\mathbf{X}'$ in $\mathbf{X}'$, is given by the expression (viz. Chap. 28)

$$P\left(\mathbf{X}''/\mathbf{X}'\right)d\mathbf{X}'' = \rho^{(2)}\left(\mathbf{X}',\mathbf{X}''\right)d\mathbf{X}'d\mathbf{X}''/\rho^{(1)}(\mathbf{X}')d\mathbf{X}'$$

i.e.,

$$P\left(\mathbf{X}''/\mathbf{X}'\right)d\mathbf{X}'' = \rho^{(1)}\left(\mathbf{X}''\right)\,g\left(\mathbf{X}',\mathbf{X}''\right)d\mathbf{X}''$$

In the present case, one also defines the new functions:

$$\rho_{\mathrm{AB}}\left(\mathbf{R}'/\mathbf{R}''\right) = {\rho^{(2)}}_{\mathrm{AB}}\left(\mathbf{R}'\mathbf{R}''\right)/{\rho^{(1)}}_{\mathrm{B}}\left(\mathbf{R}''\right)$$
$$\rho_{\mathrm{AB}}\left(\mathbf{R}'/\mathbf{R}''\right) = {\rho^{(1)}}_{\mathrm{A}}(\mathbf{R}')g_{\mathrm{AB}}\left(\mathbf{R}',\mathbf{R}''\right)$$

$\rho_{\mathrm{AB}}(\mathbf{R}'/\mathbf{R}'')$ is the density of particles A in the configuration $\mathbf{R}'$ whereas a particle B is fixed in the configuration $\mathbf{R}''$. The other new conditional distribution function $\rho_{\mathrm{BA}}(\mathbf{R}'/\mathbf{R}'')$ exhibit analogous properties.

Chapter 42
Kirkwood–Buff's Theory: Changes of the Solutes Chemical Potentials with the Concentrations at Constant Pressure and Temperature

Abstract Kirkwood–Buff's theory (1951) provides new relations between some thermodynamic quantities such as the chemical potential and the spatial pair correlation functions $G_{\alpha\beta}$ also called Kirkwood–Buff integrals. It, especially, offers expressions linking the chemical potential changes of solution components and their concentrations, at constant pressure and temperature. These expressions are all the more interesting as this kind of solutions is the most often encountered.

Expressions stemming from this theory probably set up the best means to begin to grasp the physical significance of activities and of their coefficients. This point is tackled in the next three following chapters.

The chapter is devoted to the sole study, according to this theory, of binary, homogeneous and isotropic mixtures of nonelectrolytes. It is set up within the grand ensemble framework. The starting point of the reasoning leading to the theory is the setting up of two mathematical relations expressing the concentration fluctuations. One of these relations links the fluctuations to the Kirkwood–Buff integrals $G_{\alpha\beta}$, the other links the same fluctuations to the partial derivatives of the mean number of particles with respect to the different chemical potentials.

Keywords Kirkwood–Buff's theory • Chemical potentials changes with concentrations at constant temperature and pressure • Kirkwood–Buff's integrals • Spatial pair correlation function • Concentration fluctuations • Thermodynamic quantities as a function of Kirkwood–Buff's integral • A very important relation stemming from the Kirkwood–Buff's theory • Kirkwood–Buff's theory (some aspects)

Kirkwood–Buff's theory (1951) provides new relations between some thermodynamic quantities such as the chemical potential and the spatial pair correlation functions $G_{\alpha\beta}$ also called Kirkwood–Buff integrals. It, especially, offers expressions linking the chemical potential changes of solution components and their concentrations, at constant pressure and temperature. These expressions are all the more interesting as this kind of solutions is the most often encountered.

Expressions stemming from this theory probably set up the best means to begin to grasp the significance of activities and their coefficients. This point is tackled in the next three following chapters.

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We commit ourselves to the sole study, according to this theory, of binary, homogeneous and isotropic mixtures of nonelectrolytes.

42.1 An Overview of Kirkwood–Buff’s Theory

The theory calls up a reasoning of classical mechanics and of statistical thermodynamics. It is set up within the grand ensemble framework. It consists of a link between some macroscopic thermodynamic properties of a system and the concentration fluctuations of its components.

The starting point of the reasoning leading to the theory is the setting up of two mathematical relations expressing the concentration fluctuations. Their setting up is followed by their “matching.” This is the reason why the theory is also named “Fluctuation Solution Theory.” One of these relations links the fluctuations to the Kirkwood–Buff integrals $G_{\alpha\beta}$, the other links the same fluctuations to the partial derivatives of the mean number of particles with respect to the different chemical potentials. After some mathematical developments, the theory leads to a link between the changes in concentrations and the thermodynamic properties of an isothermal and isobaric system. The corresponding expressions make allowance for the Kirkwood–Buff integrals $G_{\alpha\beta}$.

Kirkwood–Buff’s theory is an exact one. It is valid for any kind of solution.

42.2 Kirkwood–Buff Integrals $G_{\alpha\beta}$

The theory makes allowance for functions (42.1), named Kirkwood–Buff integrals:

$$\overline{G_{12}} = \int_0^{\infty} [\overline{g_{12}}(R) - 1]4\pi R^2 dR \tag{42.1}$$

which are an extension of the G function, already encountered and defined in the case of a pure liquid (viz.: Chap. 31) by the expression:

$$G = \int_0^{\infty} [\overline{g}(R) - 1]4\pi R^2 dR$$

where R is the distance between both particles 1 and 2. Just as it is written above with R being a scalar, they apply to homogeneous and isotropic media. G functions are themselves related to pair correlation functions $g_{\alpha\beta}$ and, then, to radial distribution functions (viz. Chap. 31).

In the present case of a binary function, the functions of interest for us are G_{11}, G_{12}, G_{21}, and G_{22}. They are defined below. (1 refers to the first component and so forth. Indices α and β refer indifferently to 1 or 2).

Before expliciting the Kirkwood–Buff's theory, it is interesting to qualitatively recall the physical significance of the integrals $G_{\alpha\beta}$, all the more because some expressions of activities and of their coefficients make allowance for them (viz. Chaps. 31, 32, and 33).

Let us suppose that we choose a particle 1 and that we observe the local density of 2 in the spherical shells centered on molecule 1. The local density of molecules 2 at distance R from particle 1 is given by the term $\rho_2 g_{21}(R)$. (ρ_2 is the density number of (42.2), g_{21} the radial distribution function between 1 and 2 which is the correlation function between 1 and 2). The mean number of particles 2 in the spherical shell of thickness dR at the distance R from 1 is $\rho_2 g_{21}(R)4\pi R^2 dR$. Otherwise, $\rho_2 4\pi R^2 dR$ is the mean number of particles 2 in the same spherical shell but, the center of which is a particle 1 chosen randomly.

Thus the expression $\rho_2[g_{21}(R) - 1]4\pi R^2 dR$ is a measure of the excess (or of the deficit) of particles 2 in a spherical shell of volume $4\pi R^2 dR$ around a particle 1 with respect to the number which would be obtained if we would have made allowance for only the mean number ρ_2. Thus, $\rho_2 G_{21}$ is the mean excess of particles 2 all around 1. Therefore, the integral is the excess of 2 around 1 for a density of 2 equal to the unity. The reasoning would be the same if we would have considered the density of 1 around the particle 1 or that of 2 around 2. The integrals being considered would then be G_{11}, G_{12}, and G_{22}.

Figure 33.1 shows the general shape of a Kirkwood–Buff integral as the distance of integration R, measured in nm.

42.3 Different Steps of the Setting-Up of the Kirkwood–Buff's Theory

One can estimate that it is developed in three steps consisting in:

- Relating the functions $G_{\alpha\beta}$ to the mean density numbers of the components
- Setting up the mathematical relations between some partial derivatives involving the chemical potentials of the different components. These relations are necessary to carry out the third step
- Expressing some thermodynamic quantities related to functions $G_{\alpha\beta}$.

42.4 First Step: Expressions Relating Functions $G_{\alpha\beta}$ to the Average Density Numbers of the Components

Two relations involve the fluctuations of concentrations. They are (viz. Chap. 31):

$$\overline{G_{12}} = V\{[\langle N_1N_2\rangle - \langle N_1\rangle\langle N_2\rangle]/(\langle N_1\rangle\langle N_2\rangle) - \delta_{12}/\langle N_1\rangle\} \tag{42.2}$$

$$kT(\partial/\partial\mu_2)T, V, \mu_1 = \langle N_1N_2\rangle - \langle N_1\rangle\langle N_2\rangle \tag{42.3}$$

$\langle N_1\rangle$ and $\langle N_2\rangle$ being the average numbers of particles 1 and 2. δ_{12} is Kronecker's function. In the same manner, it is demonstrated that:

$$kT(\partial\langle N_2\rangle/\partial\mu_1)_{T,V,\mu 2} = \langle N_1N_2\rangle - \langle N_1\rangle\langle N_2\rangle \tag{42.4}$$

It is clear that the elimination of the right members from the relations of types (42.2) and (42.3) permits to set up the relations to be searched for between density numbers, chemical potentials, and Kirkwood–Buff's integrals, that is to say:

$$kT/V\left[(\partial\langle N_1\rangle/\partial\mu_2)_{T,V,\mu 1}\right] = \rho_1\rho_2G_{12} + \rho_2 d\delta_{12} \tag{42.5}$$

$$kT/V\left[(\partial\langle N_2\rangle/\partial\mu_1)_{T,V,\mu 2}\right] = \rho_1\rho_2G_{12} + \rho_1\delta_{12} \tag{42.6}$$

(We note, in passing, that:

$$kT(\partial\langle N_1\rangle/\partial\mu_2)_{T,V,\mu 1} = kT(\partial\langle N_2\rangle/\partial\mu_1)_{T,V,\mu 2}$$

$$(\partial\langle N_1\rangle/\partial\mu_2)_{T,V,\mu 1} = V(\partial\rho_1/\rho\mu_2)_{T,V,\mu 1}$$

and

$$(\partial\langle N_2\rangle/\partial\mu_1)_{T,V,\mu 2} = V(\partial\rho_2/\partial\mu_1)_{T,V,\mu 2}$$

knowing that $\overline{\rho_1} = \langle N_1\rangle/V$ and $\overline{\rho_2} = \langle N_2\rangle/V$, since the solution is homogeneous and isotropic).

42.5 Second Step: Mathematical Relations Between Some Partial Derivatives Involving the Chemical Potentials of the Different Components

Before describing the second step, let us recall that, when all is said and done, the Kirkwood–Buff's theory relates the partial derivatives $(\partial\mu_\alpha/\partial N_\beta)_{T,P,N\gamma}$ (at constant temperature, pressure and concentration of the other component) to the integrals $G_{\alpha\beta}$.

(The other partial derivatives $(\partial N_\alpha/\partial\mu_\beta)_{T,V,\mu\gamma}$ being already obtained (previous step—relations (42.5) and (42.6)), though they are relations between thermodynamic quantities and functions $G_{\alpha\beta}$ are not those required. Besides, they cannot be immediately handled. We know, indeed, few data about them).

As a result, the following transformation must be carried out:

$$\left(\partial N_\alpha/\partial\mu_\beta\right)_{T,V,\mu\gamma} \rightarrow \left(\partial\mu_\alpha/\partial N_\beta\right)_{T,P,N\gamma}$$

The transformation involves two steps:

- In the first one, the partial derivatives at constant chemical potentials $(\partial N_\alpha/\partial\mu_\beta)_{T,V,\mu\gamma}(\gamma \neq \beta)$ [or equivalently the following ones $(\partial\rho_\alpha/\partial\mu_\beta)_{T,\mu\gamma}$] are transformed into $(\partial\mu_\alpha/\partial N_\beta)_{T,VN\gamma}$, that is to say in the partial derivatives of the chemical potentials with respect to the average numbers of the components, at constant temperature, pressure and concentration of the other component (in the following reasoning, $\langle N_\alpha\rangle$ is replaced by N_α in order to reduce the writing)
- In the second step, the derivatives $(\partial\mu_\alpha/\partial N_\beta)_{T,V,N\gamma}$ are transformed in those at constant pressure, temperature and $N\gamma$, $(\partial\mu_\alpha/\partial N_\beta)_{T,P,N\gamma}$. (Let us recall that the partial derivatives which are the most easily handled are those at constant pressure and temperature. This is because they are the most available experimentally).

Finally, the partial derivatives $(\partial\mu_\alpha/\partial N_\beta)_{T,P,N\alpha}$ at our disposal at the end of this step are related to the functions $G_{\alpha\beta}$.

Hence, at the end of the second step, we face with some relations which permit to express the following thermodynamic quantities, $(\partial\mu_1/\partial N_2)_{T,P,N1}$ and analogous ones and also $\overline{V_1}, \overline{V_2}$, k_T as functions of the Kirkwood–Buff integrals $G_{\alpha\beta}$. These relations are:

$$(\partial\mu_1/\partial N_2)_{T,P,N1} = -kT/V\Delta'\rho_1\rho_2G_{12} - \overline{V_1}\,\overline{V_2}/V\kappa_T \tag{42.7}$$

$$(\partial\mu_2/\partial N_1)_{T,P,N2} = -kT/V\Delta'\rho_1\rho_2G_{12} - \overline{V_1}\,\overline{V_2}/V\kappa_T \tag{42.8}$$

$$(\partial\mu_1/\partial N_1)_{T,P,N2} = kT/V\Delta'\left(\rho_2{}^2G_{22} + \rho_2\right) - \overline{V_1}^2/V\kappa_T \tag{42.9}$$

$$(\partial\mu_2/\partial N_2)_{T,P,N1} = kT/V\Delta'\left(\rho_1{}^2G_{11} + \rho_1\right) - \overline{V_2}^2/V\kappa_T \tag{42.10}$$

The Gibbs–Duhem's relations:

$$\rho_1(\partial\mu_1/\partial N_1)_{T,P,N2} + \rho_2(\partial\mu_1/\partial N_2)_{T,P,N1} = 0 \tag{42.11}$$

$$\rho_1(\partial\mu_2/\partial N_1)_{T,P,N2} + \rho_2(\partial\mu_2/\partial N_2)_{T,P,N1} = 0 \tag{42.12}$$

and that linking the molar partial derivatives

$$\rho_1\overline{V_1} + \rho_2\overline{V_2} = 1 \tag{42.13}$$

Let us recall that $\overline{V_1}$ and $\overline{V_2}$ are the molar partial volumes of components 1 and 2, V that of the whole system, and k_T its compressibility isothermal coefficient. Δ' is the determinant which naturally introduces into the calculations.

42.6 Third Step: Expressions of Thermodynamic Quantities as Functions of Kirkwood–Buff Integrals

These expressions are obtained by solving the system of equations (42.7) to (42.13). We find:

$$\overline{V_1} = (1 + \rho_2 G_{22} - \rho_2 G_{12})/\eta \quad \overline{V_2} = (1 + \rho_1 G_{11} - \rho_1 G_{12})/\eta \tag{42.14}$$

$$(\partial \mu_1/\partial N_2)_{T,P,N1} = (\partial \mu_2/\partial N_1)_{T,P,N2} = -kT/V\eta \tag{42.15}$$

$$(\partial \mu_1/\partial N_2)_{T,P,N1} = \rho_2 kT/\rho_1 V\eta \tag{42.16}$$

$$(\partial \mu_2/\partial N_1)_{T,P,N2} = \rho_1 kT/\rho_2 V\eta \tag{42.17}$$

relations in which:

$$\eta = \rho_1 + \rho_2 + \rho_1\rho_2(G_{11} + G_{22} - 2G_{12})$$

(η is a parameter introduced in order to lighten the writing).

42.7 Some Important Relations Stemming from the Kirkwood–Buff's Theory

The most important relations for our purpose, issuing from the Kirkwood–Buff's theory are those giving the partial derivatives of chemical potentials of both species with respect to their density numbers, at constant temperature and pressure, that is to say $(\partial\mu_\alpha/\partial\rho_\beta)_{T,P}$ with $\alpha =$ or $\neq \beta$ and with α or $\beta = 1$ or 2. The interesting point is that they depend on functions $G_{\alpha\beta}$, because the latter ones are accessible. These experimental conditions are often encountered in solution chemistry. The expressions being searched for are found by handling partial derivatives already known.

We obtain:

$$(\partial \mu_2/\partial \rho_2)_{T,P} = kT/\rho_2(1 + \rho_2 G_{22} - \rho_2 G_{12}) \tag{42.18}$$

Using the corresponding Gibbs–Duhem, we find:

$$(\partial\mu_1/\partial\rho_2)_{T,P} = -kT/\rho_1(1+\rho_2 G_{22} - \rho_2 G_{12}) \tag{42.19}$$

In an analogous way, we would find:

$$(\partial\mu_1/\partial\rho_1)_{T,P} = kT/\rho_1(1+\rho_1 G_{11} - \rho_1 G_{12}) \tag{42.20}$$

and

$$(\partial\mu_2/\partial\rho_1)_{T,P} = kT/\rho_2(1+\rho_1 G_{11} - \rho_1 G_{12}) \tag{42.21}$$

Remarks:

- Contrary to partial derivatives $(\partial\mu_1/\partial N_2)_{T,P,N1}$ and $(\partial\mu_2/\partial N_1)_{T,P,N2}$ obtained in the second step which are equal, those above $(\partial\mu_1/\partial\rho_2)_{T,P}$ and $(\partial\mu_2/\partial\rho_1)_{T,P}$ are not:

$$(\partial\mu_1/\partial\rho_2)_{T,P} \neq (\partial\mu_2/\partial\rho_1)_{T,P}$$

- It is interesting to recall the expression giving the change in ‹*N*› (or ρ) of a pure liquid with respect to its chemical potential μ as a function of its proper pair correlation function $G_{\alpha\alpha}$, nearby those found above. It is (viz. Chap. 32):

$$(\partial\mu/\partial\rho)T = kT/\left(\rho + \rho^2 G_{\alpha\alpha}\right)$$

We note the consistency of the whole expressions. Doubtless, this is a proof of the validity of the basic theories.

42.8 Expression of the Derivative of the Chemical Potential of a Component with Respect to Its Molar Fraction at Constant Molar Concentration of the Other

As we shall see it a bit lengthily, it is of utmost importance for our purpose to get an expression of the derivative of the chemical potential of a component, for example, $(\partial\mu_1/\partial x_1)_{T,P}$, with respect to its molar fraction, the moles number N_2 of the other species being constant. It stems from the following relation which itself results from the chain rule of derivation:

$$(\partial\mu_1/\partial x_1)_{T,P,N2} = (\partial\mu_1/\partial\rho_1)_{T,P,N2} \cdot (\partial\rho_1/\partial x_1)_{T,P,N2}$$

$$(\partial\rho_1/\partial x_1)_{T,P,N2} = 1/(\partial x_1/\partial\rho_1)_{T,P,N2}$$

$$x_1 = N_1/(N_1 + N_2)$$

$$x_1 = \rho_1/(\rho_1 + \rho_2)$$

$$dx_1/d\rho_1 = \rho_2/(\rho_1 + \rho_2)^2$$

$$d\rho_1/dx_1 = (\rho_1 + \rho_2)^2 V/N_2$$

V/N_2 is the molar volume of component 2 in the medium, at constant temperature and pressure. In this case, it is of course its partial molar volume $\overline{V_2}$. As a result:

$$(\partial\mu_1/\partial x_1)_{T,P,N2} = (\partial\mu_1/\partial\rho_1)_{T,P,N2} \cdot \rho^2\overline{V_2}$$

with $\rho = \rho_1 + \rho_2$. Taking into account this latter relation, the expression giving $\overline{V_2}$ and (42.21), we immediately obtain:

$$(\partial\mu_1/\partial x_1)_{T,P} = kT\rho^2/\rho_1\eta$$

$$(\partial\mu_1/\partial x_1)_{T,P} = kT[1/x_1 - \rho_2\Delta_{12}/(1 + \rho_2 x_1\Delta_{12})] \tag{42.22}$$

relation in which:

$$\Delta_{12} = G_{11} + G_{22} - 2G_{12} \tag{42.23}$$

$$(\partial\mu_1/\partial x_1)_{T,P} = kT\rho^2/\rho_1\eta$$

$$(\partial\mu_1/\partial x_1)_{T,P} = kT[1/x_1 - \rho_2\Delta_{12}/(1 + \rho_2 x_1\Delta_{12})] \qquad (42.22)$$

Relation (42.22) is of very great interest. We shall see (viz.: Chaps. 43 and 44) that it permits to explicit the concepts of ideal solutions (the perfect ones and the very dilute ones). We shall again turn ourselves towards this quantity in Chap. 45.

42.9 Some Aspects of Kirkwood–Buff's Theory

To conclude this report upon the Kirkwood–Buff's theory, let us mention the following points, though they are not absolutely necessary for our purpose:

- It can be considered as being general because it applies to all types of particles, whatever the number of components of the mixture is. Moreover, it does not call on the hypothesis of "pairwise additivity" of the total potential energy, which is nothing else than an approximation, saying the least.

- As the McMillan–Mayer's theory (viz.: Chap. 38) with which it can be compared, let us repeat that it is a general theory, but it shows several advantages:
  - It can be applied in the whole concentration ranges of the components, whereas the other one can only be used with dilute solutions because it explicits the thermodynamic quantities only under developments in series and its coefficients are difficult to calculate and, even, to interpret.
  - From the theoretical standpoint, although we have not developed this point, one must know that the Kirkwood–Buff's integrals depend directly on mean force potentials between the pairs of solute particles, whereas the coefficients of the McMillan–Mayer's developments depend on a mean force potential at infinite dilution. This is another difference between both methods.
- Kirkwood–Buff's theory not only permits to calculate macroscopic thermodynamic quantities starting from radial distribution functions $g(R)$ but also and inversely permits to get local information from macroscopic ones through those brought by radial distribution functions which provide data upon the distance between the two members of a pair.
- It permits a study of ideal and nonideal solutions, at least at the first level of approximation (viz.: Chaps. 43 and 44).
- Finally, let us mention the fact that it only concerns the properties of solutions the study of which is possible within the framework of the great ensemble by differentiation with respect to the number of particles (or to the pressure).

Chapter 43

Chemical Potentials of the Components of Ideal Solutions of Nonelectrolytes

Abstract The expressions of the chemical potentials of the components of ideal binary solutions of nonelectrolytes are given in this chapter. They result from a reasoning of statistical thermodynamics. These expressions, not yet mentioned in the book, are interesting for the purpose of the study of an activity at least for two reasons. The first one is that they provide an intimate link existing between the chemical potential of a component and its activity. The second reason is, simply, the practical importance of solutions. It must not be forgotten, indeed, that most processes probably occur in solutions.

The study mentioned in the chapter is deliberatively limited to that of the binary ideal solutions of nonelectrolytes. This introductory step may facilitate the following study of the activities and activity coefficients of the components of every solution. As for that of electrolyte solutions, it is deferred to a later chapter because of their particular properties.

A particular stress is laid on the fact that the results mentioned here (stemming from statistical thermodynamics) are in full agreement with the experimental data which are at the origin of the definition of ideal and very dilute solutions in classical thermodynamics. In this chapter, the notion of coupling of a molecule of solute with the remaining solvent molecules and also that of a solvent molecule with the other ones is introduced.

Keywords A new statistical look on chemical potentials (components of ideal solution of nonelectrolytes) • Ideal solutions (statistical thermodynamics) • Very dilute solutions (statistical thermodynamics) • Characteristic partition function (isothermal isobaric ensemble) • Coupling of molecules (solutes and solvent) • de Broglie's thermal wavelength • Raoult and Henry's laws (statistical thermodynamics) • Perfect solutions (mixtures of very similar components) • Ideal solutions (very dilute ones) • Chemical potential of the solute

In this chapter, we give the expressions of the chemical potentials of the components of ideal binary solutions of nonelectrolytes. They result from a reasoning of statistical thermodynamics. These expressions, not yet mentioned in this book, are interesting for our purpose, at least for two reasons. The first one is that they provide an intimate link existing between the chemical potential of a component and its activity. The second reason is, simply, the practical importance of solutions. It must not be forgotten, indeed, that most processes probably occur in solutions.

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In this chapter, we deliberately choose to only study the binary ideal solutions of nonelectrolytes. This introductory step may, in our opinion, facilitate the following study of the activities and activity coefficients of the components of every solution. As for that of electrolyte solutions, it is deferred to a later chapter because of their particular properties. For the sake of simplicity, only binary solutions are investigated, here.

We already lay particular stress on the fact that the results mentioned below (stemming from statistical thermodynamics) are in full agreement with the experimental data which are at the origin of the definition of ideal solutions in classical thermodynamics.

43.1 Looking Back on the Definition of Ideal Solutions

As we have already said it (viz., Chap. 8), the classification of ideal solutions is not clear-cut. Some authors distinguish two kinds of ideal solutions. This will be our case.

Let us recall that ideal solutions are those each component i of which exhibits a chemical potential μ_i complying with the relation:

$$d\,\mu_i = RT\, d\ln\, x_i \tag{43.1}$$

where x_i is its molar fraction. R and T have their usual meaning (viz., Chap. 8). Actually, two types of ideal solutions are distinguished:

- The perfect solutions. The behavior of all the components is ideal over the whole range of composition at all temperatures and pressures. They obey Raoult's law. In order to comply with this definition, the components must be very similar.
- The very dilute solutions. Then, the solute obeys Henry's law whereas the solvent obeys Raoult's law. As soon as the solution is not dilute enough, it remains no longer ideal.

These definitions and properties stem from the framework of classical thermodynamics.

We successively consider both cases.

43.2 Perfect Solutions: Mixtures of Two Very Similar Components

In this paragraph, we seek the relations which, in this case, link the chemical potentials of the components to their "concentrations" at constant temperature and pressure. The latter conditions are interesting to be taken into account because of their frequent occurrence in practice.

Through very similar components, we mean that the potential energy of interaction in a system of N molecules in the configuration $\mathbf{X}^N$ is independent of the identity of the species i which possesses the configuration $\mathbf{X}_i$, (entering, of course, into $\mathbf{X}^N$).

Let us label both components of the solution A and B. We choose reasoning within the framework of the isothermal-isobaric ensemble $(T, \mathbf{p}, N_\mathrm{A}, N_\mathrm{B})$ (cf, Chap. 24). Given the experimental conditions which are under constant temperature and pressure, it is the most convenient ensemble to use. (These solutions are the most frequently encountered ones). Let us recall (viz., Chap. 24) that, for a sole compound, the number particles of which being N, the partition function is:

$$\Delta(T, \mathbf{p}, N) = \sum_V Q(N, V, T)\mathrm{e}^{-pV/kT}$$

In classical mechanics, it is written:

$$\Delta(T, \mathbf{p}, N) = C\int_0^\infty dVQ(N, V, T)\mathrm{e}^{-\,pV/kT}$$

where C is a constant. The characteristic thermodynamic function of this ensemble is the Gibbs energy function G of the system. It is related to the $\Delta(T, \mathbf{p}, N)$, the characteristic function of the latter, through the expression:

$$G(T, \mathbf{p}, N) = -kT\;\ln \Delta(T, \mathbf{p}, N)$$

and the chemical potential of species A is defined by the expression:

$$\mu_\mathrm{A} = (\partial G/\partial N_\mathrm{A})_{T,P,\mathrm{NB}}$$

(B being another component of the solution).

It is equal to the change in the Gibbs energy accompanying the addition of one molecule A to a system being composed of N_A molecules A and N_B molecules B, N_A and N_B being very high numbers. Thus:

$$\mu_\mathrm{A} = G(T, \mathbf{p}, N_{\mathrm{A}+1}\;, N_\mathrm{B})\; - \; G(T, \mathbf{p}, N_\mathrm{A}, N_\mathrm{B})$$

and according to Chap. 32:

$$\exp(-\beta\mu_\mathrm{A}) = \Delta(T, \mathbf{p}, N_{\mathrm{A}+1}, N_\mathrm{B})/\Delta(T, \mathbf{p}, N_\mathrm{A}, N_\mathrm{B})$$

or

$$\begin{aligned}\exp(-\beta\mu_\mathrm{A}) = q_\mathrm{A}\int dV\int d\mathbf{X}^{\mathrm{NA}+\mathit{1}}d\mathbf{X}^{\mathrm{NB}}\exp\left[-\beta\mathbf{p}V - \beta U_{\mathrm{NA}+\mathit{1},\,\mathrm{NB}}\left(\mathbf{X}^{\mathrm{NA}+\mathit{1}}, \mathbf{X}^{\mathrm{NB}}\right)\right]\\ /{\Lambda_\mathrm{A}}^3(N_{\mathrm{A}+1}) \times 8\pi^2\int dV\int d\mathbf{X}^{NA}d\mathbf{X}^{NB}\exp\left[-\beta\mathbf{p}V - \beta\mathrm{U}_{NA,NB}\left(\mathbf{X}^{\mathrm{NA}}, \mathbf{X}^{\mathrm{NB}}\right)\right]\end{aligned} \tag{43.2}$$

(Let us note that, here, the considered example regards a particle possessing an internal structure as it is indicated by the presence of symbols q and $\mathbf{X}$ in these expressions).

The "out of integrals" term $q_{\mathrm{A}}/\Lambda_{\mathrm{A}}{}^3(N_{\mathrm{A+1}})$ comes from the ratio:

$$q_{\mathrm{A}}{}^{\mathrm{NA+1}}/\left(\Lambda^{3(\mathrm{NA+1})}\right)(N_{\mathrm{A}}+1)!\left(8\pi^2\right)^{(\mathrm{NA+1})}/q_{\mathrm{A}}{}^{\mathrm{NA}}/\,\Lambda^{3\mathrm{NA}}N_{\mathrm{A}}!\left(8\pi^2\right)^{\mathrm{NA}}$$

stemming from both partition functions. $\Lambda_{\mathrm{A}}{}^3$ and q_A are, respectively, the de Broglie's thermal wavelength and the internal molecular partition function of particle A.

Let us now consider the case of a system consisting of N particles A and 0 particle B, system being at the same temperature and pressure as the previous one and into which is added 1 molecule A. The chemical potential μ_{A}^p (superscript p for pure) is given by the expression (43.3). (43.3) results obviously from the adaptation of (43.2) to the new conditions:

$$\begin{aligned}\exp\left(-\beta\mu_{\mathrm{A}}^p\right) = q_{\mathrm{A}}\int dV\int d\mathbf{X}^{N+1}\exp\left[-\beta\mathbf{p}V-\beta U_{N+1}\left(\mathbf{X}^{N+1}\right)\right]/\Lambda_{\mathrm{A}}{}^3(N+1)\left(8\pi^2\right)\\ \times\int dV\int d\mathbf{X}^{N}\exp\left[-\beta\mathbf{p}V-\beta U_{N}\left(\mathbf{X}^{N}\right)\right]\end{aligned} \tag{43.3}$$

Let us suppose, now, that N in expression (43.3) is equal to the sum $N_{\mathrm{A}}+N_{\mathrm{B}}$ in expression (43.2) and let us replace N with $N_{\mathrm{A}}+N_{\mathrm{B}}$ in (43.3). The hypothesis of the very great similitude of compounds A and B manifests itself in the following equalities:

$$\begin{aligned} d\mathbf{X}^{\mathrm{NA+NB+1}} &= d\mathbf{X}^{\mathrm{NA+1}}d\mathbf{X}^{\mathrm{NB}}\\ U_{N+1}\left(\mathbf{X}^{N+1}\right) &= U_{\mathrm{NA}\,+\,1,\,\mathrm{NB}}\left(\mathbf{X}^{\mathrm{NA}+1},\mathbf{X}^{\mathrm{NB}}\right)\\ U_N\left(\mathbf{X}^N\right) &= U_{\mathrm{NA,NB}}\left(\mathbf{X}^{\mathrm{NA}},\mathbf{X}^{\mathrm{NB}}\right)\end{aligned} \tag{43.4}$$

The three relations (43.4) must be written since, with respect to the intermediary step in which A was alone, now, the species B does exist .

The ratio of expressions (43.2) and (43.3) leads to the equality:

$$\exp\left[-\beta\mu_{\mathrm{A}}+\beta\mu_{\mathrm{A}}^p\right] = (N+1)/(N_{\mathrm{A}}+1) \tag{43.5}$$

With:

$$(N+1)\,/(N_{\mathrm{A}}+1) \approx N/N_{\mathrm{A}}$$

we obtain:

$$\mu_{\mathrm{A}}(T,\mathbf{p},N_{\mathrm{A}}) = \mu_{\mathrm{A}}^p(T,\mathbf{p}) + kT\ \ln x_{\mathrm{A}} \tag{43.6}$$

This result is in perfect agreement with the result of the integration of (43.1). Note that the resulting integral solution is satisfied for $x_{\mathrm{A}} = 1$.

The expression of the chemical potential of each component of an ideal solution of this kind complies with expression (43.6). This result is very important. It expresses Raoult's law (viz., Chap. 8).

Hence, with the help of statistical thermodynamics and through relation (43.6) *we recover Raoult' s law and all its inferences*. Let us recall that it was set up, in classical thermodynamics, on the basis of pure experimental data (viz., Chap. 8).

Relation (43.6) clearly shows that the *natural* expression of the concentration in the context of Raoult's law is the molar fraction $N_{\mathrm{A}}/N = N_{\mathrm{A}}/N_{\mathrm{A}} + N_{\mathrm{B}}$. Moreover, an analogous reasoning with compound B would show that the latter would exhibit the same behavior as A. In other words, the behavior of B is the same as that of A:

$$\mu_{\mathrm{B}}(T, \mathbf{p}, N_{\mathrm{A}}) = \mu_{\mathrm{B}}^{p}(T, \mathbf{p}) + kT \ln x_{\mathrm{B}} \tag{43.7}$$

Again, we recover the fact that in an ideal solution of this kind, Raoult's law is obeyed by all the components of the solution. This kind of solution for which the chemical potential of each component obeys the expression (43.7) or (43.6) is sometimes named symmetric ideal solution. Let us notice that for them, the standard state does exist.

All these results come from the validity of the equality (43.4), that is to say from the condition of the very great similitude of the components of the solution. Actually, the conditions of a behavior obeying Raoult's law may be less stringent than that of great similitude (viz., Chap. 44).

43.3 Ideal Solutions: Very Dilute Solutions

We know that the chemical potential μ of a fluid is given by the relation (viz.: Chap. 32):

$$\mu = kT \ln\left(\rho \Lambda^{3} q^{-1}\right) - kT \ \ln\langle \exp(-\beta \mathrm{B})\rangle \tag{43.8}$$

The term $-kT \ln \langle \exp(-\beta \mathrm{B})\rangle$ is the coupling work of a particle when it is brought from infinite to the bulk of the system. When the latter does possess as only component particles A and if the coupled one is also A, the coupling work may be symbolized by the term $W(\mathrm{A}|\mathrm{A}+\mathrm{A})$, whereas when the system is a binary solution, the components of which being A and B, the coupling work is $W(\mathrm{A}|\mathrm{A}+\mathrm{B})$ either $W(\mathrm{B}|\mathrm{B}+\mathrm{A})$ depending on the coupled particle is being A or B. Let A be the solute and B the solvent.

Now, with the aid of statistical thermodynamics, we are in position to discuss the nature of the standard states and the expressions of the chemical potentials, according to the fact that we regard either the solute or the solvent. After, we shall be able to compare the results of the reasoning and those directly stemming from classical thermodynamics.

- Chemical potential of the solute

  Its chemical potential is given by the expression (viz., Chap. 32)

$$\mu_A = W(A|A+B) + kT \ln\left(\rho_A {\Lambda_A}^3 {q_A}^{-1}\right) \tag{43.9}$$

This relation is general. It can also be written as:

$$\mu_A = W(A|A+B) + kT \ln\left(\Lambda_A^3 \mathrm{q}_A^{-1}\right) + kT \ln\rho_A \tag{43.10}$$

It strongly looks like its expression stemming from classical thermodynamics (viz. for example Chap. 6):

$$\mu_A = {\mu_A}^\circ(\rho) + kT \ln\rho_A \tag{43.11}$$

From the very fact that the chemical potential of a compound must be the same in the same thermodynamic state, we can deduce from (43.10) and (43.11) that the standard chemical potential of A is given by the expression:

$${\mu_A}^\circ = W(A|A+B) + kT \ln\left(\Lambda_A^3 q_A^{-1}\right) \tag{43.12}$$

- A first interesting particular case is that in which solute A is very dilute. One particle A cannot “see” any particle different from B all around it. Then, the coupling work is $W(A|B+B)$ and we can write for the expression of its chemical potential:

$$\mu_A = W(A|B+B) + kT \ln\left(\Lambda_A^3 q_A^{-1}\right) + kT \ln\rho_A \quad \text{(very dilute solution)} \tag{43.13}$$

Because the terms $W(A|B+B)$ and $W(A|A+A)$ differ, the standard chemical potential of A in this case is not the same as when it is pure.

Let us recall that this is a case which is often encountered in practice, in particular in analytical chemistry. It is widely studied in classical thermodynamics.

- A second interesting particular case is that where the particle B is very similar to A. The coupling work of B is then equal to that of A and:

$$W(A|A+B) = W(A|A+A)$$

  Inserting this equality into (43.10), we obtain:

$$\mu_A = W(A|A+A) + kT \ln\left(\Lambda_A^3 q_A^{-1}\right) + kT \ln\rho_A \tag{43.14}$$

Then, the standard chemical potential is that of A pure. For the sake of immediate reasoning, let us consider a system consisting of component A pure. Its density number is ρ_{A}^{p}. The chemical potential of A is, then:

$$\mu_{\mathrm{A}}^{p} = W\left(\mathrm{A}\middle|\mathrm{A}+\mathrm{A}\right) + kT\ \ln\ \left(\Lambda_{\mathrm{A}}^{3} q_{\mathrm{A}}^{-1}\right) + kT\ \ln \rho_{\mathrm{A}}^{p} \tag{43.15}$$

Comparing it to the previous system where the density number of A is ρ_{A} and supposing that both systems do possess the same total number of particles, that is to say:

$$n_{\mathrm{A}}^{p}(\text{2nd system}) = n_{\mathrm{A}} + n_{\mathrm{B}} \quad (\text{1st system})$$

the ratio of both density numbers is then evidently as follows:

$$\rho_{\mathrm{A}}/\rho_{\mathrm{A}}^{p} = n_{\mathrm{A}}/n_{\mathrm{A}}^{p} = \left(n_{\mathrm{A}}/n_{\mathrm{A}}^{p}\right)/1 = x_{\mathrm{A}}$$

We immediately deduce the relation (43.6) above from (43.14) and (43.15) in agreement with the hypothesis that A and B are very similar.

- Let us study, now, the chemical potential of solvent B when the solute A is very dilute.

  Its chemical potential is given by the expression:

$$\mu_{\mathrm{B}} = W\left(\mathrm{B}\middle|\mathrm{A}+\mathrm{B}\right) + \ kT\ \ln\ \left({\Lambda_{\mathrm{B}}}^{3} {q_{\mathrm{B}}}^{-1}\right) + kT\ \ln \rho_{\mathrm{B}}$$

We note that when the solution becomes more and more diluted:

$$W\left(\mathrm{B}\middle|\mathrm{A}+\mathrm{B}\right) \rightarrow W\left(\mathrm{B}\middle|\mathrm{B}+\mathrm{B}\right)$$

The chemical potential of the solvent goes over the one it possesses when it is pure.

Hence, thanks to the previous reasoning based on statistical thermodynamics, we notice that concerning ideal very dilute solutions, but not the perfect ones:

- The standard chemical potential of the solute does not go over its chemical potential when it is pure (viz. the previous subsection).
- When the solution is more and more dilute, the chemical potential of the solvent goes over its chemical potential when it is pure. In other words, it obeys Raoult's law (viz. previous subsection).

The whole of both sentences are no more than Henry's law.

Chapter 44

Chemical Potentials of Components of Binary Nonideal Solutions of Nonelectrolytes

Abstract The chapter mentions new expressions of the chemical potentials of the components of the binary nonideal solutions of nonelectrolytes. According to the foregoing considerations, it is logic to conceive that the comparison of the chemical potentials of components of ideal solutions with those of the components of nonideal ones may permit to get some insights into the expressions of activities and activity coefficients.

For the sake of further comparisons are set up, here, the expressions of the chemical potentials of the components of a nonideal solution, the behaviors of which are slightly different from that of a perfect solution on one hand and from that of an insufficiently dilute solution, on the other.

The reasoning leading to the expressions being searched for results from a mathematical relation stemming from Kirkwood–Buff's theory. This relation is recalled. According to it, the derivative at constant temperature and pressures of the chemical potential of a component of the solution with respect to its molar fraction is a function of its molar fraction, of the concentration of the other component and of a new parameter Δ_{AB} which is a linear combination of the Kirkwood–Buff's integrals G_{AA}, G_{BB}, and G_{AB}, where A and B symbolize the two components in interaction. When they are possible, the integrations of the foregoing derivative and of its variations (according to the experimental conditions) show the importance of this parameter.

Keywords Chemical potentials (binary nonideal solutions of nonelectrolytes) • Chemical potentials (ideal solutions) • Kirkwood–Buff's theory • Kirkwood–Buff's integrals • Derivatives of the chemical potentials (with their respect of their molar fractions) • Chemical potentials of the components of a solution (weakly deviating from a perfect solution) • Molar and molality scale • Solvent chemical potential

In this chapter, we are interested in the expressions of the chemical potentials of components of binary nonideal solutions of nonelectrolytes. According to the foregoing considerations, it is logic to conceive that the comparison of the chemical potentials of components of ideal solutions with those of the components of nonideal ones may permit to get some insights into the expressions of activities and activity coefficients.

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Here, we set up the expressions of the chemical potentials of the components of a nonideal solution, the behavior of which is:

- Slightly different from that of a perfect solution, on one hand.
- That of an insufficiently dilute solution, on the other.

The reasoning leading to the expressions being searched for results from a mathematical relation stemming from Kirkwood–Buff's theory. We begin by recalling this relation.

44.1 Derivatives of the Chemical Potentials of a Solution Components with Respect to Their Molar Fractions

Let us already mention that these derivatives are partial ones at constant pressure and temperature. For instance, in the case of compound A, it is the derivative: $(\partial\mu_{\mathrm{A}}/\partial x_{\mathrm{A}})_{\mathrm{T,P,}}$

The expression of the derivative is (viz., Chap. 42):

$$(\partial\mu_{\mathrm{A}}/\partial x_{\mathrm{A}})_{\mathrm{T,P}} = kT[1/x_{\mathrm{A}} - \rho_{\mathrm{B}}\Delta_{\mathrm{AB}}/(1+\rho_{\mathrm{B}}x_{\mathrm{A}}\Delta_{\mathrm{AB}})] \tag{44.1}$$

with:

$$\Delta_{\mathrm{AB}} = G_{\mathrm{AA}} + G_{\mathrm{BB}} - \ 2G_{\mathrm{AB}}$$

Functions $G_{\alpha\beta}$ $(\alpha, \beta^{\circ}.\mathrm{A\,and\,\,B})$ are spatial pair correlation functions or Kirkwood–Buff's integrals. They are themselves related to the radial distribution functions $g_{\alpha\beta}$ by the following expression:

$$\overline{G_{\alpha\beta}} = \int_0^{\infty} \left[g_{\alpha\beta}(R) - 1\right] 4\pi R^2 dR$$

44.2 Chemical Potentials of the Components of a Solution, the Behavior of Which Weakly Deviates from that of a Perfect Solution

For instance, this is the case of solutions, the components of which obey Raoult's law nearly in the whole range of "concentrations." Given their great similarity with symmetric ideal solutions, it is logic to choose the molar fraction as a unity of "concentration" of their components, for the sake of later comparison.

As a rule, it is possible to get an expression of the chemical potential μ_{A} by integration of (44.1). From another viewpoint, we know that an ideal solution obeys the relation (viz.: Chap. 43):

$$d\mu_{\mathrm{i}} = kT\,d\ \ln\,x_i \tag{44.2}$$

The comparison of both integrated forms may be, as a rule, interesting to carry out.

Let us formally integrate expression (44.1). By setting up:

$$\rho = \rho_{\mathrm{A}} + \rho_{\mathrm{B}}$$
$$x_{\mathrm{B}}\rho\ = \rho_{\mathrm{B}}$$

it can be also written as:

$$(\partial\mu_{\mathrm{A}}/\partial x_{\mathrm{A}})_{T,P,N} = kT[1/x_{\mathrm{A}} -\ x_{\mathrm{B}}\rho\Delta_{\mathrm{AB}}/(1+\rho x_{\mathrm{B}}x_{\mathrm{A}}\Delta_{\mathrm{AB}})] \tag{44.3}$$

or:

$$d\mu_{\mathrm{A}} = kT[1/x_{\mathrm{A}} -\ x_{\mathrm{B}}\rho\Delta_{\mathrm{AB}}/(1+\rho x_{\mathrm{A}}x_{\mathrm{B}}\Delta_{\mathrm{AB}})]dx_{\mathrm{A}} \qquad (dT = 0,\ d\mathbf{p} = 0)$$

Taking into account that the solution is binary, that is to say that $x_{\mathrm{A}} + x_{\mathrm{B}} = 1$,

$$dx_{\mathrm{A}} = -dx_{\mathrm{B}}$$

we obtain by integration:

$$\mu_{\mathrm{A}}(T,\mathbf{p},x_{\mathrm{A}}) = \mu_{\mathrm{A}}^{P}(T,\mathbf{p}) +\ kT\ \ln\,x_{\mathrm{A}} + kT\int_0^{x\mathrm{B}} \left[x_{\mathrm{B}}'\rho\Delta_{\mathrm{AB}}/(1+\rho x_{\mathrm{A}}'x_{\mathrm{B}}'\Delta_{\mathrm{AB}})\right]dx_{\mathrm{B}}' \tag{44.4}$$

Quite evidently, the definite integral $kT\int_0^{x\mathrm{B}} [x_{\mathrm{B}}'\rho\Delta_{\mathrm{AB}}/(1+\rho x_{\mathrm{A}}'x_{\mathrm{B}}'\Delta_{\mathrm{AB}})]dx_{\mathrm{B}}'$ must be related to the expression of the activity coefficient of compound A on the molar fractions scale.

44.3 Chemical Potentials of Components of Nonideal, Insufficiently Dilute, Solutions

44.3.1 Chemical Potentials in Nonideal, Dilute Solutions on the Density Numbers Scale

Let A be the most dilute component (the solute). We have seen (viz., Chap. 43) that it is more natural and also in any case more practical to adopt the scale of the density numbers in order to describe the behavior of the solutes. Since we are now on this scale, the expressions of chemical potentials of components are obtained by starting from their partial derivatives with respect to their density number ρ, directly set up by Kirkwood–Buff's theory (viz.: Chap. 42).

Three partial derivatives are of interest from the practical viewpoint. They are:

- $(\partial\mu_A/\partial\rho_A)_{T,\mu B}$ at constant chemical potential of the solvent and temperature. This derivative is interesting for the study of the osmotic pressure (viz.: Chap. 38).
- $(\partial\mu_A/\partial\rho_A)_{T,P}$ at constant temperature and pressure. It is the most important derivative because it concerns the kind of solution the most encountered in chemistry.
- $(\partial\mu_A/\partial\rho_A)_{T,\rho B}$ at constant temperature and density number of the solvent. (Obeying the latter condition is equivalent saying that the solvent volume is constant). This derivative is less important than the previous ones.

The expressions of these derivatives are known. They are given by Kirkwood–Buff's theory (viz.: Chap. 22). They are:

$$(\partial\mu_A/\partial\rho_A)_{T,\mu B} = kT/\left(\rho_A + {\rho_A}^2 G_{AA}\right)$$

It is also written as follows:

$$(\partial\mu_A/\partial\rho_A)_{T,\mu B} = kT[1/\rho_A - G_{AA}/(1+\rho_A G_{AA})] \tag{44.5}$$

$$(\partial\mu_A/\partial\rho_A)_{T,P} = kT/[\rho_A(1+\rho_A G_{AA} - \rho_A G_{AB})]$$

It is also written as:

$$(\partial\mu_A/\partial\rho_A)_{T,P} = kT[1/\rho_A - (G_{AA} - G_{AB})/(1+\rho_A G_{AA} - \rho_A G_{AB})] \tag{44.6}$$

$$(\partial\mu_A/\partial\rho_A)_{T,\rho B} = kT\left\{1/\rho_A \ - \ \left[G_{AA} + \rho_B\left(G_{AA}G_{BB} - {G_{AB}}^2\right)\right]/D\right\} \tag{44.7}$$

with:

$$D = 1 + \rho_A G_{AA} \ + \rho_B G_{BB} \ + \rho_A\rho_B\left(G_{AA}G_{BB} \ - \ G_{AB}^2\right)$$

Relation (44.7) also stems from the Kirkwood–Buff's theory by taking into account the relation:

$$V/kT(\partial\mu_A/\partial N_A)_{T,V,NB} = 1/kT\ (\partial\mu_A/\partial\rho_A)_{T,\rho B}$$

Some interesting results can be inferred from relations (44.5)–(44.7).

- Partial derivatives are divergent for $\rho_A \rightarrow 0$
- If $\rho_A \rightarrow 0$, the solution is ideal. The first term of relations (44.5)–(44.7) is dominant. As a result:

$$(\partial\mu_{\mathrm{A}}/\partial\rho_{\mathrm{A}})_{T,\mu\mathrm{B}} = (\partial\mu_{\mathrm{A}}/\partial\rho_{\mathrm{A}})_{T,P} = (\partial\mu_{\mathrm{A}}/\partial\rho_{\mathrm{A}})_{T,\rho\mathrm{B}} = kT/\rho_{\mathrm{A}} \quad (\rho_{\mathrm{A}} \to 0)$$

Then, the integration of the three partial derivatives leads to the three following expressions:

$$\begin{aligned} \mu_{\mathrm{A}\left(T,\mu\mathrm{B},\rho\mathrm{A}\right)} &= \eta^{\circ}{}_{\mathrm{A}(T,\mu\mathrm{B})} + kT\,\ln\rho_{\mathrm{A}} \\ \mu_{\mathrm{A}\left(T,P,\rho\mathrm{A}\right)} &= \mu^{\circ}{}_{\mathrm{A}(T,P)} + kT\,\ln\rho_{\mathrm{A}} \quad (\rho_{\mathrm{A}} \to 0) \\ \mu_{A\left(T,\rho\mathrm{B},\rho\mathrm{A}\right)} &= \mu^{\circ}{}_{\mathrm{A}\left(T,\rho\mathrm{B}\right)} + kT\,\ln\rho_{\mathrm{A}} \end{aligned} \tag{44.8}$$

These expressions are evidently different although they exhibit the same kind of mathematical expression since the three integration constants $\mu^{\circ}{}_{\mathrm{A}}$ (called the standard potential of A in the specified conditions) apply in different conditions as it is indicated by the indices of the partial derivatives.

Here is a new reason, which is different from that involving the choice of the scale of "concentrations," of the diversity of choices of the conditions which constitute the definition of standard states.

However, the similarity of the three expressions must be highlighted.

Returning to expressions (44.5)–(44.8), two observations must be made:

- The standard chemical potentials do not correspond to an actual standard state of the system. (When $\rho_{\mathrm{A}} = 1$, indeed, the solution is not sufficiently dilute to remain ideal—viz. Chap. 11). Let us recall that standard states of the components of symmetric ideal solutions do actually exist. They are defined as being their pure state in the conditions of the process ($x_{\mathrm{A}}\mathrm{and}x_{\mathrm{B}} = 1$).
- It is quite evident that the conditions underlying the fact that the term $1/\rho_{\mathrm{A}}$ may be much higher than others are different according to the investigated case. They can depend only on G_{AA} values for the first one, whether on both G_{AA} and G_{AB} for the second or, even, on the three G_{AA}, G_{AB}, G_{BB} for the third. This is a striking illustration of the interest of Kirkwood–Buff's theory.

44.3.2 Some Supplementary Considerations Concerning the Chemical Potential of the Solute at Constant Temperature and Pressure: The Part Played by the Scale of Concentrations

Chemical potentials and activities at constant temperature and pressure are quantities very often handled in the course of solutions studies. This is the reason why we focus ourselves on them. In this case, several concentration scales can happen to be used. As a result, activity values (and also those of their coefficients) vary. Besides, the already tackled density numbers scale, we now consider the scale of molar fractions and that of molalities.

- The molar fraction scale

The relation (44.3) stemming from the Kirkwood–Buff's theory remains valid since the reasoning leading to it is a general one. We observe that when $x_A \to 0$ (ideal solution), the term $1/x_A$ is dominant. Then:

$$(\partial\mu_A/\partial x_A)_{T,P} = kT/x_A \qquad (x_A \to 0) \tag{44.9}$$

whence

$$\mu_{A(T,P,xA)} = \mu^{\circ x}{}_A(T,\mathbf{p}) + kT \ \ln x_A \qquad (x_A \to 0) \tag{44.10}$$

$\mu^{\circ x}{}_A(T,\mathbf{p},x_A)$ is the integration constant, also named the standard potential. This new standard potential is different from that at constant temperature and pressure already encountered above (relation (8)):

$$\mu^{\circ x}{}_A(T,\mathbf{p},x_A) \neq \mu^{\circ}{}_A(T,\mathbf{p},\rho_A)$$

This accounts for the occurrence of a different superscript. We must indicate the adopted scale of concentration. $\mu^{\circ}{}_A(T,\mathbf{p},\rho_A)$ is, indeed, as it is recalled above, the standard chemical potential (at constant pressure and temperature) entering in the definition of the activity when it is related to the density number, whereas the writing $\mu^{\circ x}{}_A(T,\mathbf{p},x_A)$ indicates the concentration is expressed in molar fractions.

The expression relating one standard state to the other is:

$$\mu^{\circ}{}_A(T,\mathbf{p}) = \mu^{\circ x}{}_A(T,\mathbf{p}) - kT \ \ln\rho_B \tag{44.11}$$

It results from the relation existing between the total density number ρ of the solution, that of the solute A *and its molar fraction x_A:*

$$x_A = \rho_A/\rho$$

Replacing x_A by this expression into (44.9) *gives:*

$$\mu_A = \mu^{\circ x}{}_A(T,\mathbf{p}) + kT \ \ln\rho_A - kT \ \ln\rho$$

The chemical potential of a compound in a given state can be endowed solely with only one value, whatever the chosen scale of "concentrations." As a result, we can also write:

$$\mu_A = \mu^{\circ}{}_A(T,\mathbf{p}) + kT \ \ln\rho_A$$

The comparison of both latter relations, after taking into account the fact that $\rho \to \rho_B$ when $\rho_A \to 0$, leads to that mentioned above.

- Molality scale

Another standard potential interesting to express is that applying when the molalities scale is used. Let us recall that for dilute solutions, the molality value of a solute is very close to that of its molarity (cf, Chap. 1). Both are very often used especially in physical and analytical chemistries. When the solution is sufficiently dilute, the molality m_A is related to the molar fraction through the relation:

$$m_A = 1000\, x_A/M_B$$

where M_B is the solvent molecular weigh. Replacing x_A in (44.9) by its expression stemming from the relation just above, we obtain:

$$\mu_A = [\mu^{\circ x}{}_A(T, \mathbf{p}) \ + kT\ \ln(M_B/1000)] \ + \ kT \ \ \ln\, m_A$$
$$\mu_A = \mu^{\circ m}{}_A(T, \mathbf{p}) \ + \ kT\ \ln\, m_A$$

We note that the standard potentials $\mu^{\circ m}{}_A(T, \mathbf{p})$ and $\mu^{\circ x}{}_A(T, \mathbf{p})$ are not identical, whence their difference of superscripts.

44.3.3 Solvent Chemical Potential

Of course, it is also interesting to express the solvent B chemical potential. In order to do that, we use the Gibbs–Duhem's relation which is:

$$x_B(\partial\mu_B/\partial x_A)_{T,P} + x_A(\partial\mu_A/\partial x_A)_{T,P} = 0$$

Taking into account (44.8) which is valid when $x_A \to 0$, it becomes:

$$-x_B(\partial\mu_B/\partial x_B)_{T,P} + kT \ = 0 \quad (x_A \to 0)$$

After integration, we get:

$$\mu_B(T, \mathbf{p}, x_B) = \ C(T, \mathbf{p}) \ + kT\ \ln \ \ x_B \quad (\mathrm{x}_A \to 0)$$

where $C(T, \mathbf{p})$ is the integration constant. In order to specify it, we take into account the fact that when $x_A \to 0$, $x_B \to 1$. Hence, $C(T, \mathbf{p})$ is equal to the chemical potential of the pure solvent $(x_B = 1)$, that is to say:

$$C(T, \mathbf{p}) = \mu_B^P(T, \mathbf{p})$$

and

$$\mu_{\mathrm{B}}(T, \mathbf{p}, x_{\mathrm{B}}) = \mu_{\mathrm{B}}^{P}(T, \mathbf{p}) + kT \ln x_{\mathrm{B}} \quad (x_{\mathrm{B}} \rightarrow 1)$$

This result has already been mentioned several times.

At this point, let us recall that quasi-systematically in chemistry, the solute activities are related to their molalities or molarities and the solvent activity to its molar fraction (viz.: Chap. 1).

Chapter 45

Expressions of Activity Coefficients and Activities in Relation to Kirkwood–Buff's Theory

Abstract As it has been anticipated and as it is shown in this chapter, the Kirkwood–Buff's theory can provide expressions for activities and their coefficients of the components of nonideal solutions of nonelectrolytes through the derivatives of the chemical potentials, at least at the first level of approximation. Actually, as it is described, comparisons of the expressions of the chemical potentials of the component of ideal solutions with those found (for the same conditions) by integration after the using of Kirkwood–Buff's theory, indeed, permit to get some expressions of activity coefficients and show that they are functions of some molecular parameters with probably the most important one of them, the parameter Δ_{AB} and the Kirkwood–Buff's integrals. They are different from those stemming from McMillan–Mayer's theory. Then, Kirkwood–Buff's theory may be considered as completing the latter, besides, of course, its intrinsic theoretical interest.

No doubt that the McMillan–Mayer's theory and overall the Kirkwood–Buff's theory bring a very important piece in the understanding of the physical significance of an activity.

Keywords Expressions of activities and activity coefficients in relation to Kirkwood–Buff's theory • The parameter Δ_{AB} • Chemical potentials (components of ideal solutions) in comparison with those found by integration of the theory • Different kinds of ideal solutions • Activity and activity coefficients in the case of symmetric nonideal solutions and of dilute solutions • Multiplicity of activities • Meaning of the parameter Δ_{AB} • Lattice model of solutions

We recently anticipated that Kirkwood–Buff's theory can provide expressions for activities and their coefficients of the components of nonideal solutions of nonelectrolytes, at least at the first level of approximation. Actually, we shall see that, indeed, it permits to get some expressions of activity coefficients and that they are functions of some molecular parameters. They are different from those stemming from McMillan–Mayer's theory. Then, Kirkwood–Buff's theory may be considered as completing the latter, besides, of course, its intrinsic theoretical interest.

In this chapter, again, we commit ourselves to the sole study of nonideal solutions of non electrolytes.

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45.1 Some Introductory Points: Different Kinds of Ideal Solutions

The considerations developed in the previous chapters provide us with some mathematical relations which enable us to get expressions of activity coefficients and of the corresponding activities, at least formally. But, before studying them, it is judicious to recall the different kinds of ideal solutions to which are related the nonideal ones.

We know, indeed, that the standard state is the same for both the ideal hypothetical solution and the studied nonideal one, related to the former (viz. Chap. 11).

As a rule, the important point is to recall that the choice of another ideal solution of reference than that just evocated induces the choice of another standard state. It entails the introduction of another type of activity coefficient and of activity. But, this choice is perfectly licit, because the chemical potential of a component in a given state is a constant.

The differential equation (45.1), given the manner how it has been set up (viz.: Chaps. 42 and 44), can apply to symmetrical solutions and to very dilute ones as well (for definitions of symmetrical and very dilute solutions, see just below):

$$(\partial \mu_{\mathrm{A}}/\partial x_{\mathrm{A}})_{T,P} = kT\left[1/x_{\mathrm{A}} - x_{\mathrm{B}}\rho\Delta_{\mathrm{AB}}/(1+\rho x_{\mathrm{A}}x_{\mathrm{B}}\Delta_{\mathrm{AB}})\right] \tag{45.1}$$

(Let us recall that, in this equation, ρ is the total density number: $\rho = \rho_{\mathrm{A}} + \rho_{\mathrm{B}}$; x_{A} and x_{B} are the molar fractions and Δ_{AB} the combination of the Kirkwood–Buff's integrals: $G_{\mathrm{AA}} + G_{\mathrm{BB}} - 2G_{\mathrm{AB}}$)) Fig. 45.1.

As we shall see, now, equation (45.1) permits to identify the ideality and nonideality conditions. Through them, it is possible to characterize three different types of ideal fluids.

- The first type corresponds to the case for which $\rho \rightarrow 0$. Then, the particles constituting the fluid are, on the average, very far from others. The intermolecular forces exert no effect on the properties of the mixture. Its behavior tends toward that of a perfect gases mixture, in which by hypothesis, there exists no interaction between the particles. Then, the relation (45.1) becomes:

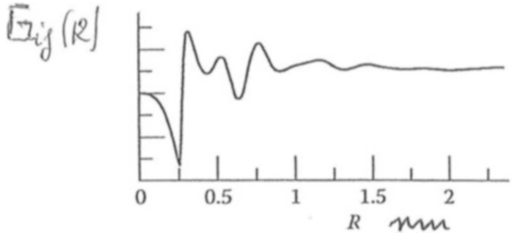

Fig. 45.1 General shape of a Kirkwood–Buff's integral as a function of the distance *R* (nm) of integration

$$(\partial\mu_A/\partial x_A)_{T,P} = kT/x_A$$

This case is of little interest for us, because we are considering the case of solutions.

- The second kind of ideal solution corresponds to the case for which $\Delta_{AB} = 0$ in (45.1). It is that for which both components are symmetrical. The partial derivative is written just as above:

  $$(\partial\mu_A/\partial x_A)_{T,P} = kT/x_A$$

  It is interesting to notice that, once the condition $\Delta_{AB} = 0$ is obeyed, the intensity of the intermolecular and the total molar fraction ρ do not preclude the "ideality" of the solution.
- The third type corresponds to the case for which $x_A \to 0$. Under these conditions, the term $1/x_A$ is by far stronger than the second in the right member of relation (45.1). Hence, the expression of the partial derivative of the chemical potential exhibits the simplified form above. It is the case of the very dilute solutions.

In order to theoretically treat a problem involving a nonideal solution, there is absolutely no objection that it would be treated as being a deviant from an ideal one, whether the latter is of the first, second, or the third types just above. In each case, the introduction of a specific activity coefficient rectifies the nonideality character, as it was thought up by Lewis.

According to the fact that the deviance from "ideality" must be related to one of the three cases, the three corresponding activity coefficients are different. As a result, the chemical potential of the solute A is written as:

$$\mu_A = c_1 + kT\ \ln\left(x_A\gamma^{gi}\right)$$

$$\mu_A = c_2\ +\ kT\ \ln(x_A\gamma^{S})$$

$$\mu_A = c_3\ +\ kT\ \ln(x_A\gamma^{D})$$

γ^{gi} (gi: for ideal gas)', γ^{S} (S: for symmetric), γ^{D} (D: for dilute) are the activity coefficients corresponding to the three types of solutions. c_1, c_2, c_3 are the integration constants. As it has been already said, the activities exhibit different expressions and values according to the case.

45.2 Expressions of the Activities and of the Activity Coefficients in the Case of Symmetric Nonideal Solutions

- General case

  Sometimes, the solubility or the miscibility of the components permits to choose their standard states, as being themselves in pure state (x_A or $x_B = 1$), at the temperature and pressure of the system. For these practical reasons, it is more convenient to adopt the molar fraction scale, since both molar fractions (x_A or $x_B = 1$) can be reached. Because of this fact, both components can be treated symmetrically. It is, then, advisable to reason with respect to the second kind of ideal fluid.

The standard states do, indeed, exist really and their thermodynamic properties are known. The curves of the fugacities and activities of the components, versus their molar fractions, are described in Chap. 11.

Hence, the activity coefficient is of the type γ^S and the activity of the type $x\,\gamma^S$. One knows (viz.: Chap. 44) that relation (45.1) leads to expression (45.2) after integration, given the fact that $x_A + x_B = 1$.

$$kT\ \ln\ \gamma_A^S = kT\int_0^{xB}\left[x'_B\rho\Delta_{AB}/\left(1+\rho x'_A x'_B\Delta_{AB}\right)\right]dx'_B \tag{45.2}$$

(45.2) can be also written as (45.3):

$$\begin{aligned}\gamma_A^S &= \exp\left[\int_0^{xB}\left[x'_B\rho\Delta_{AB}/\left(1+\rho x'_A x'_B\Delta_{AB}\right)\right]dx'_B\right]\\ a_A^S &= x_A\exp\left[\int_0^{xB}\left[x'_B\rho\Delta_{AB}/\left(1+\rho x'_A x'_B\Delta_{AB}\right)\right]dx_B\right]\end{aligned} \tag{45.3}$$

The Relations (45.3) are the expressions of the activity coefficients and of the activities of the components of nonideal symmetric solutions on the molar fraction scale, at the first level of approximation.

Unfortunately, these expressions remain purely formal because the integration cannot be carried out, since we do not know the variations of the function Δ_{AB} with the molar fractions. (Besides, we do not know them more with molalities and molarities than with molar fractions).

We notice that activities and activity coefficients are a function of the total density number ρ, the molar fractions x_A, x_B, and the quantity $\Delta_{AB.}$ Moreover, the function is more complicated than it seems at first sight because $\Delta_{AB.}$ depends itself on ρ, x_A, x_B. Furthermore, it must not be forgotten that these expressions result from truncatures of series developments leading to simplifications.

Actually, few binary systems are in this case for solubility or miscibility reasons. An usual example is provided by some mixtures of liquids.

– Particular cases

At this point of the study, it is interesting to investigate some particular cases.

- We can consider the case in which the product $\rho\Delta_{AB}$ is independent of the composition.

  The integration:

$$\int_0^{xB}\left[x'_B\rho\Delta_{AB}/\left(1+\rho x'_A x'_B\Delta_{AB}\right)\right]dx_B$$

is then possible. We obtain:

$$\mu_{\mathrm{A}}(T,P,x_{\mathrm{A}}) = \mu_{\mathrm{A}}^{\mathrm{P}}(T,P) \ + kT\ln x_{\mathrm{A}} + 1\ /2kT\rho x_{\mathrm{B}}^{2}\Delta_{\mathrm{AB}} \tag{45.4}$$

Let us introduce the quantity $\gamma_{\mathrm{A}}^{\prime\mathrm{S}}$ for the sake of argument. $\gamma_{\mathrm{A}}^{\prime\mathrm{S}}$ is defined by the equality:

$$\gamma_{\mathrm{A}}^{\prime\mathrm{S}} = \exp\left(1/2\rho x_{\mathrm{B}}^{2}\Delta_{\mathrm{AB}}\right) \tag{45.5}$$

(The exponent S recalls that the solution is related to a symmetric one and the prime that we are facing a particular case). Relation (45.4) can, now, be written:

$$\mu_{\mathrm{A}}(T,P,x_{\mathrm{A}}) = \mu_{\mathrm{A}}^{\mathrm{P}}(T,P) + kT\ln\left(x_{\mathrm{A}}\gamma_{\mathrm{A}}^{\prime\mathrm{S}}\right) \tag{45.6}$$

After examination of relation (45.6), it appears that the quantity $\gamma_{\mathrm{A}}^{\prime\mathrm{S}}$ is the activity coefficient of *A* and that the product $x_{\mathrm{A}}\gamma_{\mathrm{A}}^{\prime\mathrm{S}}$ is the activity of A. Such an activity is related to the scale of molar fractions. Although this double assimilation stems from a particular case, it has the great merit to induce the following comments:

The activity coefficient depends on the molar fraction x_{B} of the other component and also of its own molar fraction $x_{\mathrm{A},}$ since x_{A} and x_{B} are linked. It also depends on the total molar fraction ρ. The activity, for its part, directly depends, of course, on its concentration x_{A} but, moreover indirectly, also on x_{B} through the activity coefficient.

Relation (45.5) brings a theoretical support to Margules relation, the origin of which is purely experimental. Let us recall that it permits to express the activity of a component in the same conditions (viz. Chaps. 8 and 12) according to the relation:

$$f_{\mathrm{A}} = f_{\mathrm{A}}^{0}x_{\mathrm{A}}\exp\left[1/2\beta_{1}x_{\mathrm{B}}^{2} \ + \cdots\right]$$

We recall that f_{A} and f_{A}^{0} are the fugacities of A in the solution and in the pure liquid state, the ratio $f_{\mathrm{A}}/f_{\mathrm{A}}^{0}$ being the activity of the compound. We can, in particular, notice the dependence of the activity coefficient with the exponential, the exponent of which is the square of the molar fraction of the other component. Thus, such an exponent, somewhat unexpected at first sight, is found in both relations: the experimental and theoretical ones. It is a satisfactory point.

* Another interesting particular case is that in which $\Delta_{\mathrm{AB}} = 0$.

As a result, the chemical potential μ_{A} is given by the expression:

$$\mu_A(T, P, x_A) = \mu_A^P(T, P) + kT\ln x_A \quad (\Delta_{AB} = 0)$$

The activity coefficient γ_A^S is, then, equal to unity. We must notice that such an expression does not obligatorily mean that there exists no interaction between the components. It may also mean that these interactions may counterbalance themselves according to the equality:

$$G_{AA} + G_{BB} - 2G_{AB} = 0$$

Remark: Standard state—Raoult's law

In the case of symmetric nonideal solutions, the standard state chosen in order to define the activities of both components is the component in pure state at temperature and pressure of the solution. If $x_A = 1$, *indeed, the activity is equal to unity (since* $a_A = x_A\gamma_A^S$*) and the solution is ideal. The activity coefficient is, then, referred to Raoult's law.*[1]

45.3 Expressions of Activity Coefficients and Activities of the Components of Nonideal Dilute Solutions

This case has already been studied from the viewpoint of classical thermodynamics (viz. Chap. 11). It is of great importance in analytical and physical chemistry.

We have already said that essentially for practical reasons of solubility of the solutes, it is convenient to relate their activities to the concentration scale expressed in density numbers, whereas the solvent activity remains related to its molar fraction.

Now, we successively investigate the expressions of the activity coefficients and of activities for both kinds of components.

- Concerning the solute:

  Because of the choice of the concentration scale, the activity coefficients are of the type γ^D and the behaviors of the components are related to the third type of an ideal fluid.

  We know (viz.: Chap. 44) that several partial derivatives $(\partial\mu_A/\partial\rho_A)$ exist according to the experimental conditions. Their expressions are directly found from Kirkwood–Buff's theory (viz. Chap. 42). They are:

$$(\partial\mu_A/\partial\rho_A)_{T,\mu B} = kT[1/\rho_A - G_{AA}/(1 + \rho_A G_{AA})] \tag{45.7}$$

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[1] Let us recall that in this case, the activity coefficient must be symbolized by f according to IUPAC. We prefer to keep the symbol γ in order to avoid any confusion with the fugacity.

$$(\partial\mu_{\mathrm{A}}/\partial\rho_{\mathrm{A}})_{T,P} = kT[1/\rho_{\mathrm{A}} - (G_{\mathrm{AA}} - G_{\mathrm{AB}})/(1 + \rho_{\mathrm{A}}G_{\mathrm{AA}} - \rho_{\mathrm{A}}G_{\mathrm{AB}})] \qquad (45.8)$$

$$(\partial\mu_{\mathrm{A}}/\partial\rho_{\mathrm{A}})_{T,\rho_B} = kT\left\{1/\rho_{\mathrm{A}} - \left[G_{\mathrm{AA}} + \rho_{\mathrm{B}}\left(G_{\mathrm{AA}}G_{\mathrm{BB}} - G^2_{\mathrm{AB}}\right)\right]/D\right\} \qquad (45.9)$$

with:

$$D = 1 + \rho_{\mathrm{A}}G_{\mathrm{AA}} + \rho_{\mathrm{B}}G_{\mathrm{BB}} + \rho_{\mathrm{A}}\rho_{\mathrm{B}}\left(G_{\mathrm{AA}}G_{\mathrm{BB}} - G^2_{\mathrm{AB}}\right)$$

Let us consider expressions (45.7), (45.8), and (45.9) and develop in series the integrals $G_{\alpha\beta}$ of their right members in powers of ρ_{A} and finally only retain the first two terms according to:

$$G_{\mathrm{AA}}(\rho_{\mathrm{A}}) = G_{\mathrm{AA}}(\rho_{\mathrm{A}} = 0) + (\partial G_{\mathrm{AA}}/\partial\rho_{\mathrm{A}})_{\rho_{\mathrm{A}}=0}\rho_{\mathrm{A}} + \cdots$$

$$G_{\mathrm{AB}}(\rho_{\mathrm{A}}) = G_{\mathrm{AB}}(\rho_{\mathrm{A}} = 0) + (\partial G_{\mathrm{AB}}/\partial\rho_{\mathrm{A}})_{\rho_{\mathrm{A}}=0}\rho_{\mathrm{A}} + \cdots$$

$$G_{\mathrm{BB}}(r_{\mathrm{A}}) = G_{\mathrm{BB}}(\rho_{\mathrm{A}} = 0) + (\partial G_{\mathrm{BB}}/\partial\rho_{\mathrm{A}})_{\rho_{\mathrm{A}}=0}\rho_{\mathrm{A}} + \cdots$$

Symbolizing $G_{\mathrm{AA}}(\rho_{\mathrm{A}} = 0)$, $G_{\mathrm{AB}}(\rho_{\mathrm{A}} = 0)$, $G_{\mathrm{BB}}(\rho_{\mathrm{A}} = 0)$, respectively, by $G^{\circ}{}_{\mathrm{AA}}$, $G^{\circ}{}_{\mathrm{AB}}$, $G^{\circ}{}_{\mathrm{BB}}$, we obtain:

$$(\partial\mu_{\mathrm{A}}/\partial\rho_{\mathrm{A}})_{T,\mu B} = kT\left(1/\rho_{\mathrm{A}} - G^{\circ}_{\mathrm{AA}} + \cdots\right) \qquad (45.10)$$

$$(\partial\mu_{\mathrm{A}}/\partial\rho_{\mathrm{A}})_{T,P} = kT\left[1/\rho_{\mathrm{A}} - \left(G^{\circ}_{\mathrm{AA}} - G^{\circ}_{\mathrm{AB}}\right) + \cdots\right] \qquad (45.11)$$

$$(\partial\mu_{\mathrm{A}}/\partial\rho_{\mathrm{A}})_{T,\rho_B} = kT\left\{1/\rho_{\mathrm{A}} - \left[G^{\circ}_{\mathrm{AA}} + \rho^{\circ}_{\mathrm{B}}\left(G^{\circ}_{\mathrm{AA}}G^{\circ}_{\mathrm{BB}} - G^{\circ 2}_{\mathrm{AA}}\right)\right]/\left(1 + \rho^{\circ}_{\mathrm{B}}G^{\circ}_{\mathrm{BB}}\right) + \cdots\right\} \qquad (45.12)$$

As far as the truncatures are legitimate, the three above expressions can, then, be integrated. We obtain:

$$\mu_{\mathrm{A}}(T,\mu_{\mathrm{B}},\rho_{\mathrm{A}}) = \mu^{\circ}_{\mathrm{A}}(T,\mu_{\mathrm{B}}) + kT\ln\rho_{\mathrm{A}} - kTG^{\circ}_{\mathrm{AA}}\rho_{\mathrm{A}} + \cdots \qquad (45.13)$$

$$\mu_A(T,P,\rho_{\mathrm{A}}) = \mu^{\circ}_{\mathrm{A}}(T,P) + kT\ln\rho_{\mathrm{A}} - kT\left(G^{\circ}_{\mathrm{A}} - G^{\circ}_{\mathrm{AB}}\right)\rho_{\mathrm{A}} + \cdots \qquad (45.14)$$

$$\begin{aligned}\mu_{\mathrm{A}}(T,\rho_{\mathrm{A}},\rho_{\mathrm{B}}) = \mu^{\circ}_{\mathrm{A}}(T,\rho_{\mathrm{B}}) + kT\ln\rho_{\mathrm{A}} \\ - kT\left\{G^{\circ}_{\mathrm{AA}} - \left[\rho^{\circ}_{\mathrm{B}}\left(G^{\circ}_{\mathrm{AB}}\right)^2\right]/\left(1 + \rho^{\circ}_{\mathrm{B}}G^{\circ}_{\mathrm{BB}}\right)\right\}\rho_{\mathrm{A}} + \cdots\end{aligned} \qquad (45.15)$$

These three expressions suggest defining the activity coefficients by the relations (45.16), (45.17), (45.18) and the activities by relations (45.19), (45.20), (45.21), (the arguments of the logarithms in the three latter relations being the activities of the solute):

$$kT\ \ln\gamma_A^D(T,\mu_B,\rho_A) = -kT\overset{\circ}{G}_{AA}\rho_A \tag{45.16}$$

$$kT\ \ln\gamma_A^D(T,P,\rho_A) = -kT\left(\overset{\circ}{G}_{AA} - \overset{\circ}{G}_{AB}\right)\rho_A \tag{45.17}$$

$$kT\ \ln\gamma_A^D(T,\rho_B,\rho_A) = -kT\left\{\overset{\circ}{G}_{AA} - \left[\overset{\circ}{\rho}_B\left(\overset{\circ}{G}_{AB}\right)^2\right]/\left(1+\overset{\circ}{\rho}_B\overset{\circ}{G}_{BB}\right)\right\}\rho_A \tag{45.18}$$

$$\mu_A(T,\mu_B,\rho_A) = \overset{\circ}{\mu}_A(T,\mu_B) + kT\ \ln\left[\rho_A\gamma_A^D(T,\mu_B,\rho_A)\right] \tag{45.19}$$

$$\mu_A(T,P,\rho_A) = \overset{\circ}{\mu}_A(T,\mathbf{p}) + kT\ \ln\left[\rho_A\gamma_A^D(T,P,\rho_A)\right] \tag{45.20}$$

$$\mu_A(T,\rho_A,\rho_B) = \overset{\circ}{\mu}_A(T,\rho_B) + kT\ \ln\left[\rho_A\gamma_A^D(T,\rho_B,\rho_A)\right] \tag{45.21}$$

Relations (45.16) to (45.21) are the expressions of the activity coefficients and of the activities of the solute of nonideal dilute solutions on the scale of density numbers, at the first level of approximation.

Unfortunately, they remain also essentially formal. However, they induce the following conclusions:

- According to the conditions defining the system (viz. the partial derivatives indices), the activities differ since the respective activity coefficients are not the same.

  Here, again, we are facing up with the important fact that, according to the experimental conditions, there exist different activities of a solute of a dilute solution.

  In strict scientific rigor, this fact would force to use cumbersome symbolism which is not perceptible in literature. The reason of this matter of fact is that the parameters defining a system are often (if not always) known. As a result, there is omission of some symbols.
- Relations (45.16), (45.17), and (45.18) show that the activity coefficients depend on the density numbers ρ_A and ρ_B and on the different integrals $G_{\alpha\beta}$. Evidently, it is the same for activities. In this case, the dependence on ρ_A is double, since besides that on the activity coefficients, the value of an activity is equal to the product of a density number by the corresponding activity coefficient.
- Relations (45.16), (45.17), and (45.18) also show that when ρ_A tends toward zero, the activity coefficients γ^D, whatever they are, tends toward 1, in full agreement with the Lewis' definition:

$$\lim\gamma^D(\rho_A \to 0) = 1$$

- The above reasoning, especially the limited development in series shows that, in the considered conditions, the standard state retained in order to define the activities is the infinite dilute solution. In other words, for solutes, activities are defined in such a way that Henry's law is obeyed.

  - Coefficients γ^{D} are evidently different from coefficients γ^{S}.
  - Again, we can also notice the presence of the Kirkwood–Buff's integrals in these expressions.

- Concerning the solvent
  It is also interesting to consider the expression of the solvent chemical potential in a dilute solution. The simplest way to grasp it is to use the relation related to the solvent B, stemming from the Kirkwood–Buff's theory:

$$(\partial\mu_{\mathrm{B}}/\partial x_{\mathrm{B}})_{T,P} = kT[1/x_{\mathrm{B}} - \rho_{\mathrm{A}}\Delta_{\mathrm{AB}}/(1 + \rho_{\mathrm{A}}x_{\mathrm{B}}\Delta_{\mathrm{AB}})]$$

For a solution, the behavior of which is very weakly different from that exhibited by an ideal very dilute solution ($\rho_{\mathrm{A}} \to 0$), the relation becomes:

$$(\partial\mu_{\mathrm{B}}/\partial x_{\mathrm{B}})_{T,P} \approx kT(1/x_{\mathrm{B}} - \rho_{\mathrm{A}}\Delta_{\mathrm{AB}}\cdots)$$

or

$$(\partial\mu_{\mathrm{B}}/\partial x_{\mathrm{B}})_{T,P} = kT(1/x_{\mathrm{B}} - \rho x_{\mathrm{A}}\Delta_{\mathrm{AB}}\ldots)$$

and after the development in series according to the powers of x_{A}:

$$(\partial\mu_{\mathrm{B}}/\partial x_{\mathrm{B}})_{T,P} = kT\left(1/x_{\mathrm{B}} - \rho^{\circ}x_{\mathrm{A}}\overset{\circ}{\Delta}_{\mathrm{AB}}\ldots\right) \quad (x_{\mathrm{A}} \to 0)$$

By integration of this expression, we obtain:

$$\mu_{\mathrm{B}}(T,P,x_{\mathrm{B}}) = \mu_{\mathrm{B}}^{\mathrm{P}}(T,P) + kT\ \ln x_{\mathrm{B}} + kT\int_0^{x\mathrm{A}} \rho^{\circ}\overset{\circ}{\Delta}_{\mathrm{AB}}x'_{\mathrm{A}}dx'_{\mathrm{A}} \quad (x_{\mathrm{A}} \to 0)$$

$$\mu_{\mathrm{B}}(T,P,x_{\mathrm{B}}) = \mu_{\mathrm{B}}^{\mathrm{P}}(T,P) + kT\ \ln x_{\mathrm{B}} + 1/2kT\overset{\circ}{\rho}_{\mathrm{B}}\overset{\circ}{\Delta}_{\mathrm{AB}}x_{\mathrm{A}}^2 \quad (x_{\mathrm{A}} \to 0\ \ x_{\mathrm{A}} \to 1)$$

Contrary to the case of the solute, the chosen standard state for the solvent is itself in pure state at the pressure and temperature of the system. It is a real state. Here, we again find the fact that it obeys Raoult's law.

45.4 Multiplicity of Activities: Other Kinds of Activities

A striking fact is the multiplicity of the possible activities of different values characterizing notably a solute in a given system. We saw just above that nothing but three activities can be effective when the scale of concentrations is based on the density numbers. There remain other possibilities. For example, for the solutes, the concentration scale may be that of molar fraction (even if it is often inconvenient) but, also, those of molalities and molarities. In each case, the standard states are not the same and the activities of one component in a given thermodynamic system exhibit different values (viz.: Chap. 11).

45.5 Meaning of the Parameter $\varDelta_{AB}$

All these results highlight the importance of the parameter $\varDelta_{AB}$:

$$\varDelta_{AB} = G_{AA} + G_{BB} - 2G_{AB} \tag{45.22}$$

in which the $G_{\alpha\beta}$ are Kirkwood–Buff's integrals (viz.: Chap. 42). We have already mentioned that Kirkwood–Buff's integrals represent the particles β in excess around one α for a density unity and conversely. The expression $\rho_B[g_{BA}(R) - 1]4\pi R\ ^2dR$, indeed, measures the excess (or the deficit) of particles B in a spherical shell of volume $4\pi R^2dR$ around a particle A with respect to the number which would be found if we would have only taken into account the average density $\rho_{B.}$ Thus, we may consider that $G_{\alpha\beta}$ represents the affinity of α for β and conversely. (The term affinity, used here, must not be endowed with the meaning it possesses in classical thermodynamics.)

Owing to these last considerations plus the previous ones concerning solutions which are weakly deviant from the ideal symmetric ones, we may acknowledge that the linear combination $\varDelta_{AB}$ is a measure of the similarity of components A and B.

The mathematical structure of expression (45.22) refers to relation (45.23) representing the lattice-model of solutions. According to it, the condition of the status of ideal symmetric solution is (viz. Chap. 16):

$$W_{AA} + W_{AB} - 2W_{AB} = 0 \tag{45.23}$$

$W_{\alpha\beta}$ are the interaction energies between the species α and β located on the neighbor lattice points.

Finally, from a mathematical viewpoint, we notice that when $\varDelta_{AB} = 0$, G_{AB} is the arithmetic average of the integrals G_{AA} and G_{BB}. This point must be compared with the term ($G_{11}G_{22}$–G_{12}^2) arising in the definition of ζ found into Kirkwood–Buff's theory (viz.: Appendix D supplement 3) in which G_{12} is the geometrical average of G_{11} and G_{12} when $\Delta_{AB} = 0$.

Chapter 46
Debye–Hückel Theory

Abstract According to the state of the art, it is impossible to determine the activity or the activity coefficient of an ion. However, one knows how to approach their numerical values, at least for the sufficiently dilute solutions in ions, solutions qualified of weak ionic strengths. This calculation is possible thanks, notably, to the Debye–Hückel relations. Hence, the Debye–Hückel's theory is of utmost interest not only, evidently, from the theoretical standpoint but also from the practical one. In order to illustrate this point, the following example of the electrochemical methods of chemical analysis may be mentioned. Some of them respond, indeed, to the activities of species to which they are sensitive. Moreover, from the theoretical standpoint, the Debye–Hückel relations are greatly useful as soon as calculations of the "concentrations" of the ions must be refined.

In this chapter, the setting up of the Debye–Hückel theory is given and its validity is thoroughly discussed. It is particularly the case for some simplifications accompanying the theory which, despite their occurrence, do not preclude its validity, at least in some conditions. It can be said, indeed, that the Debye–Hückel works better than it is awaited!

Some other relations which can be considered as being extensions of the previous ones are also given in the chapter. They are devised in order to be useful in the cases of solutions of less weak ionic strengths as those to which Debye–Hückel relations can legitimately apply.

A brief review concerning the forces exerting between atoms and molecules precede these considerations in order to better specify the range in which Debye–Hückel laws apply and why.

Keywords Debye–Hückel's relations (theory) • Electrochemical methods and activities • Ionic strength • Intermolecular forces • Electrostatic potential • Poisson–Boltzmann's equation • Absolute permittivity • Debye–Hückel's length • Ionic interactions • Ion-size parameter • Ion solvatation • Ion pairs • Hypothesis on which is based the Debye–Hückel's theory • Agreement theory of the Debye–Hückel relations (limited and extended) with experiments • Solvation of the ions • Changes of the dielectric constants with the ions concentrations • Ion-pairs formation

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According to the state of the art, one does not know how to measure the activity or the activity coefficient of an ion. However, one knows how to approach their numerical values, at least for the sufficiently dilute solutions in ions, solutions qualified of weak ionic strengths. This calculation is possible thanks, notably, to the Debye–Hückel relations. Hence, the Debye–Hückel theory is of utmost interest not only, evidently, from the theoretical standpoint but also from the practical one. In order to illustrate this point, let us take the following example of the electrochemical methods of chemical analysis. Some of them respond, indeed, to the activities of species to which they are sensitive. Moreover, from the theoretical standpoint, the Debye–Hückel relations are greatly useful as soon as calculations of the "concentrations" of the ions must be refined.

In this chapter, we study the Debye–Hückel theory, the validity of which is discussed. We also mention some other relations which can be considered as being extensions of the previous ones. They are devised in order to be useful in the case of solutions of less weak ionic strengths as those to which Debye–Hückel relations can legitimately apply.

But, before, we begin with a brief review concerning the forces exerting between atoms and molecules in order to better specify the range in which Debye–Hückel laws apply and why.

46.1 Intermolecular Forces

The forces exerting between atoms, molecules, and ions are from electrostatic origin. They are of different kinds. Finally, their theoretical basis is Coulomb's law which commands the attraction and the repulsion of the electrical charges. According to the type of molecular interactions, one speaks of long-range or short-range forces. For example, it is evident that the force exerting between two particles, which is expressed by a relation in $1/r^2$ (r being the distance between both particles), does possess a range of action by far greater than that of the force which is expressed in $1/r^7$.

Let us consider one system constituted by two charges (ions i and j). One knows (viz. Appendix P) that the force occurring at the distance r_o of one of both charges is, in absolute value, equal to the gradient of the potential energy of electrostatic interaction between both charges, that is to say:

$$f = -\left(dU_{ij}/dr\right)_{ro}$$

The intermolecular potential energy exhibits different forms according to the kinds of interactions between the particles. One distinguishes the interaction energies between:

- Two ions. It is expressed by a relation of the kind:

  $$U_{ij} = k/r$$

  where k is a constant. It gives rise to a long-range force. The corresponding potential interaction energy is of the order of 250 kJ mol^{-1}.
- One ion and a permanent dipole. It is expressed by a relation of the type:

  $$U_{ij} = k/r^2$$

  Its energy is of the order of 15 kJ mol^{-1}.
- Two permanent dipoles. It is expressed by an expression of the kind:

  $$U_{ij} = k/r^6$$

  This interaction gives rise to Keesom's forces.
- A permanent dipole and the induced dipole in the other molecule by the first one, with:

  $$U_{ij} = k/r^6$$

  relation analogous to the previous one. This interaction gives rise to Debye's forces.
- Molecules or atoms, electrically neutral species, as it is the case for the rare gases with, also, a relation of the type:

  $$U_{ij} = k/r^6$$

  giving rise to London's forces, which are essentially of quantum origin. The last three types of interactions exhibit an energy of the order of 1 kJ mol^{-1}.

All these interactions generate attractions between particles. Keesom, Debye, and London's forces are generally classified under the heading of Van der Waals' forces, although there exists some incertitude in the literature concerning the forces entering under this denomination. Let us notice that the Van der Waals forces entail no electrical charges neither permanent dipoles. Moreover, among the three, the London's forces are the most intense.

46.2 Strategy Followed in the Drawing Up of the Debye–Hückel Theory

The impossibility to determine the activity of an ion alone is due to the fact that it is not possible to experimentally measure the part of the Gibbs energy of a system which can be assigned to the interaction of ion i (that the activity coefficient of which is wanted) with the other ions of the solution (viz. Chap. 15).

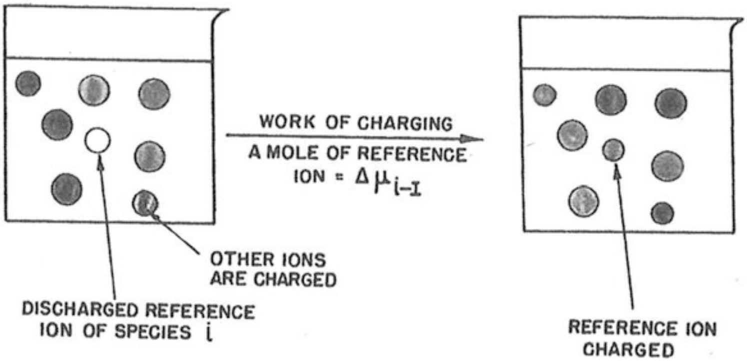

Fig. 46.1 Initial and final states of the charging process of the ion *i.(Reprinted from John O'M. Bockris and Amulya K.N. Reddy in "Modern electrochemistry 1 Ionics,* 2nd *edition, with kind permission from Springer Science plus Media LLC)*

The following process has been devised.

At the initial point of the process, all the ions of the solution are mutually in interactions. Among them, only one, ion *i*, is supposed, at the beginning of the process to be electrically uncharged and to be located in the point O. O is chosen as being the coordinates center. In the final state, *i* is endowed with the electrical charge $z_i e_o$ (z_i being the number of charges of the ion and e_o the elementary charge). The strategy consists in calculating the work *w* developed between both instants in order that the ion should be charged (Fig. 46.1). The charging work is equal to the reversible, isothermal one necessary in order to charge one mole of ion *i* at the point O. Il is developed again in 46.3 under. The intermolecular forces are of electrostatic origin. They stem from the remaining of the solution.

The charging work *w* multiplied by the avogadro number N_A is equal to the change in the chemical potential $\Delta\mu(i - \mathrm{I})$ due to the interactions between the ion *i* and other ions:

$$\Delta\mu(i - I) = WN_A \qquad (46.1)$$

(The symbolism $(i - I)$ means the interaction between the ion *i* and the whole of other ions I).

From a general standpoint in electrostatics, a charging work in a point requires to know the electrostatic potential at this point. Hence, the electrostatic potential due to the electric charges located around it must be calculated (Fig. 46.2). To be more precise, this electrostatic potential Ψ_{cloud} is the electrostatic potential occurring at the distance *r* from the central ion *i*. It is due to the distribution of other ions around *i*, distribution so-called ionic atmosphere (Fig. 46.2). At this point, the occurrence of several existing electrostatic potentials must be emphasized.

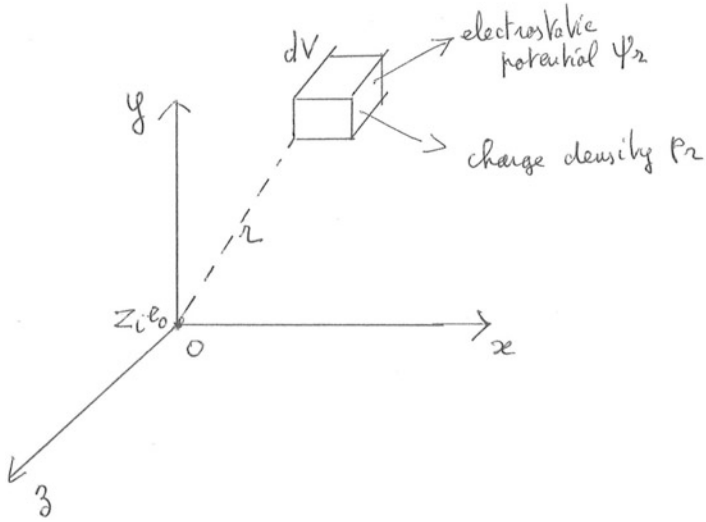

Fig. 46.2 Reference point and electrostatic potential at distance *r* of it

They are:

- The electrostatic potential Ψ_{cloud} which is due to the distribution of the ions around the central one *i*.
- That due to the central ion *i* itself, Ψ_{ion}.
- The mean electrostatic potential Ψ_r at the distance *r* of the central ion *i*, which is due to the whole ions of the solution, included *i* (for the term mean, see paragraph 5).

They must not be confused. According to the principle of the superposition of electrostatic potentials, they are linked by the relation:

$$\psi_r = \psi_{\text{ion}} + \psi_{\text{cloud}}$$

As it has been already said just above, of interest in the Debye–Hückel theory is the potential Ψ_{cloud} since the foundation of the theory is to find one relation of the kind:

$$\Delta\mu(i - I) = kN_{\text{A}}\Psi_{\text{cloud}}$$

where *k* is a constant, the meaning of which will be given by the following calculations.

Already, it is interesting to mention that Ψ_{cloud} is calculated from the two other potentials Ψ_r and Ψ_{ion}.

46.3 Hypotheses on Which Is Based the Debye–Hückel Theory

Debye and Hückel have made some hypothesis in order to perform this calculation. They are:

- The strong electrolytes are fully dissociated. With this hypothesis, Debye and Hückel have purely and simply retained the conclusions of S. Arrhenius.
- The difference in the behaviors of the solution of one electrolyte and of a nonideal one is that the electrolyte solution becomes ideal only when it is, by far, more dilute than the latter. This is because of, in the former, the particles of the solute are charged. Without the electrostatic interactions between the ions, the solution would behave as an ideal one. Then, the deflection with regard to the "ideality" is only ascribed to mutual interactions between the electrical charges brought by the ions.
- In order to specify this point, let us write the general expression (ideal solution or not) of the chemical potential of the ion *i*:

$$\mu_{i\,x} = \mu_i{}^{\circ}{}_x + RT\ln a_{ix} \tag{46.2}$$

or

$$\mu_{ix} = \mu_i{}^{\circ}{}_x + RT\ln x_i + RT\ln\gamma_{x\,i} \tag{46.3}$$

Let us confine ourselves to study the case for which the activity coefficients are related to the molar fraction scale. Considerations relative to other scales are analogous to those presently developed.

In both relations, the chemical standard potential is the same since the solution tends to be ideal when it is more and more dilute (viz. Chaps. 11 and 12). Hence, it is evident that the term RT ln $\gamma_{x\ i}$ quantifies the deflection with regard to the "ideality." Then, RT ln $\gamma_{x\ i}$ is the change in the Gibbs energy accompanying the crossing of one mole of particle *i* from the ideal system (where it would not bring any electrical charge) to the actual system where it is charged. As a result, according to what is preceding:

$$RT\ln\gamma_{x\,i} = \Delta\mu\,(i - I) \tag{46.4}$$

At this level of reasoning, it is essential to specify what is meant by the term "electrostatic interactions" in the Debye–Hückel interactions. They are only the coulombic interactions, the force of which being in $1/r^2$. All the other interactions which are in $1/r^n$ with $n > 2$, responsible for the dispersible forces, etc., are not taken into account by the theory. Hence, the only interactions which are taken into account are those which are considered as being long-range ones, as it is indicated by the term in $1/r^2$. This point is very important because it is only for the solutions sufficiently diluted in electrolytes that the ions are sufficiently distant from each other to no longer undergo these "short-range" interactions.

The fact that only the long-range interactions are taken into account may bring about (and brings about), as a rule, some problems concerning the validity of the theory. This is actually the case. From the experimental viewpoint, the activities, indeed, take into account all the kinds of deflections with regard to the ideal behavior. In other words, the values of the activities are blind to the phenomena they lessen. They do not see the origin of the deflections they quantify. Here, a source of discrepancy may happen between the reality and the theory. The latter may explain the occurrence of several phenomena by taking only into account one of them !This is irrational. *To sum up, we can, already, assert that the theory can represent the reality only when the interactions in* $1/r^2$ *overcome all other phenomena which may be at the origin of the deflections, that is to say, solely in the case of sufficiently dilute solutions.*

– The ions are supposed to be spherical and unpolarizable.

For some authors, this constitutes the primitive model. It would be more judicious to take into account all the kinds of interactions, not only those of electrostatic origin.

46.4 Schematic Representation of the Solution of an Electrolyte

The displacement of ions in the solution is not random because of the electrostatic interactions. A great feature of electrolytes solutions to which the Debye–Hückel theory leads, indeed, is that every ion of the solution is surrounded by an atmosphere constituted in majority by ions of electric charges opposed to its proper one. Let us consider, for example, the central positive ion i of charge $z_i e_o$ (e_o being the charge of the electron) located in a particular point of volume dV situated at the distance r of this point (Fig. 46.2).

Because of the motions from thermal origin of ions, at a given moment, some positive and negative ions go into and away from the element dV. But owing to the fact that, by hypothesis, the central ion is positively charged, it happens that an excess of negative ions is present in the element. The probability to find an excess of negative ions in dV is larger than that to find an excess of positive charges. Hence, the displacement of the ions is not random.

Then, from these last considerations, it is already possible to infer that every ion is associated with an ionic atmosphere surrounding it, the sign of which is opposite to its proper one. We can also infer that the density of the atmosphere close to the central ion is larger than that existing farther where it tends to cancel. Furthermore, intuitively, one can already imagine that the whole atmosphere of an ion does possess an electrical charge equal and opposite to that of its central ion, since the solution is electrically neutral.

The Debye–Hückel theory justifies these preliminary assertions.

46.5 The Basic Equation of the Debye–Hückel Theory: The Poisson–Boltzmann Equation

The calculation of the charging work involved in the second paragraph involves not only to know the charge of the ion *i* but also to know the electrostatic potential in which it is located (viz. Appendix P). The potential ψ_r prevailing in the volume dV, located at the distance r of the ion *i* must be calculated. It is important to recall that ψ_r is the total electrostatic potential. This means that it is due to the whole ions included the ion *i* itself.

The potential ψ_r in a point is related to the charge density ρ_r prevailing at this point. This relation is given by Poisson's equation (46.5) given under (Appendix Q):

$$\partial^2\psi_r/\partial x^2 + \partial^2\psi_r/\partial y^2 + \partial^2\psi_r/\partial z^2 = -4\pi\rho_r/\varepsilon \tag{46.5}$$

ε is the absolute permittivity of the medium.

The absolute permittivity ε *(or simply permittivity) is equal to the product of the permittivity of the vacuum* ε_0 *by the relative permittivity* ε_r *of the medium:*

$$\varepsilon = \varepsilon_0\,\varepsilon_r$$

The vacuum permittivity ε_0 *has for unity the Faraday per meter (F* m^{-1}*) or the coulomb per mole per meter (C* $mol^{-1}\,m^{-1}$*). The relative permittivity* ε_r *(formerly called dielectric constant of the medium) is a dimensionless number.*

For the aqueous solutions, Debye and Hückel have adopted the value of the permittivity of pure water for ε. It is interesting and somewhat surprising to notice that the solvent plays a part in this equation solely through the constant value ε and that it is considered as being a continuum medium. This is a condition of validity of Poisson's equation. Actually, the medium is not truly a continuum medium since the distribution of the ions is not homogeneous within it. The objection can be overcome by considering the average location of the different ions.

Remark: Since the Debye–Hückel theory is mainly centered on the behavior of the solute and since it considers the solvent as being a continuum, it is classified at the level so-called McMillan–Mayer level, on a scale devoted to the taking into account all the phenomena constituting a process in a solution.

For the following calculations, it is easier to express the previous equation (46.5) as being a function of the sole coordinate r instead of the coordinates x, y, z. The variable r is the radius of a sphere centered on the central ion *i*. No doubt, indeed, that the outer cover of the other ions of the solution around *i* does possess a spherical symmetry. The coordinate r is sufficient to describe the system. Equation (46.5) becomes:

$$1/r^2 d/dr\left(r^2 d\psi_r/dr\right) = -4\pi\rho_r/\varepsilon \tag{46.6}$$

(The transformation of (46.5) into (46.6) is easy to perform—viz. Appendix R).

The resolution of the equation (46.6) involves knowing the density ρ_r or, rather, to know how it changes with the function ψ_r. It is only when the expression of ρ_r as a function of ψ_r is introduced into (46.6) that it becomes possible to determine ψ_r. Actually, it is the case.

ψ_r is, then, one judicious solution of the obtained differential equation. The ionic density is given by the expression:

$$\rho_r = \sum\nolimits_k N_k z_k e_o \tag{46.7}$$

where the indice k permits to mark out every kind of ions, z_k being their number of charges. The density ρ_r is related to the number N_k of ions k per cm^3 of the element of volume dV. *At this point of the reasoning is coming a very important hypothesis of Debye and Hückel. It is thoroughly discussed below, in this chapter*. The number N_k and hence ρ_r for every ion k are related to the number $N_k{}^\circ$ thanks to the Boltzmann equation (46.8) (viz. Appendix S):.

$$N_k = N_k{}^\circ\, e_o z_k \exp(-\, z_k e_o \psi_r/kT) \tag{46.8}$$

$N_k{}^\circ$ is the number of ions k per cm^3 of the whole solution. The term $z_k e_\mathrm{o} \psi_r$ is the electrostatic energy U that some ions k may acquire because of the occurrence of the electrostatic potential ψ_r in the volume dV. The electrostatic energy is:

$$U = -z_k e_o \psi_r$$

ψ_r is called potential of average force because it results from electrostatic forces due to the charges of the whole ions.

Hence, the equation which plays the part of the basis of the Debye–Hückel theory is:

$$1/r^2 d/dr\left(r^2 d\psi_\mathrm{r}/dr\right) = -4\pi/\varepsilon \sum_k z_k N_k{}^\circ e_o \exp\left(-z_k e_o \psi_r/kT\right) \tag{46.9}$$

Its resolution permits to determine the potential ψ_r as a function of r. The relation (46.9) is often called the Poisson–Boltzmann equation.

46.6 On the Legitimacy of the Poisson–Boltzmann Equation

A very important point concerning the legitimacy of the Poisson–Boltzmann equation must be, already, highlighted, before we come back on it. It concerns the calculation of the density ρ_r and more specifically the use of the Boltzmann's exponential—relation (46.8).

In all scientific rigor, ρ_r is given by the expression (viz. Chap. 42):

$$\rho_r = \rho_k g_{ik} \tag{46.10}$$

$g(r)_{ik}$ is the classical symbol of the pair correlation function. The indices i and k recall that, in the occurrence, $g(r)_{ik}$ relates the central ion i to an ion k of the ionic cloud. The symbol (r) recalls that g_{ik} depends on r. ρ_k is the density of the ion k in the bulk solution. $g_{ik}(r)$ is the factor by which the local density of the ion k $\rho_k g_{ik}(r)$ differs from its density in the bulk solution, where the electrostatic disturbances of concentrations are negligible. The relation (46.10) must be equivalent to the following (46.11):

$$\rho_r = \rho_k \exp[-w_{ik}(r)/kT] \tag{46.11}$$

where $w_{ik}(r)$ is the potential of average force between the ions i and k. (The gradient of $w_{ik}(r)$ with its sign inverted is the acting force between i and k). The weakness of the Poisson–Boltzmann equation lies in the fact that the correlation by pairs function is not an exponential in the great majority of cases as it has been admitted, as a rule, by Debye and Hückel. As a result, the following relation which has been settled by Debye and Hückel:

$$w_{ik}(r)/kT = z_k e_o \psi_r \tag{46.12}$$

cannot always be applied. Because of that, the theory can be considered as being only approximate. In the case of a gas, we have seen (visualize Chap. 29) that it is only when it is extremely dilute we can assimilate the correlation function to one exponential. (The demonstration has already been realized that it is the case when only two molecules of gas are in interaction (cf Chap. 29)!

46.7 A Solution of the Poisson–Boltzmann Equation and Some Inferences

An important point of the resolution process of the Poisson–Boltzmann equation is the truncation of the series expansion of the Boltzmann's exponential, the first two terms of which are only kept. Debye and Hückel have, indeed, expressed the hypothesis that the electrical energy of each particle $z_k e_o \psi_r$ is small with respect to the thermal factor kT. The merits and the interest of this hypothesis are studied in paragraph 14.5. Hence, the exponential is approximated according to:

$$\exp[-z_k e_o \psi_r/kT] \approx 1 - z_k e_o \psi_r/kT$$

The charge density becomes:

$$\rho_r = \sum\nolimits_k N_k{}^\circ z_k e_o - \sum\nolimits_k N_k{}^\circ z_k{}^2 e_o{}^2 \psi_r/kT$$

The first term of the right member of this equation is null because the whole solution is electrically neutral. As a result, the Poisson–Boltzmann equation which remains to be solved becomes:

$$1/r^2\left[d\left(r^2 d\psi_r/dr\right)/dr\right]\chi^2\psi_r = \left[(4\pi/\varepsilon kT)\sum_k N_k{}^\circ z_k{}^2 e_o{}^2\right]\psi_r \tag{46.13}$$

It is called the linearized Poisson–Boltzmann equation.

- In equation (46.13), the term on the right between brackets is nothing different from a collection of constants for a given solution at a given temperature. Hence, it is a constant which is symbolized by χ^2:

  $$\left[(4\pi/\varepsilon kT)\sum_k N_k{}^\circ z_k{}^2 e_o{}^2\right] = \chi^2 \tag{46.14}$$

  The constant χ is not only interesting to introduce for the facility of writing, it is also interesting for the following fact. Its inverse χ^{-1} does possess a physical unambiguous meaning (see under).

  Now, the linearized Poisson–Boltzmann equation is:

  $$\frac{1}{2}\left[d\left(\pi^2 d\psi_2/d\pi\right)/d\pi\right]\chi^2\psi_2 \tag{46.15}$$

  The appropriate solution of (46.15) is (viz. Appendix T);

  $$\psi_r = (z_i e_o/\varepsilon)[\exp(-\chi r)/r] \tag{46.16}$$

  ψ_r is the total electrostatic potential, that is to say that due to the whole of ions k *plus* ion i, at the distance r of the central ion i.

  The solution (46.16) leads to the following results:

- The charge density at the distance r of the central ion is given by the relation:

  $$\rho_r = -(z_i e_o/4\pi)\chi^2(e^{-\chi r}/r) \tag{46.17}$$

- The total charge in excess q_{cloud} (ionic atmosphere) around the central ion is given by the relation:

$$q_{\text{cloud}} = -z_i e_o \tag{46.18}$$

This result is a very interesting one. It shows that the central ion, the charge of which is $+z_i e_o$, is surrounded by an ionic cloud, the total charge of which is exactly equal, but opposed to its proper one. This result is in full agreement with the fact that the whole solution is electrically neutral. Concerning this result, a point deserves a particular comment. It is the fact that the value 0 has been retained (in order to obtain this result), as the lowest limit of an integral intervening in the calculations (viz. Appendix U). This choice entails that the central ion is assimilated to a point charge. This working hypothesis is thoroughly discussed in paragraph 12.

- The geometrical locus of the maximal charge around the central ion is the sphere of radius r, the length of which is given by:

$$r = \chi^{-1} \tag{46.19}$$

It is for this reason that χ^{-1} is called radius or thickness of the ionic cloud surrounding the central ion. A simple analysis of the dimension of relation (46.20) given below shows that, actually, χ^{-1} does possess the dimension of a length.

When we look, indeed, at the equality:

$$\chi^{-1} = \left[(\varepsilon kT/4\pi) \cdot 1/\left(\sum_k N_k{}^{\circ} z_k{}^2 e_o{}^2\right)\right]^{1/2} \tag{46.20}$$

we see that $e_0{}^2$ is expressed in C^2, $N_k{}^{\circ}$ number of ions per volume unit is expressed in m^{-3}, z_k is a dimensionless number, and ε in C mol^{-1} m^{-1}. It is for this reason that χ^{-1} is also called *Debye and Hückel's length*. We notice that when the concentration tends toward 0, the cloud tends to spread out. This property is interesting.

- The electrostatic potential ψ_{cloud} only due to the ionic cloud is given by the expression:

$$\psi_{\text{cloud}} = (z_i e_o/\varepsilon r)(\mathrm{e}^{-\chi r} - 1) \tag{46.21}$$

This relation is very important because of the fact that it is the calculation of Ψ_{cloud} which permits to determine the corrective term of Gibbs energy due to the ionic interactions (viz. paragraph 2). Its fruitfulness gets clearer in the case of sufficiently dilute solutions. The sum $\Sigma_k N_k{}^{\circ} z_k{}^2 e_o{}^2$ is, then, sufficiently weak in order the product χr to be markedly weaker than 1. Under these conditions:

$$\mathrm{e}^{-\chi r} - 1 \approx -\chi r$$

$$\psi_{\text{cloud}} = -z_i \mathrm{e}_o / \varepsilon \chi^{-1} \tag{46.22}$$

The relation (46.22) shows that the central ion i may be considered as being submitted to a potential due to a sole ion of charge $-z_i e_o / \varepsilon$ located at the distance χ^{-1} from it.

It is interesting to notice that it is only when this potential value takes precedence that the Debye–Hückel relations apply.

46.8 Limiting Equation of Debye–Hückel

The change in the chemical potential $\Delta\mu(i - I)$ due to interactions ion–ion is equal to the charging work W of the central species I multiplied by the Avogadro's number.

46.8.1 Calculation of the Corrective Term of the Gibbs Energy of Ions–Ions Interactions

The charging work W of i is developed under the potential ψ_{cloud} due to the ionic atmosphere around i. Because of this work, the charge of the ion i changes from the null value up to the charge $z_i e_o$,

From the general physical standpoint, we know that:

$$dW_{\acute{e}lectric} = \psi dq$$

Thus, for the ion i:

$$dW_{\acute{e}lectric} = \psi_{\text{cloud}} dq$$

$$dW_{\acute{e}lectric} = -\left(z_i e_o / \varepsilon \chi^{-1}\right) dq$$

Since $z_i e_o$ is a charge, let us write for simplicity:

$$q = z_i \, e_o$$

$$W_{\acute{e}lectr.} = -\int_0^{z_i \, e_o} q dq / \varepsilon \chi^{-1}$$

$$W_{\acute{e}lectr.} = -z_i^2 e_o^2 / 2\varepsilon \chi^{-1}$$

and

$$\Delta\mu(i-I) = -N_{\mathrm{A}}(z_i e_{\mathrm{o}})^2/2\varepsilon\chi^{-1} \tag{46.23}$$

46.8.2 Expression of the Activity Coefficient γ_x of One Ion

The result (46.23) permits the calculation of the activity coefficient of the ion *i*. According to paragraphs 2 and 3, we obtain:

$$RT\ln\gamma_{x\,i} = -N_{\mathrm{A}}(z_i e_{\mathrm{o}})^2/2\varepsilon\chi^{-1} \tag{46.24}$$

46.8.3 Introduction of the Ionic Strength

It is easy to verify that, in literature, using the scale of molalities (or of molarities) in order to quantify the « concentrations » of the solutes largely prevails on that of molar fractions in solution chemistry. Concerning this purpose, there are two points to remark in the previous theory:

- The activity coefficients are quantified on the basis of the molar fractions. This point has no practical interest since we have seen that, for the sufficiently dilute solutions, the values of the different activity coefficients γ_x, γ_m, and γ_{c} differ very little from each other (viz. Chap. 11). This is the case, notably, when the limit and extended Debye–Hückel can legitimately be used.
- Before the Debye–Hückel theory has been stated, Lewis had, already, introduced the parameter I on a purely experimental basis, which he defined by the relation:

$$I = 1/2\sum_k C_k z_k^{\,2}$$

He had identified this parameter as being an important one in order to take correctly into account the behavior of the solutions, and he has named it *the ionic strength of the solution*. According to the Lewis's definition, C_k is the concentration of the ion *k* expressed in molarities in the whole solution. The term χ^{-1} is expressed in number of moles per cm^3. Thus, it must be expressed in mol L^{-1}. $N_k{}^\circ$ being the number of ions in 1 cm^3 of solution and N_{A} the Avogadro's number, the relation permitting the correction is:

$$N_k{}^\circ = N_{\mathrm{A}} C_k/1000$$

C_{k} is the concentration (mol L^{-1}) of the ion. As a result:

$$\sum_k N_k{}^\circ z_k{}^2 e_o{}^2 = e_o{}^2 N_{\mathrm{A}}/1000\sum\nolimits_k C_k z_k{}^2 \tag{46.25}$$

and:

$$\chi = \left(8\pi e_o{}^2 N_A / 1000\varepsilon kT\right)^{1/2} \cdot \sqrt{I}$$

Usually, the term in braces is symbolized by B, i.e.:

$$B = \left(8\pi e_o{}^2 N_A / 1000\varepsilon kT\right)^{1/2}$$

and

$$\chi = B\sqrt{I}$$

46.8.4 The Limit Debye–Hückel Equation

According to what is preceding and adopting the decimal logarithm, we obtain:

$$\ln\gamma_{x\,i} = -\left(z_i{}^2 e_o{}^2 N_A / 2\varepsilon RT\right) B\sqrt{I}$$
$$\log\gamma_{x\,i} = -(1/2.303)\left(e_o{}^2 N_A / 2\varepsilon RT\right) B_{Z_i}{}^2\sqrt{I}$$

Introducing, now, the factor A:

$$A = (1/2.303)\left(e_o{}^2 N_A / 2\varepsilon RT\right) \tag{46.26}$$

one finally obtains:

$$\log\gamma_{x\,i} = -Az_i{}^2\sqrt{I} \tag{46.27}$$

It is the limit Debye–Hückel law. A is a constant which is independent of the nature of the ion i. It depends on the temperature and on the nature of the solvent through its permittivity ε absolute which, also, depends on the temperature. For water at 298 K, $\varepsilon_r = 78{,}54$:

$$A = 0.509\,\mathrm{mol}^{-1/2}\mathrm{L}^{1/2}$$

(Other values of A are given in the literature depending on those retained for the value ε of water. Thus, with $\varepsilon = 78.54$, $A = 0.5085$, whereas with $\varepsilon = 78.30$, $A = 0.5115$) B is a function of the temperature and of ε. For water at 298 K

$$B = 0.329 \cdot 10^{\,8}\,\mathrm{cm}^{-1}\,\mathrm{mol}^{1/2}\,\mathrm{L}^{1/2}$$

To the ionic strengths for which the Debye–Hückel equations are legitimate, the constants appearing in the limit equation above are the same, whether the ionic strength is expressed in molalities or in molarities. This is due to the fact that for the sufficiently dilute solutions, the values of the “concentrations” of a species in solution are quasi-equal when they are expressed in molalities or in molarities.

An important point to underline is that the Debye–Hückel limiting law equation does not only apply (when its use is legitimate) to strong electrolytes, it also applies to the ions of solutions containing weak electrolytes, provided its true ionic strength is taken into account. That is to say, the dissociation extent of the electrolyte must be known (viz. Chap. 19).

46.9 On the Agreement of the Limit Equation with Experiments

46.9.1 Relation Derivating from the Limit Equation the Results of Which Can Be Directly Confronted with the Experimental Results

It is impossible to experimentally determine the activity coefficient of an ion. Hence, equation (46.27) cannot be directly confronted with the experience. However, the value of the mean ionic activity coefficient of one electrolyte is experimentally attainable (viz. Chaps. 14 and 15). Hence, if it were possible to modify the limit equation (46.27) (permitting to separately calculate the activities of the ion and of its counterion of one electrolyte) in order to obtain an equation which would permit to calculate their mean coefficient, the values obtained in such a way could be confronted with the experience. Evidently, the potential fit between the calculated and measured values found would then only give an indirect proof of the validity of the limit equation permitting to calculate the activity coefficient of a simple ion, at least in the conditions for which it can be used. However, such an agreement would be very convincing.

The transformation of the limit equation into another taking into account the mean coefficients is easily feasible. The mean activity coefficient of an electrolyte is given by the expression (viz. Chaps. 14 and 15):

$$\gamma_{\pm} = \left(\gamma_{+}^{v+} \cdot \gamma_{-}^{v-}\right)^{1/v}$$

ν is the total number of ions given by one molecule of the electrolyte:

$$v = v_{+} + v_{-}$$

By taking the logarithm, we obtain

$$\ln\gamma_{\pm} = \left(v_{+}\ln\gamma_{+} + v_{-}\ln\gamma_{-}\right)/(v_{+} + v_{-})$$

and, at this step of reasoning, by expressing $\log \gamma_+ \log \gamma_-$ by relations (46.24):

$$\ln\gamma_\pm = -1/v\left[\left(N_A {e_o}^2/2\varepsilon RT\right)\chi\left(v_+ {z_+}^2 + v_- {z_-}^2\right)\right]$$

It is easy to verify that:

$$\left(v_+ z_+^2 + v_- {z_-}^2\right)/(v_+ + v_-) = z_+ z_-$$

because of the fact that each electrolyte being neutral,

$$\left|v_+ z_+\right| = \left|v_- z_-\right|$$

As a result:

$$\ln\gamma_\pm = -\left[\left(N_A {e_o}^2/2\varepsilon RT\right)\left|z_+ z_-\right|\right]\chi$$

Replacing χ by its expression (46.21), and proceeding as above lead to the relation:

$$\log\gamma_\pm = -A(z_+ z_-)\surd I \tag{46.28}$$

i.e., to say at 25 °C

$$\log\gamma_\pm = -0.509\left|z_+ z_-\right|\surd I \tag{46.29}$$

This is the limit equation of Debye–Hückel, but applying to the whole electrolyte. For a monovalent electrolyte, at the concentration C

$$I = C$$

and

$$\log\gamma_\pm = -0.509\surd C \quad \left(\text{electrolyte monovalent } \textit{at } 25\,^\circ\text{C}\right) \tag{46.30}$$

Equations (46.28),(46.29), and (46.30) can be, then, directly compared with the experiments.

46.9.2 Agreement of the Debye–Hückel Limiting Law with Experiments

The Debye–Hückel limiting law (46.28) or (46.29) shows that:

- The logarithm of the activity coefficient of an electrolyte must linearly decrease with the square root of the ionic strength of the solution. In the case of an electrolyte 1-1, it must decrease linearly with the square root of its "concentration."
- The slope of the straight line $\log \gamma_\pm/\sqrt{I}$ can be computed without ambiguity by starting from fundamental physical constants and using the values z_+ and z_-.
- It must not depend on the nature of the electrolyte. It only depends on the kind of the electrolyte, that is to say according to their types 1-1, 2-2…
- At null ionic strength, the mean activity coefficient must be equal to 1.

By considering the relations (46.28) or (46.29), we already notice that the theory subscribes to the latter condition: indeed, for $I = 0$, $\gamma_\pm = 1$. Now, by taking the example of the aqueous solutions of an electrolyte 1-1 shown (Fig. 46.3), we see that the condition 1 is satisfied for the very weak concentrations.

Figure 46.4 shows that, on one hand, the slopes are actually different according to the type of the electrolyte and, on the other, that their values are those calculated.

Finally, the change of the slope of the limiting law with the permittivity (dielectric constant of the medium) is also in agreement with the theory. According to the relation (46.26) and the expression of B, indeed, the slope of the line $\log \gamma_\pm/\sqrt{I}$, at constant temperature, must be proportional to the inverse of the value $\varepsilon^{3/2}$. Figure 46.5 exhibits this behavior for low values of I in the cases, for example, of solutions in

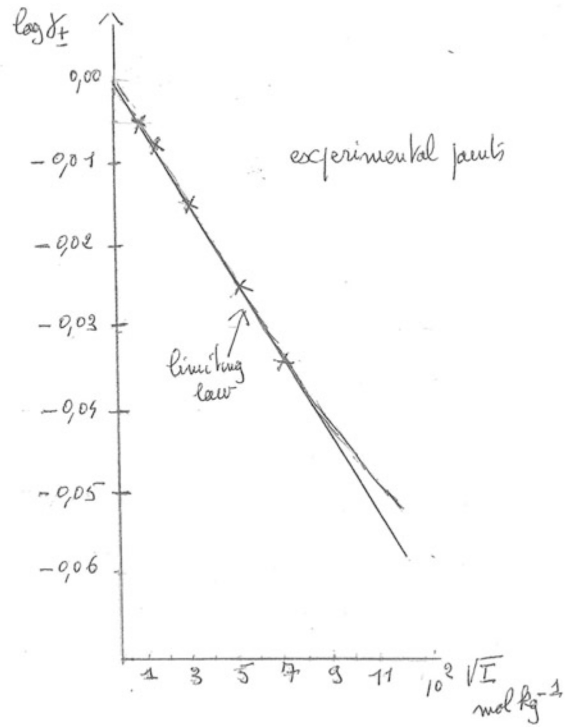

Fig. 46.3 Debye–Hückel limiting law: approximate range of validity

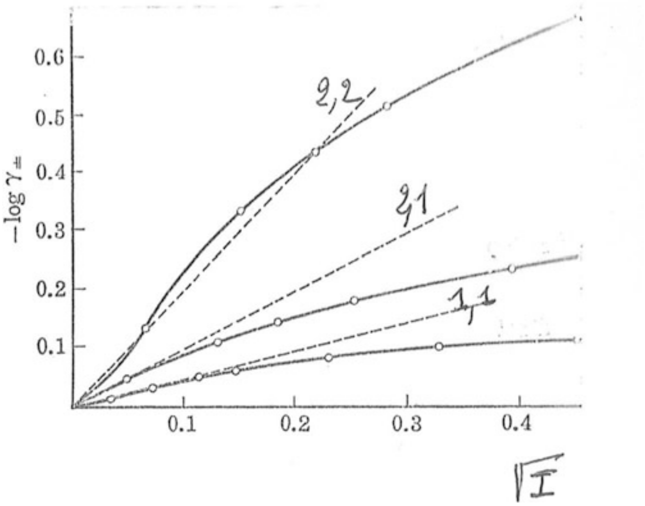

Fig. 46.4 Calculated and experimentally obtained slopes according to the kind of electrolyte (i, j: charges of the cation and of the anion)

methanol, ethanol as well as in the mixtures water-dioxan, the dielectric constant values of which being located in the interval 9.53–78.6.

Now, concerning the changes of the slope of the limit equation as a function of the temperature, according to the realized studies, they are in full agreement with the experience, although they are difficult to interpret, since, when the temperature changes, some other factors do also change. This is, for example, the case of the dielectric constant.

All this information, strengthening the theory, constitutes what is called by some authors: the great triumph of the Debye–Hückel theory.

46.10 Limitations of Debye–Hückel Limiting Equation

However, the Debye–Hückel limiting law exhibits serious limits.[1]

The essential observation of its imperfection appears at the examination of Figs. 46.3 and 46.4 which shows that all the conclusions it predicts are only accurate for very weak ionic strengths. These figures show that, broadly speaking, beyond the ionic strength $I = 0.01$ mol L^{-1}, the activity coefficient decreases less quickly than it is predicted by the limit theory.

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[1] It has been endowed with a considerable success, but it is not perfect. P. Debye, himself, said that the theory did not merit such a success!

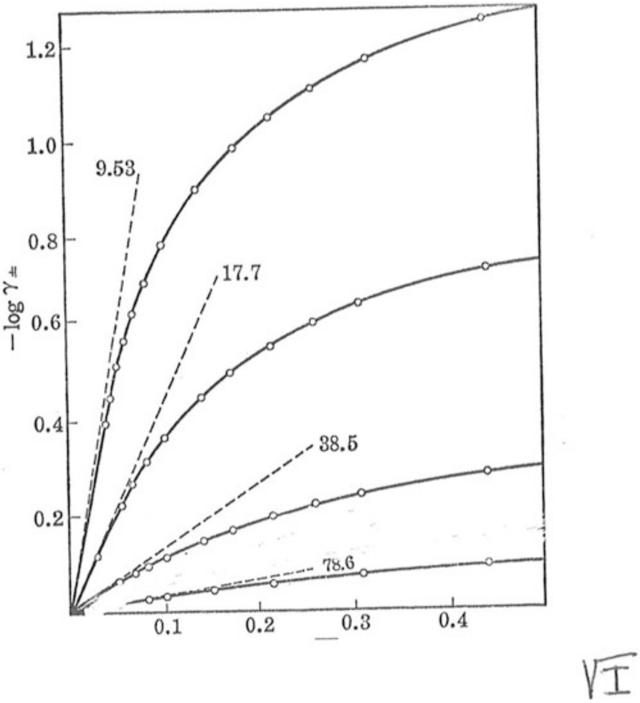

Fig. 46.5 Obtained Debye–Hückel limiting law as a function of the dielectric constant of the medium

Figure 46.5 shows that above an ionic strength such as $\sqrt{I} > 0.3$ mol L^{-1}, the electrolytes of the same kinds are, actually, "distinguishable" from each other (Table 46.1).

46.11 Possible Causes of the Limitations of the Debye–Hückel Limiting Equation

According to the starting hypothesis and the followed reasoning to set up this theory, one can infer that there exist several causes to the limitations of the limiting law, that is to say:

- The ions and especially the central ion have a finite size. They cannot be assimilated to charged points.
- The series development of the exponential in the Poisson–Boltzmann's equation is not justified.
- The fact to only consider the interactions in $1/r^2$ may be an error. Are there any reasons not to take into account other interactions in the reasoning and even

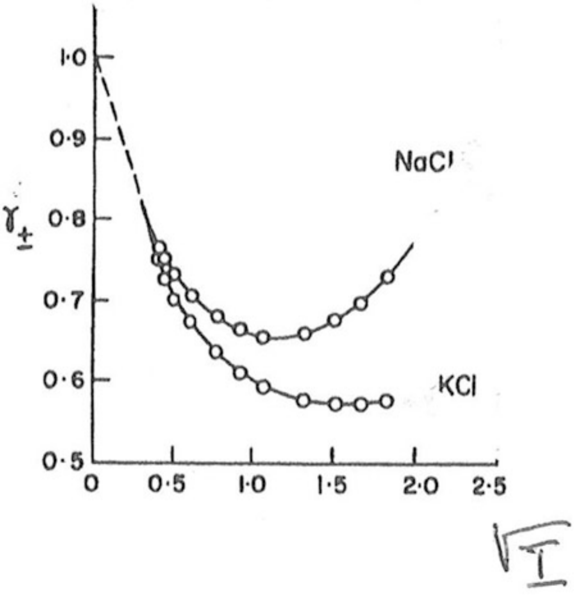

Fig. 46.6 Differences of behaviors between two electrolytes of the same type (NaCl and KCl) once the ionic strength exceeds some value

Table 46.1 Comparison of the calculated and experimental mean activity coefficients $\gamma_\pm$ of NaCl at 298 K *(according to J.O'M. Bockis and Amulya K.N. Ready "Modern Electrochemistry" 1 Ionics,* 2nd *edition, Plenum Press, New York and London, 1998)*

Molalities	$\log\gamma_\pm$ (experimental)	$\log\gamma_\pm$ (calculated)
0.001	0.0155	0.0162
0.002	0.0214	0.0229
0.005	0.0327	0.0361
0.01	0.0446	0.0510
0.02	0.0599	0.0722

other processes such as, for example, the formation of ions-pairs or, also, the occurrence of dispersion forces?

- Finally, another cause merits to be considered. It is the fact that, in this theory, the solvent is assimilated to a continuum and plays a part solely through its dielectric constant. From a different viewpoint it would play, for example, it is, simply, that of solvating ions!

46.12 Ions Have a Finite Size Radius: The Extended Debye–Hückel Theory

A way in order to improve the previous theory came, immediately, in mind: it was to consider that the ions, actually, have a finite radius.

Taking into account the fact that the central ion having the finite radius *a* leads to the equation so-called the extended Debye–Hückel equation—viz. Appendix U, it is:

$$\log\gamma_i = -Az_i{}^2\sqrt{I}/\left(1 + Ba\sqrt{I}\right) \tag{46.31}$$

A and *B* are the same constants as those occurring in the limiting equation. *a* is believed to be the radius of the ion in solution (viz. the discussion below). *a* is called "ion size parameter" or the shorter distance of approach to every ion with the central one. Thus, the extended Debye–Hückel relation law differs from the reduced one by the presence of the denominator $1 + Ba\sqrt{I}$. For the whole electrolyte, the relation is:

$$\log\gamma_\pm = -A(z_+z)\sqrt{I}/\left(1 + Ba\sqrt{I}\right) \tag{46.32}$$

Then, the value of *a* may be assimilated to a kind of mean value of the ion size parameters of the ions constituting the electrolyte.

46.13 On the Meaning of the "Ion Size Parameter"

- From the theoretical standpoint, we can notice that:
  - If one writes the expression of the mean ionic activity coefficient under the following equivalent form (viz. Appendix T and relation (46.16):

$$\log\gamma_\pm = -A(z_+z_-)\sqrt{I}/\left(1 + a/\chi^{-1}\right)$$

we can notice that the more dilute the solution is, the larger the radius of the ionic cloud χ^{-1} is. Then, the ratio a/χ^{-1} tends to be negligible with respect to 1 and the extended equation becomes the limiting one. This behavior is in full agreement with the physical intuition. (The principle, so-called the correspondence principle in physics, is obeyed). The result of the existence of the denominator in the extended law is that the value of $-\log\gamma_\pm$ is slightly larger than that given by the limiting equation. This effect is all the more significant as the ionic strength is larger. By applying the following series development:

$$1/(1+x) = 1 - x + x^2/2!\ldots$$

to the term $1 + Ba\surd I$ and by only retaining the first two terms, we obtain:

$$1/\left(1 + Ba\surd I\right) \approx 1 - Ba\surd I$$

and:

$$\log\gamma_{\pm} = -A\left|z_{+}z_{-}\right|\surd I + C_{\mathrm{te}}I \tag{46.33}$$

where the symbol C_{te} means constant. Actually, it appears a positive correction for the calculation of log $\gamma_{\pm}$ with respect to the limiting equation. Let us recall that in the determination of the activity coefficients of electrolytes by conductometry (viz. Chap. 18) some extrapolation relations of the type (46.33) are used. However, even if the presence of the term $(1 + Ba\surd I)$ in the extended equation bends the curve $-\log\gamma_{\pm}/\surd I$ (of the limiting equation), definitively, it cannot give rise, from the pure mathematical standpoint, to the occurrence of a minimum in the curve.

- According to the experimental results, that is to say after the fitting of the theoretical curve (calculated values $\log\gamma_{\pm}/\surd I$) to the corresponding experimental ones, it appears that, for weak ionic strengths, the value a is larger than the sum of the crystallographic radius of the positive and negative ions of the solution and is lower than the sum of the radius of the solvated ions. That is to say, it lies in the range 0.35–0.45 nm. This is a reasonable value. However, from some less weak value of the ionic strength, that of a may considerably vary when the latter increases. Thus, for molalities of sodium chloride in aqueous solutions located in the range $9 \cdot 10^{-2}$ mol kg^{-1} to 1 mol kg^{-1}, a varies from 6 up to 14 Å (1 angström: 10^{-10} m)! Likewise, for aqueous solutions of hydrochloric acid of molalities varying from 1 up to 1.8 mol kg^{-1}, a varies from 1.38 up to 8.50 nm. Even, for larger concentrations, a may be endowed with aberrant values. Thus, for a molality of 2 mol kg^{-1} in hydrochloric acid, $a = -41.12$ nm! For a molality 2.5 mol kg^{-1} in lithium chlorid, $a = -14.19$ nm! These results explain why a, now, is considered as being an adjustable parameter permitting to get the best fit between the experimental and calculated values of $-\log\gamma_{\pm}$ as a function of $\surd I$, rather than a quantity possessing a true physical meaning.
- The limits of using the extended Debye–Hückel equation are the following ones. *Roughly,* it permits to calculate the mean ionic activity coefficient of an electrolyte up to an ionic strength of 0.1 mol L^{-1} with reasonable values a.

Clearly, even if it is undeniable that taking into account the radius of the ions improves the capabilities of calculation of reasonable values of activity coefficients, it is true that the model remains imperfect. In this respect, the aberrant values taken by the parameter a for some ionic strengths provide us with a dazzling proof of this assertion.

46.14 Other Causes of Discrepancy Between the Experiments and the Debye–Hückel Laws

46.14.1 Solvation of the Ions of the Electrolyte

We know, that in solutions, ions are surrounded by several sheaths of solvent molecules which solvate the former ones. As a result, the effective "concentrations" and hence the activities of the ions and of the solvent may not be those forecast by the simple consideration of the "concentrations." We name effective "concentrations," i.e., activities, the quantities which govern the value of their chemical potential. The number of solvent molecules mobilized for the solvation is evidently all the larger as the electrolyte "concentration" is. The Debye–Hückel theories do not take into account this phenomenon. Therefore, it is easy to conceive that (by taking, for example, the solvent water), the number of water molecules available to play the part of the bulk water is weaker than forecast. As a result, the effective "concentration" of the ions is greater than that estimated as a rule. The number of water molecules solvating the two antagonist ions in their first solvation layers may be important. For example, the total hydration number n_{h} would be of the order of 8. Thus for 1 mol L^{-1} of NaCl, the solvatation of both ions leads to the concentration 48.5 mol L^{-1} of bulk water instead of 55.5 mol L^{-1}. The value 55.5 mol L^{-1} only takes into account the stoichiometric concentration and not the latter phenomenon.

Concerning, now, the experimental value of the activity, it is sure that it takes it into account. The solute activity being equal to the product of the "concentration" by the activity coefficient, the latter becomes larger than forecast since the effective "concentration," the only one which matters according to this theory, is larger. A simple theory shows that the two following terms:

$$-2.303RT(n_{\mathrm{h}}/n)\log a_{\mathrm{w}} + 2.303RT\log[(n_{\mathrm{w}}+n)/(n_{\mathrm{w}}+n-n_{\mathrm{h}})]$$

must be added to the "classical" one—$\log\gamma_{\pm}$ of the Debye–Hückel theory for the calculation of the activity coefficients. n_{w} is the total number of water molecules, n_{h} that of water molecules linked to both ions per mole of ions, n the number of moles of electrolytes, a_{w} the activity of water after the addition of the ions (a_{w} is slightly less than the unity), and C the analytical concentration of an electrolyte 1-1. The modified Debye–Hückel is the following one:

$$\begin{aligned} RT\log\gamma_{\pm} = -A\sqrt{C}/\left(1+Ba\sqrt{C}\right) - 2.303RT(n_{\mathrm{h}}/n)\log a_{\mathrm{w}} \\ + 2.303RT\log[(n_{\mathrm{w}}+n)/(n_{\mathrm{w}}+n-n_{\mathrm{h}})] \end{aligned} \tag{46.34}$$

The encouraging results found by using this relation must be tempered with the fact that the Debye–Hückel term $-A\sqrt{C}/(1+Ba\sqrt{C})$ is maintained, in this occurrence, at high levels of ionic strengths of the order of 2–4 mol L^{-1}. They may, no longer, remain pertinent. It is not sure at all that with such concentrations, the solution surrounding the ion may be, still, considered as being a continuum, a basic hypothesis formulated by Debye and Hückel.

46.14.2 *The Adoption of the Boltzmann's Definition for the Density* ρ_r

This point has been already discussed in paragraph 6 above. Let us recall that, in principle, ρ_r is given by the expression:

$$\rho_r = \rho_k g_{ik}(r) \tag{46.10}$$

$g(r)_{ik}$ being the pair correlation function between the central ion *i* and one ion *k* of the ionic cloud. According to the Debye–Hückel hypothesis, the relation (46.10) is equivalent to the following one (46.11):

$$\rho_r = \rho_k \exp[-w_{ik}(r)/kT] \tag{46.11}$$

where $w_{ik}(r)$ is the potential of the mean force between the ion *i* and one ion *k* of the ionic cloud. The approximation of the Poisson–Boltzmann's equation lies in the fact that the following equality has been set up:

$$w_{ik}(r)/kT = z_k e_o \psi_r$$

This equality is only accurate when the solutions are very dilute. When the distance *r* is short, $w_{ik}(r)$ takes into account not only the interactions between ions (this is done by the Boltzmann's term) but also the indirect interactions due to the solvent (this is not done by the Boltzmann's term). As we know, the more dilute the solutions are, the farther from each other are the ions.

46.14.3 *Change of the Dielectric Constant with the Ions Concentrations in the Solution*

Actually, the permittivity (i.e., the dielectric constant) changes with the ions concentrations, that is to say also with the distance *r*. The Poisson–Boltzmann's equation does not take this factor into account. The medium is not one without any structure.

Moreover, using the Poisson's equation entails a continued charges density around the central ion. This is not the case. However, assimilating the solution comprising discrete charges to a continued cloud of charges may be justified by introducing a mean and continued location of charges in the time.

According to the cosphere theory, there is no sufficient taking into account of the solvation phenomena (viz. paragraph 14-1) and of the changes in the relative permittivity of the solvent close to the ions in the Debye–Hückel theory. For this reason, a more complicated potential of electrostatic interaction than that retained in the Debye–Hückel theory has been chosen in it.

According to the theoretical calculations which result from it, it is proved that this approach differs in its conclusions from that of Debye–Hückel because the equation stemming from the theory involves a term which is specific of the involved ions. Hence, according to the Debye–Hückel limiting law, indeed, there is only dependence on the ionic strength of the activity coefficients. According to the cosphere theory, solutions of equal molarities in sodium chloride and sodium hydroxide, even for weak concentrations, exhibit different mean ionic activity coefficients. Moreover, it shows that the linear term present in the Guggenheim (viz. Chap. 15) and Davies' relations is characteristic of the electrolyte. The cosphere theory is due to Gurney and Friedmann.

46.14.4 Formation of Ion-Pairs and of Superior Aggregates

Here, we only evocate the formation of ion-pairs, although in some cases, the formation of triple ions and even that of superior aggregates must be taken into account. It can disrupt the fit between the mean activity coefficients (and hence, indirectly, the activity coefficients of the constituting ions alone) and the calculated coefficients. The Debye–Hückel theory does not take into account the formation of ion-pairs and of other aggregates. It is usual to neglect their formation in the solvents of large dielectric constant such as water. But it is an error as soon as the solution contains ions which are not monovalent (viz. below). The formation of pair-ions AM_{ip} can be represented by the following equilibrium (ip: ion-pairs):

$$A^+ + M^- \rightleftharpoons AM_{ip}$$

the constant K_{ip} of which is given by the expression:

$$K_{ip} = a_{AM}/a_{A+}\,a_{M-}$$

A theory, due to N. Bjerrum, relative to the formation of ion-pairs, indicates that the factors which favor the formation of ion-pairs are a weak dielectric constant of the solvent, a weak ionic radius of the ions and strong electrical charges. If there exist few ion-pairs involving monovalent ions in water ($\varepsilon_r = 78.6$), it seems that it is no longer the case as soon as the solvent contains bivalent ions and *obviously* ions of superior electrovalence, and that even in water. One example is provided by an aqueous solution of zinc sulfate for which $K_{ip} = 240$.

The ion-pairs being neutral, they must not, as a rule, play a direct part in the value of the ionic strength of a solution. (It is not the case of triple-ions which are of the types A+ M− A+ and M− A+ M−). They are randomly distributed in the whole solution. However, the formation of aggregates, whatever they are, plays an indirect part. The Debye–Hückel theory cannot give the accurate answer as soon as there are the formations of ion-pairs and aggregates in non-negligible amounts. It disturbs, indeed, the normally foreseeable "concentration" of the free ions. Only the ions non-engaged in ion-pairs and aggregates must be considered in order to study the ionic atmosphere surrounding the central ion. The result is analogous to that resulting from the phenomenon of ion solvation (see above). This is all the more true as the ion-pairs pairs and all the kinds of aggregates are themselves more and less solvated! The effective "concentration" which must be considered for the study is evidently weaker than the analytical concentration. If one only takes into account the ion-pairs formation and if the fraction θ of the total number of ions gives rise to the formation of ion-pairs, it is only the fraction $(1 - \theta)$ which can enter the Debye–Hückel theory. One relation giving the mean theoretical ionic activity coefficient $\gamma_{\pm\text{th}}$ taking into account the formation of ion-pairs does exist.

The fraction θ of formed ion-pairs can be calculated as a function of the size of the ions, the dielectric constant of the solvent and the analytical concentrations, thanks to Bjerrum's theory. One demonstrates that the observed mean ionic activity coefficient $\gamma_{\pm\ \text{obs}}$ is linked to the theoretical one $\gamma_{\pm\text{th}}$ by the relation:

$$\log\gamma_{\pm\text{obs}} = \log\gamma_{\pm\text{th}} + \log(1 - \theta)$$

46.14.5 Legitimacy of the Series Development of the Boltzmann's exponential

Another possible cause of the shortcomings of the Debye–Hückel theory may lie in the legitimacy of the truncature of the series development of the Poisson–Boltzmann's equation. Actually, the answer to this question may be qualified as being unexpected.

The demonstration has been done that the non-linearization of this exponential would entail the existence, unexpectedly, of a theoretical contradistinction! The linearization, as it has been performed above, is necessary in order to avoid this contradistinction! The demonstration has been based by performing the calculations involving the entire exponential. (Besides, they have necessitated the use of computers). The results obtained in this manner are inaccurate and are proved to be inconsistent).

We have seen that the linearization leads, indeed, to the relation:

$$\rho_r = -\sum\nolimits_k \left(N_k{}^\circ z_i{}^2 e_o{}^2/kT\right)\psi_r$$

that is to say to a linear relation between ρ_r and ψ_r. In the case of the "unlinearized" Poisson–Boltzmann's equation, the relation between these two quantities is no longer linear. But, the obtention of the Debye–Hückel relations comes from the legitimacy and the use of the electrostatics theorem known under the name of "principle of linear superposition of fields." It stipulates that the total potential due to two (or more) systems of charges located at two well-defined points is equal to the sum of the potentials due to both systems. This can no longer be the case if the charge at a point is in an exponential relation with the potential.

From a general viewpoint, some authors note that a pitfall of the Debye–Hückel theory is that it does not take into account the potential energy stemming from some electrostatic interactions (viz. paragraph 3), whence the name of primitive model with which it is endowed. Neither, does it take into account other factors such as the formation of hydrogen bonds, the existence of quantum effects and of donor–acceptor properties of the solvent.

Chapter 47
Radial Distribution Functions and Electrolytes Solutions Theory

Abstract Recent progresses concerning the theory of solutions, in particular those of electrolytes, are based on statistical thermodynamic reasonings. For example, it is possible to calculate changes of chemical potentials of some electrolytes with their concentrations, thanks to the radial distribution function, that is to say by applying the Kirkwood–Buff's theory. Hence, it is possible to have access to activity coefficients in various conditions. But obtaining these results involves performing very complex calculations, impossible to do without the help of computers. Among the informatic methodologies used, the so-called "technique of informatic simulations" deserve some considerations.

Keywords Radial distribution functions • Electrolytes solutions theories • Kirkwood–Buff's theory • Informatics and simulation theories (algorithm) • Monte Carlo method • Molecular dynamics method • Cost function • Particular Kirkwood–Buff's integrals • Least squares regressions (linear and not linear) • Ion-pairs

Recent progresses concerning the theory of solutions, in particular those of electrolytes, are based on statistical thermodynamic reasoning. For example, it is possible to calculate changes of chemical potentials of some electrolytes with their concentrations, thanks to the radial distribution function, that is to say by applying the Kirkwood–Buff theory. Hence, it is possible to have access to activity coefficients in various conditions. But obtaining these results involves performing very complex calculations, impossible to do without the help of computers. Among the informatic methodologies used, that so-called "technique of informatic simulation" deserves some considerations.

47.1 Informatic Simulation Techniques

In this paragraph, we confine ourselves to mention some considerations on the general principles.

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47.1.1 Generalities

Informatic methods of simulation consist in obtaining the calculated results of some studied physicochemical experimental processes and in comparing them to the corresponding experimental results. The latter ones must be obtained in exactly the same conditions as those prevailing in the calculations. The comparison permits to verify the accuracy of the initially chosen physicochemical model governing the calculations (through judicious algorithms) and the accuracy of these calculations themselves. When they are satisfactory, the data to which they lead are chosen to eventually give a better starting base of calculations than previously and so forth. The great advantage of these methodologies is that they "work" with a great number of experimental data. In other words, they benefit from a consequent number of experimental information. This characteristic strengthens the accuracy and the precision of the determination.

These techniques require to know the studied process as well as possible in order to write the most plausible as possible initial mathematical model permitting the calculations mentioned above. Actually, the writing of the model entails adopting hypothesis which, at the end of the simulation, proves to be verified or to be invalided. For example, the validation of a hypothesis (through the comparison of the results) may permit to evidence the occurrence of some electrostatic interaction. (We have already, in this book, given a very simple example of informatic simulation—viz. Chap. 19).

A simulation involves several successive steps. They are:

- To acquire a knowledge as accurate as possible of the studied physical or chemical process. This step is called the writing (or the conception) of the physicochemical model.
- To write its corresponding mathematical model. This step is crucial. It consists in writing all the equations describing and quantifying all the processes envisaged in the previous step. It also consists in linking them in order that their more or less simultaneous resolution permits to obtain the results.
- To perform the calculations with a computer. This step entails to write the algorithm corresponding to the preceding steps. Let us notice that its writing also entails the conception of a strategy (eventually) permitting *the automatic* continuation of the steps and also the end of the whole process. It also entails the adoption of constraints in order to minimize the calculation times and to avoid the obtaining of intermediary aberrant results.

For our purpose, two great techniques of informatic simulations are used. They are those so-called "Monte Carlo" and "molecular dynamics" ones.

47.1.2 The “Monte Carlo” Approach

According to its principle, the method consists in calculating and summing all the potential energies due to the electrostatic interactions between (in the most simple case) each pair of particles in a given configuration, as a function of their distance and, then, to average the obtained results over all the configurations. The major interest of the technique is that every possible and conceivable interaction between the particles may be introduced in the model for calculations. It is very important to notice that, in this first description, the potential energies are calculated by only taking into account the electrostatic interactions between two particles. We shall come back to this point in paragraph 4.

In order to take into account the interactions between two particles, one can, for example, adopt the Lennard–Jones’ relation:

$$U_{ij} = -A/r^6 + B/r^{12}$$

where A and B are two constants. Their values are automatically found during the simulation process in order to give the best fit.[1]

The strategy is as follows. The particles are placed in the starting configuration which must be chosen (arbitrarily) as judiciously as possible in order to minimize the calculation time. Then, each particle is randomly displaced, hence the name of the method. Then, the following question is asked: does the displacement of the particle decrease the potential energy of the system? If the answer is yes, the algorithm accepts the displacement of the particle. If the answer is no, the displacement is rejected. (Some softenings of this constraint are sometimes adopted.)

The operation is repeated numerous times until the system is in equilibrium, that is to say when it becomes impossible to get any more decrease in its energy. Some thermodynamic quantities may be calculated in this manner. For example, as soon as in 1970, period during which the computers were, by far, less powerful than to day, with a sampling as weak as a number of particles of the order of one hundred (compare with the Avogadro’s number!), some authors could again find the exact location of the minimum of the curve $\log \gamma_{\pm}$ of one electrolyte as a function of $\sqrt{C}$ (viz. Chap. 15).

47.1.3 Molecular Dynamic Technique

In this technique, the computer is used in order to calculate how the particles system evolves with time. The calculations are performed by applying the laws of classical mechanics. At each beginning of the micromotion of one particle, the resolution of the movement equations of classical mechanics allows to define the trajectories of

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[1] A and B are not the same constants as those of the Debye–Hückel equations.

all the particles and, hence, to guide them for a new displacement. Thus, contrary to the "Monte Carlo" technique, the sequence of the events is not random since it obeys the solutions of the movement equations. The global force playing a part in the movement equations is from electrostatic origin. It results from the occurrence of an average potential due to the presence of the other particles.

The major hypothesis on which the technique is based is that the global force which, finally, commands the displacement of particles is constant during a time interval which must be very short, in order that the parameters governing the motion equations can be considered as being constant. In practice, it is of the order of the femtosecond (10^{-15} s). It must be noticed that in this technique, there is no true condition of arrest of the process. One way to know that the process is finished is to look at the obtained numerical values. Then, when it is the case, they do not vary anymore when the process is still continuing. Furthermore, one can, also, repeat the whole same process by starting from other initial conditions than previously and verify that, finally, the same equilibrium as previously is found. Besides, this test is advised for every simulation process, in order not to be the victim of a mirage!

47.1.4 Some Remarks

Actually, these methods appear as being special processes of numerical evaluation of multidimensional integrals. Hence, they permit to calculate the average value $\langle F \rangle$ of the integrals:

$$\langle F\rangle = \int \dots \int d\mathbf{R}^N \mathbf{P}\left(\mathbf{R}^N\right) F\left(\mathbf{R}^N\right)$$

where $P(\mathbf{R}^N)$ is the distribution function (or the basic probability density) (viz. Chap. 28) and $F(\mathbf{R}^N)$ the function in the configuration $\mathbf{R}^N$. It can be the radial distribution function.

The very stringent limit of using these methods and from which it is not possible to go away is the capability of calculation of the computers. Having the Avogadro's number in mind (6.023×10^{23} mol^{-1}), one can easily conceive that a computer cannot treat such a sampling of one mole, overall if one reminds that each particle must be described by three cartesian coordinates and by three moment coordinates. Furthermore, we only, here, mention the case of spherical particles devoided of any internal structure. When it is not the case, the handling of one or two supplementary coordinate(s) per molecule is necessary (viz. Chap. 27 and Appendix F). It must be noticed that this lack of power of calculation inevitably raises the question of the legitimacy of the obtained results with a limited number of particles, of the order of 10^3 up to 10^4.

47.2 General Principle of the Calculation of the Activity Coefficients of the Electrolytes Through the Use of the Kirkwood–Buff Theory

As in the case of nonelectrolytes solutions, the activity coefficients are obtained from the spatial pair correlation functions $\overline{G_{\alpha\beta}}$, also called Kirkwood–Buff integrals:

$$\overline{G_{\alpha\beta}} = \int_0^\infty \left[\overline{g}(r)_{\alpha\beta} - 1\right] 4\pi r^2 dr$$

They depend themselves on the radial distribution functions $\overline{g}\,(r)_{\alpha\beta}$. Let us recall that the theory leads to mathematical relations linking some thermodynamic quantities (among them the chemical potential) and the Kirkwood–Buff integrals. The latter are themselves related to the radial distribution functions $g(r)_{\alpha\beta}$. The results obtained through the theory notably allow to obtain the chemical potentials changes with the species "concentrations" at constant temperature and pressure. It is through the occurrence of these relations that the activity coefficients are reached (viz. Chap. 42).

Let us also recall that the radial distribution functions can be experimentally evaluated and eventually even calculated. Some mixed methodologies based both on experimental results and on theoretical calculations, as for example those involving informatic simulations are also used (viz. Chap. 29).

It is important to notice that, up to now, the mentioned radial distribution functions involve interactions exerting between two species. In the Debye–Hückel theory, this is not the case.

47.3 Radial Distribution Functions and the Corresponding Theory of the Electrolytes

47.3.1 *Radial Distribution Functions Only Involving Interactions Between Two Species*

In the case of nonelectrolytes, α may be identical to β, as they may not be. For solutions of electrolytes, it is necessary to define and to use special radial distribution functions. Thus, for those describing the interactions between two ions (of general type $g^{(2)}(r)$) the functions $g^{(2)}{}_{++}(r), g^{(2)}{}_{+-}(r)$ and $g^{(2)}{}_{--}(r)$ are introduced. In the symbols, the first index is that of the charge of the central ion and the second that of the other ion. It must be noticed that:

$$g^{(2)}{}_{+-}(r) = g^{(2)}{}_{-+}(r)$$

because the central ion may also be in the ionic sheath of another ion.

It is certain that only considering the interactions between two species (ionic or not) is the easiest means to perform the calculations. The reason is as follows: the calculation of the radial distribution functions, that is to say that of the potential electrostatic energy (due to the electrostatic interaction between both species as a function of their distance r) can be strictly solved, that is to say without any approximation. There exists an analytical solution to the differential equations describing the process.

The criticism concerning the fact that one bases the calculations by only considering the interactions exerting between two particles is evident. This way to perform the calculations is purely and simply one approximation since more than two particles may interact simultaneously. The consequence of this state of matter is the following: even when the calculated result is in full agreement with the experimental data, it remains, however, the fruit of an approximate process. This fact means that the fitting technique compensates an imperfect approach by a process, which because of that, is obligatorily itself imperfect! If we again consider the example of the calculation based on the Lennard–Jones' model, we have said that the values A and B tidy themselves automatically to obtain the best fit with the experimental data. According to that we have just said, the apparent validity of the result is not necessarily the reflection of the strict scientific reality. A and B are, certainly, endowed with values optimizing the simulation but, despite this positive point, they do not adopt realistic values.

However, it remains true that this methodology is particularly fruitful in the study of fluids.

47.3.2 Radial Distribution Functions More Complex

Intuitively, one can imagine that taking into account the interactions between several ions rather than between only two may significantly improve the approach to the reality. Thus, distribution functions of the types $g^{(3)}(r_{12}, r_{13}, r_{23})$, $g^{(4)}$, $g^{(5)}$, $g^{(6)}$, … and hence, of course in the cases of electrolyte solutions, the functions of types $g^{(3)}{}_{+++}$, $g^{(3)}{}_{++-}$, $g^{(3)}{}_{+--}$, $g^{(3)}{}_{---}$ have been introduced. Let us mention in passing, without insisting that there exists a theory permitting to relate the functions $g^{(4)}$ to $g^{(3)}$, $g^{(3)}$ to $g^{(2)}$, …, step by step.

A very serious difficulty is appearing as soon as radial distribution functions $g^{(n)}$ such as $n > 2$ are handled. Then, it is no longer possible to exactly calculate the corresponding radial distribution functions and more precisely the electrostatic potential energy of the n species in interactions as a function of the distances separating them. It is the problem of the three bodies in astronomy. Therefore, for the calculations, one must operate through approximations, for example, the following one:

$$g^{(3)}\left(r_{\alpha\beta}, r_{\beta\gamma}, r_{\alpha\gamma}\right) = g^{(2)}r_{\alpha\beta}g^{(2)}r_{\beta\gamma}g^{(2)}r_{\alpha\gamma}$$

It appears that this kind of approximations is far from being satisfactory.

47.4 Debye–Hückel Theory and Radial Distribution Function

Finally, it is interesting to recall the difference of approaches of the solutions of electrolytes between the Debye–Hückel theory and that based on the radial distribution function.

47.4.1 The Radial Distribution Function in the Debye–Hückel Theory

Let us recall that in the Debye–Hückel theory, the Maxwell–Boltzmann distribution:

$$n_k = n_k{}^{\circ}\exp(-z_k e\psi_{\text{cloud}}/RT)$$

has been arbitrarily retained by the authors (viz. Chap. 46). $z_k e$ is the charge of one ion k and ψ_{cloud} is the mean electrostatic potential due to the other particles. The average is taken over the whole configurations of all the particles. The choice of this distribution is the essential approximation of the Debye–Hückel theory.

It amounts to introducing the ratio $n_k/n_k{}^{\circ}$ as the function of radial distribution, that is to say:

$$g(r) = n_k/n_k{}^{\circ}$$
$$g(r) = \exp(-z_k e\psi_{\text{cloud}}/kT)$$

47.4.2 Some Advantages of the Approach Through the Radial Distribution Functions

The approach through the radial distribution functions permits to take into account:

- All the interactions that can be conceived between the different particles constituting the system. The Debye–Hückel theory takes only into account the electrostatic interactions. This is done through the use of functions G_{AB}, which are themselves related to the radial functions $g(r)$. In this chapter, we have seen this case. We have seen, indeed, that the study of electrolytes solutions entails the introduction of functions $g^{(2)}{}_{++}$, etc. It is true that taking into account all the possible interactions between the particles make significantly more complex the calculations and these ones would not been possible without the use of computers without great calculation capacities. At this point of the description of the methods of study of the solutions, it is quite legitimate to assert that the couple distribution function/computer works in perfect synergy for the study of solutions.

- The interactions between the solutes (whichever they are) and the solvent, whence the introduction of the functions of the kinds $g^{(2)}{}_{-\mathrm{solv}}$, $g^{(2)}{}_{+\mathrm{solv}}$, $g^{(2)}{}_{\mathrm{solv-solv}}$. In brief, the part played by the solvent is no longer proved. Besides, the Poisson's equation does not appear in the last calculations. Hence, the theory takes into account the molecular structure of the solvent. This is absolutely not the case in the theory of Debye–Hückel. Hence, the treatment of solutions through the radial distribution functions permits to begin to study the solutions at the level so-called "the Born–Oppenheimer" level. The Debye–Hückel, as we have already said, remains to the Mc-Millan level.
- The formation of ion-pairs. They are implicitly considered in the calculations.

47.5 Some Results

Concerning the activity coefficients, some arguments and very complex calculations of statistical thermodynamics allow to obtain new pieces of information concerning the relations which link them to the ion concentrations. For example, in the case of a symmetrical electrolyte, the following conclusions have been retained:

$$(\partial \ln\gamma_{\pm}/\partial C_{+})_{T,P} = [1 - 2C_{+}N_{\mathrm{A}}(G_{+-} - G_{+\mathrm{solv}})]/\left[2C_{+}{}^{2}N_{\mathrm{A}}(G_{+--} - G_{+\mathrm{solv}})\right]$$

and

$$(\partial \ln\gamma_{\pm}/\partial C)_{T,P} = [1 - 2CN_{\mathrm{A}}(G_{+-} - G_{+\mathrm{solv}})]/\left[2C^{2}N_{\mathrm{A}}(G_{+-} - G_{+\mathrm{solv}})\right]$$

where C_{+} or C is the cation or the whole electrolyte concentration and N_{A} the Avogadro's number. (Let us notice in passing that these expressions entail functions of the type $g^{(3)}$).

- A first interesting point appears. The mean ionic activity coefficient of the electrolyte explicitly depends on the interactions solute–solvent.

- A second one lies in the fact that it does not depend on the other interactions, as it is proved by the absence of the radial distribution functions g_{++}, g_{--} $g_{-\ \mathrm{solv}}$, $g_{\mathrm{solv-\ solv}}$ in the preceding relations.

  Some other conclusions do appear:

- The values $g(r)$ and their dependence with the distance r which separates the particles in interactions depend on the nature of the ions and not only of their charges.
- When the ions have different sizes (a hypothesis which is absolutely not envisaged in the Debye–Hückel theory) one finds that the values:
  - $g^{(2)}{}_{--}$ do vary a little when the cation size is changed
  - $\mathrm{g}^{(2)}{}_{++}$ decreases when the cation size decreases
  - $g^{(2)}{}_{+-}$ increases when its size decreases.

Chapter 48
The Activity Concept in Retrospect

Abstract The chapter essentially summarizes the interest of the notion of activity. As it is well known in classical thermodynamics, the chemical potential function, introduced by Gibbs in 1875, permits to treat physicochemical problems as mathematical ones. The difficulty is, once the mathematical solution found, to transform it into numerical physicochemical answers because the relations between the chemical potential and real parameters such as the temperature, pressure, and molar fractions are difficult to grasp at first sight.

Using activities simplify the problem, in the opinion of the author, activities play the part of an auxiliary function facilitating the understanding of the experimental reality, once the behaviors are no longer ideal. But, their exact physical significance is not known. However, as it has been shown, Mc-Millan–Mayer and Kirkwood–Buff's theories have brought some insights in this field.

Keywords Lewis definition of activities • Interesting features of the notion of activity/summary

As it is well known in classical thermodynamics, the chemical potential function, introduced by Gibbs in 1875, permits to treat physicochemical problems as mathematical ones. The difficulty is, once the mathematical solution found, to transform it into numerical physicochemical answers because the relations between the chemical potential and real parameters such as the temperature, pressure, and molar fractions are difficult to grasp at first sight.

Using activities simplify the problem, since as we have seen it, they are related to these experimental parameters without, besides, knowing their significance. In our opinion, such a part of auxiliary function played by activities together with their exact physical significance, which can be approached as we have seen, deserve a summing-up of its principal features.

48.1 Lewis' General Definition of Activity

G.N. Lewis defined the activity of a compound in a given state of a thermodynamic system as being:

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> an active density member which bears the same relation to the chemical potential μ at any density that $\overline{N}/V$ does as $\overline{N} \rightarrow 0$.

If we take the example of a solute in a very dilute solution, we know that its chemical potential μ is given by a relation of kind (48.1):

$$\mu = \mathrm{Cte} + RT \ln C \quad \text{(very dilute solution)} \tag{48.1}$$

where C is an expression of its concentration and Cte is a constant. When the solution is not diluted enough, relation (48.1), no longer, correctly describes the behavior of the solute. In order that the case remains, the chemical potential must be expressed by relation (48.2):

$$\mu = \mathrm{Cte} + RT \ln a \quad \text{(every solution)} \tag{48.2}$$

where a is the activity of the solute. It is a quantity arbitrarily introduced by Lewis. It permits to correctly describe the behavior of the compound through the value it confers to its chemical potential μ.

We observe that, owing to the fact that relation (48.2) applies to every solution and in particular to very dilute ones, the constant Cte is the same in both expressions (48.1) and (48.2) for identical pressure and temperature of the systems, since for dilute solutions, indeed, the activity is defined as being equal to its concentration):

$$a = C \quad \text{(very dilute solutions)}$$

In brief, an activity may be considered as being a kind of fictitious concentration of a component in a given thermodynamic system, in such a manner that it does exhibit an ideal behavior under these conditions, while it keeps the value of the chemical potential it actually possesses.

The activity is a thermodynamic quantity depending on the nature of the substance it qualifies, on its concentration, temperature, pressure, and on the nature of the rest of the system. It is a quantity without any unity. It has been exclusively introduced within the framework of classical thermodynamics.

48.2 Interesting Features of the Introduction of Activities

Handling activities is of a major interest when a system does no longer exhibit an ideal behavior, whichever its composition is.

When, indeed, the behavior of the compound or, more generally, of the system is studied by making an allowance for its chemical potential (as it must be the case), but when the latter is expressed in terms of concentrations, the results of the process become incorrect once the dilution considerations are no longer obeyed. As an interesting example coming from the realm of chemistry, let us take that of an equilibrium. If we base our reasoning on the concentrations of the reactants and products, the prediction of the characteristics of the equilibrium state (its thermodynamic equilibrium constant) becomes false when the dilution conditions are no longer obeyed. They remain correct if activities are used.

Very highly also, G.N. Lewis has introduced the activity notion in such a manner that its handling allows the (correct) study of the physical and chemical processes by using the same reasoning and mathematical formalism as those used to describe the courses of ideal systems in concentration terms.

48.3 Ideal Solutions: Causes of Deviation from the Ideal Case

We know that a gas is ideal when there exists no interaction between its atoms or molecules. Both classical and statistical thermodynamics clearly show that, then, gases obey the perfect gases law. Of course, strictly and scientifically speaking, actually, it always remains some interactions between particles, even when the quantity of matter is very low and when it is confined into a very large container. Hence, the notion of ideal gas is a fiction. But, it is an experimental fact that gases obey the perfect law in some instances.

The “ideality” notion in the case of solutions is more complex than with gases for the following reason. In a solution (containing two components obligatory at least), there remain interactions between the solute and the solvent even at very high dilution.

Some authors distinguish two kinds of ideal solutions. They are actually limiting cases.

- The first one results from the fact that the solute and the solvent do possess structures which are very close to each other. The interactions between solute molecules, between solute solvent molecules, and between solvent–solvent molecules are of the same intensity. Then, both solute and solvent obey Raoult’s law. This is one of the two criteria of ideality. This case corresponds to the so-called ideal symmetric solutions, also named perfect solutions.
- The second case is that in which the solute is very dilute. One solute particle can only see solvent molecules all around it. Then, the solute obeys Henry’s law. This is the other criterion of ideality. Let us recall that when the solute obeys Henry’s law, then the solvent obeys Raoult’s law.
- Deviations from the ideal case are the mark of electrostatic interactions between the different particles of the system. As an example of such a case, this affirmation applies to those of nonelectrolytes and of electrolytes as well. The result is the occurrence of a potential energy of interaction.
- Concerning now:

- The solutions of nonelectrolytes, two theories stemming from statistical thermodynamics strengthen this affirmation, at least in some conditions (see under paragraph 10).
- The solutions of electrolytes, several theories of different levels of complexity, theories of which the most well-known are those of Debye and Hückel and their extensions, quantify the interactions between the ions.

48.4 The Activity Coefficient

From a general viewpoint, the activity a_i of a compound i is related to its "concentration" C_i through the following general relation:

$$a_i = \gamma_i C_i$$

where γ_i is its activity coefficient. The activity coefficient function is an arbitrary one, quite evidently inseparable from that of the activity coefficient. The value of the activity coefficient is a measure of the deviation of behavior of i from the ideal case. The activity coefficient is a quantity without any dimension, as the activities are.

We must pay attention to the fact that the above relation is not a linear function between the activity and the "concentration" despite its appearance because the coefficient γ_i is not a constant. In the case of electrolytes solutions, for instance, it changes with the ionic strength of the medium (viz.: Paragraph 12).

48.5 Multiplicity of the Activities of a Species in a Given Thermodynamic State

The above relation does not give all the links between activities and concentrations, although it is general from the formal standpoint. It masks the fact that a given species in a given thermodynamic state may exhibit several activities of different values. The reason is the arbitrary character of the definition of an activity.

48.6 On the Arbitrary Character of the Definition of an Activity: The Standard State

The arbitrary character of the definition of an activity lies in the fact that the activity value of a species depends on the choice of a standard state which is necessary to define it. The choice of a standard state is itself arbitrary. An activity, indeed, can only be defined with respect to the definition of a standard state. In the standard state, its chemical potential is $\mu°$ and its activity is equal to the unity.

In every thermodynamic state, the activity of a substance (and its coefficient) is linked to its chemical potential through the relation:

$$\mu_i = \mu_i{}^{\circ} + RT\ln a_i (1) \quad \text{with} \quad a_i = \gamma_i C_i$$

According to its choice, the standard state $\mu_i{}^{\circ}$ of a species is defined by characteristic values which change with its nature and its activity value is also defined in such a manner that the chemical potential remains the same for a given thermodynamic system. In other words, fixing an arbitrary value to an activity (this is always possible) entails the choice of a defined standard state.

Finally, the invariance of the chemical potential in a given state is not surprising because the change of the Gibbs energy accompanying a given process at constant temperature and pressure must be a constant. This is a consequence of the definition of the Gibbs energy, the change of which accompanying a definite process is a constant.

48.7 Standard States Usually Chosen

For practical reasons, some standard states are quasi-systematically chosen by the community of the physico-chemists. In the case, for instance, of binary solutions:

- For symmetric solutions, the standard state of each component is itself in pure state at the pressure and temperature of the system. In these conditions, according to relation (48.1), RT ln a_i is, hence, the (measurable) Gibbs energy change accompanying the transformation of one mole of i from the pure state into its state in the system. The concentration scale to which is related the activity is that of molar fractions x. This scale permits to easily scan the whole range of concentrations, since the molar fraction can vary only between 0 and 1:

$$a_i{}^{\mathrm{S}} = \gamma_{i,x}{}^{\mathrm{S}} x_i \quad (\mathrm{S}: \text{ symmetrical});$$

- For dilute solutions, the standard state of solvent B is itself in pure state at temperature and pressure of the system. The concentration scale to which is referred its activity is that of molar fractions. When it is pure $x_{\mathrm{B}} = 1$. For the solute A, the standard state is that in which it would exhibit an ideal behavior at temperature and pressure of the system, usually at a “concentration” $m = 1$ mol kg^{-1} or $c = 1$ mol L^{-1}. For solubility reasons, the standard state is a hypothetical one. Let us recall that in the standard state, the solution exhibits an ideal behavior as it does in the reference state in which the solute is very dilute. The reference state has the very important property to be actual. Therefore, the thermodynamic properties of the standard state are obtained by extrapolation of those of the reference state. Whether the scale of concentration is the molality one or molarity one, the activity is given by the following expressions:

$$a_A{}^D = \gamma_{A,m}{}^D m_A \quad \text{or} \quad a_A{}^D = \gamma_{Ac}{}^D c_A \quad (\mathrm{D}: \text{ dilute})$$

It is clear that the solute shows different values of its activity according to the adopted "concentration" scales.

In literature, one also adopts the following conventions quasi-systematically:

- The activity of pure liquids and solids in equilibrium with their solutions is exactly equal to the unity. They are themselves their proper standard state;
- Gases in equilibrium with a solution have an activity equal to their fugacity.

These conventions are followed for nonelectrolytes and for electrolytes solutions as well.

48.8 Activities, Equilibrium Constants, and Gibbs Energy Changes Accompanying Processes

Thermodynamic constants of chemical equilibria (which quantify the so-called mass action law) are expressed in activity terms. They are not endowed with a dimension.

Although it is not frankly apparent in literature because of the agreement ruling on the choice of the standard states and hence on the activities, the values of the equilibrium constants do vary with the kind of activity retained. However, despite the activity values which may vary, the chemical processes which are quantified through them show a constant Gibbs energy change.

This phenomenon can be summarized by saying that in the expression of the chemical potential, there exists a subtle balancing of the chemical potential and of the activity values.

Again, quite evidently here, we meet the fact that Gibbs energy is a state function.

48.9 Other Definition of the Activity of a Species

The activity a_i of a species is also defined as being the ratio of its fugacity f_i and its fugacity f_i° in the standard state:

$$a_i = f_i / f_i^\circ$$

Actually, with judicious choices of standard states permitting to anchor both fugacities and activities values, for the same thermodynamic state, the activity values found from the fugacities are made identical to those coming from the chemical potentials.

48.10 Activity Coefficients, Activities, and Deviations from the Ideal Behavior in the Case of a Liquid or a Solution

Statistical thermodynamics and the pairwise-additivity hypothesis (which postulates that the potential energy of interaction between the whole particles is equal to the sum of energy interactions of these ones taken two by two), lead to the expression:

$$\mu = kT\ln\left(\rho\Lambda^3 q^{-1}\right) \; - \; kT\ln\langle\exp(-\beta B)\rangle$$

μ is the chemical potential of the species, the factor $kT\ln\left(\Lambda^3 q^{-1}\right)$ its standard chemical potential in the gaseous state $\mu^{\circ g}$, ρ its density number and β the ratio $1/kT$. B is the sum of the interaction energies U_{ij} between two particles. The factor ‹exp $(-\beta B)$› is the average exponential of the same term. We notice that the previous expression can be written strictly equivalently as:

$$\mu = kT\ln\left(\Lambda^3 q^{-1}\right) + kT\ln\rho - kT\ln\langle\exp(-\beta B)\rangle$$

or:

$$\mu = kT\ln\left(\Lambda^3 q^{-1}\right) + kT\ln[\rho/\langle\exp(-\beta B)\rangle]$$

The term in brackets $[\rho/\langle\exp(-\beta B)\rangle]$ is the activity.

48.11 Activities of Nonelectrolytes and Molecular Quantities

Classical thermodynamics does not provide answers to this question. In no case, it is surprising since, sensu stricto, in its whole *corpus*, it has no need to recognize the very existence of atoms, molecules, ions whereas statistical thermodynamics provide some insight in this realm. It is its vocation.

Two theories stemming from the handling of the grand ensemble permit to approach and to begin expressing the activities in terms of molecular parameters. They are McMillan–Mayer and Kirkwood–Buff's theories.

- McMillan–Mayer's theory leads to the following expressions (among others):
  - For the definition of the activity z of a real gas:

$$z = Q_1\lambda/V$$

where λ is the absolute activity of the gas, V the volume of the system, and Q_1 the canonical partition function corresponding to the presence of only one particle in the system. The activity z of the gas is related to its density number ρ by a power series of the kind:

$$z = \rho + a_2\rho^2 + a_3\rho^3 + \ldots$$

This relation is a true scientific advance. It permits, at least formally, to calculate the activity starting from the corresponding value of the concentration. This was not conceivable, before. Another interesting point is that we know the significance of every coefficient of the power series. It is not always the case for every coefficient of power series in physics. It is one of the most remarkable achievements of statistical thermodynamics that it provides explicit expressions for the virial coefficients in terms of the intermolecular interaction energy of groups of 2 particles, 3 particles …n particles, respectively, for the coefficients a_2, a_3…a_n particles.

Coefficients a_2, $a_{3,}$ …are indirectly related to those of the virial of the gas. Hence, they are indirectly accessible experimentally. They show the great following feature: the coefficient a_2 expresses and quantifies the interactions between two particles of the gas, a_3 those between three particles … and so forth. Hence, when the number density is very weak, the interactions between more than two particles are most unlikely to occur. As a result, we can only keep the first two terms of the series in order to explicit the activity of the compound.

It is evident that activity coefficients are also accessible through the calculation of the ratio z/ρ. Let us stress the fact that the above relation, as a rule, permits to express an activity as a function of the corresponding concentration.

Likewise, McMillan–Mayer and Hill's theories provide a power series of the same kind which relates an activity of a solute to its molality in a solution at constant pressure and temperature. They also permit, in this case, to introduce a new type of activity coefficient having the property to take into account the interactions existing between only one molecule of solute and the whole solvent molecules, that is to say when it obeys Henry's law. In this state, the studied particle is immerged in an average electrostatic field stemming from the whole of the other ones. This kind of interactions does not exist, of course, in a gas because of the occurrence of the vacuum between the particles.

- Kirkwood–Buff's theory is grounded on the properties of spatial pair-correlation functions $G_{\alpha\beta}$ (or Kirkwood–Buff integrals) defined by the expression:

$$G_{\alpha\beta} = \int_0^\infty \left[g_{\alpha\beta}(R) - 1\right] 4\pi R^2 dR$$

where $g_{\alpha\beta}(R)$ is the radial distribution function (which is experimentally accessible) between both molecules α and β, R being the distance between them. $g_{\alpha\beta}(R)$ is the factor quantifying the deviance (at the distance R between them) of the behavior of the average local density $\rho g_{\alpha\beta}(R)$ related to the real density ρ. The theory leads to several interesting results. Among them let us mention several expressions of chemical potentials and hence, through them, expressions of activities and of their relevant coefficients of components of solutions in different conditions. In particular, it demonstrates the importance of the following parameter:

$$\Delta_{\alpha\beta} = G_{\alpha\alpha} + G_{\beta\beta} - 2G_{\alpha\beta}$$

where symbols $G_{\alpha\alpha}$, $G_{\beta\beta}$, $G_{\alpha\beta}$ are the Kirkwood–Buff's integrals in the binary mixture. Let us recall that the theory reduces the interactions between particles to the electrostatic ones within pairs. The expression of $\Delta_{\alpha\beta}$ permits to characterize three kinds of ideal fluids. They are those which exhibit the behavior of:

Perfect gases
Symmetric solutions
Dilute solutions

As it has been already said, to these behaviors are related different choices of different standard states, of concentration scales and of activities.

The Kirkwood–Buff's theory, notably, leads to the following relations:

- For symmetric solutions in which A and B are the two components, x_A and x_B their molar fractions, ρ the total density number and for which the activities are related to the molar fractions:

$$kT \ln\gamma_A{}^S = kT\int_0^{xB} \left[x'_B\rho\Delta_{AB}/\left(1+\rho x'_A x'_B\Delta_{AB}\right)\right]dx_B$$
$$a_A{}^S = x_A \exp\int_0^{xB} \left[x'_B\rho\Delta_{AB}/\left(1+\rho x'_A x'_B\Delta_{AB}\right)\right]dx_B]$$

- For dilute solutions, at constant temperature and pressure and with the activities related to the density numbers:

$$kT \ln\gamma^D{}_A(T,P,\rho_A) = -kT\left(G^{\circ}_{AA} - G^{\circ}_{AB}\right)\rho_A$$
$$\mu_A(T,P,\rho_A) = \mu^{\circ}{}_A(T,P) + kT\ln[\rho_A\gamma^D{}_A(T,P,\rho_A)]$$

$G^{\circ}{}_{AA}$ and $G^{\circ}{}_{AB}$ are the first terms of the series developments of Kirkwood–Buff's integrals G_{AA}, G_{AB} as functions of density numbers.

According to the Kirkwood–Buff's theory, it appears that the parameter $\Delta_{\alpha\beta}$, linear combination of Kirkwood–Buff's integrals, is a parameter of utmost importance since it commands the behavior of a solution from the standpoint of "ideality," at least in great part. $\Delta_{\alpha\beta}$ can be considered as being the deviation of the mixture behavior with respect to that of an ideal symmetric solution.

Otherwise, Kirkwood, by grounding its reasoning on the notion of radial distribution, has demonstrated that the chemical potential of a gas is given by the expression:

$$\mu = kT\ln\left(\rho\Lambda^3 q^{-1}\right) + \rho\int_0^1 d\xi\int_0^1 U(R)\, g(R,\xi)4\pi R^2 dR$$

Λ is the de Broglie's thermal wavelength and q is its internal molecular partition function. ρ is its density number. ξ is a coupling parameter for the electrostatic interactions of one particle of the system with all others. It can change from 0 to 1. When the added particle is completely discharged $\xi = 0$. When it is fully charged, $\xi = 1$.

$g(R, \xi)$ is the radial distribution function between the added particle charged at the value ξ and every other one located at distance R from the former. $U(R)$ is the interaction energy between them. Its occurrence is the mark of the fact that the activity coefficient (and the activity) takes into account the electrostatic interactions. Considering the last relation, it is evident that:

$$kT\ln\gamma = \rho\int_0^1 d\xi\int_0^\infty U(R)\, g(R,x)4\pi R^2 dR$$

γ being the activity coefficient of the gas and the term $kT\ \ln(\Lambda^3 q^{-1})$ its standard potential.

Now, putting the theories of McMillan–Mayer and of Kirkwood–Buff in a brief comparison, the first point to stress is that they are both exact. Hence, necessarily, they must be equivalent. However, they are somewhat different because the McMillan–Mayer theory appeals to the pairwise-additivity of the total potential energy hypothesis, whereas the Kirkwood–Buff's does not in any case.

It seems that the McMillan–Mayer approach is more convenient to use in applications if we consider the study of the solution from an unsymmetrical viewpoint of the components. The typical example is that of the osmotic pressure. On the other hand, the Kirkwood–Buff's theory is more convenient if we want to consider the components from a symmetrical point of view, that is to say as having the same status. Actually, the latter is easier to handle.

48.12 Activities of Electrolytes: Expressions of Activities and of Activity Coefficients of Electrolytes in Terms of Molecular Parameters

Concerning the activities of ions, the most important point to highlight is the fact that it is impossible to measure the activity of an ion, whereas it is possible to measure that of the whole electrolyte it stems from. However, the calculation of the activity of an ion is feasible thanks to some theoretical equations, at least in some experimental conditions.

The great difference between the behaviors of electrolytes and nonelectrolytes in solutions lies in the fact that the interionic interactions are by far much stronger than those existing between nonelectrolytes. They occur through very much greater interionic distances than those between nonelectrolytes do. As a result, even in very dilute solutions in which the ions are statistically far from others all the more the solutions dilute are, "long range" interactions are still perceptible. This is not the case with solutions of nonelectrolytes.

Numerous theoretical models permit to calculate activities of ions and of whole electrolytes through their activity coefficients. The most well known are those of Debye and Hückel. One distinguishes the limit and extended Debye–Hückel's equations.

- The limit equation follows from two starting hypothesis according to:
  - An ion can be assimilated to a simple electrically charged point
  - It is supposed as being immersed in a continuum medium possessing the same permittivity as the pure solvent

  In these conditions, from the laws of electrostatics and thermodynamics, it follows:

$$\log\gamma_{xi} = -\,A{z_i}^2\sqrt{I}$$

γ_x is the activity coefficient of the ion, z_i its charge, and I the ionic strength of the solution, defined by the relation:

$$I = 1/2\sum_i C_i{z_i}^2$$

The ionic strength is half the sum applying to all the ions in solution of the products of their squared charge and of their concentration, usually expressed in molarities, whereas the activity coefficient links the ion activity to its concentration expressed in molar fraction.

A is a composite constant for given temperature and solvent. It is interesting to notice that when I tends toward 0, γ_x tends toward 1 in agreement with the general considerations devoted to the activities. We also notice that all the ions, cations whether anions, exhibit the same activity coefficients provided they bring the same relative charge. In water at 25 °C, the limit equation can apply to the sole solutions, the ionic strengths of which are less than about 10^{-3} mol L^{-1}.

- The extended Debye–Hückel equation follows from the same basements as the previous one but after having taking into account the fact that a ion does possess a finite radius. Its expression is:

$$\log\gamma_i = -A{z_i}^2\sqrt{I}/\left(1 + Ba\sqrt{I}\right)$$

B is a constant depending only on the nature of the solvent through its permittivity and on the temperature. The parameter a can be considered as being an adjustment parameter after having been considered very wrongly as the radius of the hydrated ion. In any case, it occurrence permits the individualization of every ion. This was not possible with the equation limit. The extended relation can be applied for ionic strengths weaker than 10^{-1} mol L^{-1}.

Debye–Hûckel equations only apply in some ionic strengths ranges, otherwise they lead to spurious values, even absurd, of ionic activities. Their failures at too high values of the ionic strengths have several causes. They are:

- The solvation of the ions of the electrolytes that the theory does not take into account,
- The arbitrary adoption of a Boltzmann's distribution for the density of the counter-ions all around a reference ion of the solution. This approximation is justified only when solutions are very dilute in ions. This assertion is perfectly demonstrated by the study of solutions by the consideration of the corresponding radial distribution functions,
- The changes in the values of the dielectric constant in the bulk solution with the concentration of ions which are not taken into account,
- The formation of ions-pairs and of ionic aggregates, which are also not taken into account,
- The false hypothesis according to which the deviant behavior of an electrolyte solution with respect to that of an ideal solution is exclusively due to the fact that the solute particles are electrically charged and that, without the electrostatic interionic interactions, the solutions would be ideal. Here is one of the hypothesis on which is founded the theory. In other words, the deviation from ideality is only attributed to the mutual interactions of the electric charges of the ions. Of course, at weak and average distances between ions, the already existing interactions existing in solutions without electrolyte add up the "long-range" ones existing in electrolytes solutions.

  It is an experimental fact that expressions of the type:

$$\log\gamma_{\pm} = -A\left|z_{+}z_{-}\right|\surd I/\left(1 + \surd I\right) + bI$$

in which the term bI is of a purely empirical origin enhances the fit between the values experimentally found and those calculated (the calculations being carried out on the average activity coefficients). More complicated expressions have been proposed. The followed one is due to Guggenheim:

$$\log\gamma_{\pm} = -A\left|z_{+}z_{-}\right|\surd I/\left(1 + \surd I\right) + bI + cI^{2} + dI^{3} + \cdots$$

where b, c, d, ... are empirical coefficients.

- Another approach consists in starting from excess functions, putting them under a polynomial form after having found the best fit with the experimental data and, finally, in proceeding to some derivations in order to find the activity coefficients.

For this purpose, let us recall the Pitzer's relations linking the excess Gibbs energies to the moles numbers of the different electrolytes. They are very often used. When water is the solvent, they are of the kind:

$$G^E/RT = w_\mathrm{w} f(I) + 1/w_\mathrm{w} \sum_{ij} \lambda_{ij}(I)\, n_i n_j + 1/{w_\mathrm{w}}^2 \sum_{ijk} \mu_{ijk} n_i n_j n_k$$

w_w is the weight of the solvent (water) in the solution. n_i, n_j, n_k are the mole numbers of species i, j, k. $f(I)$ is a function of the ionic strength, of the nature of the solvent and of the temperature. It takes into account the "long range" interactions. From the mathematical standpoint, $f(I)$ can take the form of the Debye–Hückel's term or of that issuing from the radial distribution function. $\lambda_{ij}(I)$ is also a function of the ionic strength of the solution. It takes the interactions at short distances into account, but these interactions are only those developing between two ions. The parameter μ_{ijk} reflects the interactions between three molecules.

- Let us finally mention that the progresses of the last decades in the realm of the solution theory, progresses founded on the use of statistical thermodynamics, permitted to calculate the changes of the average activity coefficients of electrolytes with their concentrations. This was possible by handling the radial distribution function. But these calculations are extremely complicated, not tractable without the use of computers.

48.13 Determination of Activities

The determination of the activities of nonelectrolytes is possible, that of a whole electrolyte also. It is the same for that of an average activity coefficient of an electrolyte. This fact permits to indirectly check the possibility of applying the Debye–Hückel's relations and others.

On the contrary, the determination of the activity of an ion is impossible. Fortunately, it is reasonably calculable, at least in some ionic strength conditions, thanks due to Debye–Hückel's relations and others.

Appendix A
Mathematical Apparatus

A.1 State Functions: Mathematical Implications

Let us consider a function L of several variables x, y, z. Its total differential is given by the expression:

$$dL(x,y,z) = (\partial L/\partial x)_{y,z}\,dx + (\partial L/\partial y)_{x,z}dy + (\partial L/\partial z)_{x,y}\,dz$$

Let us also suppose that L is a state function. Physics and especially thermodynamics tell us that there exist quantities such as their changes from a state A to a state B are independent from the way along which the process is carried out. In this case:

$$\Delta L = L_{\mathrm{B}} - L_{\mathrm{A}}$$
$$\Delta L = \text{constant}$$

From the mathematical viewpoint, in order a function L be a state function, its total differential must be exact. A convenient criterion of the exact character of a total differential is that partial derivatives related to this function obey to the relation given under. For the sake of simplification, let us suppose that L is a function of only two variables. Its total differential is:

$$dL(x,y) = (\partial L/\partial x)_y\,dx + (\partial L/\partial y)_x\,dy$$

The most often, both partial derivatives are functions of x and y, that is to say:

$$(\partial L/\partial x)_y = M(x,y) \quad \text{and} \quad (\partial L/\partial y)_x = N(x,y)$$

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The total differential can be written:

$$dL(x,y) = M(x,y)\,dx + N(x,y)\,dy$$

The condition in order the total differential be an exact one is the following equality:

$$[\partial M(x,y)/\partial y]_x = [\partial N(x,y)/\partial x]_y$$

A.2 Homogeneous Functions: Euler's Theorem

Let us consider the function:

$$y = ax^2 + bxy + cy^2$$

and replace the variables x and y, respectively, by the products λx and λy, where λ is a parameter. The function y is transformed into y' which is written:

$$\begin{aligned} y' &= a(\lambda x)^2 + b(\lambda x)(\lambda y) + c(\lambda y)^2 \\ y' &= \lambda^2(ax^2 + bxy + cy^2) \\ y' &= \lambda^2\, y \end{aligned}$$

The result of the multiplication of variables x and y by λ is the multiplication of the whole function y by the term λ^2. The possibility to put the former function y (in which the factor λ is not present) in a common factor entails that it is homogeneous. Since, in the present case, the parameter λ is at the square order, the function y is defined as being a *homogeneous function of second order*.

Euler's theorem rationalizes and generalizes this result. Let us consider the function of two variables x and y $f(x, y)$ for the sake of simplification. According to the theorem, $f(x, y)$ is homogeneous and of order n when the following expression is satisfied:

$$x[\partial f(x,y)/\partial x]_y + y[\partial f(x,y)/\partial y]_x = n\,f(x,y)$$

This expression may be easily generalized to the case of n independent variables. A straightforward example is the case of the volume V of a mixture of two liquids. The experience shows that V is a homogeneous function of order 1 of the numbers of moles n_1 and n_2 of each component, that is to say:

$$V = f(n_1, n_2)$$

and, hence, according to Euler's theorem:

$$n_1[\partial V/\partial n_1] + n_2[\partial V/\partial n_2] = V$$

The notion of homogeneous function is particularly useful when the partial molar quantities are handled.

A.3 Schwartz's Theorem

The Schwartz's theorem stipulates that for a function of two independent variables x and z, the derivation order in order to obtain the cross derivative is of no importance. Hence, for the function:

$$y = f(x, z) \quad (x \text{ and } z \text{ independent variables})$$
$$\partial^2 f/\partial x \partial z = \partial^2 f/\partial z \partial x$$

the second mixed derivatives are equal.

A.4 Method of Lagrangian Multipliers

The method of lagrangian multipliers permits to localize the maximum or the minimum of a function $f(x, y, z)$ when there are one or more constraints imposed on the system. (This limits the domains of x, y, and z in which one can hunt for a maximum or a minimum.) One can write:

$$df = (\partial f/\partial x)_{y,z} dx + (\partial f/\partial y)_{x,z} dy + (\partial f/\partial z)_{x,y} dz$$

At the maximum, $df = 0$ whichever the choice of dx, dy, dz is. In other words, the variations of x, y, z are independent from each other. Hence, the only way to get $df = 0$ is to obtain the values of x, y, z such as the three following relations are simultaneously verified:

$$(\partial f/\partial x)_{y,z} = 0, \quad (\partial f/\partial y)_{x,z} = 0, \quad (\partial f/\partial z)_{x,y} = 0$$

Let us suppose that we are seeking a maximum (or a minimum) in the domain of the three variables in which they obey to the function $G(x, y, z) = a$ where a is a constant.

The method consists in building the function:

$$F(x, y, z) = f'(x, y, z) + \lambda G(x, y, z)$$

Where λ is an arbitrary constant called Lagrangian multiplier. (The method involves an equal number of multipliers as that of constraints.) Then, the method consists in setting up the partial derivatives $(\partial F/\partial x)_{y,z}$, $(\partial F/\partial y)_{x,z}$, $(\partial F/\partial z)_{x,y}$ become equal to 0. As a result, with the help of the three (in the present case) found relations, it becomes possible to express two of the three variables as a function of the third and, since the three are related to each other through the function $f(x, y, z)$, to deduce the values making the latter maximum or minimum. The method also permits to calculate the value of this function at its maximum (or minimum). Usually, knowing the multipliers values is unnecessary, excepted in statistical thermodynamics.

Example: Searching for the maximum of the function $x^m y^n z^p$ to which the constraint $x + y + z = a$ (a: constant) is imposed.

$$F(x, y, z) = x^m y^n z^p + \lambda(x + y + z)$$

$$(\partial F/\partial x)_{y,z} = m x^{m-1} y^n z^p + \lambda = 0$$

$$(\partial F/\partial y)_{x,z} = x^m y^{n-1} z^p + \lambda = 0$$

$$(\partial F/\partial x)_{x,y} = x^m y^n z^{p-1} + \lambda = 0$$

Starting from the last three relations, one finds:

$$x = my/n; \quad z = py/n$$

and:

$$my/n + y + py/n = a$$

whence:

$$y = an/(m + n + p)$$

and so far…

A.5 Maximum-Term Method

The method consists in replacing the logarithm of a sum by the logarithm of the most important term of this sum. Strictly speaking, the method appears to be approximate but, in some conditions, it can be considered as being quasi-exact.

As an example, let us consider the sum $\sum$ defined by the expression:

$$\sum = \sum_{N}^{M} t_N \quad (N = 0 \ldots M)$$

where

$$t_N = M!x^N / N!(M - N)! \tag{A.1}$$

The sum $\sum$ is strictly equal to the following expression:

$$\sum = (1 + x)^M$$

and:

$$\ln \sum = M \ln(1 + x) \tag{A.2}$$

One is searching for the most important term $t_N{}^*$ of the sum (A.1). Since the term $t_N{}^*$ is also the highest of the $\ln t_N$ sum, it is more judicious to reason about this last series.

Let us use the Stirling's approximation which permits to approximate the factorial of a very large number without detectable error. It is:

$$\ln y! = y \ln y - y$$

whence:

$$\ln t_N = M \ln M - N \ln N - (M - N) \ln(M - N) + N \ln x \tag{A.3}$$

The condition

$$\partial \ln t_N / \partial N = 0$$

leads to the expressions:

$$N^* / \left(M - N^*\right) = x \text{ and } N^* = xM/(1 + x)$$

N^* is the value of N which confers the maximum value on the term t_N. Introducing this expression into (3), one finds:

$$\ln t_N^* = M \ln(1 + x) \tag{A.4}$$

The comparison of (A.2) and (A.4) shows that:

$$\ln \sum t_N = \ln t_N^*$$

This result may appear to be illogical but we must not forget that it is obtained at the price of a starting approximation, that of Stirling. Owing to the fact that the Stirling's approximation is all the more exact as the factorial in question is large, one may deduce that this kind of reasoning is all the more accurate as the logarithm arguments are large. Fortunately, it is the case in statistical thermodynamics.

Appendix B
Relation Between the Activity $a_{C\ i}$ and the Fugacity of a Gas (viz. Chap. 10)

The partial pressure of gas *i* in an ideal gaseous mixture is given by the relation:

$$p_i = n_i RT/V$$

or

$$p_i = RTc_i$$

After introduction of the relation (7.15) of Chap. 7 into this expression,

$$\mu_i = \mu_i^* + RT\ln p_i$$

we obtain (in numerical values):

$$\mu_i = \mu_i^* + RT\ln RT + RT\ln c_i$$

Now, we can introduce the new standard chemical potential $\mu_{ci}{}^\circ$ such as:

$$\mu_{ci}^o = \mu_i^* + RT\ln RT$$

whence:

$$\mu_i = \mu_{ci}^\mathrm{o} + RT\ln c_i$$

We notice, indeed, that when $C_i = 1\ \mathrm{mol\ L^{-1}}$

$$\mu_i = \mu_{ci}^o$$

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(Let us notice in passing that μ^{o}_{ci} only depends on the temperature and on the nature of the gas.) The expression of the chemical potential of the gas *i* with this new standard potential is, whatever its behavior is:

$$\mu_i = \mu^{\mathrm{o}}_{ci} + RT\ln a_{ci}$$

or

$$\mu_i = \mu^{*}_i + RT\ln RT + RT\ln a_{ci}$$

The chemical potential expressed with the usual chemical potential is (viz. relation (10.13) Chap. 10):

$$\mu_i = \mu^{*}_i + RT\ln a_i$$

The comparison of the last two relations gives:

$$RT\ln RT + RT\ln ac_i = RT\ln a_i$$

i.e.:

$$a_{ci} = a_i/RT \tag{B.1}$$

and since in the standard state:

$$a_i = f_i/f^{\circ}_i$$

and since in the usual standard state $f_i^{\circ} = 1$ atm:

$$a_{ci} = f_i/RT \tag{B.2}$$

Expressions (B.1) and (B.2) are only valid when they are expressed in numerical values. With this new standard state, the proportionality constant relating the activity to the fugacity is now equal to 1/*RT* (in numerical values).

The relations are pertinent only because, as standard states, we have adopted those for which there exists a perfect behavior of the component *i*, respectively, for $p_i^{\circ} = 1$ atm and $C_i^{\circ} = 1$ mol L^{-1}.

Appendix C
Integration of the Equation $d\ln a_{\pm} = d\theta/\nu\lambda m + \alpha\theta d\theta/\nu m$

The problem is to integrate the following relation:

$$d\ln a_{\pm} = d\theta/v\lambda m \;+\; \alpha\theta d\theta/vm \tag{C.1}$$

The integration involves the use of the intermediary function j defined by the relation:

$$j = 1 \;-\; \theta/v\lambda m \tag{C.2}$$

The function j tends toward zero when m tends toward zero since, then, the ratio $\theta/\nu\lambda m$ tends toward unity. In the case of a nonelectrolyte, indeed, we must admit (it is demonstrated) that:

$$\theta \approx \lambda m$$

The more diluted the solution is, the more exact this relation is. The generalization to the case of the electrolytes is immediate.

Differentiating the relation (C.2) by keeping in mind that m and θ are, indeed, variables, whereas ν and λ are constant gives:

$$dJ = \theta dm/v\lambda m^2 - d\theta/v\lambda m$$

or

$$dJ = (1 - J)\; dm/m - d\theta/v\lambda m$$
$$d\theta/v\lambda m = (1 - J)d\ln m \;-\; dJ$$

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Combining this relation with the expression which is to be evaluated:

$$d\ln a'_{\pm} = d\theta/v\lambda m + \alpha\theta d\theta/vm$$

leads to the relation:

$$d\ln a'_{\pm} = (1 - J)d\ln m - dJ + \alpha\theta d\theta/vm \tag{C.3}$$

given that:

$$\gamma_{\pm} = a_{\pm}/m_{\pm}$$

and that,

$$m_{+}^{v+} \cdot m_{-}^{v-} = m^{v}\left(v_{+}^{v+} \cdot v_{-}^{v-}\right)$$

we obtain:

$$\ln\gamma_{\pm} = \ln a_{\pm} - \ln m - \ln\left(v_{+}^{v+} \cdot v_{-}^{v-}\right)^{1/v}$$

Hence

$$d\ln\gamma_{\pm} = d\ln a_{\pm} - d\ln m$$

and the relation (C.3) becomes:

$$d\ln\gamma_{\pm} = -Jd\ln m - dJ + \alpha\theta d\theta/vm$$

The integration gives, since when $m = 0, j = 0$ and since in very dilute solution, the ratio $\theta/\nu\lambda m$ tends toward 1 and j tends toward unity:

$$\ln\gamma_{\pm} = -\int_{0}^{m} jd\ln m - j + (\alpha/v)\int_{0}^{m} (\theta/m)d\theta$$

Appendix D
Determination with Cells with Transference

One example is provided by the determination of the mean activity coefficient of a solution of hydrochloric acid with the following cell:

$$\mathrm{Pt}\left|\mathrm{H_2}(1\,\mathrm{atm.})\right|\mathrm{HCl}\;(\mathrm{m'})\left|\right|\mathrm{HCl}(\mathrm{m})\left|\mathrm{H_2}(1\;\mathrm{atm.})\right|\mathrm{Pt}$$

Both solutions of different molarities in hydrochloric acid are in contact through a device permitting the flow of current.

The principle of the determination is based on the fact that as soon as the value of the transference number of an ion is known as a function of its “concentration,” its activity coefficient may be obtained from the measurement of the emf of a suitable cell with transference.

Let us suppose that the galvanic cell have reversibly debited 1 faraday. Let us study the processes that occur in the cell.

The electrochemical reactions are:

$$\begin{array}{ll} \text{at the anode} & 1\,/\,2\mathrm{H_2} \rightleftharpoons \mathrm{H^+} + 1\mathrm{e^-} \\ \text{at the cathode} & \mathrm{H^+} + 1\mathrm{e^-} \rightleftharpoons 1\,/\,2\mathrm{H_2} \end{array}$$

The left-hand solution, in a first step, grows richer of one mole of ions H^+ but one part of the latter ones migrates into the solution toward the compartment on the right. Let t_+ be the transference number of ion H^+ and t_- that of the chloride ion. One knows that $t_+ + t_- = 1$ (viz. electrochemistry). But, in the solution, the current is ensured by t_+ ions H^+ flowing toward the right and by t_- anions Cl^- flowing toward the left. The fluxes of these ions in solution actually constitute the current in solution, current so-called ionic current. By these displacements, the ionic current ensures the neutrality of the solutions. As a result, after a flow of 1 faraday, it remains $(1 - t_+) = t_-$ mole of ions H^+ in the left compartment. In order to maintain the electrical neutrality in this compartment, t_- mole of ions Cl^- migrate from the right toward the left in the solution. Concerning the left compartment, in total, there

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is a gain of t_- mole de HCL for 1 debited faraday. For the right compartment, there is a loss of 1 mol of hydrogen ions because of the electrolyse but compensated by the arrival of t_+ ions by the solution. There is a loss of $(1-t_{+)}=t_-$ ions H^+ by the right compartment. The neutrality of the compartment is maintained by the migration in solution of t_- ions Cl^- from the right toward the left, already mentioned.

Finally, for one debited faraday, the left compartment gains t_- moles of HCl and the right one loses t_- moles of HCl.

Naming μ'_+ the chemical potential of the positive ion (here H+) in the left compartment and μ'_+ that of the anion (here Cl^-) whereas μ_+, μ_- are the chemical potentials of the same ions of the right compartment, the change in the Gibbs energy accompanying the flow of one faraday (flow of one electron from the left toward the right in the external circuit) is:

$$\Delta G = -\left[t_-\left(\mu'_+ - \mu_+\right) + t_-\left(\mu'_- - \mu_-\right)\right]$$

This relation is nothing different from a balance of the transformation. In order to relate the emf of the cell (that is to say ΔG) to the mean ionic activity $a_\pm$ of the electrolyte in the cell, one must takes into account the fact that the values of the transference numbers change with the “concentration” of the ion. This is done by setting up the previous expression under the form of differentials and after by integration.

$$\mu'_+ = \mu_+ + d\mu_+ \quad \text{and} \quad \mu'_- = \mu_- + d\mu_-$$

As a result, the following relation is obtained:

$$dG = - t_-\left(d\mu_+ + d\mu_-\right)$$

By introducing the general definition of the chemical potential $\mu = \mu^\circ + RT\ln a$, the previous relation becomes:

$$dG = -t_-RT(d\ln a_+ + d\ln a_-)$$

and since:

$$\begin{aligned} a_\pm &= (a_+a_-)^{1/2} \\ dG &= -2t_-RTd\ln a_\pm \end{aligned} \tag{D.1}$$

According to the equation (viz. Chap. 5):

$$dG = - FdE$$

where dG is the variation of the Gibbs energy corresponding to the debit of one faraday and where dE is the emf of the cell when the concentrations of both solutions differ from each other by an infinitesimal quantity. Hence, relation (D.1) becomes:

$$dE = 2t_{-}(RT/F)\, d\ln a_{\pm} \tag{D.2}$$

For the integration, we begin by replacing the mean ionic activity by the product of the mean ionic molality $m_{\pm}$ by the mean ionic activity coefficient $\gamma_{\pm}$. This permits to introduce the latter:

$$a_{\pm} = m_{\pm}\gamma_{\pm}$$

(We would define the mean ionic concentration in an analogous manner as that followed in order to define the mean molality, that is to say by the expression:)

$$c_{\pm}^{v} = \left(c_{+}^{v+}c_{-}^{v-}\right)$$

For the above example of an electrolyte 1-1, $m_{\pm} = m$. The relation (D.2) can be written:

$$dE = 2t_{-}(RT/F)(d\ln m + d\ln\gamma_{\pm})$$

or

$$dE/t_{-} = (2RT/F)(d\ln m + d\ln\gamma_{\pm}) \tag{D.3}$$

m is the molality of the solution, E the emf of the cell, t_{-} the transference number of the anion, and $\gamma_{\pm}$ the mean activity coefficient.

Appendix E
Kielland's Tables

An approached calculation of the activity coefficient of an ion is possible by starting from the values mentioned in Tables E.1 and E.2 resulting from the compilation by Kielland in 1937 of data present in the literature. The first gives the values of *a* for the listed ions which are classified as a function of their electrical charge. For example, the proton appears with the value $a = 9$. In the second table are mentioned the activity coefficients of the ions as a function of the ionic strength of the solution, once their values a are known. Then, for the ionic strengths 10^{-3} and 10^{-1} mol L^{-1}, the proton exhibits the following respective values $\gamma = 0.967$ and 0.83. The anion citrate 3^- would possess the value $a = 5$. Its activity coefficients for the ionic strengths 10^{-3} and 10^{-1} mol L^{-1} would present the respective values 0.728 and 0.115. In this occurrence, the activities considerably differ from the concentrations. Here, we again find the influence of the charge of the ion.

Tables E.1 and E.2, respectively, contain the values a for 130 ions and the values of the activity coefficients as a function of the ionic strength.

From a practical viewpoint, the following questions can come in mind:

- For the relation (15.6) (Chap. 15), what value a must we choose? that of the cation or that of the anion? Answer: it is judicious to choose the mean value;
- What strategy must we adopt when the ion is not listed? Answer: generally, one takes the values of a listed one of the same charge and of about the same volume as that studied.

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Table E.1 Values of the *a* parameter of several ions

Charge 1	
9	H^4
8	$(C_6H_5)_2CHCOO^-$, $(C_3H_7)_4N^+$
7	$OC_6H_2(NO_3)_3$, $(C_3H_7)_3NH^+$, $CH_3OC_6H_4COO^-$
6	Li^+, $C_6H_5COO^-$, $C_6H_4OHCOO^-$, $C_6H_4ClCOO^-$, $C_6H_5CH_2COO^-$, $CH_2^{2-}CHCH_2COO^-$, $(CH_3)_2CCHCOO^-$, $(C_2H_5)_4N^+$, $(C_3H_7)_2NH_2^+$
5	$CHCl_2COO^-$, CCl_3COO^-, $(C_2H_5)_3NH^+$, $(C_3H_7)NH_3^+$
4	Na^+, $CdCl^+$, ClO_2^-, IO_3^-, HCO_3^-, $H_2PO_4^-$, HSO_3^-, $H_2AsO_4^-$, $Co(NH_3)_4(NO_2)_2^+$, CH_3COO^-, CH_2ClCOO^-, $(CH_3)_4N^+$, $(C_2H_5)_2NH_2^+$, $NH_2CH_2COO^-$, $^+NH_3CH_2COOH$, $(CH_3)_3NH^+$, $C_2H_5NH_3^+$
3	OH^-, F^-, CNS^-, CNO^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_4^-, MnO_4^-, K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-, Rb^+, CS^+, NH_4^+, Tl^+, Ag^+, $HCOO^-$, H_2 (citrate)$^-$, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$
Charge 2	
8	Mg^{2+}, Be^{2+}
7	$(CH_2)_5(COO)_2^{2-}$, $(CH_2)_6(COO)_2^{2-}$, (congo red)$^{2-}$
6	Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, $C_6H_4(COO)_2^{2-}$, $H_2C(CH_2COO)_2^{2-}$, $(CH_2CH_2COO)_2^{2-}$
5	Sr^{2+}, Ba^{2+}, Ra^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}, $S_2O_4^{2-}$, WO_4^{2-}, Pb^{2+}, CO_3^{2-}, SO_3^{2-}, MoO_4^{2-}, $Co(NH_3)_5Cl^{2+}$, $Fe(CN)_5NO^{2-}$, $H_2C(COO)_2^{2-}$, $(CH_2COO)_2^{2-}$, $(CHOHCOO)_2^{2-}$, $(CCO)_2^{2-}$, H (citrate)$^{2-}$
4	Hg_2^{2+}, SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_8^{2-}$, SeO_4^{2-}, CrO_4^{2-}, HPO_4^{2-}, $S_2O_6^{2-}$
Charge 3	
9	Al^{3+}, Fe^{3+}, Cr^{3+}, Sc^{3+}, Y^{3+}, La^{3+}, In^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}
6	Co (ethylenediamine)$_3^{3+}$
5	Citrate^{3-}
4	PO_4^{-3}, $Fe(CN)_6^{-3}$, $Cr(NH_3)_6^{+3}$, $Co(NH_3)_6^{+3}$, $Co(NH_3)_5H_2O^{3+}$
Charge 4	
11	Th^{4+}, Zn^{4+}, Ce^{4+}, Sn^{4+}
6	$Co(S_2O_3)(CN)_5^{4-}$
5	$Fe(CN)_6^{4-}$
Charge 5	
9	$Co(S_2O_3)_2(CN)_4^{5-}$

Table E.2 Values of the activity coefficients as a function of the ionic strength and of the parameter *a (According to J. Kielland, J .Am. Chem. Soc., 1937, 59, 1675)*

Ionic strength							
a	0.001	0.0025	0.005	0.01	0.025	0.05	0.1
Charge 1							
9	0.967	0.950	0.933	0.914	0.88	0.86	0.83
8	0.966	0.949	0.931	0.912	0.88	0.85	0.82
7	0.965	0.948	0.930	0.909	0.875	0.845	0.81
6	0.965	0.948	0.929	0.907	0.87	0.835	0.80
5	0.964	0.947	0.928	0.904	0.865	0.83	0.79
4	0.964	0.947	0.927	0.901	0.855	0.815	0.77
3	0.964	0.945	0.925	0.899	0.85	0.805	0.755
Charge 2							
8	0.872	0.813	0.755	0.69	0.595	0.52	0.45
7	0.872	0.812	0.753	0.685	0.58	0.50	0.425
6	0.870	0.809	0.749	0.675	0.57	0.485	0.405
5	0.868	0.805	0.744	0.67	0.555	0.465	0.38
4	0.867	0.803	0.740	0.660	0.545	0.445	0.355
Charge 3							
9	0.738	0.632	0.54	0.445	0.325	0.245	0.18
6	0.731	0.620	0.52	0.415	0.28	0.195	0.13
5	0.728	0.616	0.51	0.405	0.27	0.18	0.115
4	0.725	0.612	0.505	0.395	0.25	0.16	0.095
Charge 4							
11	0.588	0.455	0.35	0.255	0.155	0.10	0.005
6	0.575	0.43	0.315	0.21	0.105	0.055	0.027
5	0.57	0.425	0.31	0.20	0.10	0.048	0.021

Appendix F
Classic Canonical Partition Function

The following explanations only consist in a qualitative approach of expressions (27.1) and (27.3) of Chap. 27. (They are, respectively, numbered (F.1) and (F.2) here.) It is the classical canonical partition function for a system of spherical particles, devoided of any internal structure. Here is only an attempt to explicate it and to give its origin:

$$\begin{aligned} Q(N,T,V) &= \left[1/\left(N!h^{3N}\right)\right]\bullet \\ &\int_{-\infty..}^{+\propto}\int \exp\left[-H(x_1,y_1,z_1\ldots x_N y_N z_N;\ \ p_{x1},p_{y1}p_{z1}\ldots p_{xN}p_{yN}p_{zN})\right]/kT\bullet \\ &dx_1,dy_1,dz\ldots dp_{xN},dp_{yN},dp_{zN} \end{aligned} \tag{F.1}$$

$$Q(N,T,V) = \left[1/\left(N!h^{3N}\right)\right]\int_{-\infty..}^{+\propto}\int \exp[-H/kT]d\mathbf{R}^N d\mathbf{p}^N \tag{F.2}$$

Expression (F.2) is strictly equivalent to the previous one (F.1).

After some elementary recallings concerning the probability theory, we justify relations (F.1) and (F.2) in two steps.

- In the first step, we mention the genesis of the following relation:

$$Q(N,T,V) = \left[1/\left(N!h^{3N}\right)\right]\int_{-\infty..}^{\infty}\int f\left(\mathbf{R}^N,\mathbf{p}^N\right)d\mathbf{R}^N d\mathbf{p}^N \tag{F.3}$$

We note the occurrence of the function $f(\mathbf{R}^N, \mathbf{p}^N)$, which is undetermined at this point. The purpose of its introduction is on one hand to favor the discovery of the link existing between the studied expressions and some elements of the probability theory.

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– In the second step, we introduce an exponential function instead of the function $f(\mathbf{R}^N, \mathbf{p}^N)$. This step deserves a particular treatment, as we shall see.
  The cornerstone of the explanation of the mathematical expression of the $Q(T, V, N)$ function is the concept of *phase space*.

F.1 Some Elements of the Probability Theory

- Let us consider a trial which leads to a finite number of distinct events. A value X of the random variable x and a probability $\mathbf{P}(x)$ are associated to each of these events. $\mathbf{P}(x)$ is a function of x and exhibits a well-defined value for each X_i value. The function $\mathbf{P}(x)$ is a discontinuous probability function.
  The random variable is discrete and of finite order. The sum of all the values $\mathbf{P}(X_i)$ is equal to 1. (The considered trial, indeed, obligatorily leads to the events $E_i \ldots E_j$ which are mutually exclusive.) This condition is called the "normalization condition." We know that the average $\langle X_i \rangle$ is given by the expression:

$$\langle X_i \rangle = \sum_i X_i P(X_i)$$

It is also called the "expected value."

- The random variable can, in some instances, lead to an infinity of eventualities. Then, it can exhibit any value in a defined interval. It is continuous. From a more general standpoint, when the random variable x can exhibit any value between a and b (included from $-\infty$ till $+\infty$), one can define a distribution law by choosing a function $f(x)$ called the *density probability function*, which is always positive or null for the values x located in the interval $[a, b]$. The probability for the event x located in the interval $[x_1, x_2]$ is $\int_{x1}^{x2} f(x)dx$ (viz.: Fig. F.1).

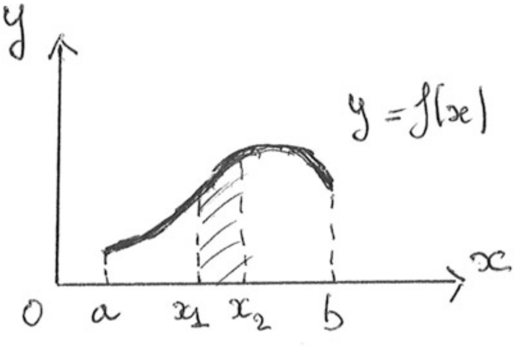

Fig. F.1 Example of one continuous density probability function at one dimension x

The probability for x could be located at the value x_1 in the very very small interval dx is $f(x_1)dx$. As previously, the function $f(x)$ is such that:

$$\int_a^b f(x)dx = 1$$

The notion of average can be generalized to the continuous case. Given the different values X_i of the random variable and supposing that x can take all the possible values between a and b, we can cut out the interval [a, b] in partial intervals, the length of which tending toward 0. These "subintervals" are the following ones:

$$a, x_1 - x_1, x_2 - \cdots x_i, x_j \cdots x_{N-1}, b$$

The probability that x_i will belong to any of these intervals is $(x_{i-1}, x_i) f(X_i)$, X_i being a value of this interval. In it, x values differ all the less from X_i than the interval is small. When its length tends toward zero, one can admit that all the values x lying between x_{i-1} and x_i can be merged with $X_{i.}$ The average value is the limit of the expression:

$$\langle X \rangle = \sum_{i=1} X_i f(X_i)(x_i - x_{i-1}) \quad (x_i - x_{i-1}) \rightarrow 0$$

that is to say:

$$\langle X \rangle = \int_a^b x f(x)dx$$

The reasoning can be extended to the calculation of the average of any other quantity, provided it, mathematically, depends on x. From a general standpoint, let us consider the function $F(x)$. In these conditions, its value is given by the expression

$$\langle F(x) \rangle = \int_a^b F(x) f(x)dx \tag{F.4}$$

- One can extend the previous relations and reasonings to the case of two dimensions. Let us suppose there are two continuous random variables x and y. The density probability function is of the kind $f(x, y)$.
  Thus, the probability that the point (x, y) locating in the area element $dxdy$ will be at $x = x_1$ and at $y = y_1$ is $f(x_1, y_1)dxdy$. The probability that x and y will be located in the intervals [a, b] and [α, β] is:

$$\int_\alpha^\beta \int_a^b f(x, y)dxdy$$

In this case, the averages of the variables x and y

$$\langle X \rangle = \int_{\alpha}^{\beta}\int_{a}^{b} x f(x,y)dxdy$$
$$\langle Y \rangle = \int_{\alpha}^{\beta}\int_{a}^{b} yf(x,y)dxdy$$

These considerations can be immediately extended for N random variables.

F.2 Genesis of Expression (F.2)

Let us recall that the configuration of a system, in its most general meaning, expresses both the location of its particles and their orientation. For the following discussion, we only consider their position. It is actually this type of system that equations (F.1), (F.2), and (F.3) describe as it is shown by the symbolism **R** instead of **X**. (It must be noticed, however, that the choice of these conditions does not impair the generality of the reasoning, at all.) In other words, we only consider the spherical particles without any internal structure. Only, the space coordinates are of importance for us in these conditions. We are not interested, now, in the momenta coordinates for reasons that we will give at the end of this appendix.

- Let us explicit the analogy between the canonical partition functions occurring in quantum and classical mechanics. In quantum mechanics, the function is (viz.: Chap. 22):

$$Q(T,V,N)_{\text{quant}} = \sum_j \exp\left[-E_j(N,V,T)\right]$$

that, uniquely for the sake of the presentation, we write here:

$$Q(T,V,N)_{\text{quant}} = \sum_j f(T,V,N)$$

Let us notice that the function $f(T, V, N)$ implies the intervention of space coordinates x_1, y_1, $z_1 \ldots x_n$, y_n, z_n through the volume V of the system. We know, indeed, that according to the very principles of quantum mechanics, the permitted energy levels depend on the volume and on the number of particles of the system. Thus, it appears clearly that, since the results of classical mechanics can be considered as being identical to those stemming from quantum mechanics when the energy levels become near to each other, the canonical partition function must be of the type for a space of $3N$ dimensions (viz. the following paragraph):

$$Q(N,T,V)_{\text{class}} \rightarrow\ ??\int_{-\infty}^{+\infty} ..\int f(x_1,y_1,z_1\ldots x_N y_N\, z_N)\ \ dx_1,dy_1,dz_1\ldots dx_N dy_N dz_N$$

- It remains to explain the presence of the « out-integral » terms in the right-hand members of equations (F.1) and (F.2) and to consider the integration over the momenta coordinates.

  The presence of factorial $N!$ in the denominator comes from the fact that the particles are interchangeable and that identical configurations would be counted several times without this presence, owing to the manner how the expressions are built. h is Planck's constant. It appears in calculations as integration constants. h is a remnant of quantum mechanics existing, somewhat surprisingly, in the calculations of classical mechanics.

  Finally, so far, during these explanations, we have not taken the momenta into account. Concerning the integrations over these coordinates, visualize the paragraph 4.

F.3 Phase Space

The following considerations are grounded in the concept of classical phase space of a *macroscopic* isolated system of volume V containing N molecules of a species.

- The total number n of space coordinates defining the location of all the particles of the system is $n = 3N$. The number n is huge, of the order of about 10^{23} (Avogadro's number.) Moreover, momenta p_{xi}, p_{yi}, p_{zi} coordinates of each species must be added to the previous ones in order to fully describe the state of the system at the molecular level. (This is, indeed, the ultimate goal of statistical thermodynamics!). Hence, $2n$ coordinates are necessary to define the system. Thus, the classical phase space is conceived to be at $2n$ dimensions, n for the space and n for the momenta coordinates.
- The state of the system at instant t (included its dynamical state) is known if the location and speed components of each particle present in it are specified. All the information is gathered by the location of the point of phase space defined by its corresponding space and momenta coordinates. Every one of these points is named "phase point." Owing to the classical mechanics laws, once a point is positioned at an instant t, its future position (and even its past position) in the phase space is known. According to the theory, in order to know its future position, it is sufficient to integrate the $2n$ differential equations of first order to obtain the expressions $x_1(t)$, $y_1(t)$, $z_1(t)$…$x_N(t)$, $y_N(t)$, $z_N(t)$!!!. Since the coordinates number is huge, it is illusory to hope to carry out this tremendous work of integration.

  The result of these considerations is the statistical method proposed by Gibbs.
- The foundation of the statistical method lies in the fact that *a point of the phase space represents an isolated system (T, V, N) and not a particle*. One studies an

isolated system of characteristics T, V, N, that is to say a canonical system. (Let us remark in passing that space coordinates do intervene through the volume V.) In Gibbs' statistical theory, one is forced to consider 1 ensemble of $\aleph$ isolated systems with $\aleph \to \infty$. All the systems of the ensemble are endowed with the same thermodynamic characteristics as that studied (same temperature, volume, and particles number). Nothing precludes to figure the detailed state of each of these systems by a point in the same phase space. The fact that a point in the phase space does not represent the state of a *particle but a system* (which contains a great number of particles) must be emphasized. In the phase space, a system is represented by a point defined by $2n$ coordinates located on $2n$ axes. Every particle of the system contributes to supply to the point figuring the system six coordinates values.

Since ($\aleph \to \infty$), the whole ensemble is represented by a continuous cloud, more and less dense, of the representative points of every system. The cloud is moving with time since the dynamical state of the system is described. As time goes along, each point constituting the cloud has its own trajectory defined by the mechanics laws. The fact that we consider a continuous cloud implies that the ensemble contains an infinite number of systems.

- The concept of a continuous density of points permits, at least formally, to define the function:

$$f\left(x_1, y_1, z_1 \ldots x_N y_N z_N\ , p_{x1}, p_{y1} p_{z1} \cdots p_{xN} p_{yN} p_{zN}\ ; t\right)$$

in such a way that it represents the fraction of the $\aleph$ points (systems) present at any instant t in the volume element [dx_1, dy_1, dz_1, dp_{x1}, dp_{y1}, dp_{z1}. . .dx_N, dy_N, dz_N, dp_{xN}, dp_{yN}, dp_{zN}] of the phase space. From now on, we symbolize this function as $f(x, p; t)$. Hence, the number of points of the phase space in that volume element symbolized by $dxdp$ is:

$$\aleph f(x, p; t)\ dxdp$$

The function $f(x, p; t)$ is named *probability density function* since if a system is randomly chosen in the ensemble at an instant t, the probability that the point representative of its dynamical state will be located in the volume element $dpdx$ is:

$$f(x, p; t) dxdp$$

- The probability density function $f(x, p; t)$ is such that:

$$\int \ldots \int f(x, p; t) dxdp\ = 1$$

This means that the whole systems of the ensemble must be located in the phase space. This the normalization condition.

- Thus, $f(x, p; t)$ being the probability density function, one can admit that the probability that the point phase representative of the dynamic state of the studied system will be in the domain $f(x, p; t)dxdp$ is:

$$f(x,p;t)dxdp/\int\ldots\int f(x,p;t)dxdp \tag{F.5}$$

In agreement with the postulates of statistical mechanics, that is to say with the ergodic theory of matter which stipulates that the average value of a mechanical quantity over a very brief moment is equal to the average of the same quantity established over the whole ensemble of systems replicating the previous one. In these conditions, the average of the ensemble of every function $\varphi(x, p)$ is given by the expression:

$$\langle\varphi\rangle = \int\ldots\int \varphi(x,p)f(x,p;t)\ dxdp/\int\ldots\int f(x,p;t)dxdp$$

and taking into account the normalization condition:

$$\langle\varphi\rangle = \int\ldots\int \varphi(x,p)f(x,p;t)dxdp$$

When the system is at equilibrium, it does not further evolve with time. Then, we can write:

$$\langle\varphi\rangle\ = \int\ldots..\int \varphi(x,p)f(x,p)dxdp \quad \text{(equilibrium)}$$

At equilibrium, the average $\langle\varphi\rangle$ is independent of time.

F.4 The Distribution Function; *Boltzmann's Law*

Here, we are in the field of the postulate.

For a closed, isotherm system for which the independent variables T, V, N are fixed, the function $f(x, p; t)$, introduced in (F.4) is postulated as being of the type:

$$f(x,p;t) = \text{ constant} \cdot \exp[-\beta H(x,p)]$$

where $\beta = 1/kT$. Actually, this assigning is not a true postulate. However, it logically and directly results from a true postulate related to the distribution function of the microcanonical ensemble which leads to *Boltzmann's law*. Only the exponential function is, indeed, compatible with Boltzmann's theory.

F.5 Exponential Function and Integration

From the strict mathematical standpoint, the fact that the function $f(x, p; t)$ is an exponential greatly simplifies integrations and reasoning. Hamilton's function falls in this case. Its exponential can be written:

$$\exp[-\beta H(x,p)] = \exp\left[-\beta\sum_{i=1}\left(\mathbf{p}_i^2/2m\right)\right]\cdot\exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right.$$

For this reason, the integrations involved in relation (F.2):

$$\int\limits_{-\infty}^{+\propto}..\int\exp[-H/kT]d\mathbf{R}^N d\mathbf{p}^N$$

can be equivalently written under the form of the following product:

$$\int_{-\infty}^{+\propto}..\int\exp\left[-\beta\sum_{i=1}\left(\mathbf{p}_i^2/2m\right)\right]d\mathbf{p}^N\cdot\int_{-\infty}^{+\propto}..\int\exp\left[-\beta U_N\left(\mathbf{R}^N\right)d\mathbf{R}^N\right.$$

The integration of the part devoted to the momenta of Hamilton's function is possible.

Appendix G
The Concept of Fugacity

From the mathematical standpoint, the problem is to calculate the derivate: $(\partial \ln[q^N Z_N/N!]/\partial T)_{V,N}$

In this expression, both q^N and Z_N depend on temperature. q^N depends on temperature through Λ. After having split the logarithm according to:

$$\ln\left[q^N Z_N/N!\right] = \ln q^N/N! \ + \ln Z_N$$

one successively derives both terms of the right member of this relation with respect to temperature and in both cases one uses the derivative chain rule.

– For the first derivation, one obtains:

$$\begin{aligned} \ln q &= -3\ln\Lambda \\ \ln\Lambda &= \ln h - ½\ln(2\pi mkT) \\ \ln\Lambda &= \ln h - 1/2\ln 2\pi mk - ½\ln T \end{aligned}$$

whence:

$$\partial \ln q/\partial T = 3/2\partial \ln T/\partial T$$

and finally

$$NkT^2 \ln q^N/N! = 3/2NkT$$

– The second derivate to evaluate is:

$$kT^2\partial \ln Z_N/\partial T$$

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with:

$$Z_N = \int \ldots \int d\mathbf{R}^N \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right]$$
$$\partial \ln Z_N / \partial T = \partial \ln\left\{\int \ldots \int d\mathbf{R}^N \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right]\right\} / \partial T$$

For sake of shortness, let us set up:

$$\left\{\int \ldots \int d\mathbf{R}^N \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right]\right\} = \{\ \}$$

The chain rule of derivation permits us to write:

$$\partial \ln Z_N / \partial T = \ \partial \ln\{\} / \partial\{\} \bullet \partial\{\} / \partial T$$
$$\partial \ln Z_N / \partial T = \ 1/\{\} \bullet \partial \int \ldots \int d\mathbf{R}^N \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right] / \partial T$$

Let us notice that variables $\mathbf{R}^N$ and T are independent. Owing to this point, it is allowed to derivate the exponential with respect to temperature while staying under the sign sum. Let us use the chain rule for the second time by setting up:

$$\partial \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right] / \partial T = \partial \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right] / \partial\left[-\beta U_N\left(\mathbf{R}^N\right)\right] \bullet \partial\left[-\beta U_N\left(\mathbf{R}^N\right)\right] / \partial T$$

Since $\beta = 1/kT$, we obtain:

$$\partial \ln Z_N / \partial \mathrm{T} = 1/\{\} \cdot \int \ldots \int d\mathbf{R}^N \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right] U_N\left(\mathbf{R}^N\right)\ \partial(-1/kT)/\partial T$$
$$\partial \ln Z_N / \partial \mathrm{T} = 1/\{\} \cdot \int \ldots \int d\mathbf{R}^N \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right] U_N\left(\mathbf{R}^N\right)\ \left(1/kT^2\right)$$

Finally:

$$kT^2 \partial \ln Z_N / \partial T \ = \int \ldots \int d\mathbf{R}^N \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right]\left[U_N\left(\mathbf{R}^N\right)\right]\ /Z_N$$

whence the relation being searched for.

Appendix H
Ideal Solutions

Obtaining the expression: $p = kT(\partial \ln Z_N / \partial V)_{T,N}$

In order to calculate this partial derivative, it is evident that we must express Z_N in relation to V. Given the fact that for a macroscopic system we can assume that pressure is independent from the geometrical shape of the system, we adopt a cube of side equal to $V^{1/3}$ as the volume of the system. The configurational partition function Z_N is then:

$$Z_N = \int_0^{V1/3} \ldots \int_0^{V1/3} \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right] dx_1 dy_1 dz_1 \ldots dx_N dy_N dz_N$$

Let us introduce the variables:

$$x'_i = V^{-1/3} x_i; \quad y'_i = V^{-1/3} y_i; \quad z'_i = V^{-1/3} z_i$$

Now, the integrand is independent from the volume V. Z_N can now be written:

$$Z_N = V^N \int_0^1 \cdots \int_0^1 \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right] dx'_1 \ldots dz'_N$$

After derivation of this expression, we obtain

$$\begin{aligned}(\partial Z_N / \partial V)_{N,T} = {} & N V^{N-1} \int_0^1 \ldots \int_0^1 \exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right] dx'_1 \ldots dz'_N \\ & + V^N \left\{ \partial \left[\int_0^1 \ldots \int_0^1 dx'_1 \ldots dz'_N \left[\exp\left[-\beta U_N\left(\mathbf{R}^N\right)\right] \left(-\beta \partial U_N\left(\mathbf{R}^N\right)\right] / \partial V_{N,T} \right\} \right.\right.\end{aligned} \tag{H.1}$$

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It is at this step that the "pairwise additivity" hypothesis is adopted. It is written as:

$$U_N\left(\mathbf{R}^N\right) \;=\; 1/2\sum_{ij} U\left(\mathbf{R}_{ij}\right) \quad (i \neq j)$$

where, as we shall immediately demonstrate it,

$$U_N\left(\mathbf{R}^N\right) \;= 1/2\sum_{ij} U\left(V^{1/3}\mathbf{R}'_{ij}\right) \quad (i \neq j)$$

According to the metric properties of space, we can indeed set up:

$$\boldsymbol{R}_{ij} = \left[\left(x_i - x_j\right)^2 + \left(y_i - y_j\right)^2 + \left(z_i - z_j\right)^2\right]^{1/2}$$
$$\boldsymbol{R}_{ij} = V^{1/\,3}\left[\left(x'_i - x'_j\right)^2 + \left(y'_i - y'_j\right)^2 + \left(z'_i - z'_j\right)^2\right]^{1/2}$$

and for sake of shortness

$$\boldsymbol{R}_{ij} \;=\; V^{1/\,3}\sigma$$

σ being the square root of the term between the square brackets. One also writes:

$$\sigma \;= \boldsymbol{R}'_{ij}$$

According to the previous considerations, for the operation of derivation, one can write:

$$\begin{aligned}
\partial U_N\left(\mathbf{R}^N\right)/\partial V \;&= 1/2\sum_{ij}\left[\partial U\left(\mathbf{R}_{ij}\right)/\partial \mathbf{R}_{ij}\right]\left[\partial \mathbf{R}_{ij}/\partial V\right] \quad (i \;\neq\; j)\\
\partial U_N\left(\mathbf{R}^N\right)/\partial V \;&=\; 1/2\sum_{ij}\left[\partial U\left(\mathbf{R}_{ij}\right)/\partial \mathbf{R}_{ij}\right](1/3)V^{-2/3}\mathbf{R}'_{ij}\\
\partial U_N\left(\mathbf{R}^N\right)/\partial V \;&= (1/6V)\sum_{ij}\left[\partial U\left(\mathbf{R}_{ij}\right)/\partial \mathbf{R}_{ij}\right]\mathbf{R}_{ij}
\end{aligned} \tag{H.2}$$

Let us inject (H.2) into (H.1) and return to the previous variables x_i, y_i, z_i. We obtain:

$$(\partial \ln Z_N/\partial V)_{T,N} = \; N/V \;-(\beta/6V)\int\ldots\int d\mathbf{R}^N P\left(\mathbf{R}^N\right)\sum_{ij}\left[\partial U\left(\mathbf{R}_{ij}\right)/\partial \mathbf{R}_{ij}\right]\mathbf{R}_{ij}$$

The multiple integral is the average value of the function $[\partial U(\mathbf{R}_{ij})/\partial \mathbf{R}_{ij}]\mathbf{R}_{ij}$ in the framework of the "pairwise additivity" hypothesis. Hence, the reasoning of the first paragraph can be used. We obtain (viz. Chap. 30) the following expression:

$$p = kT\rho - \left(\rho^2/6\right)\int_0^\infty R[\partial U(R)/\partial R]\, g(R) 4\pi R^2 dR \tag{H.3}$$

as in the case already encountered in which R'-R' is only a function of R (a scalar).

Appendix I
Definitions of Activity

Let us begin by recalling that the square root of the variance σ_E (or root mean-square deviation from the mean or fluctuation) of a statistical series of some experimental quantity E is defined by the expression:

$$\sigma_\mathrm{E} = \overline{\left[\left(E - \overline{E}\right)^2\right]}^{1/2}$$

It is easy to check that:

$$\begin{aligned}\overline{\left[\left(E - \overline{E}\right)^2\right]} &= \overline{\left[E^2 - 2E\left(\overline{E}\right) + \left(\overline{E}\right)^2\right]} \\ \overline{\left[\left(E - \overline{E}\right)^2\right]} &= \overline{E}^2 - \left(\overline{E}\right)^2\end{aligned} \tag{I.1}$$

Obligatorily, it is a positive quantity.

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Appendix J
Activity of a Gas

Demonstration of the relation: $kT\left(\partial\langle\overline{N}\rangle/\partial\mu\right)_{V,T}=\overline{N}^2-\left(\overline{N}\right)^2$

Let us differentiate the following equality (viz. Chap. 24):

$$\overline{N}\sum_N Q(N,V,T)\exp(N\mu/kT)\;=\sum_N NQ(N,V,T)\exp(N\mu/kT)$$

with respect to μ without forgetting that $\overline{N}$ is a function of μ. (For the origin of this expression, visualize Chap. 24 given the fact that the probability $P(N)$ that the system possesses N particles (whichever its energy is) is $P(N)=Q(N,V,T)\exp(N\mu/kT)/\Xi$). After derivation and division by Ξ, we obtain:

$$\begin{aligned}&\left(\partial\overline{N}/\partial\mu\right)_{V,T}+\left(\overline{N}/\Xi kT\right)\sum_N NQ(N,V,T)\exp(N\mu/kT)\\&=(1\;/\Xi kT)\sum_N N^2Q(N,V,T)\,\exp(N\mu/kT)\end{aligned}$$

We notice that in the last two terms of this equality, we again find the expression of the probability that the system possesses N particles. Hence, with the help of (I.1) and of expression $P(N)$, we obtain:

$$kT\left(\partial\overline{N}/\partial\mu\right)_{V,T}=\overline{N}^2-\left(\overline{N}\right)^2$$

or

$$\left\langle(N-\langle N\rangle)^2\right\rangle\;=kT\left(\partial\overline{N}/\partial\mu\right)_{V,T}$$

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Appendix K
Activities of Nonelectrolytes in Solutions

Establishing relation (32.22) of Chap. 32:

$$\mu \;=\; kT\,\ln\left(\rho\Lambda^3 q^{-1}\right) \;+\rho\int_0^1 d\xi\int_0^\infty U(R)g(R,\xi)4\pi R^2 dR$$

Kirkwood has defined an auxiliary potential energy $U(\xi)$ such as:

$$U(\xi) = U_N(\mathbf{R}_1,\ldots,\mathbf{R}_N) \;+\xi\sum_j U\left(\mathbf{R}_0,\mathbf{R}_j\right) \quad 1 \;\le j \le N \tag{K.1}$$

the added particle, named central particle, being labeled by the indice 0.

The "pairwise additivity" hypothesis applies to the factor $\sum_j U(\mathbf{R}_0, \mathbf{R}_j)$. It entails that the potential energy of interactions between the whole particles of the system is equal to the sum of interaction energies for each possible pair of them.

When we compare expressions (32.10) and (32.12) of Chap. 32, it appears that:

$$U(\xi = 0) = U_N(\mathbf{R}_1,\ldots,\mathbf{R}_N)$$
$$U(\xi = 1) = U_{N+1}(\mathbf{R}_0,\ldots,\mathbf{R}_N)$$

The reasoning consists in admitting that while ξ changes from zero till 1, function $U(\xi)$ changes in a continuous manner between $U(\xi=0)$ and $U(\xi=1)$. It is based on the introduction of the following auxiliary configurational partition function:

$$Z(\xi) \;= \int\ldots\int d\mathbf{R}_0, d\mathbf{R}_1\ldots d\mathbf{R}_N \exp[-\beta U(\xi)]$$

Its comparison with equation (9.3) (Chap. 9) shows that this relation has the structure of a configuration integral. It appears that:

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$$Z(\xi = 0) = \int \ldots \int d\mathbf{R}_0, d\mathbf{R}_1 \ldots d\mathbf{R}_N \exp[-\beta U_N]$$
$$= V Z_N$$

When $\xi = 0$, according to the above definition of $U(\xi)$, $U(\xi)$ does not indeed depend on $\mathbf{R}_0$ and the integration over $\mathbf{R}_0$ is immediate since $d\mathbf{R}_0$ can be taken out the multiple integral. It is also clear that:

$$Z(\xi = 1) \ = Z_{N+1}$$

where

$$Z_{N+1} \ \ = Z(\xi = 1)$$

The expression (32.15) of Chap. 32 can be also written after introduction of function $Z(\xi)$:

$$\mu \ = kT\ln\left(\rho \Lambda^3 q^{-1}\right) \ - \ kT\ln Z(\xi = 1) \ + \ kT\ln Z(\xi = 0)$$

by setting up:

$$kT\ln\left\langle \exp\left(- B/kT \right\rangle = kT\ln Z(\xi = 1) \ - \ kT\ln Z(\xi = 0)$$

since the function $U(\xi)$ is introduced in order to take into account of the interactions. By using the mathematical identity:

$$kT\ln Z(\xi = 1) - kT\ln Z(\xi = 0) \ = \ kT\int_0^1 (\partial \ln Z(\xi)/\partial \xi) d\xi$$

we obtain:

$$\mu \ = \ kT\ln\left(\rho \Lambda^3 q^{-1}\right) - \ kT\int_0^1 (\partial \ln Z(\xi)/\partial \xi) d\xi \tag{K.2}$$

Let us differentiate with respect to ξ in order to calculate the integrand. By applying the chain rule several times and by taking into account relation (K.1):

$$\begin{aligned} &kT(\partial \ln Z(\xi)/\partial \xi) = \ kT/Z(\xi)\int \ldots \int d\mathbf{R}_o \ldots d\mathbf{R}_N \{\exp[-\beta U(\xi)]\} \bullet \\ &\left[- \beta \sum_j U\left(\mathbf{R}_0, \mathbf{R}_j\right)\right] \qquad\qquad 1 \le j \le N \end{aligned} \tag{K.3}$$

The derivation process is given at the end of this appendix.

Since:

$$\exp[-\beta U(\xi)]\,/Z(\xi) \;=\; P\left(\mathbf{R}^{N+1},\xi\right)$$

where $P(\mathbf{R}^{N+1}, \xi)$ is the probability density (or the basic distribution function) for the observation of the configuration $\mathbf{R}^{N+1}$ with the value ξ of the coupling constant, we obtain:

$$kT(\partial \ln Z(\xi)/\partial\xi) = -\int\ldots\int d\mathbf{R}_{\text{o}}\ldots d\mathbf{R}_N P\left(\mathbf{R}^{N+1},\xi\right)\left[\beta\sum_j U\left(\mathbf{R}_0,\mathbf{R}_j\right)\right]$$

$$kT(\partial \ln Z(\xi)/\partial\xi) = -\sum_j\int\ldots\int d\mathbf{R}_{\text{o}}\ldots d\mathbf{R}_N\ \left(\mathbf{R}^{N+1},\xi\right)\big)U\left(\mathbf{R}_0,\mathbf{R}_j\right)$$

By arbitrarily privileging the pair 0,1 (all the pairs being equivalent):

$$kT(\partial \ln Z(\xi)/\partial\xi) = -N\iint dR_o dR_1 U(R_o R_1)\int\ldots\int d\mathbf{R}_2\ldots d\mathbf{R}_N P\left(\mathbf{R}^{N+1},\xi\right)$$

Owing to the fact (viz.: Chap. 28)

$$\int\ldots\int d\mathbf{R}_2\ldots d\mathbf{R}_N P\left(\mathbf{R}^{N+1},\xi\right) = P^{(2)}(\mathbf{R}_{\text{o}},\mathbf{R}_1,\xi)$$

and that:

$$P^{(2)}(\mathbf{R}_{\text{o}},\mathbf{R}_1,\xi) = [1/N(N-1)]\rho^{(2)}(\mathbf{R}_{\text{o}},\mathbf{R}_1,\xi)$$

we obtain:

$$kT(\partial \ln Z(\xi)/\partial\xi) = -1/(N-1)\iint d\mathbf{R}_{\text{o}} d\mathbf{R}_1 U(\mathbf{R}_{\text{o}}\mathbf{R}_1)\rho^{(2)}(\mathbf{R}_{\text{o}},\mathbf{R}_1,\xi)$$

and since

$$\rho^{(2)}(\mathbf{R}_{\text{o}},\mathbf{R}_1,\xi) = g(\mathbf{R}_{\text{o}},\mathbf{R}_1,\xi)\rho^2$$

By taking into account the spherical symmetry and the isotropic character of the system:

$$kT(\partial \ln Z(\xi)/\partial\xi) = -\rho^2/(N-1)\iint d\mathbf{R}_{\text{o}} d\mathbf{R}_1 U(\mathbf{R}_{\text{o}}\mathbf{R}_1) g(\mathbf{R}_{\text{o}},\mathbf{R}_1,\xi)$$

expression which can be written:

$$kT(\partial \ln Z(\xi)/\partial \xi) = -\rho^2/(N-1)\int d\mathbf{R}_o \int d\mathbf{R}_1 U(\mathbf{R}_o\mathbf{R}_1)g(\mathbf{R}_o, \mathbf{R}_1, \xi)$$

By carrying out the first integration, taking into account that $N - 1 \approx N$ and, finally, owing to the spherical symmetry and the isotropy of the system, we obtain:

$$kT(\partial \ln Z(\xi)/\partial \xi) = -\rho \int_0^\infty U(R)g(R, \xi)4\pi R^2 dR$$

which injected into relation (K.2), leads the searched for relation.

Calculating the partial derivative $\partial \ln Z(\xi)/\partial \xi$

It consists, once more, in applying the chain rule, that is to say:

$$\partial \ln Z(\xi)/\partial \xi = [\partial \ln Z(\xi)/\partial Z(\xi)][\partial Z(\xi)/\partial \xi]$$
$$\partial \ln Z(\xi)/\partial \xi = [1\ /Z(\xi)][\partial Z(\xi)/\partial \xi]$$

Thus, the derivative to be calculated is:

$$\partial Z(\xi)/\partial \xi = \partial\left\{\int_V .. \int d\mathbf{R}_o d\mathbf{R}_1 \ldots d\mathbf{R}_N \exp\left|-\beta\left[U_N\left(\mathbf{R}_1 \ldots \mathbf{R}_N + \xi \sum_j U\left(\mathbf{R}_o, \mathbf{R}_j\right)\right]\right|\right\}/\partial \xi$$

It is perfectly legitimate to derivate with respect to the coupling ξ under the signs sum since the variables $\mathbf{R}_o$, $\mathbf{R}_N$, and ξ are independent. The term under the signs sum which depend on ξ is $\xi\sum_j U(\mathbf{R}_o, \mathbf{R}_j)$. Thus, the derivation to carry out is: $\partial \exp[-\beta\xi\sum_j U(\mathbf{R}_o, \mathbf{R}_j)]/\partial \xi$.

$$\begin{aligned}
&\partial \exp\left[-\beta\xi\sum_j U\left(\mathbf{R}_o, \mathbf{R}_j\right)\right]/\partial \xi \\
&\quad = \partial \exp\left[-\beta\xi\sum_j U\left(\mathbf{R}_o, \mathbf{R}_j\right)\right]/\partial \xi / \partial\left[-\beta\xi\sum_j U\left(\mathbf{R}_o, \mathbf{R}_j\right)\right] \bullet \\
&\quad \partial\left[-\beta\xi\sum_j U\left(\mathbf{R}_o, \mathbf{R}_j\right)\right]/\partial \xi
\end{aligned}$$

whence the relation being searched for.

Appendix L
Partition Functions in the McMillan–Mayer's Theory

The grand ensemble partition function, in the case of a system of two components, is given by the expression (viz. Chap. 35):

$$\Xi(T, V, \lambda_1, \lambda_2) = \sum_{N1 \geq 0} \sum_{N2 \geq 0} Q(T, V, N_1, N_2) \lambda_1^{N1} \lambda_1^{N2} \tag{L.1}$$

where the functions $Q(T, V, N_1, N_2)$ are the canonical partition ones corresponding to all the possible arrangements of the numbers of moles N_1 and N_2, evidently changing since the study is performed within the realm of the great ensemble. Given the fact that from a general standpoint,

$$\Xi = e^{PV/kT}$$

P is the pressure in the inside compartment and V the volume of the system. One can, starting from these two last relations, write the following expressions, once the osmotic equilibrium is reached (with $P = p + \pi$):

$$\begin{aligned} \exp[(p+\pi)V/kT] &= Q_{00}\lambda_1^0\lambda_2^0 + Q_{01}\lambda_1^0\lambda_2^1 + Q_{02}\lambda_1^0\lambda_2^1 + Q_{03}\lambda_1^0\lambda_2^1 + \ldots \\ &+ Q_{10}\lambda_1^1\lambda_2^0 + Q_{11}\lambda_1^1\lambda_2^1 + Q_{12}\lambda_1^1\lambda_2^2 + Q_{13}\lambda_1^1\lambda_2^3 + \ldots \\ &+ Q_{20}\lambda_1^2\lambda_2^0 + Q_{21}\lambda_1^2\lambda_2^1 + Q_{22}\lambda_1^2\lambda_2^2 + Q_{23}\lambda_1^2\lambda_2^3 + \ldots \\ &+ Q_{30}\lambda_1^3\lambda_2^0 + Q_{31}\lambda_1^3\lambda_2^1 + Q_{32}\lambda_1^3\lambda_2^2 + Q_{33}\lambda_1^3\lambda_2^3 + \ldots \end{aligned} \tag{L.2}$$

π is the osmotic pressure. **p** is the pressure of the system before the osmotic phenomenon has arisen. The expression (L.2) is by no means mysterious. Function Ξ is simply the grand ensemble partition function adapted to the problem.

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Expression (L.2) can also be written under the equivalent form (L.3):

$$\exp[(p+\pi)V/kT] \ = \sum_{N1\geq 0}\sum_{N2\geq 0} Q_{N1,N2}(V,T)\lambda_1^{N1}\lambda_2^{N2} \tag{L.3}$$

For the inside solution (that developing the osmotic pressure after the solute have been added), the grand partition function can be expressed under a more concise form than above, by setting up:

$$\exp[(p+\pi)V/kT] \ = \sum_{N2\geq 0} \Psi_{N2}(\mu_1,V,T)\lambda_2^{N2} \tag{L.4}$$

where:

$$\Psi_{N2} \ = \sum_{N1\geq 0} Q_{N1,N2}\lambda_1^{N1} \tag{L.5}$$

$\Psi_{N2}(\mu_1, V, T)$ may be regarded as being the partition function of a system at constant temperature and volume, open to the component 1 but closed to the component 2. (Being not open to all the components, one speaks, rather of the partition function of the "semi-grand ensemble.") The expression (L.5) corresponds to a vertical reading, column after column, of the expression (L.2), i.e., at a constant composition of the solute 2 (N_2 constant) and at a variable solvent (N_1 variable). However, the expression (L.4) corresponds to the horizontal reading of (L.2), i.e., to a constant composition in solvent and to a variable composition in solute 2. Let us remark that when $N_2 = 0$ (solvent alone—first vertical column of (L.2)), no osmotic pressure, of course, develops and one can write:

$$\exp[pV/kT] \ = \ \Psi_o \tag{L.6}$$

with

$$\begin{aligned} \Psi_o &= \Psi(N2=0) \\ \Psi_o &= \sum_{N1\geq 0} Q_{N1}\lambda_1^{N1} \end{aligned} \tag{L.7}$$

Given the fact that the values of the activities tend to become equal to those of the concentrations when the latter ones become very weak, it is clear that, in order to relate the meaning of the activity of the solute b z_2 to its density number ρ_2 in this case, the functions Ψ_o, $\Psi_1(\Psi_{N2=1})$, $\Psi_{2,}$ ..., expressing the fact that the considered solutions are very dilute, will have to be handled in the following reasoning.

The ratio Ψ_1/Ψ_o arises as being interesting. It is written in terms of partition functions. It is pertinent to wonder about its physical meaning. According to what is preceding:

$$\Psi_o = \sum_{N1 \geq 0} Q_{N1} \lambda_1^{N1}$$

$$\Psi_1 = \sum_{N1 \geq 0} Q_{N1N2} \lambda_1^{N1} \lambda_2^1$$

By developing,

$$\Psi_o = \left[Q_{00}{\lambda_1}^0 + Q_{10}{\lambda_1}^1 + Q_{20}{\lambda_1}^2 + \ldots\right]{\lambda_2}^0$$

since $Q_{00} = 1$ and ${\lambda_1}^0 = 1$ together with ${\lambda_2}^0$:

$$\Psi_o = 1 + Q_{10}{\lambda_1}^1 + Q_{20}{\lambda_1}^2 + \cdots$$

$$\Psi_1 = \left[Q_{01} + Q_{11}{\lambda_1}^1 + Q_{21}{\lambda_1}^2 + \cdots\right]\lambda_2$$

we obtain:

$$\Psi_1/\Psi_o = \left[Q_{01} + Q_{11}{\lambda_1}^1 + Q_{21}{\lambda_1}^2 + \cdots\right]\lambda_2/\left(1 + Q_{10}{\lambda_1}^1 + Q_{20}{\lambda_1}^2 + \cdots\right) \tag{L.8}$$

The ratio Ψ_1/Ψ_o appears as being the mark of the interaction of one molecule of solute with the pure solvent. The latter plays its part through the denominator of the ratio and also through the term in square brackets of the numerator. The molecule of solute intervenes through its absolute activity λ_2 at the order 1 and also through the term in square brackets of the numerator. Moreover, one knows (viz. Chap. 23) that the canonical functions Q_{ij} are directly related to the Helmholtz energy of the systems that they represent. Given the equivalence Helmholtz energy/work (in the conditions of reversibility), one can forecast that the ration Ψ_1/Ψ_o is an expression of the energy of interaction between the molecule of solute and the molecules of pure solvent.

Appendix M
Relations Between π and the Virial Coefficients and Also with the Density Number ρ_2 (First Step)

The followed reasoning is analogous to that permitting to relate the density number of a gas to its activity. From a pure mathematical standpoint, we can say that the introduction of the term Ψ_0/Ψ_1 permits to work out the case of a dilute solution of a nonelectrolyte in a similar manner as that followed in the case of real gases.

According to what is preceding:

$$\begin{aligned} \Xi &= \exp[(p+p)V/kT] \\ \Xi &= \sum_{N2\geq 0} \Psi_{N2}(\mu_1, V, T)\lambda_2^{N2} \end{aligned} \tag{M.1}$$

where (viz. Appendix L):

$$\Psi_{N2}(\mu_1, V, T) = \sum_{N1\geq 0} Q_{N1,N2}\lambda_1^{N1}$$

In order to simplify the writing, let us set up $N \equiv N_2$ and replace λ_2 by its expression

$$\lambda_2 = z_2 V/Q_{01}$$

We obtain (by simplifying further the writing):

$$\Xi = \sum_N \Psi_N \left(V^N/Q_{01}^N\right) z_2^N \tag{M.2}$$

By replacing z_2 by its expression:

$$\begin{aligned} z_2 &= \gamma_2^0 \delta_2 \\ \Xi &= \sum_N \Psi_N \left(V^N/Q_{01}^N\right) \gamma_2^{0N} \delta_2^N \end{aligned} \tag{M.3}$$

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and by replacing $\gamma_2{}^\circ$ by its expression (viz. preceding chapter),

$$\gamma_2{}^\circ = Q_{01}\Psi_0/\Psi_1$$

we obtain:

$$\Xi = \sum_{N\geq 0} \Psi_N(\Psi_0/\Psi_1)^N V^N \delta_2{}^N \tag{M.4}$$

or

$$\exp[(p+\pi)V/kT] = \sum_{N\geq 0} \Psi_N[(\Psi_0 V/\Psi_1)\delta_2]^N \tag{M.5}$$

$$\exp[(p+\pi)V/kT] = \Psi_0 + \Psi_1(\Psi_0 V/\Psi_1)\delta_2 + \Psi_2(\Psi_0 V/\Psi_1)^2\delta_2^2 + \Psi_3(\Psi_0 V/\Psi_1))^3\delta_2^3 + \cdots$$

in which the functions Ψ_1, Ψ_2, Ψ_3 are defined in the preceding appendix. The expression (M.5) can also be written:

$$\exp[(p+\pi)V/kT] = \Psi_0 + \Psi_0\sum_{N\geq 1} \Psi_N\left(\Psi_0^{N-1}/\Psi_1^N\right)V^N\delta_2^N$$

$$\exp[(p+\pi)V/kT] = \Psi_0\left(1 + \sum_{N\geq 1} \Psi_N\left(\Psi_0^{N-1}/\Psi_1^N\right)V^N\delta_2^N\right)$$

Starting from (M.5), we obtain:

$$\exp(\pi V/kT) = 1 + \sum_{N\geq 1} \Psi_N\left(\Psi_0^{N-1}/\Psi_1^N\right)V^N\delta_2^N$$

The analogy with the following relation regarding an imperfect gas (viz. Chap. 34)

$$\Xi = 1 + \sum_{N\geq 1}\left[Z_N(V,T)/N!\right]z^N \quad \left(\text{relation (34.12)—Chap. 34}\right)$$

is quasi-perfect. It becomes definitively perfect by setting up:

$$Z_N^*(\mu_1, V, T) = N!\Psi_N\left(\Psi_0^{N-1}/\Psi_1^N\right)V^N \tag{M.6}$$

The expression is now:

$$\exp(\pi V/kT) = 1 + \sum_{N\geq 1}\left[Z_N^*(\mu_1, V, T)/N!\right]\delta_2^N \tag{M.7}$$

Appendix N
Relations Between π and the Virial Coefficients and Also with the Density Number ρ_2 (Second Step)

The following expansion in series is quite analogous to that followed in the case of real gases:

$$\exp[\Pi V/kT] = \left[1 + \sum_{N\geq 1} \left(Z_N^*/N!\right)\delta_2^N\right]$$

$$\Pi V/kT = \ln\left[1 + \sum_{N\geq 1} \left(Z_N^*/N!\right)\delta_2^N\right]$$

relation analogous to that (34.17) of Chap. 34. Then, we proceed to the expansion in series of the logarithm. We obtain, limiting it to the term of order 2:

$$\Pi V/kT = \sum_{N\geq 1} \left(Z_N^*/N!\right)\delta_2^N - 1/2\left\{\sum_{N\geq 1} \left(Z_N^*/N!\right)\delta_2^N\right\}^2 \ldots$$

i.e.:

$$\Pi/kT = \left(Z_1^*/V\right)\delta_2 + 1/2V\left(Z_2^* - Z_1^{*2}\right)\delta_2^2 + \cdots$$

admitting that, from the strict mathematical viewpoint,

$$-1 \leq \sum_{N\geq 1} \left(Z_N^*/N!\right)\delta_2^N \leq 1$$

Setting up:

$$b_1 = Z_1^*/V, \quad b_2 = 1/2V\left(Z_2^* - Z_1^{*2}\right), \ldots$$

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we obtain:

$$\Pi/kT = \sum_{j\geq 1} b_j \delta_2^j \tag{N.1}$$

Let us notice at this point that the coefficients b_j depend on μ_1 and T.

The obtention of the relation expressing the osmotic pressure π as a function of the density number ρ_2 involves that of the expression of ρ_2 as a function of δ_2. The latter is obtained according to the following reasoning.

According to the properties of the grand canonical ensemble:

$$\overline{N_2} \;=\; kT(\partial \Xi/\partial \mu_2)_{V,T}$$

Moreover:

$$\ln\Xi = \exp[(p+\pi)V/kT]$$

whence:

$$\begin{aligned}\overline{N_2} &= \; kT(\partial(p+\pi)V/kT/\partial\mu_2)_{V,T}\\ \overline{N_2} &= \; (\partial(p+\pi)V/\partial\mu_2)_{V,T}\end{aligned}$$

p being constant, we obtain:

$$\begin{aligned}\overline{N_2}/V &= \partial\pi/\partial\mu_2\\ \rho_2 \; &= \partial\pi/\partial\mu_2\end{aligned} \tag{N.2}$$

$d\mu_2$ is obtained as follows:

$$\begin{aligned}\lambda_2 \; &= \exp[\mu_2/kT]\\ \ln\lambda_2 &= \mu_2/kT\\ d\mu_2 &= kTd\ln\lambda_2\end{aligned}$$

Transferring into relation (N.2), we find:

$$\rho_2 \;=\partial(\pi/kT)/\partial\ln\lambda_2$$

In the preceding reasoning, it was set up by definition that:

$$\lambda_2 = \delta_2\Psi_0 V/\Psi_1$$

i.e.:

$$\ln\lambda_2 = \ln\delta_2 + \ln(\Psi_0 V/\Psi_1)$$

whence

$$d\ln\lambda_2 = d\ln\delta_2$$

As a result:

$$\rho_2 = \delta_2((\partial\pi/kT)/\partial\delta_2)$$

and according to (N.1):

$$\rho_2 = \sum_{j\geq 1} jb_j\delta_2^j \tag{N.3}$$

whence:

$$\delta_2((\partial\pi/kT)/\partial\delta_2) = \sum_{j\geq 1} jb_j\delta_2^j$$

This relation must be compared with that expressing the development of the virial of the osmotic pressure:

$$\pi/kT = \rho_2 + \sum_n B_n^*\rho_2^n \quad (n \geq 2) \tag{N.4}$$

The virial coefficients $B_n{}^*$ are related to the b_j through relation (N.4) by taking into account the fact that $\delta_2 \to \rho_2$ when $\rho_2 \to 0$.

As in the case of imperfect gases, it is interesting to express the osmotic pressure as a function of the density number ρ_2 in order to express the activity coefficients in statistical thermodynamics terms. This would permit to better grasp their physical meaning. Although the preceding reasoning permits to answer this question, we can proceed as follows. We use the expressions (N.1) and (N.3). In a first step, we set up (after having noticed that, evidently, $m_1 = b_1 = 1$):

$$\delta_2 = \rho_2 + m_2\rho_2^2 + m_3\rho_2^3 + \cdots$$

Limiting the development to the term of order 3, we immediately find:

$$\delta_2^2 = \rho_2^2 + 2m_2\rho_2^3 + \cdots$$
$$\delta_2^3 = m_3\rho_2^3 + \cdots$$

By transferring these powers δ_2 into (N.3) and by identifying term to term, we obtain the following identities:

$$m_2 \equiv -2b_2, \quad m_3 \equiv 8b^2 - 3b_3, \quad \ldots$$

It must be noticed that the coefficients m_2, $m_3, \ldots m_j \ldots$ depend only on the coefficients b$_i$ for which i cannot be superior to j. Hence, we find:

$$\delta_2 = \rho_2 + (-2b_2)\rho_2^2 + (8b_2 - 3b_3)\rho_2^3 + \cdots$$

By reporting this expression into (N.1), we obtain the following expression of the type (N.5):

$$\pi/kT = \sum_{n \geq 2} B_n \rho_2^n \tag{N.5}$$

The coefficients B_n are only functions of the b_i and only depend on μ_1 and T.

Appendix O
Meaning of the Ratio $\Delta_N \Delta_0^{N-1}/\Delta_1^N$

The significance of the ratio is based on the general relation (viz. Chap. 24):

$$G(T,p,N) = -\,kT\ln\Delta(T,p,N)$$

and on the following calculation. Let us take the logarithm of the studied ratio. We obtain:

$$\begin{aligned}
\ln\left(\Delta_N\Delta_0^{N-1}/\Delta_1^N\right) &= \ln\Delta_N + \ln\left(\Delta_0^{N-1}\right) \; - \ln\left(\Delta_1^N\right)\\
-\ln\left(\Delta_N\Delta_0^{N-1}/\Delta_1{}^N\right) &= -\ln\Delta_N \; - \ln\left(\Delta_0^{N-1}\right) \; + \ln\left(\Delta_1{}^N\right)\\
-\,kT\ln\left(\Delta_N\Delta_0^{N-1}/\Delta_1^N\right) &= -kT\ln\Delta_N - \; kT\ln\left(\Delta_0^{N-1}\right) \; + kT\ln\left(\Delta_1^N\right)\\
-\,kT\ln\left(\Delta_N\Delta_0^{N-1}/\Delta_1^N\right) &= -\,kT\ln\Delta_N - \; kT\ln\left(\Delta_0^{N-1}\right) \; + kT\ln\left(\Delta_1^N\right)
\end{aligned}$$

i.e.:

$$\begin{aligned}
-kT\ln\left(\Delta_N\Delta_0^{N-1}/\Delta_1^N\right) &= G_N + (N-1)G_0 - NG_1\\
-kT\ln\left(\Delta_N\Delta_0^{N-1}/\Delta_1^N\right) &= G(N_1, N_2 = N, p, T)\\
&\quad +(N-1)G(N_1, N_2 = 0, P, T) \; - NG(N_1, N_2 = 1, \; p, T)
\end{aligned}$$

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Appendix P
Work and Electrostatic Interactions Energy

When the state of a system is such that it only gives rise to electrostatic interactions:

- The work done on it is equal to its total energy change
- It is equal to the change in its kinetic energy plus its potential energy change.

P.1 Potential Electrostatic Energy

Let us suppose that the system is constituted by two electric charges z_1e and z_2e. When the forces exerted by the surroundings on both charges force them to move extremely slowly, one can consider that the kinetic energy of the system is constant. In these conditions:

- The work supplied to the system for the charge z_2e to be moved from the distance a to the distance b of the other charge z_1e is equal to the change in the potential energy due to the electrostatic interactions
- It is hence equal to the difference in the potential energy of both charges at the points b and a.

P.2 Expression of the Work to Do

Hence, obtaining the electrostatic potential energy entails to know the work to be done in order to perform the preceding displacement. The results obtained in this case may be, besides, generalized without difficulty. The general definition of the work permits to write that the one w supplied to the system in the above example is of the type:

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$$w = \int_a^b f dr$$

where f is the electrostatic interactions force exerting between both charges and r being the distance between both charges. According to Coulomb's law, f is given by the expression:

$$f = z_1 z_2 e^2 / 4\pi\varepsilon_o \varepsilon_r r^2$$

Where ε_o is the vacuum permittivity (expressed in F m^{-1}), ε_r the relative permittivity (dimensionless) of the vacuum ($\varepsilon_r = \varepsilon/\varepsilon_o$), and ε the permittivity of the medium expressed in (F m^{-1}). The force developed by the surroundings to do the work must be equal and opposed to the interaction force f. As a result, the work supplied by the surroundings is given by the relation:

$$w = -\int_a^b \left(z_1 z_2 e^2 / 4\pi\varepsilon_o \varepsilon_r\right)\left(1/r^2\right) dr$$

$$w = \left(z_1 z_2 e^2 / 4\pi\varepsilon_o \varepsilon_r\right)(1/r)\Big|_a^b$$

$$w = \left(z_1 z_2 e^2 / 4\pi\varepsilon_o \varepsilon_r\right)(1/b) - \left(z_1 z_2 e^2 / 4\pi\varepsilon_o \varepsilon_r\right)(1/a)$$

From these results, we can deduce that:

- The potential energies of the system constituted by the two charges located in points a and b are, respectively, $(z_1 z_2 e^2/4\pi\varepsilon_o\varepsilon_r)(1/a)$ and $(z_1 z_2 e^2/4\pi\varepsilon_o\varepsilon_r)(1/b)$
- The potential energy of both charges at every distance r is given by the expression $(z_1 z_2 e^2/4\pi\varepsilon_o\varepsilon_r)(1/r)$
- The value of the derivative of the potential energy with respect to the distance r is equal (but with the opposite sign) to the force exerting in this point r:

$$d(\text{potential energy})/dr\big)r = -\text{force at the point } r$$

P.3 Relation Between the Potential Electrostatic Energy and the Electrostatic Potential

We have just seen that the potential energy of interaction between the two charges located at the distance r is given by the relation $(z_1 z_2 e^2/4\pi\varepsilon_o\varepsilon_r)(1/r)$. This relation can also be written:

$$[(z_1 e/4\pi\varepsilon_o\varepsilon_r r)]z_2 e \quad \text{and} \quad [(z_2 e/4\pi\varepsilon_o\varepsilon_r r)]z_1 e$$

The two terms in square braces only depend on the charge in r. The term [$(z_1 e/4\pi\varepsilon_o\varepsilon_r r)$] is the electrostatic potential Ψ_1 due to the charge $z_1 e$ located at the distance r from the charge z_2e. The term $[(z_2e/4\pi\varepsilon_o\varepsilon_r r)]$ is the electrostatic potential Ψ_2 due to the charge z_2e located at the distance r from the charge z_1e. Therefore, it is possible to set up in a general way *that the potential (electrostatic) energy of interaction between two charges located at the distance r from each other is equal to the product of the potential by the charge on which the potential is acting*.

It is interesting to notice that the electrostatic potential at one point only depends on its charge. It does not depend on the value of the charge on which it is acting or, more simply on the fact that whether there exists another charge or not.

Appendix Q
Poisson's Relation

Poisson's equation results from the expression of the total force flux $d\phi$ (for example, of charges) which goes away from a volume dV through the external surfaces. It also results from the Gauss' theorem. The total force flux is given by the following expression (its setting up is given in the second part of this appendix):

$$d\phi = -\left(\partial^2\psi/\partial x^2 + \partial^2\psi/\partial y^2 + \partial^2\psi/\partial z^2\right)dx\,dy\,dz \qquad \text{(Q.1)}$$

(the following term in braces is the laplacian operator:

$$\left(\partial^2/\partial \mathrm{x}^2 + \partial^2/\partial \mathrm{y}^2 + \partial^2/\partial \mathrm{z}^2\right)$$

which, here, applies to the potential Ψ from which stems, in the present case, the electrostatic operating force.

Gauss' theorem stipulates that the total flux of charges going away from a closed volume through the external surface is equal to the term $k\sum q$ in air where $\sum q$ is the algebraic sum of the electrical charges contained by this volume and k a constant characterizing the medium (the insulator). Let us consider the case in which the medium possesses free electric charges and let ρ the charges density, i.e., the ratio of the charges and of the volume. The total charge dq contained in the volume element $dxdydz$ is:

$$dq = \pi dxdydz$$

The conjunction of these theoretical principles leads to the equality:

$$-\left(\partial^2\psi/\partial x^2 + \partial^2\psi/\partial y^2 + \partial^2\psi/\partial z^2\right)dx\,dy\,dz = k\rho\,dx\,dy\,dz$$

This is the Poisson's relation.

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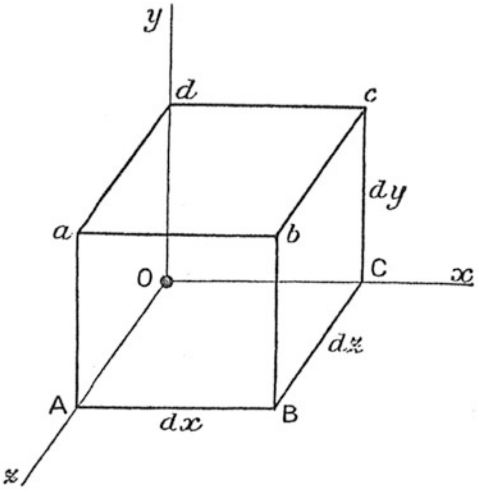

Fig. Q.1 Volume element through which circulates the flux

The demonstration leading to the relation (Q.1) is the following one. Let us calculate the flux of forces through the total surface S of the volume element $dV = dx\ dy\ dz$ (Fig. Q.1).

One names the force flux through the surface S the product of S by the component force perpendicular to the surface. Let us recall that F is changing in every point of the space. At the point O, the components of F are X, Y, Z but after a displacement during which x is varying from dx, y from dy, and z from dz, the components become:

on the x axis	$X + (\partial X/\partial x)dx$
on the y axis	$Y + (\partial Y/\partial y)dy$
on the z axis	$Z + (\partial Z/\partial z)dz$

By arbitrarily adopting the convention that a going away flux is positive and that an incoming one is negative, one obtains the following results:

– The entering flux through the surface OAad is

$$\phi x = -XdS = -Xdzdy$$

and the going away flux through the parallel surface cCBb is:

$$\phi x + d\phi x = [X + (\partial X/\partial x)dx]dzdy$$

The algebraic sum is:

$$d\phi_x = (\partial X/\partial x)\ dxdydz$$

It is the same thing for the fluxes going out through the axis z and y. One obtains:

$$d\phi_z = (\partial Z/\partial z)\, dzdxdy \quad \text{and} \quad d\phi_y = (\partial Y/\partial y)dydzdx$$

The total flux going away from the volume element dV is:

$$d\phi = (\partial X/\partial x + \partial Y/\partial y + \partial Z/\partial z)dx\, dydz \tag{Q.2}$$

But, in the case of the flux of an electrostatic field (viz. electrostatics),
one can write:

$$X = -(\partial\psi/\partial x) \quad Y = -(\partial\psi/\partial y) \quad Z = -(\partial\psi/\partial z) \tag{Q.3}$$

(This is true because the work done by the electrostatic force when the point to which it applies crosses from a point A to a point B is independent from the followed path. According to relation (Q.3), $\partial X/\partial x$ which lies in (Q.2) becomes:

$$\partial X/\partial x = -\left(\partial^2\psi/\partial x^2\right)$$

Likewise,

$$\partial Y/\partial y = -\left(\partial^2\psi/\partial y^2\right) \quad \partial Z/\partial z = -\left(\partial^2\psi/\partial z^2\right)$$

The introduction into (Q.2) leads to (Q.1).

Appendix R
Change of Coordinates in Poisson's Equation

This corresponds to the crossing from the equation (46.5) to equation (46.6)—viz. Chap. 46

$$\partial^2\psi_r/\partial x^2 \; + \; \partial^2\psi_r/\partial y^2 + \; \partial^2\psi_r/\partial z^2 \; = -\, 4\pi\rho_r/\varepsilon \quad ((46.5)\text{—Chap. } 46)$$

$$1/r^2 d\;/dr\;(r^2 d\psi_r/dr) \; = \; - \; 4\pi\rho_r/\varepsilon \quad ((46.6)\text{—Chap. } 46)$$

The crossing is easily performed by using the chain rule law of derivation. Let us consider the partial second derivative $\partial^2\Psi_r/\partial x^2$ and write (according to this rule):

$$\partial\psi_r/\partial x = (\partial\psi_r/\partial r)\cdot(\partial r/\partial x)$$

$$\partial^2\psi_r/\partial x^2 \; = \partial[(\partial\psi_r/\partial r)\cdot(\partial r/\partial x)]/\partial x$$

By doing the same process with the two other second partial derivatives lying in the laplacian and doing the sum, one obtains the expression (46.6) given the relation:

$$x^2 + y^2 + z^2 = r^2$$

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Appendix S
General Principles of Calculations of Ionic Species Concentrations in Solutions Involving Activities

Used exponential in the Poisson–Boltzmann equation

Let $N°_k$ be the number of ions k in 1 cm^3 of solution. The number of ions k in the volume dV would be $N°_k\, dV$ without electrostatic energy. Because of the occurrence of the electrostatic potential Ψ_{r} in the volume dV, the average number of ions k in dV is not this one. It is given by the Boltzmann's relation, i.e.:

$$\overset{\circ}{N}_k dV \exp(-z_k \varepsilon_o \psi_r / kT) = N_k dV$$

The charge in the volume dV, due to the ion k, is:

$$z_k e_o \overset{\circ}{N}_k dV \; \exp(-z_k \varepsilon_o \psi_r / kT)$$

The total charge due to the whole ions contained in the volume dV is:

$$e_o \Sigma_k z_k \overset{\circ}{N}_k dV \exp(-z_k e_o \psi_r / kT)$$

As a result, the charge density ρ_r is given by the expression:

$$\rho_r \; = \sum_k \overset{\circ}{N}_k z_k e_o \exp(-z_k e_o \psi_r / kT)$$

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Appendix T
Solution of Poisson–Boltzmann's Equation and Inferences

The indexes of the equations of this appendix are labelized "in primes" in order to distinguish them from those coming from Chap. 46 which keep their previous numerotation.

T.1 Solution of the Differential Equation

The general solution of this kind of differential equation is known. It is of the type:

$$\psi_r = A[\exp(-\chi r)\ /r]\ + A''[\exp(\chi r)/r]$$

A and A' are the two integration constants which are fixed by the limit conditions. The first condition is that the potential Ψ_r must vanish for the distance r infinite. As a result, A' must be null. Hence, it remains as a solution:

$$\psi_r\ =\ A[\exp(-\chi r)/r]$$

The second condition concerns the limit case in which the central ion is alone. Then, χ is null and the potential Ψ_r reduces to that due to the central ion i. Let us assume that the central ion is a point charge. (We shall come back on this hypothesis in the following appendix.) From the general standpoint, the potential due to a punctual charge q located at the distance r from the chosen point in order to evaluate it and occurring in a medium of dielectric constant ε is:

$$\psi_r\ =\ q/\varepsilon$$

i.e., here,

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$$\psi_{(\text{ion central})} = z_i e_o / 4\pi\varepsilon r$$

This expression added to the fact that $\chi = 0$ leads to the equality:

$$z_i e_o / 4\pi\varepsilon \ = A$$

Therefore, the appropriate solution of the linearized Poisson–Boltzmann's equation is:

$$\psi_r = z_i e_o / 4\pi\varepsilon \exp(-\chi r)/r \tag{T.1}$$

This relation expresses the potential Ψ_r due to all the ions (included ion *i*) at the distance r of the central ion as a function of the concentrations of the ions.

T.2 Charge Density at the Distance *r* of the Central Ion

Given the relations (46.6), (46.15), and (46.16) of Chap. 46, we obtain:

$$-4\pi\rho_r/\varepsilon = \chi^2\psi_r \tag{T.2}$$

and according to (T.1):

$$\rho_r = -(z_i e_o/4\pi)\chi^2 \mathrm{e}^{-\chi r}/r$$

It is the relation (46.17) of Chap. 46

T.3 Total Charge in Excess All Around the Central Ion

Let us consider a spherical sheath of thickness *dr* at the distance *r* of the central ion. The charge *dq* of this sheath is equal to the charge density $d\rho_r$ multiplied by its volume:

$$dq \ = \rho_r 4\pi r^2 dr$$

As a result, the total charge is given by the expression:

$$q = \int_{\text{lower limit}}^{\infty} \rho_r 4\pi r^2 dr \tag{T.3}$$

lower limit

$$q = - \int_{\text{lower limit}}^{\infty} (z_i e_o/4\pi)\chi^2 (\mathrm{e}^{-\chi r}/r) 4\pi r^2 dr$$

This charge is the total one but without that of the central ion. For the process of integration, the question of the lower limit of r is open. In a first time, Debye and Hückel have put forward the hypothesis that the ion is nothing different from a point charge. As a result, one can write:

$$q_{\text{cloud}} = \int_0^{\infty} (z_i e_o/4\pi)\chi^2 (\mathrm{e}^{-\chi r}/r) 4\pi r^2 dr$$

that can be equivalently written, χ being a constant:

$$q_{\text{cloud}} = -z_i e_o \int_{r=0}^{r=\infty} \mathrm{e}^{-\left(\chi r\right)} (\chi r)\ d(\chi r)$$

Integrating by parts gives:

$$q_{\text{cloud}} = \ - z_i e_o$$

T.4 Locus of the Maximal Charge Around the Central Ion

The net charge of a spherical sheath of thickness dr around the central ion, at the distance *r*, is given by the expression:

$$dq = \rho_r 4\pi r^2 dr$$
$$dq = \ - z_i e_o \mathrm{e}^{-\chi r} \chi^2 r dr$$

The *r* value for which there is the maximum of charge is given by setting up:

$$dq/dr = 0$$

The result is:

$$r = \chi^{-1}$$

Hence, the maximal value of the charge contained in a sheath located around the central ion is such that the distance from the latter one is given by the expression:

$$r = \chi^{-1}$$

T.5 Electrostatic Potential Only due to the Ionic Atmosphere

The potential Ψ_r calculated above is the total electrostatic potential. It is equal to the sum of the potential due to the ionic atmosphere (cloud) and of that due to the central ion:

$$\psi_r = \psi_{\text{ion central}} + \psi_{\text{atm ionique}}$$

According to what is preceding:

$$\psi_{\text{cloud}} = (z_i e_o/\varepsilon)(\mathrm{e}^{-\chi r}/r) - z_i e_o/\varepsilon r$$
$$\psi_{\text{cloud}} = z_i e_o/\varepsilon r(\mathrm{e}^{-\chi r} - 1)$$

For the case in which the sum $\sum_k N_k {z_k}^2 {e_o}^2$ becomes sufficiently weak for the product χr to be largely weaker than 1, one can set up:

$$\mathrm{e}^{-\chi r} \approx 1 - \chi r$$
$$\mathrm{e}^{-\chi r} - 1 \approx -\chi r$$

Then, Ψ_{cloud} becomes:

$$\psi_{\text{cloud}} = -z_i e_o/\varepsilon \chi^{-1}$$

Appendix U
Extended Debye–Huckel Equation

It is convenient to consider again the theory which leads to the limit equation. Let us recall that in the latter, the central ion is assimilated to a charge point. We know that, in these conditions, the solution of the linearized Poisson–Boltzmann equation is of the type:

$$\psi_r = A\mathrm{e}^{-\chi r}/r$$

The evaluation of the constant *A* permits to introduce the radius a of the central ion that, henceforth, we suppose to be spherical and of finite dimension.

The charge *dq* in a spherical sheath of thickness dr located at the distance *r* of *i* is given by the expression:

$$dq \;= \rho_r 4\pi r^2 dr$$

The charge density is given by the expression:

$$\rho_r = -(\varepsilon/4\pi)\chi^2\psi_r$$

By introducing into the latter relation the expression of Ψ_r as a function of *A*, we obtain:

$$\rho_r = -(\varepsilon/4\pi)\chi^2 A\mathrm{e}^{-\chi r}/r$$

By combining the latter relations, we obtain:

$$dq = -A\chi^2\varepsilon(\mathrm{e}^{-\chi r} r dr)$$

The total charge of the ionic atmosphere must remain equal, as previously, to $-z_i e_\mathrm{o}$ in order to respect the neutrality of the solution (for a central ion of charge $+z_i e_\mathrm{o}$).

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Let a be the radius of the central ion. The latter is calculated according to the expression:

$$z_i e_o = -\int_a^\infty dq$$

$$-z_i e_o = -A\chi^2\varepsilon \int_a^\infty \mathrm{e}^{-\chi r} r dr$$

which can be equivalently written

$$-z_i e_o = \ - \ A\varepsilon \int_a^\infty \mathrm{e}^{-\chi r}\,(\chi r) d(\chi r)$$

$$-z_i e_o = \ - \ A\varepsilon \mathrm{e}^{-\chi a}(1 + \chi a)$$

The value of A obtained by taking into account the radius a is:

$$A = (z_i e_o/\varepsilon)[\mathrm{e}^{\chi a}/(1 + \chi a)]$$

The solution of the corresponding Poisson–Boltzmann equation is, given the relation (46.31) of Chap. 46:

$$\psi_r \ = (z_i e_o/\varepsilon)[\mathrm{e}^{\chi a}/(1 + \chi a)](\mathrm{e}^{-\chi r}/r)$$

In order to follow the same strategy as previously, the electrostatic potential Ψ_{cloud} acting on the central ion must be known. It is given as previously by the expression:

$$\psi_{\text{cloud}} \ = \psi_r - \psi_{\text{central ion}}$$

$$\psi_{\text{cloud}} = (z_i \mathrm{e}_{\mathrm{o}}/\varepsilon r) \cdot \mathrm{e}^{\chi(a-r)}/(1 + \chi a) - z_i e_o/\varepsilon r$$

$$\psi_{\text{cloud}} = \left(z_i \mathrm{e}_{\mathrm{o}}/\varepsilon r\right)\left[\mathrm{e}^{\chi(a-r)}/(1 + \chi a) - 1\right]$$

But the difference with the preceding case lies in the fact that the potential due to the cloud begins at the point at which ends the radius of the ion, i.e., for $r = a$. As a result, by replacing r by a in the preceding relation, we obtain:

$$\psi_{\text{cloud}} = -\left(z_i e_o/\varepsilon\chi^{-1}\right)[1/(1 + \chi a)]$$

and

$$\ln\gamma_i = -N_{\mathrm{A}}\left[(z_i e_o)^2/2\varepsilon RT\chi^{-1}\right]\left(1/(1 + \ \chi a\right)$$

By following the same process as previously, we obtain:

$$\ln\gamma_{\pm} = -A\left|z_{+}z_{-}\right|\surd I/(1+\chi A)$$

and according to the relation (46.27) of Chap. 46 which remains valid:

$$\chi = B\surd I$$

we obtain:

$$\ln\gamma_{\pm} = -A\left|z_{+}z_{-}\right|\surd I/\left(1\ +Ba\surd I\right)$$

This is the equation of the extended Debye–Hückel theory.

Appendix V
Demonstration That the Function *PV* Is the Function Characteristic of the Grand Canonical Ensemble

Let us substitute the expression below (viz. Chap. 24):

$$P_j(N : V, T, \mu) = \mathrm{e}^{-Ej(N,V)/kT}\mathrm{e}^{N\mu/kT}/\Xi$$

into the expression:

$$S = -k\sum_j \sum_N P_j(N)\ln P_j(N)$$

We obtain:

$$S = \overline{E}/T - \overline{N}\mu/T + k\ln\Xi$$

Let us identify this equation to the following coming from thermodynamics:

$$S = E/T - N\mu/T + PV/T$$

We find:

$$kT\ln\Xi = PV$$

Remark: This reasoning is rigorous only when the integrations leading to the two expressions of the entropy above involve a null integration constant. This hypothesis is very reasonable since the entropy is an indicator of the number of microstates accessible to a system and since in particular, there subsists only one microstate when the number of moles of the components of a system tends toward zero.

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I.M. Klotz, *Chemical Thermodynamics: Basic Theory and Methods* (W.A. Benjamin, New York, 1964) (A very didactic book and, hence, very popular. A magistral graphic presentation of the notions of standard states and activities)

G.N. Lewis, M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, 1st edn. (McGraw-Hill, New York, 1923) (Historical monument of the literature devoted to chemical thermodynamics. Still precious as our book shows it)

K.S. Pitzer, *Thermodynamics, 3rd Edition of the Book "Thermodynamics" of G.N. Lewis* (McGraw-Hill, New York, 1925) (Third edition of the preceding book. For our purpose, it essentially highlights the interesting feature to develop considerations on excess Gibbs free energies which permit the obtaining of activity coefficients)

Activity Coefficients in Electrolyte Solutions. Collective volumes, ed. by R.M. Pytkowics vols. 1 and 2 (CRC Press Inc, Boca Raton, 1979) (Besides some theoretical aspects, this book is essentially devoted to the activities in the natural waters)

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Fluctuation Theory of Solutions: Applications in Chemistry, Chemical Engineering and Biophysics. Collective volume, ed. by P.E. Smith, E. Matteoli, J.P.O'Connell (CRC Press/Taylor and Francis Group, Boca Raton, 2013) (Books containing recent essentials on the Kirkwood–Buff's theory and its applications in the chemistry of solutions)

Physical Chemistry of Electrolyte Solutions: Modern Aspects. Collective volume, ed. by J. Barthel, H. Krienke, W. Kunz (Springer, Heidelberg, 1998) (Presentation of modern theories of the chemistry of ions in solution. The theoretical level of this book is higher than that of our own)