

Statistical Thermodynamic and Surface Chemistry

Course No. Chem3102

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Statistical Thermodynamics

Topic to be covered:

1. Introduction
 - 1.1. Terminology and Basic Concepts
 - 1.2. Basic Statistics
 - 1.3. Statistics of Particles
 - 1.4. Distribution Functions
 - 1.5. Partition Function
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1. Introduction

With the development of atomic and molecular theories in the late 1800s and early 1900s, thermodynamics was given a molecular interpretation. This field is called **statistical thermodynamics**, which can be thought of as a bridge between macroscopic and microscopic properties of systems. Essentially, statistical thermodynamics is an approach to thermodynamics situated upon statistical mechanics, which focuses on the derivation of macroscopic results from first principles. It can be opposed to its historical predecessor phenomenological thermodynamics, which gives scientific descriptions of phenomena with avoidance of microscopic details.

Since any observed equilibrium property of matter must be some kind of an average of a large number of molecules, it is evident that we must use statistical methods to determine this property. *The discipline which deals with the computation of the macroscopic properties of matter from the data on the microscopic properties of individual atoms (or molecules)* is called **statistical Thermodynamics** or **statistical mechanics**.

Statistical mechanics can be applied easily to simple ideal systems such as monoatomic and diatomic gases. For application to interacting systems such as liquids (where strong intermolecular forces exist), the details of the intermolecular potential energy, which is not always known accurately, have also to be taken into account. That is why statistical mechanics of liquids is a difficult but fascinating subject. Gases under high pressures, too, are difficult to treat statistically since they deviate strongly from ideality. In recent years statistical methods have been applied successfully to simple liquids and dense gases. Progress in this area have made possible by the application of both the advanced mathematical methods and high-speed computers which can numerically solve the otherwise highly intractable differential and integro-differential equations involved in advanced theoretical treatments. Before starting our actual statistical calculation we will try to understand some of the theories like partition function and equipartition function.

1.1. Terminology and Basic Concepts

Probability

If an event can occur in n ways (i.e. there are n possible outcomes) and a particular result can occur in m ways, then the probability of the particular result occurring is m/n .

Example

Spinning a coin gives rise to 2 possible outcomes: H (Heads) or T (Tails) H occurs in 1 way; therefore the probability of a H result is $\frac{1}{2}$

Note:

1. The sum of the probabilities for all possible results is unity: in the above example, the probability of T occurring is also $\frac{1}{2}$ and the probability of obtaining either an H or a T (i.e. encompassing all possible results) is therefore equal to $(\frac{1}{2} + \frac{1}{2}) = 1$
2. Probabilities may be expressed as fractions, in decimal format or as percentages; so the following probabilities are all equivalent - $\frac{1}{2}$, 0.5, 50%.

Example

A standard dice has six faces (with faces numbered 1 ... 6) and rolling it gives rise to 6 possible outcomes. A 3 occurs in 1 way; therefore the probability of throwing a 3 is $\frac{1}{6}$

Permutations and Combinations

If we have n different items, then the number of ways of arranging them in a row is given by the factorial $n!$

Proof by Example

Consider how many arrangements are possible for the 26 letters of the alphabet. The first letter could be chosen in 26 different ways - leaving 25. Thus 25 choices are possible for the second letter. The third choice is then made from the 24 remaining letters and so on. The number of different arrangements possible for just the first two choices is thus 26×25 ; and when the third is included, $26 \times 25 \times 24$. This process can be continued until all the letters of the alphabet are used up and the number of different possible arrangements is $26 \times 25 \times 24 \times 23 \times \dots \times 4 \times 3 \times 2 \times 1$ - such a multiplication series is called a *factorial* and in this case the number of arrangements would be written as $26!$

Example

With three different letters, ABC, then $n = 3$ and $n! = 6$, corresponding to the six possible arrangements which are: ABC, ACB, BAC, BCA, CAB, CBA

Example 1 : Cl and Cl₂

Chlorine has two stable isotopes of RAM 35 and 37. Their relative abundance is about 3:1. This can be expressed as " the chance of encountering a Cl atom of mass 35 in a collection of free chlorine atoms is 75% " or the *probability* of any particular Cl atom having mass 35 is 0.75.

This means that a mass spectrum of chlorine atoms shows two peaks at masses 35 and 37, the former three times as intense as the latter.

What happens in the chlorine molecule (Cl₂)? Clearly several combinations of isotopes are possible, (i) both atoms are of mass 35, giving ³⁵Cl₂ , (ii) one 35 and one 37, giving ³⁵Cl³⁷Cl, or (iii) both are of mass 37, giving ³⁷Cl₂ . These possible combinations give rise to three peaks in the mass spectrum, corresponding to Cl₂⁺ ions with relative masses of 70, 72, and 74.

There are several ways of tackling the problem of identifying the exact probability of each molecular mass occurring. We will start with the least sophisticated approach.

If we choose the first atom in the molecule to be ³⁵Cl then this choice has a probability of 0.75; this atom may then be associated with either another ³⁵Cl atom, again with a probability of 0.75, or with a ³⁷Cl atom, with a probability of 0.25.

The pattern of all possible combinations, taking account of these relative probabilities is shown in Table 1. For this table we have chosen to work with four chlorine atoms in the first instance, since the relative abundances then indicate that on average three will be 35 and one 37. *Each* of these atoms can then be associated with four other atoms, and again three will be 35 and one 37, giving the sixteen possible Cl₂ molecules shown in the table.

Table 1: Possible Ways of Combining Chlorine Isotopes

First Cl	35				35				35				37			
Second Cl	35	35	35	37	35	35	35	37	35	35	35	37	35	35	35	37
Total mass	70	70	70	72	70	70	70	72	70	70	70	72	72	72	72	74

Total number of molecules = 16

No. of molecules of mass 70 = 9 ⇒ Relative probability = $\frac{9}{16} = 0.5625$

No. of molecules of mass 72 = 6 ⇒ Relative probability = $\frac{6}{16} = 0.3750$

No. of molecules of mass 74 = 1 ⇒ Relative probability = $\frac{1}{16} = 0.0625$

Cross-checking:

Total number of molecules = 9 + 6 + 1 = 16

Total probability of all outcomes = 0.5625 + 0.3750 + 0.0625 = 1.0000

Note that the total number of possible isotopic arrangements in the final molecule arises by

multiplying the number of choices for the first atom by the number of choices for the second. In this case four for the first times four for the second i.e. sixteen.

If the only way in which these molecules can be distinguished is by mass then the relative probabilities will be as shown on the right hand side of the lower part of the table – of the sixteen arrangements, nine correspond to a total molecular mass of 70, six correspond to a total mass of 72 and one corresponds to a total mass of 74.

1.2. Basic Statistics

Different physical situations encountered in nature are described by three types of statistics, *viz.*, *the Maxwell-Boltzmann (or M-B) statistics, the Bose-Einstein (or B-E) statistics and the Fermi-Dirac (or F-D) statistics.* The *M-B* statistics, developed long before the advent of quantum mechanics, is also called **classical statistics** whereas the **Bose-Einstein and Fermi-Dirac statistics** are collectively called **quantum statistics**. The characteristics of the three types of statistics are summed up as follows:

1. In **M-B** statistics, the particles are assumed to be distinguishable and any number of particles may occupy the same energy levels. Particles obeying **M-B** statistics are called *boltzmannons or maxwellons*.
2. In **B-E** statistics, the particles are indistinguishable and any number of particles may occupy a given energy level. This statistics is obeyed by particles having integral spin, such as hydrogen (H_2), Deuterium (D_2), nitrogen (N_2), helium-4 (He^4) and photons. Particles obeying **B-E** statistics are called *bosons*.
3. In **F-D** statistics, the particles are indistinguishable but only one particle may occupy a given energy level. This statistics is obeyed by particles having half-integral spin, e.g., the protons, electrons, helium-3 (He^3) and nitric oxide (NO). Particles obeying **F-D** statistics are called *fermions*.

Fermions are those species whose wave functions are *antisymmetric* with respect to the exchange of particles whereas **bosons** are those species whose wave functions are symmetric with respect to the exchange of particles.

1.3. Statistics of Particles

(i) Maxwell-Boltzmann Statistics

Consider a system of N *distinguishable* particles occupying energy levels $\epsilon_0, \epsilon_1, \epsilon_2$, etc. The total number of arrangements for placing n_0 particles in the ground state energy level ϵ_0 , n_1 particles in the first excited energy level ϵ_1 , n_2 particles in the second excited energy level ϵ_2 , and so on, is known as the **thermodynamics probability, W** , of the given macrostate. It is, in general, a very large number. Our problem is to determine W , i.e., to determine how many microstates correspond to a given macrostate. It can be shown that W is given by

$$W = \frac{N!}{n_1!n_2!n_3!\dots n_j!} = \frac{N!}{\prod n_i!} \quad (1)$$

Where $N = \sum n_i$

In Eq.1, N is the total number of particles and the summation is over all the energy levels. It is possible to realize a given energy level in more than one way, i.e., more than one quantum state has the same energy. When this happens, the energy level is said to be degenerate, let g_i be the **degeneracy (multiplicity)** of the energy level ϵ_i . This means that if there is one particle in the i th energy level, there are g_i ways of distributing it. For two particles in the i th level, there are g_i^2 possible distributions. Thus, for n_i particles in the i th level, there are $g_i^{n_i}$ possible distributions. Hence, the thermodynamic probability for the system of N particles is given by

$$W = N! \prod_i \frac{g_i^{n_i}}{n_i!} \times \text{constant} \quad (2)$$

It is well known that the entropy S and probability W of a given state of a system are related by the Boltzmann equation, the most famous equation in statistical mechanics, viz.,

$$S = k \ln W \quad (3)$$

The probability must be a maximum for an equilibrium state so that at equilibrium

$$S = k \ln W_{\max} \quad (4)$$

We are thus interested in finding a distribution that will make W a maximum. It is more convenient, however, to maximize the logarithm of W . It is known from calculus that at the maximum, the derivative of a function vanishes. Hence, at equilibrium,

$$\begin{aligned} d \ln W &= \frac{\partial \ln W}{\partial n_1} dn_1 + \frac{\partial \ln W}{\partial n_2} dn_2 + \dots \\ d \ln W &= \sum_i \frac{\partial \ln W}{\partial n_i} dn_i = 0 \end{aligned} \quad (5)$$

If we confine our investigation to a *closed system of independent particles*, it meets the following two requirements:

- (i) The total number of particles is *constant*, i.e.,

$$N = \sum_i n_i = \text{constant} \quad (6)$$

- (ii) The total energy, U , of the system is *constant*, i.e.,

$$U = \sum n_i \varepsilon_i = \text{constant} \quad (7)$$

The constancy of the total number of particles implies that

$$dN = \sum dn_i = 0 \quad (8)$$

And the constancy of the total energy implies that

$$dU = \sum dn_i \varepsilon_i = 0 \quad (9)$$

From Eq. 2, taking logarithms both sides, we get

$$\ln W = \ln N! + \sum_i n_i \ln g_i - \sum_i \ln n_i! + \text{constant} \quad (10)$$

Using *Stirling's approximation* according to which, for large x ,

$$\ln x! = x \ln x - x \quad (11)$$

Using this approximation for $\ln N!$, Eq. 10 becomes

$$\begin{aligned} \ln W &= \ln N! + \sum_i n_i \ln g_i - \sum_i n_i \ln n_i + \sum_i n_i + \text{constant} \\ \ln W &= (N \ln N - N) + \sum_i n_i \ln g_i - \sum_i n_i \ln n_i + N + \text{constant} \\ \ln W &= N \ln N + \sum_i n_i \ln g_i - \sum_i n_i \ln n_i + \text{constant} \end{aligned} \quad (12)$$

Differentiating and bearing in mind that N and g_i are constants, we get

$$d \ln W = \sum_i \ln g_i dn_i - \sum_i \ln n_i dn_i - \sum n_i d \ln n_i \quad (13)$$

Now,
$$\sum_i n_i d \ln n_i = \sum_i n_i \frac{dn_i}{n_i} = \sum_i dn_i = 0 \quad (14)$$

Hence, at equilibrium,

$$d \ln W = \sum \ln g_i dn_i - \sum \ln n_i dn_i = 0 \quad (15)$$

Eq. (15) gives the change in $\ln W$ which results when the number of particles in each energy level is varied.

If our system were *open*, then n_i would vary without restriction and the variations would be *independent* of one another. It would then be possible to solve **Eq. 15** by setting each of the

coefficients of the dn_i terms in Eq. 15 equal to zero. However, our system is not open but closed and since N is constant, the values of dn_i are not independent of one another, as is seen from Eq.14. Again, the energy of the system is constant, too.

The desired solution is obtained by applying the method of *Lagrange's undetermined multipliers*. Rewriting Eq. 15, we have

$$\sum_i \ln \frac{g_i}{n_i} dn_i = 0 \quad (16)$$

Multiplying Eqs. 8 and 9 by the arbitrary constants α and β (known as **Lagrange's undetermined multipliers**) and subtracting from Eq. 16, we get

$$\sum_i \left[\ln \frac{g_i}{n_i} - \alpha - \beta \epsilon_i \right] dn_i = 0 \quad (17)$$

We can now select values of α and β in such a manner that one of the terms in the summation (say, $i = 1$) is zero, the value of dn_i being immaterial. The remaining dn_i terms then become independent of one another since dn_i can be obtained from these dn_i terms (Eq. 8). We are now in a position to set each of the coefficients of dn_i in Eq. 17 equal to zero. Thus,

$$\ln \frac{g_i}{n_i} - \alpha - \beta \epsilon_i = 0 \quad \text{or} \quad \ln \frac{g_i}{n_i} = \alpha + \beta \epsilon_i \quad \text{or} \quad \ln n_i = \ln g_i - \alpha - \beta \epsilon_i \quad \text{or}$$

$$n_i = g_i e^{-\alpha - \beta \epsilon_i} \quad (18)$$

Eq. (18) which is one form of the **Boltzmann distribution law**, gives the **most probable distribution for a macrostate**, *i.e.*, it gives the occupation numbers of the molecular energy levels for the most probable distribution in terms of the energies ϵ_i , the degeneracy g_i and the undetermined multipliers α and β .

(ii) Bose – Einstein Statistics

Consider a system of N *indistinguishable* particles such that n_i particles are in the *i*th energy level with degeneracy g_i . The n_i particles have to be distributed among g_i states. For the sake of simplicity, imagine that the *i*th energy level has $g_i - 1$ partition which is sufficient to separate the energy level into g_i intervals. Now the possible number of distributions of n_i particles among the g_i states may be determined by permuting the array of partitions and particles. The total number of permutations of n_i particles and $(g_i - 1)$ partitions is $(n_i + g_i - 1)!$. However, *the partitions and the particles are indistinguishable*. This implies that interchanging two

partitions does not alter an arrangement; also interchanging two particles does not alter an arrangement. Hence, we must divide is $(n_i + g_i - 1)!$ by the number of permutations of the $(g_i - 1)$ partitions, viz., $(g_i - 1)!$ and the number of permutations of n_i particles, viz., $n_i!$ to obtain the number of possible arrangements of the n_i particles in the energy level ϵ_i . Thus,

$$\text{The number of arrangements} = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \quad (1)$$

As in the case of **Maxwell – Boltzmann** statistics, we assume that in the present case also the total number of particles is constant and the total energy of the system is also constant, i.e.,

$$N = \sum_i n_i = \text{constant}$$

$$U = \sum_i n_i \epsilon_i = \text{constant}$$

Thus, the thermodynamic probability **W** for the system of N particles (i.e., the number of ways of distributing N particles among the various energy levels) is given by

$$W = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \quad \text{x constant} \quad (2)$$

Taking logarithms of both sides of Eq. 2, we get

$$\ln W = \sum_i [\ln(n_i + g_i - 1)! - \ln n_i! - \ln(g_i - 1)!] + \text{constant} \quad (3)$$

Here, too, since n_i and g_i are very large numbers, we can invoke *Stirling's approximation*, viz.,

$\ln x! = x \ln x - x$, to obtain

$$\ln W = \sum_i [(n_i + g_i) \ln(n_i + g_i) - n_i \ln n_i - g_i \ln g_i] + \text{constant} \quad (4)$$

Where we have set $n_i + g_i - 1 = n_i + g_i$ and $g_i - 1 = g_i$. Since, n_i is very large, it can be treated as a *continuous variable*. Differentiation of Eq. 3, with respect to n_i and setting the differential equal to zero gives for the most probable thermodynamic state of the system,

$$\delta \ln W = \sum_i [\ln n_i - \ln(n_i + g_i)] \delta n_i = 0 \quad \text{or} \quad \sum_i \left[\ln \frac{n_i}{(n_i + g_i)} \right] \delta n_i = 0 \quad (5)$$

We know that,

$$\delta N = \sum_i \delta n_i = 0 \quad (6)$$

$$\delta U = \sum_i \epsilon_i \delta n_i = 0 \quad (7)$$

Applying the method of Lagrange's undetermined multipliers to Eqs. 5, 6 and 7, we get

$$\sum_i \left[\ln \frac{n_i}{(n_i + g_i)} + \alpha + \beta \epsilon_i \right] \delta n_i = 0 \quad (8)$$

Since the variations δn_i are independent of one another, hence

$$\ln \frac{n_i}{(n_i + g_i)} + \alpha + \beta \varepsilon_i = 0 \quad (9)$$

Whence $\ln \left[\frac{g_i}{n_i} + 1 \right] = \alpha + \beta \varepsilon_i$ or $\frac{g_i}{n_i} + 1 = e^{\alpha + \beta \varepsilon_i}$ (10)

$\therefore n_i = g_i / [\exp(\alpha + \beta \varepsilon_i) - 1]$ (11)

Eq. 11 is the expression for the most probable distribution of N particles among the various energy levels according to the **Bose – Einstein** statistics.

(iii) **Fermi – Dirac Statistics**

Consider that the n_i particles are distributed among the g_i states ($n_i < g_i$) where g_i , as before, is the degeneracy of the i^{th} energy level. Imagine that the particles are *indistinguishable*. This implies that the first particle may be placed in any one of the g_i states and for each one of these choices, the second particle may be placed in any one of the remaining $g_i - 1$ states, and so on. Thus, the number of arrangements is given by the expression $g_i! / (g_i - n_i)!$. Since the particles are *indistinguishable*, the above expression has to be divided by the possible number of permutations of n_i particles, *viz.*, $n_i!$. Hence, the number of arrangements of n_i particles in the i^{th} energy level is given by the expression, $g_i! / (n_i! (g_i - n_i)!)$.

Thus, the thermodynamics probability W for the system of N particles (i.e., the number of ways of distributing N particles among the various energy levels) is given by

$$W = \prod_i \frac{g_i!}{n_i! (g_i - n_i)!} \times \text{constant} \quad (1)$$

Taking logarithms of both sides of Eq. 1, we have

$$\ln W = \sum_i [\ln g_i! - \ln n_i! - \ln (g_i - n_i)!] + \text{constant} \quad (2)$$

Assuming that n_i , g_i and $g_i - n_i$ are very large, we can apply Stirling's approximation, obtaining

$$\ln W = \sum_i [(n_i - g_i) \ln (g_i - n_i) - n_i \ln n_i + g_i \ln g_i] + \text{constant} \quad (3)$$

Thus, for the most probable state,

$$\delta \ln W = \sum_i [\ln n_i - \ln (g_i - n_i)] \delta n_i = 0$$

or
$$\sum_i \left[\ln \frac{n_i}{(g_i - n_i)} \right] \delta n_i = 0 \quad (4)$$

Since $N = \sum_i n_i = \text{constant}$ and $U = \sum_i n_i \varepsilon_i = \text{constant}$,

Hence,
$$\delta N = \sum_i \delta n_i = 0 \text{ and } \delta U = \sum_i \varepsilon_i \delta n_i = 0 \quad (5)$$

Applying Lagrange's method of undetermined multipliers, we obtain

$$\sum_i \left[\ln \frac{n_i}{(g_i - n_i)} + \alpha + \beta \varepsilon_i \right] \delta n_i = 0 \quad (6)$$

Since the variations δn_i are independent of one another, hence.

$$\ln \frac{n_i}{(g_i - n_i)} + \alpha + \beta \varepsilon_i = 0 \text{ or } \ln[(g_i/n_i) - 1] = \alpha + \beta \varepsilon_i$$

or
$$(g_i/n_i) - 1 = e^{\alpha + \beta \varepsilon_i} \quad (7)$$

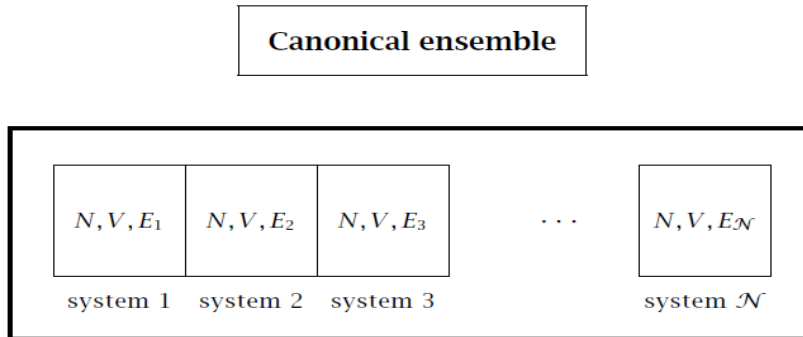
$\therefore n_i = g_i / [\text{Exp}(\alpha + \beta \varepsilon_i) + 1] \quad (8)$

Eq. 8, is the expression for the most probable distribution of N particles among the energy levels according to the **Fermi – Dirac** statistics.

1.4. Partition Function

In statistical mechanics, the **partition function**, q , is an important quantity that encodes the statistical properties of a system in thermodynamic equilibrium. It is a function of temperature and other parameters, such as the volume enclosing a gas. Most of the aggregate thermodynamic variables of the system, such as the total energy, free energy, entropy, and pressure, can be expressed in terms of the partition function or its derivatives.

There are actually several different types of partition functions, each corresponding to different types of statistical ensemble (or, equivalently, different types of free energy.) The **canonical partition function** applies to a canonical ensemble, in which the system is allowed to exchange heat with the environment at fixed temperature, volume, and number of particles.

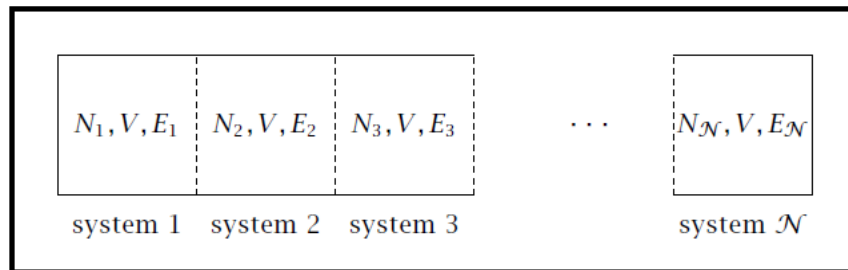


Suppose we have a thermodynamically large system that is in constant thermal contact with the environment, which has **temperature T** , with both the volume of the system and the number of constituent particles fixed. This kind of system is called a **canonical ensemble**. Let us label with n ($n = 1, 2, 3, \dots$) the *exact* states (**microstates**) that the system can occupy, and denote the total energy of the system when it is in microstate n as E_n . Generally, these microstates can be regarded as discrete quantum states of the system.

Canonical ensemble: The word ‘ensemble’ means ‘collection’ but it has been sharpened and refined into a precise significance. The word ‘canon’ means ‘according to rule’. We take a closed system of specified volume, composition and temperature which can be replicated to N times. All the identical closed systems are regarded as being in thermal contact with one another, so they can exchange energy. The total energy of all the systems is E and, because they are in thermal equilibrium with one another, they all have the same temperature, T . This imaginary collection of replications of the actual system with a common temperature is called the **Canonical ensemble**.

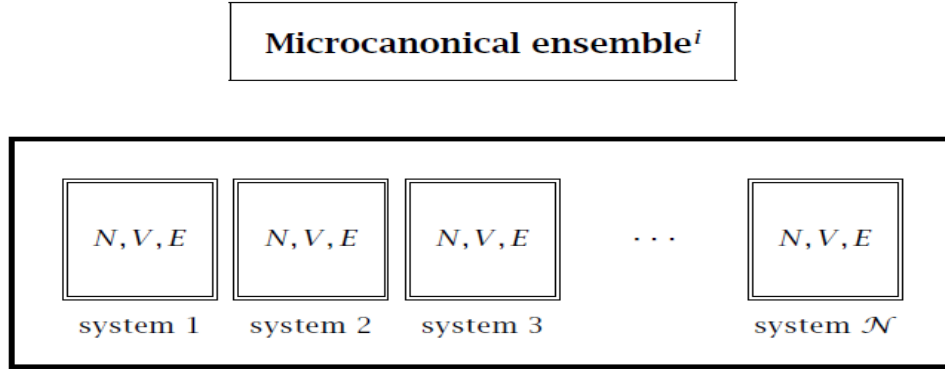
The **grand canonical partition function** applies to a grand canonical ensemble, in which the system can exchange both heat and particles with the environment, at fixed temperature, volume, and chemical potential. Other types of partition functions can be defined for different circumstances.

Grand canonical ensemble



In the **grand canonical ensemble** the volume and temperature of each system is the same, but they are open, which means that matter can be imagined as able to pass between the systems; the composition of each one may fluctuate, but now the chemical potential is the same in each system

There are two other important ensembles. They are **micro canonical ensemble** and **grand canonical ensemble**. In the **microcanonical ensemble** the condition of constant temperature is replaced by requirement that all the systems should have exactly the same energy; each system is individually isolated.



Micro canonical Ensemble: **N, V, E common**

Canonical ensemble: **N, V, T common**

Grand canonical ensemble: **μ, V, T common**

Since an ensemble is a collection of imaginary replications of the system, so we are free to let the number of members be as large as we like; when appropriate, we can let N become infinite. The number of members of the ensemble in a state with energy E_i is denoted n_i , and we can speak of the configuration of the ensemble.

1.5. Thermodynamic Functions

We can use the **Boltzmann** distribution law and the related partition functions to calculate the macroscopic (thermodynamic) properties such as internal energy, enthalpy, entropy, free energy, *etc.*, of matter from molecular properties. The partition functions are, therefore, of great importance in statistical thermodynamics.

Internal Energy, U : The internal energy, U , of a system consisting of N independent particles (atoms or molecules) is equal to the sum of the energies of individual particles. Thus,

$$U = \sum_i N_i \epsilon_i = N \bar{\epsilon} \quad (1)$$

Where $\bar{\epsilon}$ is the *average energy* of the particles defined by

$$\bar{\epsilon} = \frac{\sum_i N_i \epsilon_i}{\sum_i N_i} = \frac{\sum_i \epsilon_i e^{-\beta \epsilon_i}}{\sum_i e^{-\beta \epsilon_i}} = \frac{\sum_i \epsilon_i e^{-\beta \epsilon_i}}{q} \quad (2)$$

Now,

$$\left(\frac{\partial q}{\partial \beta} \right)_V = \frac{\partial [\sum e^{-\beta \epsilon_i}]}{\partial q} = \sum_i \epsilon_i e^{-\beta \epsilon_i} \quad (3)$$

where the differentiation is carried out at *constant volume* since the energies ϵ_i depend upon the volume. Hence,

$$\bar{\epsilon} = \frac{1}{q} \left(\frac{\partial q}{\partial \beta} \right)_V = - \left(\frac{\partial \ln q}{\partial \beta} \right)_V \quad (4)$$

Therefore, from Eqs. 1 and 4 for a system containing N particles,

$$U = -N \left(\frac{\partial \ln q}{\partial \beta} \right)_V \quad (5)$$

Since $\beta = 1/kT$ and $Nk = nR$ (where n is the number of moles), we have

$$U = -nR \left(\frac{\partial \ln q}{\partial (1/T)} \right)_V$$

Or
$$U = nRT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V \quad (6)$$

Molar Heat Capacity, C_V : For one mole of a system ($n = 1$), differentiation of U with respect to T at constant V , yields the molar heat capacity C_V . Hence,

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = R \frac{\partial}{\partial T} \left[T^2 \left(\frac{\partial \ln q}{\partial T} \right)_V \right] = \frac{R}{T^2} \left[\frac{\partial^2 \ln q}{\partial \left(\frac{1}{T} \right)^2} \right]_V \quad (7)$$

Entropy, S : If the particles are considered *indistinguishable*, then the thermodynamic probability for the system, must be divided by $N!$ to yield the new thermodynamic probability of the **Boltzmann** distribution as

$$W = \prod_i g^{n_i} / n_i! \quad (8)$$

Using the **Boltzmann** equation for entropy, *viz.*,

$$S = k \ln W \quad (9)$$

We have,
$$S = k (\sum_i n_i \ln g_i - \sum_i \ln n_i!) \quad (10)$$

Using the Stirling approximation, *viz.*,

$$\ln n_i! = n_i \ln n_i - n_i \quad (11)$$

We obtain
$$S = k \sum_i n_i \ln (g_i/n_i) + kN \quad (12)$$

Since,
$$\ln (g_i/n_i) = \ln (q/N) + \epsilon_i/kT$$

Substituting in Eq. 12, we have

$$S = k \sum_i n_i \ln q/N + k \sum_i \frac{n_i \epsilon_i}{kT} + kN = kN \ln \frac{q}{N} + \frac{U}{T} + kN \quad (13)$$

For n moles of the system, $kN = nR$. Also, using the expression for U given by Eq. 6, we have

$$S = nR \left[\ln \frac{q}{N} + T \left(\frac{\partial \ln q}{\partial T} \right)_V + 1 \right] \quad (14)$$

Helmholtz Function or Work Function, A: $A = U - TS$

Hence, after substituting for U from Eq. 6 and for S from Eq. 14,

We have
$$A = nRT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V - nRT \left[\ln \frac{q}{N} + \left(\frac{\partial \ln q}{\partial T} \right)_V + 1 \right]$$

$$A = -nRT \left[\ln \frac{q}{N} + 1 \right] \quad (15)$$

Since $nR = Nk$, we can write Eq. 15 as

$$A = -kT [\ln q^N - (N \ln N - N)] = -kT \ln (q^N / N!) \quad (16)$$

$$A = -kT \ln Q \quad (17)$$

Where Q is the *molar* partition function, *i.e.*, the partition function for one mole, *viz.*, for Avogadro's number of particles and q is the *molecular* partition function, *viz.*, the partition function for a single molecule.

Pressure, P: By definition, pressure is given by

$$P = - \left(\frac{\partial A}{\partial V} \right)_T \quad (18)$$

Differentiating Eq. 16 with respect to V at constant T , we have

$$\left(\frac{\partial A}{\partial V} \right)_T = -nRT \left(\frac{\partial \ln q}{\partial V} \right)_T \quad (19)$$

\therefore
$$P = -nRT \left(\frac{\partial \ln q}{\partial V} \right)_T \quad (20)$$

Gibbs Function, G: The Gibbs free energy defined as

$$G = H - TS = (U + PV) - TS = A + PV$$

Substituting Eq. 15 for A and Eq. 20 for P , we obtain

$$G = -nRT \left[\ln \frac{q}{N} + 1 - V \left(\frac{\partial \ln q}{\partial V} \right)_T \right] \quad (21)$$

Enthalpy, H: Enthalpy is defined as $H = U + PV$

Substituting Eq. 6 for U and Eq. 20 for P , we have

$$H = nRT \left[\left(\frac{\partial \ln q}{\partial \ln T} \right)_V + \left(\frac{\partial \ln q}{\partial \ln V} \right)_T \right] \quad (22)$$

The chemical potential

In equilibrium, a system is in steady state. Thus, a simple chemical reaction in equilibrium, of the form



has to have as many molecules going from $\mathbf{A} \rightarrow \mathbf{B}$ as from $\mathbf{B} \rightarrow \mathbf{A}$ in equilibrium. Another way to say this is that there should be no change in free energy for a reacting molecule, or that the total chemical potential (change in free energy per molecule) is zero

$$\mu_A = \mu_B \quad (2)$$

in equilibrium. The equilibrium condition can be related to the free energy for the different ensembles by

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{T,P} = \left(\frac{\partial A}{\partial N} \right)_{T,V} = \left(\frac{\partial E}{\partial N} \right)_{S,V} \quad (3)$$

For gas phase reactions in the Canonical ensemble, where $A = -kT \ln Q$, and $Q = \frac{q^N}{N!}$ the chemical potential is

$$\mu = \left(\frac{\partial A}{\partial N} \right) = -kT \frac{\partial \ln \left(\frac{q^N}{N!} \right)}{\partial N} \quad (4)$$

using Stirling's approximation, $\ln N! = N \ln N - N$. This gives a simple relation for reacting gas particles, for which the system partition function $Q = Q_A Q_B$ is the product of the partition function for each species. In this case, the condition for equilibrium

$$\begin{aligned} -kT \frac{Q}{N_A} &= -kT \frac{Q}{N_B} \\ \ln \left(\frac{q_A}{N_A} \right) &= \ln \left(\frac{q_B}{N_B} \right) \\ \left(\frac{q_A}{N_A} \right) &= \left(\frac{q_B}{N_B} \right) \end{aligned} \quad (5)$$

where N_A and N_B are the number of \mathbf{A} and \mathbf{B} molecules respectively

The equilibrium constant

The equilibrium condition can be written as a constant with respect to N because q_A and q_B are both single particle partition functions with no N dependence

$$K_N = \frac{N_B}{N_A} = \frac{q_B}{q_A} \quad (6)$$

The equilibrium constant can also be written in terms of concentrations, which are independent of volume. Substituting the density $\rho = N/V$

$$K_C = \frac{\rho_B}{\rho_A} = \frac{q_B/V}{q_A/V} = \frac{q_B}{q_A} \quad (7)$$

The single particle partition function q is equal to the volume times a function of T , so that q/V is independent of volume, which makes K_C also a constant with respect to volume. For simple reactions, given by Eq. 7, these two constants are equal, $K_N = K_C$.

We can also find an equilibrium pressure constant, using the ideal gas relation $PV = NkT$,

$$K_P = \frac{P_B}{P_A} = \frac{N_B kT/V}{N_A kT/V} = \frac{N_B}{N_A} \quad (8)$$

which again reduces to K_N and K_C .

Thermodynamic Properties of an Ideal Monoatomic Gas

A monoatomic gas, such as helium, neon, argon, etc., has only translational and electronic degree of freedom. Hence, molecular partition function is given by

$$q = q_{tr} q_{el} \dots \dots \dots (26)$$

However, we know that

$$q_{el} = g_0$$

where g_0 is the degeneracy of the electronic ground state. Hence

$$q = g_0 q_{tr} \dots \dots \dots (27)$$

Using Eq. for q_{tr}

$$q_{tr} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \times V$$

$$q = g_0 \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \times V \dots \dots \dots (28)$$

Taking $g_0 = 1$ for most atomic systems,

$$q = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \times V \dots \dots \dots (29)$$

According to Eq. 6,

$$U = nRT^2 \left(\frac{\partial \ln q}{\partial T}\right)_v = nRT^2 \left(\frac{3}{2T}\right) = \left(\frac{3}{2}\right) nRT \dots \dots \dots (30)$$

The molar heat capacity is given by

$$C_V = \left(\frac{\partial U}{\partial T}\right)_v = \frac{3R}{2} \dots \dots \dots (31)$$

Entropy is obtained by substituting Eq. 29 in Eq. 15

$$S = nR \left[\frac{5}{2} - \ln(Nh) + \left(\frac{3}{2}\right) \ln(2\pi mk) + \left(\frac{3}{2}\right) \ln T + \ln V \right] \dots \dots \dots (32)$$

For one mole of an ideal gas,

$$V = \frac{RT}{P}$$

$$\ln V = \ln R + \ln T - \ln P = \ln N_A + \ln k + \ln T - \ln P$$

Substituting in Eq. 32 and simplifying, we get

$$S = nR \left[\frac{5}{2} + \left(\frac{5}{2} \right) \ln T - \ln P + \left(\frac{5}{2} \right) \ln k + \left(\frac{3}{2} \right) \ln 2\pi m - 3 \ln h \right] \dots \dots \dots (33)$$

From Eq. 22, the pressure is given by

$$P = nRT \left(\frac{\partial \ln q}{\partial V} \right)_T = nRT \left(\frac{1}{V} \right) = \frac{nRT}{V} \dots \dots \dots (34)$$

$$\text{or} \quad PV = nRT$$

which is the *equation of state* for n moles of an ideal gas.

Substituting Eqs. 30 and 34, in the relation $H = U + PV$, we have

$$H = \left(\frac{3}{2} \right) nRT + \left(\frac{nRT}{V} \right) V = \left(\frac{3}{2} \right) nRT + nRT = \left(\frac{5}{2} \right) nRT \dots \dots \dots (35)$$

From Eq. 17, the Helmholtz function

$$A = -nRT \left[\ln \left(\frac{q}{N} \right) + 1 \right] \dots \dots \dots (36)$$

Using Eq. 28 and the equation of state, $PV = RT$, we have

$$A = -nRT \left[1 - 3 \ln h + \left(\frac{3}{2} \right) \ln 2\pi m + \left(\frac{5}{2} \right) \ln k + \left(\frac{5}{2} \right) \ln T - \ln P \right] \dots \dots \dots (37)$$

From Eqs. 37 and 23, the Gibbs function for an ideal gas is given by

$$G = -nRT \ln \left(\frac{q}{N} \right) \dots \dots \dots (38)$$

This is further simplified to give

$$G = -nRT \left[-3 \ln h + \left(\frac{3}{2} \right) \ln 2\pi m + \left(\frac{5}{2} \right) \ln k + \left(\frac{5}{2} \right) \ln T - \ln P \right] \dots \dots \dots (39)$$

Statistical Derivation of the Equation of State for Non-ideal Fluids

How can a gas have three different volumes at the same time? The answer is that the term “fluid,” meaning *that which flows*, is more general than “gas.” the term fluid includes both liquids and gases sometimes we call it non-ideal gas.

The relation between pressure p and partition function Q is a very important route to the equations of state of real gases in terms of intermolecular forces, for the latter can be built into Q . The partition function for a gas of independent particles leads to the perfect gas equation of state, $pV = nRT$. Real gases differ from perfect gases in their equations of state.

$$\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots$$

where B is the second virial coefficient and C is the third virial coefficient.

The total kinetic energy of a gas is the sum of the kinetic energies of the individual molecules. Therefore, even in a real gas the canonical partition function factorizes into a part arising from the kinetic energy, which is the same as for the perfect gas, and a factor called the configuration integral, Z , which depends on the intermolecular potentials.

$$Q = \frac{Z}{\Lambda^{3N}}$$

Where Λ the *thermal de Broglie wavelength*: By comparing this equation with ($Q = q^N/N!$, with $q = V/\Lambda^3$), we see that for a perfect gas of atoms (with no contributions from rotational or vibrational modes)

$$Z = \frac{V^N}{N!}$$

For a real monatomic gas (for which the intermolecular interactions are isotropic), Z is related to the total potential energy E_p of interaction of all the particles by

$$Z = \frac{1}{N!} \int e^{-\beta E_p} d\tau_1 d\tau_2 \dots d\tau_N$$

where $d\tau_i$ is the volume element for atom i . The physical origin of this term is that the probability of occurrence of each arrangement of molecules possible in the sample is given by a Boltzmann distribution in which the exponent is given by the potential energy corresponding to that arrangement.

The second virial coefficient then turns out to be

$$B = -\frac{N\Lambda}{2V} \int f d\tau_1 d\tau_2$$

The quantity f is the Mayer f -function: it goes to zero when the two particles are so far apart that $E_p = 0$. When the intermolecular interaction depends only on the separation r of the particles and

not on their relative orientation or their absolute position in space, as in the interaction of closed-shell atoms in a uniform sample, the volume element simplifies to $4\pi r^2 dr$ (because the integrals over the angular variables in $d\tau = r^2 dr \sin \theta d\theta d\phi$ give a factor of 4π).

$$B = -2\pi N_A \int_0^{\infty} f r^2 dr \quad f = e^{-\beta E_p} - 1$$

How this equation is used by considering the hard-sphere potential, which is infinite when the separation of the two molecules, r , is less than or equal to a certain value σ , and is zero for greater separations. Then

$$\begin{aligned} e^{-\beta E_p} = 0 & \quad f = -1 \quad \text{when } r \leq \sigma \quad (\text{and } E_p = \infty) \\ e^{-\beta E_p} = 1 & \quad f = 0 \quad \text{when } r > \sigma \quad (\text{and } E_p = 0) \end{aligned}$$

$$B = 2\pi N_A \int_0^{\sigma} r^2 dr = \frac{2}{3} \pi N_A \sigma^3$$

This calculation of B raises the question as to whether a potential can be found that, when the virial coefficients are evaluated, gives the van der Waals equation of state.

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

Such a potential can be found for weak attractive interactions ($a \ll RT$): it consists of a hard-sphere repulsive core and a long-range, shallow attractive region. A further point is that, once a second virial coefficient has been calculated for a given intermolecular potential, it is possible to calculate other thermodynamic properties that depend on the form of the potential. For example, it is possible to calculate the isothermal Joule–Thomson coefficient, μ_T from the thermodynamic relation.

$$\lim_{p \rightarrow 0} \mu_T = B - T \frac{dB}{dT}$$

Equilibrium Constants for Gas Phase Reactions

Classical thermodynamics is very useful when applied to chemical or physical processes that are in a state of equilibrium. How well does statistical thermodynamics apply to equilibrium?



Where A and B represent reactants, C and D are the products, and ν_A , ν_B , ν_C , and ν_D are the molar coefficients of the balanced chemical reaction.

Algebraically,

$\nu_C C + \nu_D D - \nu_A A - \nu_B B = 0$ It is the convention to subtract the reactants from the products.

$$\sum_{i=1}^{\text{no. of components}} \nu_i \cdot \mu_i = 0$$

$$\nu_C \mu_C + \nu_D \mu_D - \nu_A \mu_A - \nu_B \mu_B = 0$$

The overall partition function of the system Q_{sys} can be written as the product of the molecular partition functions of each component:

$$\begin{aligned} Q_{\text{sys}} &= \prod_{\text{components}} \frac{(Q_i)^{N_i}}{N_i!} \\ &= \frac{Q_A(N_A, V, T)^{N_A}}{N_A!} \cdot \frac{Q_B(N_B, V, T)^{N_B}}{N_B!} \cdot \frac{Q_C(N_C, V, T)^{N_C}}{N_C!} \cdot \frac{Q_D(N_D, V, T)^{N_D}}{N_D!} \end{aligned}$$

In this equation, we are labeling each molecular partition function with the label of the relevant component. Also, each component is occupying the same volume and has the same temperature (otherwise the system is not at equilibrium), but that each component has its own characteristic amount N_i at equilibrium. Statistical thermodynamics gives an expression for the chemical potential of a component:

$$\mu_i = -kT \ln \left(\frac{\partial Q}{\partial N_i} \right)_{N_{j \neq i}, V, T}$$

where in the case of a multicomponent mixture, the partial derivative is taken with respect to only one component, N_i , and the other components remain as constants. This has the effect of eliminating all other species' partition functions from the evaluation of each particular μ_i .

$$\mu_i \approx -kT \ln \frac{Q_i(V, T)}{N_i}$$

Substituting for each in equation

$$\nu_C \left(-kT \ln \frac{Q_C(V, T)}{N_C} \right) + \nu_D \left(-kT \ln \frac{Q_D(V, T)}{N_D} \right) - \nu_A \left(-kT \ln \frac{Q_A(V, T)}{N_A} \right) - \nu_B \left(-kT \ln \frac{Q_B(V, T)}{N_B} \right) = 0$$

The $-kT$ terms cancel to yield

$$\nu_C \ln \frac{Q_C(V, T)}{N_C} + \nu_D \ln \frac{Q_D(V, T)}{N_D} - \nu_A \ln \frac{Q_A(V, T)}{N_A} - \nu_B \ln \frac{Q_B(V, T)}{N_B} = 0$$

We can use the properties of logarithms to take each coefficient and make it an exponent inside the logarithm term.

$$\ln \left(\frac{Q_C}{N_C} \right)^{v_C} + \ln \left(\frac{Q_D}{N_D} \right)^{v_D} - \ln \left(\frac{Q_A}{N_A} \right)^{v_A} - \ln \left(\frac{Q_B}{N_B} \right)^{v_B} = 0$$

using the rule that $\ln a + \ln b = \ln ab$

$$\ln \left[\left(\frac{Q_C}{N_C} \right)^{v_C} \cdot \left(\frac{Q_D}{N_D} \right)^{v_D} \right] = \ln \left[\left(\frac{Q_A}{N_A} \right)^{v_A} \cdot \left(\frac{Q_B}{N_B} \right)^{v_B} \right]$$

If the logarithms of two products are the same (as the above equation indicates), then the arguments of the two individual logarithms are the same. Another way to put this is that we can take the inverse logarithm of both sides of the above equation and still have an equality.

$$\left(\frac{Q_C}{N_C} \right)^{v_C} \cdot \left(\frac{Q_D}{N_D} \right)^{v_D} = \left(\frac{Q_A}{N_A} \right)^{v_A} \cdot \left(\frac{Q_B}{N_B} \right)^{v_B}$$

At this point, we will rearrange equation to bring all of the partition functions Q_i to one side and all of the amounts N_i to the other. The exponents v_i will appear on both sides (as a consequence of the algebra of exponents).

$$\frac{(Q_C)^{v_C} \cdot (Q_D)^{v_D}}{(Q_A)^{v_A} \cdot (Q_B)^{v_B}} = \frac{(N_C)^{v_C} \cdot (N_D)^{v_D}}{(N_A)^{v_A} \cdot (N_B)^{v_B}}$$

The partition functions Q_i are constants that are characteristic of each chemical species, and the coefficients v_i are characteristic of the balanced chemical reaction. Therefore, the left side of equation is some constant that is characteristic of the chemical reaction. This Equation shows that the characteristic of constant is related to the amounts of each chemical species *when the reaction reaches chemical equilibrium*, even though each individual Q_i itself is defined in terms of the molecule, not any extent of reaction! Since the fraction in terms of the Q_i values has a characteristic value, then the fraction in terms of the amounts N_i at equilibrium must also have a characteristic value. This value is called the *equilibrium constant* for the reaction.

For an ideal gas, the partition function Q is a simple function of volume (again, from q_{trans}) times a more complicated function of temperature (from several other q 's):

$$Q = f(T) \cdot V$$

It is convenient to divide each molecular Q by volume to get a volume independent partition function:

$$\frac{Q}{V} = f(T)$$

By substituting this volume-independent partition function into the partition function expression for the equilibrium constant, labeled $K(T)$, which is characteristic of the chemical species in the reaction and dependent solely on T .

$$K(T) \equiv \frac{\left(\frac{Q_C}{V}\right)^{\nu_C} \cdot \left(\frac{Q_D}{V}\right)^{\nu_D}}{\left(\frac{Q_A}{V}\right)^{\nu_A} \cdot \left(\frac{Q_B}{V}\right)^{\nu_B}}$$

Equilibrium constants can also be expressed in terms of the partial pressures of the gas-phase reactants and products. The pressure-base equilibrium constant, K_p , is related to K_c by the expression

$$K_p = K_c \cdot (kT)^{\sum \nu_i}$$

where $\sum \nu_i$ represents the proper combination of the stoichiometric coefficients of gas-phase substances in the balanced chemical reaction. Remember that ν_i values are positive for products and negative for reactants.

Surface Chemistry

Topic to be covered:

2. Interfacial Structure
 - 2.1. Surface Tension and Surface Free Energy
 - 2.2. Methods of Surface Tension Measurement
 - 2.3. Nature and Thermodynamics of Liquid-Gas Interface
 - 2.4. The Surface Tension of Solutions
 - 2.5. Surfaces of Solids
 - 2.6. Adsorption at the Solid Solution Interface

Introduction

Surface chemistry can be roughly defined as the study of chemical reactions at interfaces. It is closely related to surface engineering, which aims at modifying the chemical composition of a surface by incorporation of selected elements or functional groups that produce various desired effects or improvements in the properties of the surface or interface. Surface chemistry also overlaps with electrochemistry. Surface science is of particular importance to the field of heterogeneous catalysis.

In this chapter we will discuss the physical chemistry of surfaces in a broad sense. Although an obvious enough point, it is perhaps worth noting that in reality we will always be dealing with the interface between two phases (liquid-gas, solid-liquid and solid-gas) and that, in general, the properties of an interface will be affected by physical or chemical changes in either of the two phases involved.

2. Interfacial Structure

A phase defined as a part of a system that was "homogeneous throughout." Such a definition implies that the matter deep in the interior of a phase is subject to exactly the same conditions as the matter at the exterior which forms the surface. An interface is a surface forming a common boundary among two different phases of matter, such as an insoluble solid and a liquid, two immiscible liquids, a liquid and an insoluble gas or a liquid and vacuum. The importance of the interface depends on the type of system: the bigger the quotient area/volume, the more effect the surface phenomena will have. This is clearly impossible in any case, since the molecules (or

ions) in the interior are surrounded on all sides by the uniform field of force of neighbor molecules (or ions) of the same substance. The molecules at the surface were bounded on one side by neighbors of the same kind but on the other side by an entirely different sort of environment.

Consider, for example, the surface of a liquid in contact with its vapor, shown in figure below. A molecule in the interior of the liquid is in a uniform field of force. A molecule at the surface is subject to a net attraction toward the bulk of the liquid, which is not compensated by an equal attraction from the more highly dispersed vapor molecules. Thus all liquid surfaces, in the absence of other forces, tend to contract to the minimum area. For example, freely suspended volumes of liquid assume a spherical shape, since the sphere has the minimum surface-to-volume ratio.

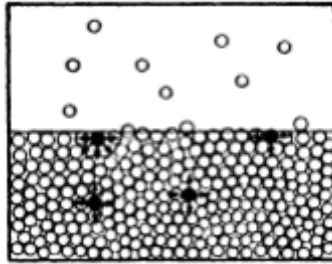


Figure: Liquid-vapor interfaces.

In order to extend the area of an interface like that in figure that is to bring molecules from the interior into the surface, works must be done against the cohesive forces in the liquid. It follows that the surface portions of the liquid have a higher free energy than the bulk liquid. This extra surface free energy is more usually described by saying that there is a *surface tension*, acting parallel to the surface, which opposes any attempt to extend the interface.

2.1. Surface Tension and Surface Free Energy

Although referred to as a free energy per unit area, surface tension may equally well be thought of as a force per unit length. Two serve to illustrate these viewpoints. Consider, first, a soap film stretched over a wire frame, one end of which is movable (Fig.). Experimentally one observes that a force is acting on the movable member in the direction opposite to that of the arrow in the diagram. If the value of the force per unit length is denoted by γ , then the work done in extending the movable member a distance dx is

$$\text{Work} = \gamma dx = \gamma dA \quad (1)$$

Where $dA = ldx$ is the change in area. In the second formulation, γ appears to be energy per unit area.

A second illustration involves the soap bubble. We will choose to think of γ in terms of energy per unit area. In the absence of gravitational or other fields, a soap bubble is spherical, as this is the shape of minimum surface area for an enclosed volume. A soap bubble of radius r has a total surface free energy of $4\pi r^2\gamma$ and, if the radius were to decrease by dr , then the change in surface free energy would be $8\pi r\gamma dr$. Since shrinking decreases the surface energy, the tendency to do so must be balanced by a pressure difference across the film



Figure: A soap film stretched across a wire frame with one movable side.

ΔP such that the work against this pressure $\Delta P 4\pi r^2 dr$ is just equal to the decrease in surface free energy. Thus

$$\Delta P 4\pi r^2 dr = 8\pi r\gamma dr \quad (2)$$

Or

$$\Delta P = 2\gamma/r \quad (3)$$

One thus arrives at the important conclusion that the smaller the bubble, the greater the pressure of the air inside relative to that outside.

The forgoing examples illustrate the point that equilibrium surfaces may be treated using either the mechanical concept of surface tension or the mathematically equivalent concept of surface free energy. A similar duality of viewpoint can be argued on a molecular scale so that the decision as to whether *surface tension* or *surface free energy* is the more fundamental concept becomes somewhat a matter of individual taste. The term surface tension is the older of the two; it goes back to early ideas that the surface of a liquid had some kind of contractile “skin”. *Surface free energy* implies only that work is required to bring molecules from the interior of the phase to the surface. Table given below shows surface tension of some liquids.

Surface tension of liquids at 20 °C

Liquid	$\gamma/(10^{-3} \text{ N/m})$	Liquid	$\gamma/(10^{-3} \text{ N/m})$
Acetone	23.70	Ethyl ether	17.01
Benzene	28.85	<i>n</i> -Hexane	18.43
Carbon tetrachloride	26.95	Methyl alcohol	22.61
Ethyl acetate	23.9	Toluene	28.5
Ethyl alcohol	22.75	Water	72.75

2.2. Methods of Surface Tension Measurement

(i) Capillary-rise Method

A capillary tube of radius r is vertically inserted into a liquid. The liquid rises to a height h and forms a concave meniscus. The surface tension (γ) acting along the inner circumference of the tube exactly supports the weight of the liquid column.

By definition, surface tension is force per 1 cm acting at a tangent to the meniscus surface. If the angle between the tangent and the tube wall is θ , the vertical component of surface tension is $\gamma \cos \theta$. The total surface tension along the circular contact line of meniscus is $2\pi r$ times. Therefore,

$$\text{Upward force} = 2\pi r \gamma \cos \theta$$

where r is the radius of the capillary. For most liquids, θ is essentially zero, and $\cos \theta = 1$. Then the upward force reduces to $2\pi r \gamma$.

The downward force on the liquid column is due to its weight which is *mass* \times *gravity*. Thus,

$$\text{Downward force} = h\pi r^2 dg$$

where d is the density of the liquid.

But

$$\text{Upward force} = \text{Downward force}$$

or

$$2\pi r \gamma = h\pi r^2 dg$$

$$\gamma = hrdg/2$$

In order to know the value of γ , the value of h is found with the help of a travelling microscope and density (d) with a pycnometer.

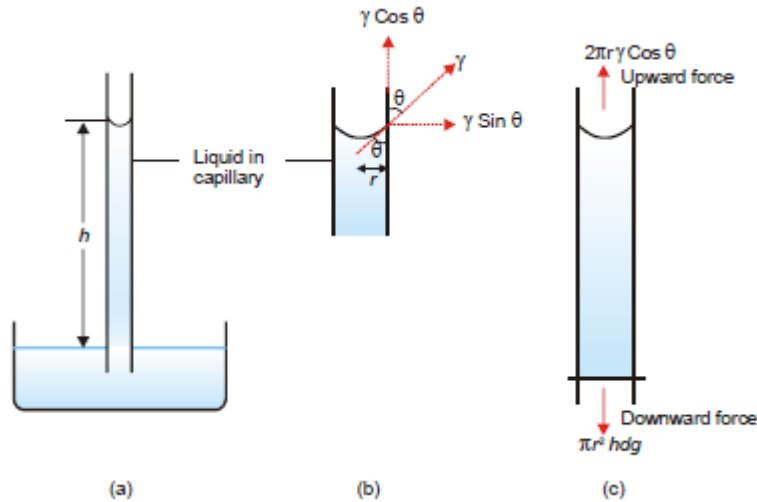


Figure: (a) Rise of liquid in a capillary tube; (b) Surface tension (γ) acts along tangent to meniscus and its vertical component is $\gamma \cos \theta$; (c) Upward force $2\pi r \gamma \cos \theta$ counter balances the downward force due to weight of liquid column, $\pi r^2 h d g$.

PROBLEM 1. A capillary tube of internal diameter 0.21 mm is dipped into a liquid whose density is 0.79 g cm^{-3} . The liquid rises in this capillary to a height of 6.30 cm. Calculate the surface tension of the liquid. ($g = 980 \text{ cm sec}^{-2}$).

SOLUTION

We know:

$$\gamma = h r d g / 2$$

Where, h = height of liquid in capillary in centimeters; r = radius of capillary in centimeters; d = density of liquid in g cm^{-3} ; g = acceleration due to gravity in cm sec^{-2}

Substituting the values from the above example, $h = 6.30 \text{ cm}$

$$r = 0.21/2 \times 1/10 = 0.0105 \text{ cm}$$

$$d = 0.79 \text{ g.cm}^{-3}$$

$$g = 980 \text{ cm.sec}^{-2}$$

Substituting these in above eq.

$$\gamma = (6.30 \times 0.0105 \times 0.79 \times 980) / 2$$

$$\gamma = 25.6 \text{ dynes cm}^{-1}$$

(ii) Drop Formation Method

A drop of liquid is allowed to form at the lower end of a capillary tube. The drop is supported by the upward force of surface tension acting at the outer circumference of the tube. The weight of the drop (mg) pulls it downward. When the two forces are balanced, the drop breaks. Thus at the point of breaking,

$$m g = 2 \pi r \gamma \quad (1)$$

where m = mass of the drop; g = acceleration due to gravity; r = outer radius of the tube

The apparatus employed is a glass pipette with a capillary at the lower part. This is called a **Stalagmometer** or **Drop pipette**. It is cleaned, dried and filled with the experimental liquid, say upto mark A. Then the surface tension is determined by one of the two methods given below.

(a) **Drop-weight Method.** About 20 drops of the given liquid are received from the drop-pipette in a weighing bottle and weighed. Thus weight of one drop is found. The drop-pipette is again cleaned and dried. It is filled with a second reference liquid (say water) and weight of one drop determined as before. Then from equation (1)

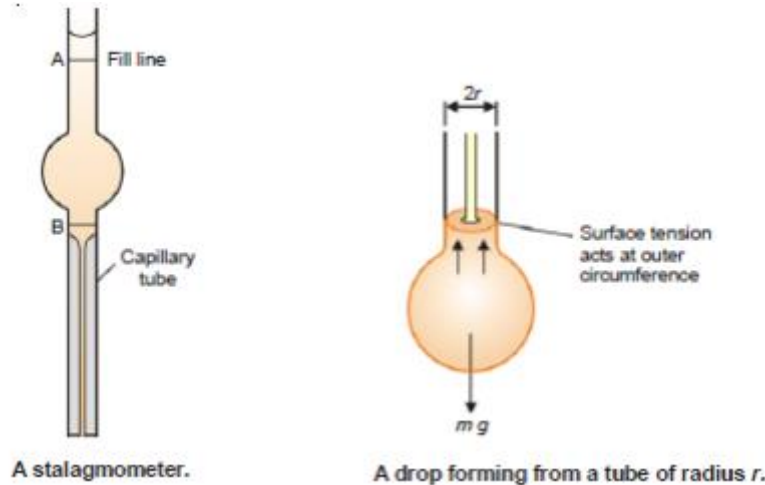
$$m_1 g = 2 \pi r \gamma_1 \quad (2)$$

$$m_2 g = 2 \pi r \gamma_2 \quad (3)$$

Dividing (2) by (3)

$$\gamma_1/\gamma_2 = m_1/m_2$$

Knowing the surface tension of reference liquid from Tables, that of the liquid under study can be found.



(b) **Drop-number Method.** The drop-pipette is filled upto the mark A with the experimental liquid (No.1). The number of drops is counted as the meniscus travels from A to B. Similarly, the pipette is filled with the reference liquid (No.2) as the meniscus passes from A to B. Let n_1 and n_2 be the number of drops produced by the same volume V of the two liquids. Thus,

$$\text{The volume of one drop of liquid 1} = V/n_1$$

$$\text{The mass of one drop of liquid 1} = (V/n_1)d_1$$

where d_1 is the density of liquid 1.

Similarly,

$$\text{The mass of one drop of liquid 2} = (V/n_2)d_2$$

Then from equation (4)

$$\gamma_1/\gamma_2 = (V/n_1)d_1/(V/n_2)d_2 = n_2d_1/n_1d_2$$

The value of d_1 is determined with a pycnometer. Knowing d_2 and γ_2 from reference tables, γ_1 can be calculated.

Problem: In the determination of surface tension of a liquid by the drop-number method, it gives 55 drops while water gave 25 drops for the same volume. The densities of the liquid and water are 0.996 and 0.800 g/cm³ respectively. Find the surface tension of the liquid if that of water is 72 dynes/cm.

Solution:

We know that

$$\gamma_1/\gamma_2 = n_2 d_1 / n_1 d_2 \quad (1)$$

Where γ_1 = Surface tension of liquid; γ_2 = Surface tension of water; n_1 = number of drops of liquid; n_2 = number of drops of water.

Therefore,

$$\gamma_2 = 72 \text{ dynes cm}^{-1}, n_1 = 55, n_2 = 25, d_1 = 0.996 \text{ g cm}^{-3}, d_2 = 0.800 \text{ g cm}^{-3}$$

Using equation (1),

$$\gamma_1 = 72 \times (0.996 \times 25) / (0.800 \times 55) = 40.7 \text{ dynes cm}^{-1}$$

Therefore, the surface tension of the given liquid is 40.7 dynes cm⁻¹

(iii) Ring-detachment Method

In this method the force required to detach a platinum ring (du Nouy ring) from the liquid surface is measured. **This force (F) is exactly equal to the downward pull due to surface tension γ acting along the circumference of the ring.** Twice the length of the circumference ($2 \times 2\pi r$) is taken since the liquid is in contact with both the inside and the outside of ring. Thus,

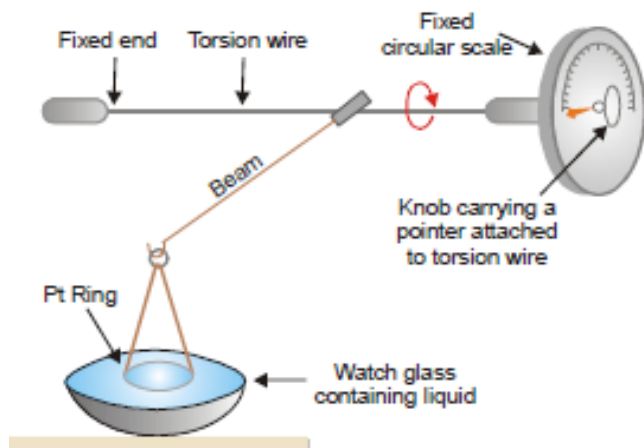
$$F = 4 \pi r \gamma$$

or

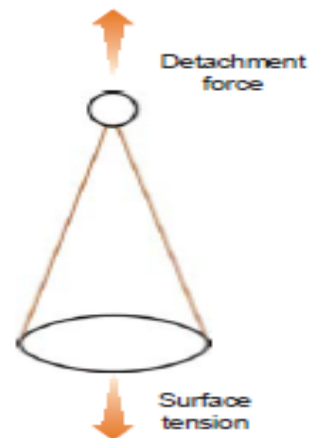
$$\gamma = F/4\pi r$$

where r is the radius of the ring.

The apparatus employed is called the **du Nouy Tensiometer**. Its essential parts are shown in Fig. One end of the torsion wire is fixed while the other is attached to a knob carrying a pointer. The pointer moves on a fixed scale. The scale is previously calibrated by taking different weights on the beam and noting the scale reading when it is lifted from the horizontal position. The liquid whose surface tension is to be determined is placed in a watch glass so that the Pt ring just touches its surface. The knob of the torsion wire is then slowly turned till the ring is just detached from the surface. The reading shown by the pointer on the scale gives the force F . The surface tension is then calculated from equation (1).



du Nouy Tensiometer



du Nouy ring with a suspending hook.

2.3. Nature and Thermodynamics of Liquid-Gas Interface

The surface tension is a definite and accurately measurable property of the interface between liquid phases. Moreover, its value is very rapidly established in pure substances of ordinary viscosity; dynamic methods indicate that a normal surface tension is established within a millisecond and probably sooner. Thus it is appropriate to discuss the thermodynamic basic for surface tension.

Surface Thermodynamic Quantities for a pure Substance

A hypothetical system consisting of some liquid that fills a box having a sliding cover; the material of the cover is such that the interfacial tension between it and the liquid is zero. If the cover is slid back so as to uncover an amount of surface dA , the work required to do so will be γdA . This is reversible work at constant pressure and temperature and thus gives the increase in free energy of the system.

$$dG = \gamma dA \quad (1)$$

The total free energy of the system is then made up of the molar free energy times the total number of moles of the liquid plus G^s , the surface free energy per unit area, times the total surface area. Thus

$$G^s = \gamma = \left(\frac{dG}{dA} \right)_{T,P} \quad (2)$$

Because this process is a reversible one, the heat associated with it gives the is *surface entropy*

$$dq = T dS = TS^s dA \quad (3)$$

where S^s is the surface entropy per square centimeter of surface.

Because $(dG/dT)_p = -S$, it follows that

$$\left(\frac{dG^s}{dA}\right)_p = -S^s \quad (4)$$

Or, in conjunction with Eq. 1,

$$\frac{d\gamma}{dT} = -S^s \quad (5)$$

Finally, the total surface enthalpy per square centimeter H^s is

$$H^s = G^s + TS^s \quad (6)$$

Often, and as a good approximation, H^s and the surface energy E^s are not distinguished, so Eq.6 can be seen in the form

$$E^s = G^s + TS^s \quad (7)$$

Or

$$E^s = \gamma - T d\gamma/dT \quad (8)$$

The total surface energy E^s generally is larger than the surface free energy. It is frequently the more informative of the two quantities, or at least it is more easily related to molecular models.

The surface specific heat C^s (distinction between C_p^s and C_v^s is rarely made), is an additional quantity to be mentioned at this point. It is given by

$$C^s = dE^s/dT \quad (9)$$

The surface tension of most liquid decreases with increasing temperature in a nearly linear fashion. The near-linearity has stimulated many suggestions as to algebraic forms that give exact linearity. An old and well-known relationship is

$$\gamma V^{2/3} = k (T_c - T) \quad (10)$$

Where V is the molar volume. One does expect the surface tension to go to zero at the critical temperature, but the interface seems to become diffuse at a slightly lower temperature replaced T_c in Eq. 10 by $(T_c - \delta)$. In either form, the constant k is about the same for most liquids and has a value of about 2.1 ergs/K.

$$\gamma = \gamma^o \left(1 - \frac{T}{T_c}\right)^n \quad (11)$$

Where n is 11/9 for many organic liquids but may be closer to unity for metals.

2.4. The Surface Tension of Solutions

The principal point of interest to be discussed in this section is the manner in which the surface tension of a binary system varies with composition. The effects of other variables such as pressure and temperature are similar to those for pure substances, and the more elaborate treatment for two-component system is not considered here.

A fairly simple treatment is useful for the case of ideal or nearly ideal solutions. An abbreviated derivation begins with the free energy of a species

$$G_i = kT \ln a_i \quad (1)$$

Where a_i is the absolute activity, $a_i = N_i g_i$, where N_i is the mole fraction of species I (unity for pure liquids), and g_i derives from the partition function Q_i . For a pure liquid 1, the surface tension may be written as

$$\gamma_1 \sigma_1 = -kT \ln a_1 / a_1^s \quad (2)$$

Or

$$\exp(-\gamma_1 \sigma_1 / kT) = g_1 / g_1^s \quad (3)$$

where the surface is viewed as a two-dimensional phase of molecular state corresponding to g_1^s and σ_1 is the molecular area. Thus, the work of bringing a molecule into the surface is expressed as a ΔG using Eq. 1.

The same relations are then applied to each component of a solution

$$\exp(-\gamma \sigma_1 / kT) = N_1 g_1 / N_1^s g_1^s \quad (4)$$

$$\exp(-\gamma \sigma_2 / kT) = N_2 g_2 / N_2^s g_2^s \quad (5)$$

where N^s denotes the mole fraction in the surface phase. Equation 4 and 5 may be solved for N_1^s and N_2^s , respectively, and substituted into the requirement that $N_1^s + N_2^s = 1$. If it is assumed that $\sigma = \sigma_1 = \sigma_2$, one then obtains

$$\exp(-\gamma \sigma / kT) = N_1 g_1 / g_1^s + N_2 g_2 / g_2^s \quad (6)$$

and, in combination with Eq. 3,

$$\exp(-\gamma \sigma / kT) = N_1 \exp(-\gamma_1 \sigma / kT) + N_2 \exp(-\gamma_2 \sigma / kT) \quad (7)$$

Hildebrand and Scott give an expansion of Eq. 7 for $\sigma_1 \neq \sigma_2$.

Guggenheim extended his treatment to the case of regular solution, that is, solutions for which

$$RT \ln f_1 = -\alpha N_2^2 \quad RT \ln f_2 = -\alpha N_1^2 \quad (8)$$

where f denotes the activity coefficient. A very simple relationship for such regular solutions comes from Prigogine and Defay:

$$\gamma = \gamma_1 N_1 + \gamma_2 N_2 - \beta N_1 N_2 \quad (9)$$

where β is a semi-empirical constant.

2.5. Surfaces of Solids

A *solid*, by definition, is a portion of matter that is rigid and resists stress. Although the surface of a solid must, in principle, be characterized by surface free energy, it is evident that the usual methods of capillarity are not very useful since they depend on measurements of equilibrium surface properties given Laplace's equation. Since a solid deforms in an elastic manner, its shape will be determined more by its past history than by surface tension forces.

Surface growth

A simple picture of a perfect crystal surface is as a tray of oranges in a grocery store (Fig. 1). A gas molecule that collides with the surface can be imagined as a table-tennis ball bouncing erratically over the oranges. The molecule loses energy as it bounces under the influence of intermolecular forces, but it is likely to escape from the surface before it has lost so much kinetic energy that it has become trapped. The same is true, to some extent, of an ionic crystal in contact with a solution. There is little energy advantage for an ion in solution to discard some of its solvating molecules and stick at an exposed position on a flat surface.

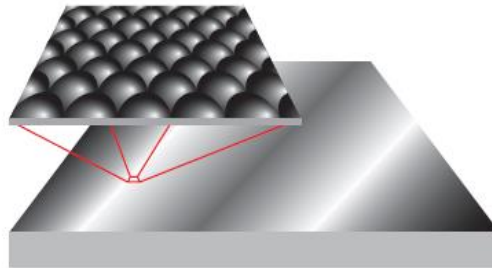


Fig. 1: A schematic diagram of the flat surface of a solid.

The picture changes when the surface has defects, for then there are ridges of incomplete layers of atoms or ions. A typical type of surface defect is a **step** between two otherwise flat layers of atoms called **terraces** (Fig. 2). A step defect might itself have defects, including kinks. When an atom settles on a terrace it migrates across it under the influence of the intermolecular potential, and might come to a step or a corner formed by a kink. Instead of interacting with a single

terrace atom, the molecule now interacts with several, and the interaction may be strong enough to trap it. Likewise, when ions deposit from solution, the loss of the solvation interaction is offset by a strong Coulombic interaction between the arriving ions and several ions at the surface defect.

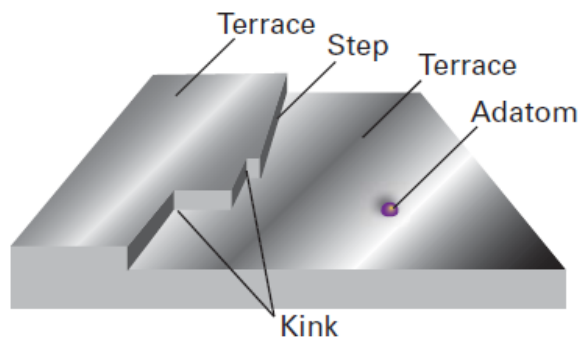


Fig. 2: Some of the kinds of defects that may occur on otherwise perfect terraces. Defects play an important role in surface growth and catalysis.

The rapidity of growth depends on the crystal plane concerned and—perhaps surprisingly—the slowest growing faces dominate the appearance of the crystal. This feature is explained in Fig. 3, where we see that although the horizontal face grows forward most rapidly, it grows itself out of existence and the more slowly growing faces survive.

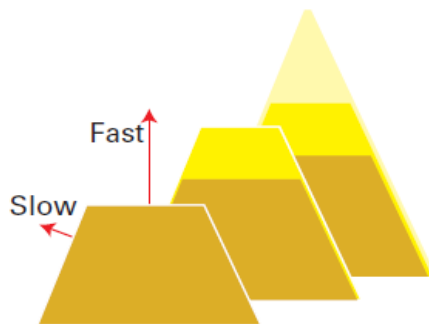


Fig. 3: The slower-growing faces of a crystal dominate its final external appearance. Three successive stages of the growth are shown.

Surface Composition and structure

Under normal conditions, a surface exposed to a gas is constantly bombarded with molecules and a freshly prepared surface is covered very quickly. Just how quickly can be estimated by using the kinetic theory of gases and the following expression for the **collision flux**, Z_w , the number of hits on a region of a surface during an interval divided by the area of the region and the duration of the interval:

$$Z_w = \frac{P}{(2\pi mk_b T)^{1/2}} \quad (1)$$

where m is the mass of the molecules. For air at 1 atm and 25°C the collision flux is $3 \times 10^{27} \text{ m}^{-2} \text{ s}^{-1}$.

Because 1 m^2 of metal surface consists of about 10^{19} atoms, each atom is struck about 10^8 times each second. Even if only a few collisions leave a molecule adsorbed to the surface, the time for which a freshly prepared surface remains clean is very short. There are various techniques which can be applied to measure the chemical composition of solid surface.

Surface Tension and Surface Free Energy

Unlike the situation with liquids, in the case of a solid, the surface tension is not necessarily equal to the surface stress. As Gibbs pointed out the surface tension is the work spent in forming unit area of surface (and may alternatively be called the surface free energy, while the surface stress involves the work spent in strengthening the surface. It is helpful to imagine that the process of forming a fresh surface of a monoatomic substance is divided into two steps: first, the solid or liquid is cleaved so as to expose a new surface, keeping the atoms fixed in the atoms in the same positions that they occupied when in the bulk phase; second, the atoms in the surface region are allowed to rearrange to their final equilibrium positions. In the case of the liquid, these two steps occur as one, but with solids the second step may occur only slowly because of the immobility of the surface region. Thus, with a solid it may be possible to stretch or to compress the surface region without changing the number of atoms in it, only their distances apart.

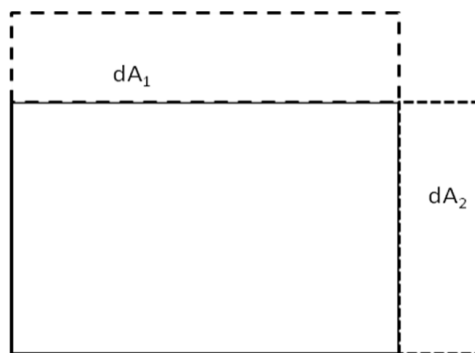


Fig. 4: Displacement in solid surface.

Surface free energy and surface stress were treated as equivalent, and both were discussed in terms of the energy to form unit additional surface. It is now desirable to consider an independent, more mechanical definition of surface stress. If a surface is cut by a plane normal to

it, then, in order that the atoms on either side of the cut remain in equilibrium, it will be necessary to apply some external force to them. The total such force per unit length is the surface stress, and half the sum of the two surface stresses along mutually perpendicular cuts is equal to the surface tension. In the case of a liquid or isotropic solid the two surface stresses are equal, but for a non-isotropic solid or crystal, this will not be true. In such a case the partial surface stresses or stretching tensions may be denoted as τ_1 and τ_2 .

For an anisotropic solid, if the area is increased in two directions by dA_1 and dA_2 , as illustrated in fig. 4. then the total increase in free energy is given by the reversible work against the surface stresses, that is

$$\tau_1 = G^s + A_1 dG^s / dA_1 \text{ and } \tau_2 = G^s + A_2 dG^s / dA_2 \quad (2)$$

where G^s is the free energy per unit area. If the solid is isotropic Eq. 2 reduces to

$$\tau_1 = \frac{d(AG^s)}{dA} = G^s + \frac{AdG^s}{dA} \quad (3)$$

For liquids, the last terms in Eq. 3 is zero, so that $\tau = G^s$ (or $\tau = \gamma$, since we will use G^s and γ interchangeably); the same would be true of a solid if the change in area dA were to occur in such a way that an equilibrium surface configuration was always maintained. Thus the stretching of a wire under reversible conditions would imply that interior atoms would move into the surface as needed so that the increased surface area was not accompanied by any change in specific surface properties. If, however, the stretching were done under conditions such that full equilibrium did not prevail, a surface stress would be present whose value would differ from γ by an amount that could be time-dependent and would depend on the term $\frac{AdG^s}{dA}$.

Adsorption

The phenomenon of concentration of molecules of a gas or liquid at a solid surface is called adsorption. The substance that deposits at the surface is called **Adsorbate** and the solid on whose surface the deposition occurs is called the **Adsorbent**.

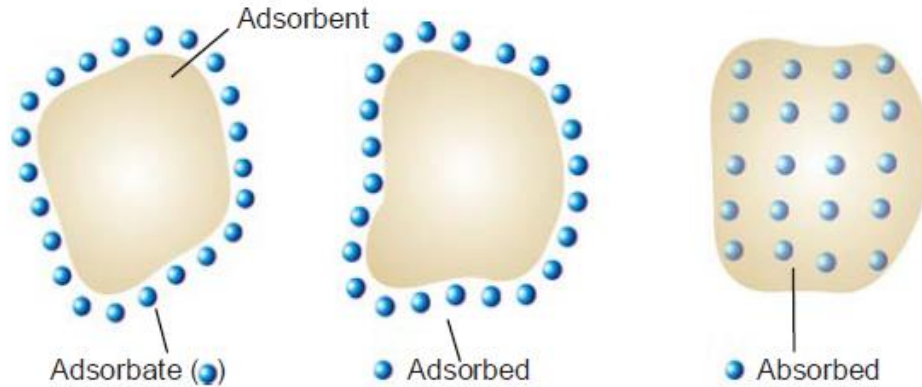


Fig. 5: Adsorption versus absorption illustration.

Adsorption versus Absorption

The term ‘adsorption’ must be carefully distinguished from another like-sounding term ‘absorption’. **While adsorption implies deposition at the surface only, absorption implies penetration into the body of the solid.** For illustration a chalk crayon when dipped in ink adsorbs the latter and on breaking it is found to be white from within. On the other hand, water is absorbed by a sponge and is distributed throughout the sponge uniformly.

Both adsorption and absorption often take place side by side. It is thus difficult to distinguish between the two processes experimentally. Mc Bain introduced the general term **Sorption** which includes both *the adsorption and absorption*.

The extent of adsorption

The attachment of molecules to a surface is called **adsorption**. The substance that adsorbs is the **adsorbate** and the underlying material that we are concerned with in this section is the **adsorbent** or **substrate**. The reverse of adsorption is **desorption**.

The extent of surface coverage is normally expressed as the **fractional coverage**, θ (theta):

$$\theta = \frac{\text{number of adsorption sites occupied}}{\text{number of adsorption sites available}} \quad (1)$$

The fractional coverage can be inferred from the volume of adsorbate adsorbed by $\theta = V/V_\infty$, where V_∞ is the volume of adsorbate corresponding to complete monolayer coverage. In each case, the volumes in the definition of θ are those of the free gas measured under the same conditions of temperature and pressure, not the volume the adsorbed gas occupies when attached to the surface. The **rate of adsorption** is the rate of change of surface coverage and is measured by observing the change of fractional coverage with time.

Physisorption and Chemisorptions

Molecules and atoms can attach to surfaces in two ways, although there is no clear frontier between the two types of adsorption. In **physisorption** (an abbreviation of ‘physical adsorption’), there is a van der Waals interaction between the adsorbate and the substrate (for example, a dispersion or a dipolar interaction of the kind responsible for the condensation of vapors to liquids). The energy released when a molecule is physisorbed is of the same order of magnitude as the enthalpy of condensation. Such small energies can be absorbed as vibrations of the lattice and dissipated as thermal motion, and a molecule bouncing across the surface will gradually lose its energy and finally adsorb to it in the process called **accommodation**. The enthalpy of physisorption can be measured by monitoring the rise in temperature of a sample of known heat capacity, and typical values are in the region of -20 kJ mol^{-1} (Table 1). This small enthalpy change is insufficient to lead to bond breaking, so a physisorbed molecule retains its identity but might be distorted. Enthalpies of physisorption may also be measured by observing the temperature dependence of the parameters that occur in the adsorption isotherm.

Table 1: Maximum observed enthalpies of physisorption, $\Delta_{ads} H_{ads}^o / (\text{kJmol}^{-1})$

CH ₄	-21
CO	-25
H ₂	-84
H ₂ O	-59
N ₂	-21
NH ₃	-38
O ₂	-21

In **chemisorption** (an abbreviation of ‘chemical adsorption’), the molecules (or atoms) adsorb to the surface by forming a chemical (usually covalent) bond and tend to find sites that maximize their coordination number with the substrate. The enthalpy of chemisorption is much more negative than that for physisorption, and typical values are in the region of -200 kJ mol^{-1} (Table 2). The distance between the surface and the closest adsorbate atom is also typically shorter for chemisorption than for physisorption. A chemisorbed molecule may be torn apart at the demand of the unsatisfied valencies of the surface atoms and the existence of molecular fragments on the surface as a result of chemisorption is one reason why solid surfaces catalyse reactions.

Table 2: Enthalpies of chemisorption, $\Delta_{ads} H_{ads}^o / (\text{kJmol}^{-1})$

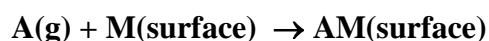
Adsorbate	Adsorbent (substrate)			
	Cr	Fe	Ni	Pt
C ₂ H ₄	-427	-285	-243	
CO		-192		
H ₂	-188	-134		
NH ₃		-188	-155	
O ₂				-293

COMPARISON OF PHYSICAL ADSORPTION AND CHEMISORPTION

Physical adsorption	Chemisorption
<ol style="list-style-type: none"> 1. Caused by intermolecular van der Waal's forces. 2. Depends on nature of gas. Easily liquefiable gases are adsorbed readily. 3. Heat of adsorption is small (about 5 kcal mol⁻¹). 4. Reversible. 5. Occurs rapidly at low temperature; decreases with increasing temperature. 6. Increase of pressure increases adsorption; decrease of pressure causes desorption. 7. Forms multimolecular layers on adsorbent surface. 	<ol style="list-style-type: none"> 1. Caused by chemical bond formation. 2. Much more specific than physical adsorption. 3. Heat of adsorption is large (20–100 kcal mol⁻¹). 4. Irreversible. 5. Increases with increase of temperature. 6. Change of pressure has no such effects. 7. Forms unimolecular layer.

Adsorption isotherms

The free gas **A** and the adsorbed gas are in a dynamic equilibrium of the form



and the fractional coverage of the surface depends on the pressure of the overlying gas. The enthalpy change associated with the forward reaction (per mole of adsorbed species) is the **enthalpy of adsorption**, $\Delta_{\text{ads}}H$. The variation of θ with pressure at a chosen temperature is called the **adsorption isotherm**.

The simplest physically plausible adsorption isotherm is based on three assumptions:

1. Adsorption cannot proceed beyond monolayer coverage.
2. All sites are equivalent and the surface is uniform (that is, the surface is perfectly flat on a microscopic scale).
3. There are no interactions between adsorbed molecules, so the ability of a molecule to adsorb at a given site is independent of the occupation of neighboring sites.

Assumptions 2 and 3 imply, respectively, that the enthalpy of adsorption is the same for all sites and is independent of the extent of surface coverage. The relation between the fractional coverage θ and the partial pressure of A, p , that results from these three assumptions is the **Langmuir isotherm**:

$$\theta = \frac{Kp}{1 + Kp} \quad K = \frac{k_a}{k_b} \quad (2)$$

where k_a and k_b are, respectively, the rate constants for adsorption and desorption. This expression is plotted for various values of K (which has the dimensions of 1/pressure) in Fig. 6. We see that as the partial pressure of A increases, the fractional coverage increases towards 1. Half the surface is covered when $p = 1/K$. At low pressures (in the sense that $Kp \ll 1$), the denominator can be replaced by 1, and $\theta = Kp$. Under these conditions, the surface coverage increases linearly with pressure. At high pressure (in the sense that $Kp \gg 1$), the 1 in the denominator can be neglected, the Kp cancel, and $\theta = 1$. Now the surface is saturated.

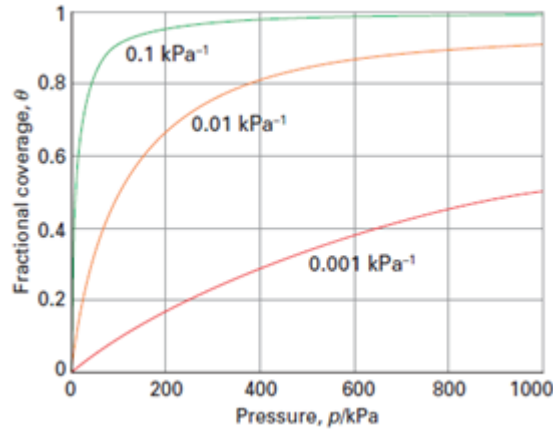


Fig. 6: Langmuir isotherm for nondissociative adsorption for different values of K .

A further point is that because K is essentially an equilibrium constant, then its temperature dependence is given by the van't Hoff equation :

$$\ln K = \ln K' - \frac{\Delta_{\text{ads}}H}{R} \left(\frac{1}{T} - \frac{1}{T'} \right) \quad (3)$$

It follows that if we plot $\ln K$ against $1/T$, then the slope of the graph is equal to $-\Delta_{\text{ads}}H/R$, where $\Delta_{\text{ads}}H$ is the standard enthalpy of adsorption. However, because this quantity might vary with the extent of surface coverage either because the adsorbate molecules interact with each other or because adsorption occurs at a sequence of different sites, care must be taken to measure K at the same value of the fractional coverage. The resulting value of $\Delta_{\text{ads}}H$ is called the **isosteric**

enthalpy of adsorption. The variation of $\Delta_{\text{ads}}H$ with θ allows us to explore the validity of the assumptions on which the Langmuir isotherm is based. There are two modifications of the Langmuir isotherm that should be noted. Suppose the substrate dissociates on adsorption, as in



The resulting isotherm is

$$\theta = \frac{(Kp)^{1/2}}{1 + (Kp)^{1/2}} \quad (4)$$

The second modification we need to consider deals with a mixture of two gases A and B that compete for the same sites on the surface. To show that if A and B both follow Langmuir isotherms, and adsorb without dissociation, then

$$\theta_A = \frac{K_A p_A}{1 + K_A p_A + K_B p_B}, \quad \theta_B = \frac{K_B p_B}{1 + K_A p_A + K_B p_B} \quad (5)$$

where K_J (with $J = A$ or B) is the ratio of adsorption and desorption rate constants for species J , p_J is its partial pressure in the gas phase, and θ_J is the fraction of total sites occupied by J . Co-adsorption of this kind is important in catalysis and we use these isotherms later.

The rates of surface processes

Figure 7, shows how the potential energy of a molecule varies with its distance above the adsorption site. As the molecule approaches the surface its potential energy decreases as it becomes physisorbed into the **precursor state** for chemisorption. Dissociation into fragments often takes place as a molecule moves into its chemisorbed state, and after an initial increase of energy as the bonds stretch there is a sharp decrease as the adsorbate–substrate bonds reaches their full strength. Even if the molecule does not fragment, there is likely to be an initial increase of potential energy as the bonds adjust when the molecule approaches the surface.

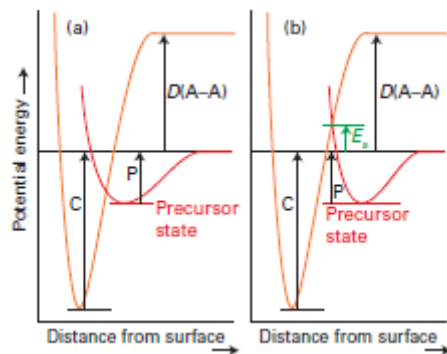


Fig. 7: *The potential energy profiles for the dissociative chemisorption of an A2 molecule. In each case, P is the enthalpy of (nondissociative) physisorption and C that for chemisorption (at T = 0). The relative locations of the curves determine whether the chemisorption is (a) not activated or (b) activated.*

In most cases, therefore, we can expect there to be a potential energy barrier separating the precursor and chemisorbed states. This barrier, though, might be low and might not rise above the energy of a distant, stationary molecule (as in Fig. 7a). In this case, chemisorption is not an activated process and can be expected to be rapid. Many gas adsorptions on clean metals appear to be nonactivated. In some cases the barrier rises above the zero axis (as in Fig 7b); such chemisorptions are activated and slower than the nonactivated kind. An example is the adsorption of H₂ on copper, which has an activation energy in the region of 20–40 kJ mol⁻¹.

One point that emerges from this discussion is that rates are not good criteria for distinguishing between physisorption and chemisorption. Chemisorption can be fast if the activation energy is small or zero; but it may be slow if the activation energy is large. Physisorption is usually fast, but it can appear to be slow if adsorption is taking place on a porous medium.

The rate at which a surface is covered by adsorbate depends on the ability of the substrate to dissipate the energy of the incoming molecule as thermal motion as it crashes on to the surface. If the energy is not dissipated quickly, the molecule migrates over the surface until a vibration expels it into the overlying gas or it reaches an edge. The proportion of collisions with the surface that successfully lead to adsorption is called the **sticking probability**, s :

$$s = \frac{\text{rate of adsorption of particles by the surface}}{\text{rate of collision of particles with the surface}} \quad (6)$$

The denominator can be calculated from kinetic theory, and the numerator can be measured by observing the rate of change of pressure. Values of s vary widely. For example, at room temperature CO has s in the range 0.1–1.0 for several d-metal surfaces, suggesting that almost every collision sticks, but for N₂ on rhenium $s < 10^{-2}$, indicating that more than a hundred collisions are needed before one molecule sticks successfully.

Desorption is always an activated process because the molecules have to be lifted from the foot of a potential well. A physisorbed molecule vibrates in its shallow potential well, and might shake itself off the surface after a short time. The temperature dependence of the first-order rate of departure can be expected to be Arrhenius-like,

$$k_d = Ae^{-E_d/RT} \quad (7)$$

where A is a pre-exponential factor and the activation energy for desorption, E_d , is likely to be comparable to the enthalpy of physisorption. In the discussion of half-lives of first-order reactions is $t_{1/2} = (\ln 2)/k$; so for desorption, the half-life for remaining on the surface has a temperature dependence given by

$$t_{1/2} = \frac{\ln 2}{k_d} = \tau_o e^{E_d/RT}, \quad \tau_o = \frac{\ln 2}{A} \quad (8)$$

(Note the positive sign in the exponent: the half-life *decreases* as the temperature is raised.) If we suppose that $1/\tau_o$ is approximately the same as the vibrational frequency of the weak molecule–surface bond (about 10^{12} Hz) and $E_d \approx 25$ kJ mol⁻¹, then residence half-lives of around 10 ns are predicted at room temperature. Lifetimes close to 1 s are obtained only by lowering the temperature to about 100 K. For chemisorption, with $E_d = 100$ kJ mol⁻¹ and guessing that $\tau_o = 10^{-14}$ s (because the adsorbate–substrate bond is quite stiff), we expect a residence half-life of about 3×10^3 s (about an hour) at room temperature, decreasing to 1 s at about 350 K.

One way to measure the desorption activation energy is to monitor the rate of increase in pressure when the sample is maintained at a series of temperatures and then to attempt to make an Arrhenius plot. A more sophisticated technique is **temperature programmed desorption** (TPD) or **thermal desorption spectroscopy** (TDS). The basic observation is a surge in desorption rate (as monitored by a mass spectrometer) when the temperature is raised linearly to the temperature at which desorption occurs rapidly; but once desorption has occurred there is no more adsorbate to escape from the surface, so the desorption flux falls again as the temperature continues to rise. The TPD spectrum, the plot of desorption flux against temperature, therefore shows a peak, the location of which depends on desorption activation energy. There are three maxima in the example shown in Fig. 8, indicating the presence of three adsorption sites with different activation energies.

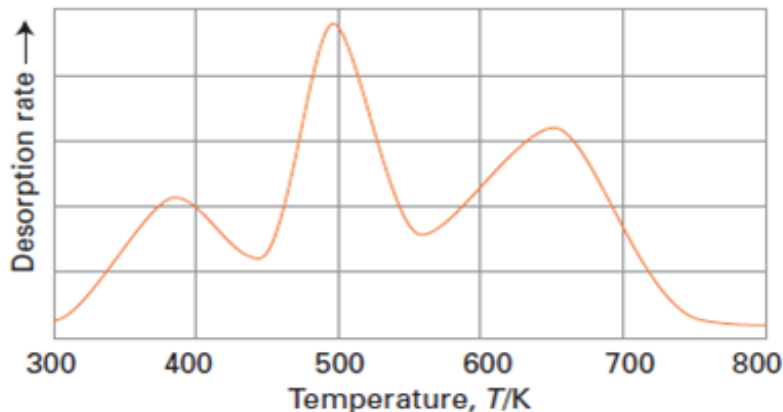


Fig. 8: The flash desorption spectrum of H_2 on the face of tungsten.

Catalytic activity at surfaces

A catalyst acts by providing an alternative reaction path with lower activation energy. A catalyst does not disturb the final equilibrium composition of the system, only the rate at which that equilibrium is approached. In this section we shall consider **heterogeneous catalysis**, in which the catalyst and the reagents are in different phases. A common example is a solid introduced as a heterogeneous catalyst into a gas-phase reaction. Many industrial processes make use of heterogeneous catalysts, which include platinum, rhodium, zeolites, and various metal oxides, but increasingly attention is turning to homogeneous catalysts, partly because they are easier to cool. However, their use typically requires additional separation steps, and such catalysts are generally immobilized on a support, in which case they become heterogeneous. In general, heterogeneous catalysts are highly selective and to find an appropriate catalyst each reaction must be investigated individually.

Computational procedures are beginning to be a fruitful source of prediction of catalytic activity. A metal acts as a heterogeneous catalyst for certain gas-phase reactions by providing a surface to which a reactant can attach by chemisorption. For example, hydrogen molecules may attach as atoms to a nickel surface and these atoms react much more readily with another species (such as an alkene) than the original molecules. The chemisorption step therefore results in a reaction pathway with lower activation energy than in the absence of the catalyst. Note that chemisorption is normally required for catalytic activity: physisorption might precede chemisorption but is not itself sufficient.

Mechanisms of heterogeneous catalysis

Heterogeneous catalysis normally depends on at least one reactant being adsorbed (usually chemisorbed) and modified to a form in which it readily undergoes reaction. Often this modification takes the form of a fragmentation of the reactant molecules. The **catalyst ensemble** is the minimum arrangement of atoms at the surface active site that can be used to model the action of the catalyst. It may be determined, for instance, by diluting the active metal with a chemically inert metal and observing the catalytic activity of the resulting alloy. In this way it has been found, for instance, that as many as 12 neighboring Ni atoms are needed for the cleavage of the C—C bond in the conversion of ethane to methane.

The decomposition of phosphine (PH₃) on tungsten is first-order at low pressures and zeroth-order at high pressures. To account for these observations, we write down a plausible rate law in terms of an adsorption isotherm and explore its form in the limits of high and low pressure. If the rate is supposed to be proportional to the surface coverage and we suppose that θ is given by the Langmuir isotherm, we would write

$$\text{Rate} = k_r \theta = \frac{k_r K p}{1 + K p} \quad (9)$$

where p is the pressure of phosphine and k_r is a rate constant. When the pressure is so low that $Kp \ll 1$, we can neglect Kp in the denominator and obtain

$$\text{Rate} = k_r K p \quad (10)$$

and the decomposition is first-order. When $Kp \gg 1$, we can neglect the 1 in the denominator, whereupon the Kp terms cancel and we are left with

$$\text{Rate} = k_r \quad (11)$$

and the decomposition is zeroth-order. Many heterogeneous reactions are first-order, which indicates that the rate-determining stage is the adsorption process.

In the **Langmuir–Hinshelwood mechanism** (LH mechanism) of surface-catalysed reactions, the reaction takes place by encounters between molecular fragments and atoms adsorbed on the surface. We therefore expect the rate law to be overall second order in the extent of surface coverage:



Insertion of the appropriate isotherms for A and B then gives the reaction rate in terms of the partial pressures of the reactants. For example, if A and B follow the adsorption isotherms given in eqn 4, then the rate law can be expected to be

$$Rate = \frac{k_r K_A K_B p_A p_B}{(1 + K_A p_A + K_B p_B)^2} \quad (12)$$

The parameters K in the isotherms and the rate constant k_r are all temperature dependent, so the overall temperature dependence of the rate may be strongly non-Arrhenius, in the sense that the reaction rate is unlikely to be proportional to $e^{-E_a/RT}$. The LH mechanism is dominant for the catalytic oxidation of CO to CO₂ on the surface of platinum.

In the **Eley–Rideal mechanism** (ER mechanism) of a surface-catalysed reaction, a gas-phase molecule collides with another molecule already adsorbed on the surface. We can therefore expect the rate of formation of product to be proportional to the partial pressure, p_B , of the nonadsorbed gas B and the extent of surface coverage, θ_A , of the adsorbed gas A. It follows that the rate law should be



The rate constant, k_r , might be much larger than for the uncatalysed gas-phase reaction because the reaction

on the surface has a low activation energy and the adsorption itself is often not activated. If we know the adsorption isotherm for A, we can express the rate law in terms of its partial pressure, p_A . For example, if the adsorption of A follows a Langmuir isotherm in the pressure range of interest, then the rate law would be

$$Rate = \frac{k_r K p_A p_B}{1 + K p_A} \quad (13)$$

If A were a diatomic molecule that adsorbed as atoms, then we would substitute the isotherm given in eqn 4 instead. According to eqn 13, when the partial pressure of A is high (in the sense $K p_A \gg 1$) there is almost complete surface coverage, and the rate law is

$$Rate = \frac{k_r K p_A p_B}{K p_A} = k_r p_B \quad (14)$$

Now the rate-determining step is the collision of B with the adsorbed fragments. When the pressure of A is low ($K p_A \ll 1$), perhaps because of its reaction, the rate law becomes

$$\text{Rate} \approx \frac{k_r K p_A p_B}{1} = k_r K p_A p_B \quad (15)$$

Now the extent of surface coverage is rate determining. Almost all thermal surface-catalysed reactions are thought to take place by the LH mechanism, but a number of reactions with an ER mechanism have also been identified from molecular beam investigations.

2.6. Adsorption at the Solid Solution Interface

Adsorption of a solute from a solution onto a solid adsorbent is more difficult to treat theoretically than the corresponding adsorption of gases on solids. It appears however that in this case, too, like the gas-solid adsorption, a monomolecular layer is formed. The solvating power of the solvent inhibits the formation of a multilayer.

For adsorption from solutions, a commonly used isotherm is the Freundlich adsorption isotherm. If x is the mass of the solute adsorbed on mass m of adsorbent and c is the concentration of the solute in the solution, then the Freundlich adsorption isotherm is expressed as

$$x/m = a = kc^n \quad (1)$$

where k and n are empirical constants. Taking logs,

$$\ln a = \ln k + n \ln c \quad (2)$$

This logarithmic form is convenient to use. If we plot $\ln a$ versus $\ln c$, the plot would be a straight line with slope equal to n and intercept equal to $\ln k$.

The Gibbs Adsorption Isotherm for Adsorption from solutions

The concentration of a solute at the surface of a solution is, in general, markedly different from that in the bulk. If the surface tension of the solute is lower than that of the liquid, it tends to accumulate at the surface of the liquid thereby decreasing the surface tension (or the surface free energy per unit area) of the liquid. A quantitative treatment of the thermodynamics of adsorption of a solute at the surface of a liquid was given in 1878 by J.W.Gibbs, the greatest 19th century American mathematical physicist.

For a system containing two components, the Gibbs free energy can be written as

$$G = n_1 \mu_1 + n_2 \mu_2 \quad (3)$$

Where n_1 and n_2 are the amounts (number of moles), μ_1 and μ_2 are the chemical potentials (*i.e.*, partial molar Gibbs free energies) of the two components, respectively. Since we are dealing with the adsorption of one of the components on the surface which results in changing the surface free energy, Eq.3 is modified to

$$G = n_1\mu_1 + n_2\mu_2 + \gamma\sigma \quad (4)$$

Where γ is the *surface energy* which is numerically the same as the surface tension and σ is the surface area. The complete differential of Eq. 4 is written as

$$dG = n_1d\mu_1 + \mu_1dn_1 + n_2d\mu_2 + \mu_2dn_2 + \gamma d\sigma + \sigma d\gamma \quad (5)$$

We see that free energy G now depends upon five independent variables, *viz.*, T , P , n_1 , n_2 and σ . Thus,

$$G = f(T, P, n_1, n_2, \sigma) \quad (6)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2, \sigma} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, \sigma} dP + \left(\frac{\partial G}{\partial n_1}\right)_{P, T, n_2, \sigma} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{P, T, n_1, \sigma} dn_2 + \left(\frac{\partial G}{\partial \sigma}\right)_{P, T, n_1, n_2} d\sigma \quad (7)$$

According to thermodynamics, the partial derivatives

$$-\left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2, \sigma}, \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, \sigma}, \left(\frac{\partial G}{\partial n_1}\right)_{P, T, n_2, \sigma}, \left(\frac{\partial G}{\partial n_2}\right)_{P, T, n_1, \sigma} \text{ and } \left(\frac{\partial G}{\partial \sigma}\right)_{P, T, n_1, n_2}$$

Eq. 7 are, respectively, equal to S , V , μ_1 , μ_2 and γ .

$$\text{Hence, } dG = -SdT + VdP + \mu_1dn_1 + \mu_2dn_2 + \gamma d\sigma \quad (8)$$

At constant temperature ($dT = 0$) and at constant pressure ($dP = 0$), Eq. 8 reduces to

$$(dG)_{T, P} = \mu_1dn_1 + \mu_2dn_2 + \gamma d\sigma \quad (9)$$

From Eqs. 5 and 9.

$$n_1d\mu_1 + n_2d\mu_2 + \sigma d\gamma = 0 \quad (10)$$

The corresponding expression for the bulk of the liquid is

$$n_1^o d\mu_1 + n_2^o d\mu_2 = 0 \quad (11)$$

Where n_1^o and n_2^o are the amounts (number of moles) of the liquid and the solute, respectively, in the bulk phase.

Since the system is in equilibrium, the chemical potential of each component in the bulk and the surface phase must be the same. The system, on being disturbed, attains a new equilibrium so that the changes in the chemical potentials must be identical in both the phases, *i.e.*, $d\mu_1$ and $d\mu_2$ in Eqs. 10 and 11 must be identical. Elimination of $d\mu_2$ from these equations gives

$$n_1 \left[-\left(\frac{n_2^o}{n_1^o}\right) d\mu_2 \right] + n_2 d\mu_2 + \sigma d\gamma = 0$$

$$\text{Or } (n_2 - n_1 n_2^o / n_1^o) d\mu_2 + \sigma d\gamma = 0$$

Or

$$-\frac{d\gamma}{d\mu_2} = \frac{n_2 - (n_1 n_2^o / n_1^o)}{\sigma} \quad (12)$$

The quantity within parenthesis of Eq. 12 gives the amount n_2^o of solute 2 associated with the amount n_1^o of liquid 1 in the *bulk* phase. On the other hand, n_2 is the amount of the solute associated with the amount n_1 of the liquid at the *surface*. Thus, the numerator on the right hand side of Eq. 12 gives the *excess amount of the solute* present in the surface of the solute per unit area of the surface, designated as Γ_2 , *i.e.*, $[n_2 - (n_1 n_2^o / n_1^o)] / \sigma = \Gamma_2$. Thus, from Eq. 12,

$$\Gamma_2 = -\frac{d\gamma}{d\mu_2} \quad (13)$$

The chemical potential of solute 2 is given by

$$\mu_2 = \mu_2^*(l) + RT \ln a_2 \quad (14)$$

where $\mu_2^*(l)$ is the chemical potential of the pure solute in the liquid phase. Hence,

$$d\mu_2 = RT d \ln a_2 \quad [Q d\mu_2^*(l) = 0] \quad (15)$$

Substituting for $d\mu_2$ in Eq. 13, we obtain

$$\Gamma_2 = -\frac{1}{RT} \left(\frac{\partial \gamma}{\partial \ln a_2} \right)_T = -\frac{a_2}{RT} \left(\frac{\partial \gamma}{\partial a_2} \right)_T \quad (16)$$

When the solution is very dilute, it behaves ideally so that the activity a_2 of the solute can be replaced by its concentration c_2 . Thus,

$$\Gamma_2 = -\frac{1}{RT} \left(\frac{\partial \gamma}{\partial \ln c_2} \right)_T = -\frac{c_2}{RT} \left(\frac{\partial \gamma}{\partial c_2} \right)_T \quad (17)$$

Eq. 17 is called Gibbs adsorption isotherm. Knowing the concentration-dependence of γ , Γ_2 can be calculated. For a solute that lowers the surface tension, the surface excess concentration Γ_2 is *positive* and for a solute that raises the surface tension, Γ_2 is *negative*.