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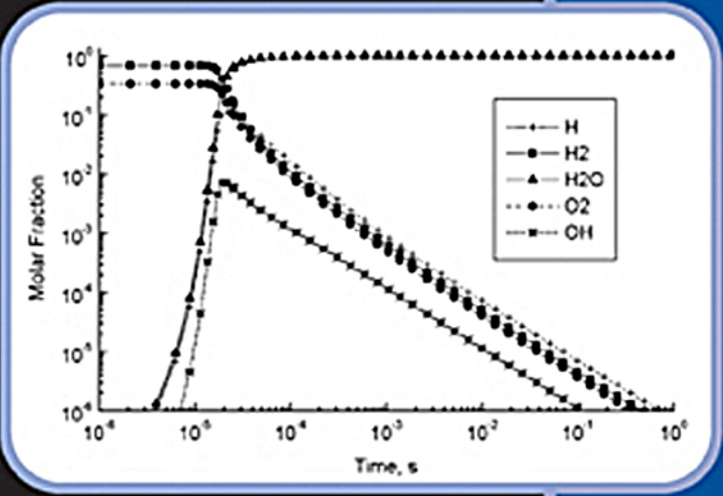

PHYSICAL AND CHEMICAL PROCESSES IN GAS DYNAMICS: PHYSICAL AND CHEMICAL KINETICS AND THERMODYNAMICS OF GASES AND PLASMAS

VOLUME II

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Paul Zarchan
Editor-in-Chief

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Physical and Chemical Processes in Gas Dynamics: Physical and Chemical Kinetics and Thermodynamics

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Contents

Preface

The Description of the medium in gas dynamics is based on modeling the processes occurring in gases and plasmas. Models of the dynamics of elementary collisional processes with the participation of atoms, molecules, ions, and electrons are considered in the first volume of this series. Models of the medium as a totality of the enormous number of particles mutually interacting in collisions are offered to the reader in this volume. If there is no physical-chemical equilibrium, the medium is described by kinetic equations. Equilibrium gases and plasmas obey the laws of thermodynamics.

The following kinetic processes are considered in this volume:

1) translational relaxation as a result of elastic collisions of atoms, molecules, ions, and electrons;
2) rotational and vibrational relaxation as a result of excitation and deactivation of rotations and vibrations of molecules and molecular ions in collisions with various particles;
3) electronic relaxation because of the formation and decay of excited electronic states of atoms, molecules, and ions;
4) macroscopic chemical transformation as a result of elementary chemical reactions in collisions between neutral particles; and
5) macroscopic kinetic processes with participation of charged particles in low-temperature plasmas.

Every problem of physical and chemical kinetics requires the answer to two basic questions: what is the kinetic mechanism, and what are the equations determining relaxation processes and reactions? The kinetic mechanism is determined by the totality of elementary processes taking place in the system and is represented as a list of the corresponding symbolic reaction formulas. Quantitative description of time evolution of the physical-chemical state of a gas or plasma, with the use of a corresponding set of kinetic equations, forms the basis of the mathematical models of medium. Coefficients in the kinetic equations (probabilities, cross sections, and rate constants of the processes) can be found in different databases or can be evaluated using the models presented in the first volume of this series.

The hierarchy of the characteristic times of physical-chemical processes in comparison with the characteristic gas dynamic time of the problem plays a crucial role in the practical development of medium models for the particular kinetic problems. Application of this principle allows one to select those process kinetics that should be considered explicitly. The faster processes will lead to the formation of equilibrium or quasi-stationary state, and the slower ones can be neglected.

In physical-chemical gas dynamics, a possibility of one or the other incomplete thermodynamic equilibrium is to be taken into account. Quite often, local thermodynamic equilibrium (i.e., equilibrium in separate, physically infinitesimally small volumes) or a partial equilibrium (equilibrium in selected parts or modes of the medium) occurs. Descriptions of the gas and plasma in local, partial, and complete equilibrium are based on the laws of thermodynamics with appropriate formulas and relations.

Equations of state are also presented in this volume. These equations relate the basic parameters (temperature, pressure, and volume) of the medium in a particular approximation with respect to density. Quite often, the ideal gas equation of state is used in gas dynamics. This equation of state is valid when the mean kinetic energy of particles is much higher than the mean potential energy of their mutual interaction.

Computer realization of the second volume of this series was implemented on the basis of the KINHELP software component of the CHEMICAL WORKBENCH reaction simulation system. References to the models from other volumes of this reference book begin from the volume number. Thus, for example, in this volume the reference to the model V.6 in the first volume is I-V.6.

Chapter 1

General Notions

I. Medium in Gas Dynamics

MEDIUM IS a matter that fills some space and consists of a large number of particles (atoms, molecules, electrons, and ions) interacting with one another and with electromagnetic fields. In gas dynamics, a neutral or ionized gas (plasma) serves as a medium being investigated.

Gas is a medium in which the constituent particles, such as atoms and molecules, move freely and randomly between collisions. The collision duration in gases is many orders of magnitude shorter than the mean time of free flight between collisions. The degree of rarefaction of a medium in gas dynamics is discussed in Refs. 1–4.

The Boltzmann gas is a medium in which the mean interparticle spacing considerably exceeds the range of action of intermolecular forces.

Plasma is an ionized gaseous medium that is electrically neutral in every physically small volume, and the characteristic length scale L^* of the problem exceeds considerably the Debye length R_D, i.e., in CGS system of units:

$$L^* \gg R_D = \left[\frac{kT_e}{4\pi e^2 n_e}\right]^{1/2}$$

where T_e is the electron temperature, e is the electron charge, and n_e is the electron number density.

Equilibrium state of a medium is the state that a medium insulated against external effects or placed in a thermal reservoir reaches after some time (see Chapter 8, Thermodynamics of Gases and Plasmas).

Steady (stationary) nonequilibrium state of a medium is the state in which the values of parameters defining the medium (for example, temperature, number densities of the components, populations of energy levels, and so on) are time independent; this state is reached in a medium that is an open system when a constant external action does not let equilibrium to be attained.

Chemically equilibrium or nonequilibrium gases are characterized by the presence or absence of chemical equilibrium, respectively.

Thermally equilibrium or nonequilibrium gases or plasma are characterized, respectively, by the presence or absence of equilibrium within and between the various degrees of freedom of particles involved in the processes occurring in these gases. The degrees of freedom include, in addition to translational degrees of freedom of molecules, atoms, ions, and electrons, also rotational and vibrational degrees of freedom of molecules and molecular ions, and electronic degrees of freedom of atoms, molecules, and ions. A chemically nonequilibrium gas may also be thermally nonequilibrium.

The concepts and criteria of ideal gases and plasmas, and of equilibrium of a medium, as well as other definitions of the parameters of a medium, are given in the appropriate sections of this volume.

A medium interacting with radiation will be treated in the fourth volume of this book (see also the description of models E.4, P.5, P.6, and C.4 in this volume).

A. Composition of a Medium—Particles

- atomic gas: atoms
- molecular gas: atoms, molecules
- atomic plasma: atoms, atomic ions, electrons
- molecular plasma: atoms, molecules, atomic and molecular ions, electrons.

Structureless particles are atoms or molecules whose internal energy (electronic energy for atoms, and rotational, vibrational, and electronic energy for molecules) does not vary during their interaction with one another and with other particles.

B. Processes in a Medium

T Translational relaxation Processes of establishment of equilibrium or quasistationary, nonequilibrium distribution of particles with respect to translational energy as a result of elastic scattering of atoms, molecules, electrons, and ions in collisions:

TT – involving translational degrees of freedom of heavy particles,
Te, TI – in collisions with electrons (e) and ions (I).

R Rotational relaxation Processes of establishment of equilibrium or quasistationary nonequilibrium distribution of molecules with respect to energy of rotational degrees of freedom as a result of excitation and deactivation of rotation of molecules and molecular ions in collisions:

RT – involving translational degrees of freedom of heavy particles,
RR – involving rotational degrees of freedom of particles,
Re, RI – in collisions with electrons (e) and ions (I).

V Vibrational relaxation Processes of establishment of equilibrium or quasistationary nonequilibrium distribution of molecules with respect to energy of vibrational degrees of freedom as a result of excitation and deactivation of vibrations of molecules and molecular ions in collisions:

VT – involving translational degrees of freedom of heavy particles,
VR – involving rotational degrees of freedom of particles,
VV – involving vibrational degrees of freedom of particles,
VRT – involving rotational and translational degrees of freedom of particles,
VE – involving electronic-vibrational energy exchange,
VC, VP – involving chemical or plasmachemical reactions,
Ve, VI – in collisions with electrons (e) and ions (I).

E Electronic relaxation Processes of establishment of equilibrium or quasistationary nonequilibrium distribution of population of electronic states of atoms, molecules, and ions in collisions:

ET – involving translational degrees of freedom of particles,
EV – involving vibrational degrees of freedom of particles,
EE – involving energy exchange between electronic states of particles,
EC, EP – involving chemical and plasmachemical reactions,
Ee, EI – in collisions with electrons (e) and ions (I).

C Chemical reactions Transformations of neutral particles (atoms and molecules) in collisions:

C – in thermally equilibrium gases,
CV – in thermally nonequilibrium gases in the absence of equilibrium in vibrational degrees of freedom of particles,
CE – in thermally nonequilibrium gases in the absence of equilibrium in electronic states,
CVE – in thermally nonequilibrium gases in the absence of equilibrium in vibrational and electronic degrees of freedom of particles.

P Plasmachemical reactions Transformations of charged particles and/or changes of their charge in collisions:

P – in a thermally equilibrium plasma,
PV – in a thermally nonequilibrium plasma, in the absence of equilibrium in vibrational degrees of freedom of particles,
PE – in a thermally nonequilibrium plasma, in the absence of equilibrium in electronic states,
PVE – in a thermally nonequilibrium plasma, in the absence of equilibrium in vibrational and electronic degrees of freedom of particles.

Elementary process is an interaction between two or three particles during their collision, which brings about a change of quantum state and/or chemical transformation of the particles (reaction).

Simple process is a plurality of identical elementary processes occurring in some volume of gas. A simple process may be a stage in a complex process.

Complex process is a combination of different simple processes (stages) in gas; for example, methane combustion in air and coal pyrolysis.

Heat of a process (reaction), or thermal effect of a process (reaction), is the heat released or absorbed by the medium in which the process occurs, under conditions when no work is performed in this medium except for the work of expansion, and the temperature remains constant. At constant volume, the process heat is equal to the change of the internal energy of the system, and at constant pressure, it is equal to the enthalpy change (see Chapter 8, Thermodynamics of Gases and Plasmas).

Exothermic process (reaction) is a process accompanied by heat release.

Endothermic process (reaction) is a process accompanied by heat absorption.

Exoergic process (reaction) is a process accompanied by energy release during transition from the ground state of particles before the process to the ground state after the process.

Endoergic process (reaction) is a process accompanied by energy absorption during transition from the ground state of particles before the process to the ground state after the process.

An exoergic process may proceed via both endothermic and exothermic channels, depending on whether the heat in this process (reaction) is released or absorbed. If the internal states of reactant particles and reaction products are not preassigned, the concept of exo(endo)ergic process (reaction) coincides with the concept of exo(endo)thermic process (reaction).

C. Models of Medium

A *physical model* of a medium is developed as concepts and assumptions regarding the medium with the particles in it and the processes occurring in this medium between interacting particles.

A *mathematical model* includes:

- a set of variables for description of the medium;
- equations determining the evolution of these variables in time and/or in space;
- initial and/or boundary conditions;
- closure relations and formulas for the variables and for the parameters and coefficients.

A combination of physical and mathematical models defines the concept of model of medium in gas dynamics.

D. Levels of Description of Medium

The levels of description of medium in gas dynamics are distinguished by the various types of variables used in the respective models of medium.

MICROSCOPIC (MOLECULAR) LEVEL OF DESCRIPTION OF MEDIUM

A medium is described as a combination of a large number of interacting particles whose motion is governed by the equations of classical or quantum mechanics.

Variables in a mathematical model are generalized coordinates and particle momenta (in classical mechanics), and eigenvalues and wave functions of coordinate and momentum operators of particles of the medium (in quantum mechanics). Modeling at the microscopic level is commonly performed with the direct simulation Monte-Carlo (DSMC) method.[5,6]

KINETIC LEVEL OF DESCRIPTION OF MEDIUM

A medium is described in terms of single-particles distribution functions of components. The distribution functions of components are the *variables* in a mathematical model.

MACROSCOPIC LEVEL OF DESCRIPTION OF MEDIUM

A medium is described by a finite number of gas dynamic parameters as functions of coordinates and time.

Examples of *variables* in a mathematical model are:

- variables that characterize density of various components; for example, number densities, molar densities, mole fractions of components, population density for quantum levels of particles, and mass density of particles;
- vector or tensor variables describing translational motion of components of the medium; for example, mean mass velocity of the medium;
- variables that characterize the energy stored in the medium and its distribution among different components and different degrees of freedom of particles; for example, translational and vibrational energy, average number of vibrational quanta, and so on.

The notation for the quantities treated in this volume is given in the appropriate chapters and descriptions of models. Helpful advices are given in Chapter 1 of the first volume of this series.

CAUTION: enumeration of excited levels in models of rotational, vibrational and electronic relaxation starts from the ground level ($k = 0, 1, 2, \ldots$), but in models of plasmachemical processes it starts from the first level ($k = 1, 2, 3, \ldots$).

II. Relaxation Processes in Gases and Plasmas

Relaxation process is a process of establishment of equilibrium or quasistationary nonequilibrium distribution in statistical systems. One treats the distribution of the number of particles with respect to:

• velocity of motion, kinetic energy of motion	for translational degrees of freedom of particles
• quantum states and internal energy of particles	for internal (rotational, vibrational, electronic) degrees of freedom of particles

Equilibrium distributions of particles:

• Maxwellian distribution in velocity and kinetic energy	See section VI of Chapter 1 in the first volume of this series for a description.
• Boltzmann distribution in quantum states and internal energy	

Temperature of different degrees of freedom of particles. See section VI of Chapter 1 in the first volume of this series for a description.

Relaxation time τ is the characteristic time of relaxation process, inversely proportional to the rate of the process:

τ_{TT} – translational relaxation time
τ_{RT} – rotational relaxation time
τ_{VT} – vibrational relaxation time
τ_E – characteristic time of electron excitation or deactivation
τ_C – characteristic time of chemical reaction
τ_P – characteristic time of plasmachemical reaction (ionization, recombination, etc.).

The relaxation times of other processes are denoted with appropriate subscripts above.

The hierarchy of relaxation times of most processes is as follows:

$$\tau_0 \sim \tau_{TT} \leq \tau_{RT} \ll \tau_{VT} \ll \tau_C \ll \tau_E \ll \tau_P$$

where τ_0 is the mean time between consecutive collisions.

The hierarchy of relaxation times does not depend on pressure, because each one of the characteristic times is proportional to pressure (a more complex pressure dependence of relaxation times is observed in processes involving electrons). The temperature dependence of relaxation time is different for each process; therefore, the order of sequence of terms in the hierarchy of relaxation times may vary with temperature. For example, at room temperatures, $\tau_{VT} \ll \tau_C$, and at high temperatures, $\tau_{VT} \sim \tau_C$.

Simplified methods for description of relaxation processes: for a known time scale τ_L of the gas dynamic problem, one must treat only the relaxation processes with relaxation times (characteristic times) of $\tau \sim \tau_L$. One can assume that the faster processes on this time scale have already ceased, and the relatively slow processes have not yet begun. This approach corresponds to the *method of quasistationary distribution functions*, in which the energy distribution function with respect to individual degrees of freedom depends only on the variables that characterize this particular degree of freedom. The completed fast processes determine the magnitude of the respective parameters in the distribution function, which characterizes results of these processes. For example, in studying vibrational relaxation of diatomic molecules, the relatively slow process of dissociation may be disregarded at $\tau_C \gg \tau_{VT}$. Faster processes of translational and rotational relaxation on a τ_{VT} scale are assumed to be terminated, and their result, that is, the formation of equilibrium energy distribution in translational and rotational degrees of freedom, enters the vibrational energy distribution function as a parameter defining the instantaneous value of translational and rotational temperature.

State-to-state or state-specific kinetics describes changes of particle population of certain energy levels.

Mode kinetics describes relaxation of a mean energy or a mean number of quanta in each vibrational and rotational mode; this method gives a simplified and compact description of state-specific kinetics and does not require information on the details of the distribution function. Basic kinetic equations in description of relaxation processes:

- *Boltzmann equation*
  quantities to be determined: velocity and translational energy distribution functions of particles,
  type of equations: integro-differential equations (see the description of models T.1 to T.3).
- *Equations of state-specific kinetics* (master equations, Pauli equations)
  quantities to be determined: populations (number of particles per unit volume) of certain energy levels,
  type of equations: ordinary differential equations (see the description of models R.1, V.1 to V.3, V.5, V.6, E.1 to E.4).
- *Diffusion equations*
  quantities to be determined: translational or internal energy distribution functions of particles,
  type of equations: partial differential equations (see the description of models R.2, V.4).
- *Equations of mode kinetics*
  quantities to be determined: mean rotational or vibrational energy,
  type of equations: ordinary differential equations (see the description of models R.4 and V.7 to V.9).

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Chapter 2

Translational Relaxation (T Models)

I. Translational Relaxation

THE PROCESS of the establishment of equilibrium in the subsystem of the translational degrees of freedom of particles (translational relaxation) is one of the fastest relaxation processes induced by molecular collisions. In an isolated system with arbitrary initial conditions, equilibrium distribution in translational velocity of particles (Maxwellian distribution) is established during the time of the order of several times between collisions. In open systems, which can exchange mass, momentum, and/or energy with the environment, the velocity distribution of particles may be substantially different from the Maxwellian one, even at steady state.

Theoretical analysis of the translational relaxation in models T.1–T.3 is performed for the spatially uniform systems for which the state of the medium varies with time only. In these models, gas dynamic variables (such as gas density and mass velocity) are assumed to be constant, external body forces are not considered, and colliding particles are assumed to be structureless (see Chapter 1, Elastic Collisions, in the first volume of the series).

A. Translational Relaxation in Single- and Two-Component Gases (T.1)

1. Purpose of the Model

The model aims at calculating the velocity distribution function for particles (atoms or molecules) in spatially uniform single- and two-component gases.

2. Assumptions

Translational motion of particles is analyzed within the framework of classical mechanics. Molecules interact by centrally symmetric forces.

3. Restrictions

a) A rarefied gas is considered, so that three-body collisions can be neglected: $NR_0^3 \ll 1$.
b) The hypothesis of molecular chaos is assumed to be valid; that is, it is assumed that the states of colliding particles are not correlated. Under the molecular chaos hypothesis, the characteristic time interval Δt is subject to the restriction depending on the molecule's velocity $\mathbf{c}$: $\Delta t \gg R_0/|\mathbf{c}|$.

4. *Boltzmann Kinetic Equations*

a) For a single-component gas,

$$\frac{\partial f}{\partial t} = \int\!\!\int\!\!\int (f'f_1' - ff_1) g b \, \mathrm{d}b \, \mathrm{d}\varphi \, \mathrm{d}\mathbf{c}_1$$

$$g = |\mathbf{c} - \mathbf{c}_1|, \quad f_1 = f(\mathbf{c}_1, t), \quad f' = f(\mathbf{c}', t), \quad f_1' = f(\mathbf{c}_1', t)$$

b) For a two-component gas of species A and B,

$$\begin{aligned}
\frac{\partial f_\mathrm{A}}{\partial t} &= \int\!\!\int\!\!\int (f_\mathrm{A}' f_\mathrm{A1}' - f_\mathrm{A} f_\mathrm{A1}) g_\mathrm{AA} b \, \mathrm{d}b \, \mathrm{d}\varphi \, \mathrm{d}\mathbf{c}_1 \\
&\quad + \int\!\!\int\!\!\int (f_\mathrm{A}' f_\mathrm{B1}' - f_\mathrm{A} f_\mathrm{B1}) g_\mathrm{AB} b \, \mathrm{d}b \, \mathrm{d}\varphi \, \mathrm{d}\mathbf{v}_1 \\
\frac{\partial f_\mathrm{B}}{\partial t} &= \int\!\!\int\!\!\int (f_\mathrm{B}' f_\mathrm{B1}' - f_\mathrm{B} f_\mathrm{B1}) g_\mathrm{BB} b \, \mathrm{d}b \, \mathrm{d}\varphi + \mathrm{d}\mathbf{v}_1 \\
&\quad + \int\!\!\int\!\!\int (f_\mathrm{B}' f_\mathrm{A1}' - f_\mathrm{B} f_\mathrm{A1}) g_\mathrm{BA} b \, \mathrm{d}b \, \mathrm{d}\varphi \, \mathrm{d}\mathbf{c}_1
\end{aligned}$$

$$f_\mathrm{A}' = f_\mathrm{A}(\mathbf{c}', t), \quad f_\mathrm{B}' = f_\mathrm{B}(\mathbf{v}', t), \quad f_\mathrm{A1}' = f_\mathrm{A}(\mathbf{c}_1', t), \quad f_\mathrm{B1}' = f_\mathrm{B}(\mathbf{v}_1', t)$$

$$g_\mathrm{AA} = |\mathbf{c} - \mathbf{c}_1|, \quad g_\mathrm{BB} = |\mathbf{v} - \mathbf{v}_1|, \quad g_\mathrm{AB} = |\mathbf{c} - \mathbf{v}_1|, \quad g_\mathrm{BA} = |\mathbf{v} - \mathbf{c}_1|$$

5. *Nomenclature*

a) Quantities calculated with the model:

$f_\mathrm{A}(\mathbf{c}, t)$ – velocity distribution function for species A
$f_\mathrm{B}(\mathbf{v}, t)$ – velocity distribution function for species B

b) Other quantities:

$\mathbf{c}, \mathbf{c}_1$ – velocities of particles A before a collision
$\mathbf{v}, \mathbf{v}_1$ – velocities of particles B before a collision
$\mathbf{c}', \mathbf{c}_1'$ – velocities of particles A after a collision
$\mathbf{v}', \mathbf{v}_1'$ – velocities of particles B after a collision
g_AA – absolute value of relative velocity for a collision of two particles A
g_BB – absolute value of relative velocity for a collision of two particles B
g_AB – absolute value of relative velocity for a collision of A and B
φ – azimuthal angle
b – impact parameter
N – number density
N^A – number density of species A
N^B – number density of species B
τ_0 – mean free time between collisions
θ – angle between the velocity vectors $\mathbf{c}_1 - \mathbf{c}$ and $\mathbf{c}_1' - \mathbf{c}'$
σ – differential cross section for elastic collisions
Θ_0 – parameter of an initial distribution conditioned on $f(\mathbf{c}, 0) > 0$
R_0 – gas kinetic radius for elastic collisions
$m_\mathrm{A}, m_\mathrm{B}$ – masses of species A and B

6. *Description of Coefficients and Parameters*

The parameters R_0 and τ_0 are defined in Chapter 1 of the first volume of the series (for example, see model I-T.1).

7. *Model Features*

a) In a gas consisting of species A and B with particle masses m_A and m_B (as well as in a one-component gas with particle mass m), the translational relaxation time, τ_0, is on the order of the mean free time τ_{TT} between collisions for either species, if $m_A \sim m_B$. At atmospheric pressure and temperature, $T \sim 300$ K, $\tau_0 \sim 10^{-10}$ s.

b) In a two-component gas with a large difference in masses between the species (e.g., $m_A \ll m_B$), translational relaxation involves three stages. At the first stage, a Maxwellian distribution is reached in the zeroth approximation for the light particles in a characteristic time, τ_A. At the second stage, a Maxwellian distribution is reached for the heavy particles in a characteristic time, τ_B. As this stage, the temperatures of the light and heavy species may differ. At the final stage, a single-temperature Maxwellian distribution is reached for the entire gas after temperatures of A and B equalize in a characteristic time, τ_{AB}. If the concentrations of A and B are almost equal, and $T_A \sim T_B$, then $\tau_A : \tau_B : \tau_{AB} = 1 : \sqrt{m_B/m_A} : m_B/m_A$.

8. *General and Particular Solutions*

a) The time-independent solution of the Boltzmann equation corresponding to an equilibrium state is the Maxwellian distribution function

$$f_A^{(0)} = N^A \left(\frac{m_A}{2\pi kT}\right)^{3/2} e^{-(m_A \mathbf{c}^2/2kT)}, \quad f_B^{(0)} = N^B \left(\frac{m_B}{2\pi kT}\right)^{3/2} e^{-(m_B \mathbf{v}^2/2kT)}$$

b) For molecules with an interaction potential of the form $U(r) = \alpha/r^4$, (Maxwellian molecules; R is the intermolecular distance, and C_4 is the parameter of potential) in a uniform gas characterized by the initial distribution function

$$f(c, 0) = \left[\frac{m}{2\pi kT(1-\Theta_0)}\right]^{3/2} \left[1 + \frac{\Theta_0}{1-\Theta_0}\left(\frac{mc^2}{2kT(1-\Theta_0)}\right) - \frac{3}{2}\right] \times \exp\left[-\frac{mc^2}{2kT(1-\Theta_0)}\right]$$

the exact solution to the Boltzmann equation is (see Refs. 13–15)

$$f(\mathbf{c}, t) = N\left(\frac{m}{2\pi kT\chi(t)}\right)^{3/2} \left[1 + \frac{1-\chi(t)}{\chi(t)}\left(\frac{mc^2}{2kT\chi(t)} - \frac{3}{2}\right)\right] \times \exp\left(-\frac{mc^2}{2kT\chi(t)}\right)$$

where $\chi = 1 - \Theta_0 e^{-\lambda t}$, $(0 \leq \Theta_0 \leq 2/5)$, $\lambda = -N(\pi/2)\int_0^\infty \alpha(\xi)(1-\xi^2)\,d\xi$

$$\xi = \cos\theta, \quad \alpha(\xi) = g_{AA}\sigma$$

The parameter λ is inversely proportional to the translational relaxation time, and may be expressed through pressure p and dynamic viscosity coefficient μ $(\lambda = p/3\mu)$. More information is available in the third volume of this series.

c) The methods of solution of Boltzmann equation are examined in Refs. 2–4, 7, 8, 15–19. Direct Simulation Monte-Carlo (DSMC) method (see Refs. 20–22) is the most effective and widely used one.

9. *Example*

Figure 2.1 illustrates evolution of the normalized velocity distribution $R(v, t)$ for Maxwellian molecules (see above), defined as $R(v, t) = f(v, t)/f(v, t = \infty)$, $v = \sqrt{mc^2/kT}$, with a dimensionless time $\tau = \lambda t - \log\Theta_0$ (Refs. 14, 15).

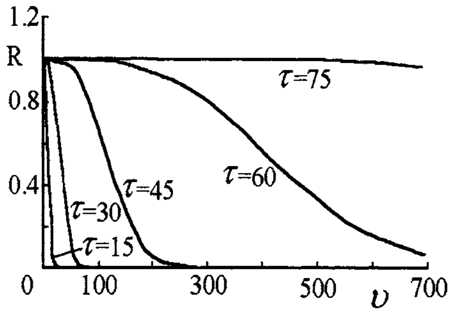

Fig. 2.1

Figure 2.1 demonstrates that the high-energy tail of the velocity distribution $f(v, t)$ approaches the Maxwellian distribution $f(v, t = \infty)$ at a slower rate as compared to the Maxwellization rate for the distribution in the thermal velocity region, $v \sim 1$. Therefore, linearized Boltzmann equation cannot describe the relaxation of $f(v, t)$ in the high-energy domain.

10. *Comments*

a) Even though the basic equation does not explicitly contain the interaction potential, knowledge of the potential is required to determine the velocities $\mathbf{c}'$ and $\mathbf{c}'_1$ for given values of $\mathbf{c}$, $\mathbf{c}_1$, and impact parameter (see Chapter 1 of volume I).

b) The solution of the Boltzmann equation for translational relaxation in steady-state supersonic flow was studied in Refs. 4, 7, 19.

Relevant material can be found in Refs. 1–8.

B. Translational Relaxation in Lorentz and Rayleigh Gases (T.2)

1. *Purpose of the Model*

The model aims at calculation of distribution functions in absolute values of velocity or translational energy

a) for heavy species as a low-concentration impurity in a light gas (Rayleigh gas);
b) for light species as a low-concentration impurity in a heavy gas (Lorentz gas).

2. *Assumptions*

a) See Assumptions in the description of model T.1.
b) The velocity distributions for light particles in a Rayleigh gas and heavy particles in a Lorentz gas are described by Maxwellian functions with temperatures T_A and T_B, respectively.

3. *Restrictions*

a) For the Rayleigh gas:

the mass of the light species A is much smaller than the mass of the heavy species B: $m_A \ll m_B$;
the number density of A is substantially higher than the number density of B: $N^A \gg N^B$.

The characteristic time interval of interest is greater than the mean free time between collisions, τ_0, for the gas of species A. (The value of τ_0 is specified in the descriptions of models I-T.1–I-T.3).

b) For the Lorentz gas:

the mass of the light species A is much smaller than the mass of the heavy species B: $m_A \ll m_B$;
the number density of A is substantially lower than the number density of B: $N^A \ll N^B$.

The characteristic time interval of interest is greater than the mean free time between collisions, τ_0, for the gas of species B. (The value of τ_0 is specified in the descriptions of models I-T.1–I-T.5).

4. *Kinetic Equations*

a) Rayleigh gas:
for the distribution function for the absolute value of velocity,

$$\frac{\partial f_B(v, t)}{\partial t} = \frac{1}{\tau_R v^2} \frac{\partial}{\partial v}\left[\frac{v^3}{2} f_B(v, t) + \frac{kT_A}{2m_B} v^2 \frac{\partial f_B(v, t)}{\partial v}\right]$$

for the translational energy distribution function,

$$\frac{\partial f_B(\varepsilon, t)}{\partial t} = \frac{1}{\tau_R} \frac{\partial}{\partial \varepsilon}\left[\left(\varepsilon - \frac{3}{2}\right) f_B(\varepsilon, t) + \frac{\partial}{\partial \varepsilon}(\varepsilon f_B(\varepsilon, t)\right], \quad \varepsilon = \frac{m_B v^2}{2kT_A}$$

$$\frac{1}{\tau_R} = \frac{16}{3} \frac{m_A}{m_B} N^A \pi (R_0^{AB})^2 \left(\frac{2kT_A}{\pi m_A}\right)^{1/2}, \quad R_0^{AB} = R_0^A + R_0^B$$

b) Lorentz gas:
for the distribution function for the absolute value of velocity,

$$\frac{\partial f_A(c, t)}{\partial t} = \frac{1}{c^2} \frac{\partial}{\partial c}\left(\frac{kT_B}{m_B} \frac{c^3}{l_A} \frac{\partial f_A(c, t)}{\partial c} + \frac{m_A}{m_B} \frac{c^4}{l_A} f_A(c, t)\right)$$

for the translational energy distribution function,

$$\frac{\partial f_A(\varepsilon, t)}{\partial t} = \frac{1}{\tau_L}\frac{\partial}{\partial \varepsilon}\left[(\varepsilon^{3/2} - 2\varepsilon^{1/2}) f_A(\varepsilon, t) + \frac{\partial}{\partial \varepsilon}(\varepsilon^{3/2} f_A(\varepsilon, t))\right], \ \varepsilon = \frac{m_A c^2}{2kT_B}$$

$$\frac{1}{\tau_L} = 2\left(\frac{m_A}{m_B}\right)^{1/2} N^B \pi (R_0^{AB})^2 \left(\frac{2kT_B}{\pi m_B}\right)^{1/2}$$

When $l_A = [N^B \pi (R_0^{AB})^2]^{-1}$, the equations for $f_A(c, t)$ and $f_A(\varepsilon, t)$ are equivalent.

5. *Nomenclature*

a) Quantities calculated with the model:
For Rayleigh gas

$f_B(v, t)$ – distribution function for the absolute value v of particle B velocity
$f_B(\varepsilon, t)$ – distribution function for dimensionless translational energy ε of particles B

For Lorentz gas

$f_A(c, t)$ – distribution function for the absolute value c of particle A velocity
$f_A(\varepsilon, t)$ – distribution function for dimensionless translational energy ε of particles A

b) Other quantities:

$\mathbf{c}$ – velocity of light particles A
c – absolute value of the velocity of light particles A
m_A, m_B – masses of particles A and B
T_A – temperature of the gas of particles A (Rayleigh gas)
T_B – temperature of the gas of particles B (Lorentz gas)
τ_0 – mean free time between collisions
l_A – mean free path for a particle A in the gas of particles B
R_0 – hard-sphere radius (gas kinetic radius)
τ_R – characteristic time of translational relaxation of heavy particles in the Rayleigh gas
τ_L – characteristic time of translational relaxation of light particles in the Lorentz gas
N^A, N^B – number density of species A and B

6. *Description of Coefficients and Parameters*

The parameters R_0, l_A (as l_0), and τ_0 are defined in Chapter 1 of the first volume (see the description of models I-T.1–I-T.4).

7. *Model Features*

a) Translational relaxation consists in maxwellization of the velocity distribution functions for light particles A in the Lorentz gas and heavy particles B in the Rayleigh gas over times τ_R and τ_L, respectively. These relaxation times are substantially greater than the respective mean free times between collisions.

b) The modeled process is characterized by canonical invariance: evolution of the Rayleigh gas that had an initial Maxwellian distribution with temperature different from the light-gas temperature proceeds through a sequence of Maxwellian distributions with varying temperature. This means that if

$$f_B(\varepsilon, 0) = 2N^B\left(\frac{\varepsilon}{\pi}\right)^{1/2}\alpha_0^{-3/2}\exp\left(-\frac{\varepsilon}{\alpha_0}\right), \quad \alpha_0 = T(0)/T_A$$

then

$$f_B(\varepsilon, t) = 2N^B\left(\frac{\varepsilon}{\pi}\right)^{1/2}\alpha^{-3/2}\exp\left(-\frac{\varepsilon}{\alpha}\right), \quad \alpha = T(t)/T_A$$

$$\frac{d\alpha}{dt} = -\frac{1}{\tau_R}(\alpha - 1)$$

The kinetic equations for the Lorentz gas are not canonically invariant.

c) The simple relaxation equation for the Rayleigh gas characterized by a dimensionless mean translational energy E has a form:

$$\frac{dE(t)}{dt} = -\frac{1}{\tau_R}[E(t) - E_\infty], \quad E = \int_0^\infty \varepsilon f_B(\varepsilon, t)\,d\varepsilon, \quad E_\infty = \frac{3}{2}$$

The Lorentz gas cannot be described by a similar energy relaxation equation.

8. *General and Particular Solutions*

The solution to the basic kinetic equation for the translational energy of particles B in the Rayleigh gas is:

$$f_B(\varepsilon, t) = N^B\varepsilon^{1/2}e^{-\varepsilon}\sum c_\nu L_\nu^{1/2}(\varepsilon)e^{-\nu\tau}$$

$$c_\nu = \frac{\Gamma(\nu+1)}{\Gamma(\nu+3/2)}\int_0^\infty f_B(\varepsilon, 0)L_\nu^{1/2}(x)\,dx$$

where $L_\nu^{1/2}(\varepsilon)$ is a generalized Laguerre polynomial and $\tau = t/\tau_R$.

In contrast to the Rayleigh gas, Lorentz gas kinetics do not admit any simple analytical description.

9. *Example*

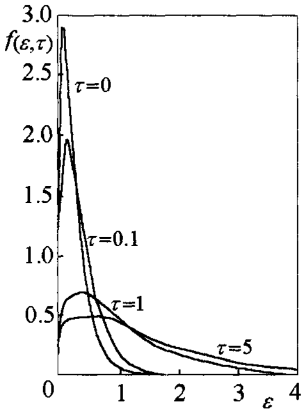

Fig. 2.2

Figure 2.2 illustrates the evolution of the distribution of particles over the dimensionless translational energy $\varepsilon = m_B v^2/2kT_A$ in the course of relaxation of an initial Maxwellian distribution $f_B(\varepsilon, 0)$ for a Rayleigh gas with $T_B(0) = (1/6)T_A$, $\tau = t/\tau_R$ (Ref. 23).

10. *Comment*

A diffusion-type kinetic equation for the translational energy distribution can be obtained for Rayleigh gas in which the light gas is characterized by a non-Maxwellian velocity distribution (see Refs. 5, 6, and 24).

Relevant material can be found in Refs. 5, 6.

C. Strong-Collision Model (T.3)

1. *Purpose of the Model*

The model aims at calculation of the velocity distribution function in a uniform gas.

2. *Assumptions*

See the description of model T.1.

Each collision is strong in a sense that it transfers the particle into the group of particles that have the Maxwellian velocity distribution.

3. *Restrictions*

For qualitative description of relaxation processes, there are no restrictions. The model is most accurate for systems close to equilibrium.

4. *Kinetic Equation*

$$\frac{\partial f}{\partial t} = \nu(f^{(0)} - f)$$

$$f^{(0)} = N\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-(mc^2/2kT)}, \quad N = \int f \, \mathrm{d}c, \quad T = \frac{2}{3kN}\int \frac{mc^2}{2} f \, \mathrm{d}c$$

5. *Nomenclature*

a) Quantity calculated with the model:

$f(\mathbf{c}, t)$ – velocity distribution function

b) Other quantities:

$\mathbf{c}$ – particle velocity
ν – empirical parameter
$f^{(0)}$ – Maxwellian distribution function
N – number density

6. *Description of Coefficients and Parameters*

The empirical parameter ν cannot be determined within the framework of the model. It is used as an adjustable parameter whose magnitude is on the order of the collision frequency per particle, i.e., the number of collisions experienced by a particle per unit time.

7. *Model Features*

a) The number density N and gas temperature T are integrals of the distribution function f. The kinetic equation is linear when both N and T are constant.

b) For a monatomic gas with particle sources, the equation has the form [6]

$$\frac{\partial f}{\partial t} = \nu(f^{(0)} - f) + q(v) - \frac{f}{\tau^*}$$

where $q(v)$ is the rate of production of particles in the velocity interval v, $v + \mathrm{d}v$, and τ^* is the characteristic lifetime of a particle. At steady state $(\nu\tau^* \gg 1)$, $f = f^{(0)} + q(v)/\nu$. In the velocity domain where $f^{(0)} < q(v)/\nu$, the particle source induces finite disturbances of the Maxwellian distribution.

8. *General and Particular Solutions*

When $\nu = \text{const}$, the solution is:

$$f(\mathbf{c}, t) = f(\mathbf{c}, 0)e^{-\nu t} + f^{(0)}(1 - e^{-\nu t})$$

9. *Example*

See the analytical solution for $\nu = \text{const}$ previously defined.

10. *Comments*

a) The strong-collision model is also known as the Bhatnagar–Gross–Krook (BGK) model (see Refs. 4, 7, and 25).

b) For a nonuniform gas with time-dependent N and T, the kinetic equation becomes a nonlinear integro-differential equation, because both N and T in $f^{(0)}$ depend on $f(\mathbf{c}, t)$ (Refs. 4 and 7).

c) The strong-collision model is employed in analyses of molecular transport processes (Ref. 26).

d) This kinetic equation is sometimes referred to as a relaxation equation (see Ref. 4).

Relevant material can be found in Refs. 4, 6–8.

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Chapter 3

Rotational Relaxation (R Models)

I. Introduction

FOR THE majority of molecules, the process of establishment of equilibrium in the subsystem of rotational degrees of freedom (rotational relaxation, see Refs. 1–4) proceeds with the characteristic time of the order of several times between collisions. There are two exceptions from this rule: first, light molecules (H_2, D_2, HD), and second, highly rotationally excited molecules, for which the rotational relaxation time at room temperature may be hundreds of times longer than the time between molecular collisions (see model R.4).

In an isolated system with arbitrary initial conditions, rotational relaxation leads to the equilibrium rotational distribution (Boltzmann distribution), see item 1 of the subsection "Model Features" of the model R.1, and also section VI in Chapter 1 of the first volume. In open systems that can exchange mass, momentum, and/or energy with the environment, for example, in laser excited gases, the rotational distribution of molecules may be substantially different from the Boltzmann one.

The physical reason for the high rate of rotational relaxation lies in the impulsive nonadiabatic nature of the RT energy transfer process: the Massey parameter $\xi = \Delta E/\hbar\tau_{col} \ll 1$, where ΔE is the energy spacing of the states between which the transition occurs, and τ_{col} is the duration of molecular collision ($\tau_{col} = \ell/\bar{u}$, where ℓ is a characteristic range of intermolecular interaction, and $\bar{u}$ is the mean velocity of relative molecular motion, see sections V and VII in Chapter 1 of the first volume). At low Massey parameters, interaction between the collision partners reduces to the elastic interaction of the nearest atoms, and the transferred energy is almost equally distributed between the rotational and translational degrees of freedom of the relaxing molecule. For light or highly rotationally excited molecules, $(\Delta E/k) \gg 1$ K, and the Massey parameter is larger than unity. Not only the atom nearest to the impinging particle, but the molecule as a whole participates in the collision in this case. With increase of the Massey parameter, symmetry of the relaxing molecule with respect to the collision partner effectively increases, and energy transferred to the rotational degrees of freedom decreases. At $\xi \to \infty$ the relaxing molecule behaves as a spherically symmetric particle, rotations of which are not excited in the collision.

Theoretical analysis of the rotational relaxation in the models R.1–R.4 is performed for the spatially uniform systems, for which the state of the media varies with time t only. In these models, gas dynamic variables (such as gas density and mass velocity) are assumed to be constant, and external body forces are not considered. When solving gas dynamic problems, the relaxation equations mentioned here should be added to the corresponding equations of gas dynamics. For example, rotational relaxation models are widely used in studies of supersonic jet and nozzle flows (for example, see Ref. 5). Rotational relaxation in a gas of polyatomic molecules with a phenomenological energy exchange model was studied in Ref. 6 with Direct Simulation Monte Carlo (DSMC) method (see Ref. 7).

A. Rotational Relaxation: State-to-State Kinetic Model (R.1)

1. *Purpose of the Model*

The model aims at the calculation of rotational state populations in various gases, including mixtures where collision partners of the relaxing molecule are treated as structureless particles.

2. *Assumptions*

a) Linear or spherical top molecules XY are considered, for which rotational energy is a function of a single quantum number.

b) The characteristic time of rotational relaxation is much longer than the translational relaxation time, so that rotational energy transfer probabilities are functions of translational temperature (that is, of the gas temperature T).

c) Three-body collisions are ignored, because the product of three-body collision rate and the probability of rotational transitions induced by those collisions is assumed to be substantially lower than the product of collision rate and transition probability for binary collisions.

d) The frequency (rate) Z of collisions of XY with other particles is independent of the rotational state of XY.

3. *Restrictions*

a) Assumption 2 implies that this model is applicable if $\tau_{RT} \gg \tau_{TT}$. This requirement is fulfilled for light molecules (H_2 and D_2) and for molecules excited to high rotational levels. In these cases, the Massey parameter is such that $(\Delta E_{n,n'}/h)(R_0/\bar{u}) \gg 1$, where R_0 is the radius of the domain of interaction between molecules, $\bar{u}$ is the mean relative velocity for the colliding particles, and $\Delta E_{n,n'} = |E_n - E_{n'}|$. Therefore, the cross section for rotational excitation $n \rightarrow n'$ is significantly smaller than the elastic collision cross section.

b) In analyses of rotational relaxation of molecules XY diluted in a gas of structureless particles M_j, the XY number density is restricted by the condition $Nk_{10}^{\mathrm{XY-XY}} \ll N^{\mathrm{M}_j}k_{10}^{\mathrm{XY-M}_j}$ $(j \geq 1)$.

c) The number densities N^{M_j} are restricted by the inequalities $k_{10}^{\mathrm{XY-M}_j\mathrm{-M}_i}N_{\mathrm{M}_j}N_{\mathrm{M}_i} \ll k_{10}^{\mathrm{XY-M}_j}N_{\mathrm{M}_j}$ $(i, j \geq 1)$ and by analogous conditions for XY–XY–XY and XY–XY–M three-body collisions and XY–XY binary collisions, which makes it possible to ignore three-body collisions.

4. *Kinetic Equations*

$$\begin{aligned}\frac{\mathrm{d}N_n}{\mathrm{d}t} = \sum_m \Bigg[& \left(k_{mn}^{\mathrm{XY-XY}} N + \sum_j k_{mn}^{\mathrm{XY-M}_j} N^{\mathrm{M}_j} \right) N_m \\ & - \left(k_{nm}^{\mathrm{XY-XY}} N + \sum_j k_{nm}^{\mathrm{XY-M}_j} N^{\mathrm{M}_j} \right) N_n \Bigg] + \sum_{\substack{m,s,l \\ s \neq l}} \left(k_{mn}^{sl} N_m N_s - k_{nm}^{ls} N_n N_l \right)\end{aligned}$$

$$n,\ m,\ s,\ l = 0,\ 1,\ 2, \ldots$$

5. *Nomenclature*

a) Quantities calculated with the model:

N_n – population density on the nth rotational level of XY molecules

b) Kinetic coefficients:

$k_{mn}^{\mathrm{XY-M}_j}$ – rate constant for the $m \to n$ transition associated with RT energy transfer in XY–M_j collisions
$k_{mn}^{\mathrm{XY-XY}}$ – rate constant for the $m \to n$ transition associated with RT energy transfer in XY–XY collisions
$k_{mn}^{sl}(T)$ – rate constant for RR energy exchange involving $m \to n$ rotational transition in one molecule and $s \to l$ transition in the other
$k_{mn}^{\mathrm{XY-M}_j\mathrm{-M}_i}$ – rate constant for the $m \to n$ transition associated with RT energy exchange in XY–M_i–M_j collisions

c) Other quantities:

i, j – indices (subscripts) referring to structureless molecules
T – translational temperature (gas temperature)
E_n – rotational energy of a molecule XY in the nth rotational level
N – number density of XY molecules
N^{M_j} – number density of M_j particles
N_0 – population density for ground state
τ_{RT} – rotational relaxation time
τ_{TT} – translational relaxation time
g_n – statistical weight (multiplicity) of the nth rotational level
B – rotational constant

6. *Description of Coefficients and Parameters*

Formulas for the rate constants $k_{mn}^{\mathrm{XY-M}_j}(T)$ of RT energy exchange were presented in Chapter 3 of the first volume. Data required to describe RR energy exchange can be found in Refs. 1 and 2.

The rotational energy E_n as a function of rotational quantum number n was described in Chapter 1 of the first volume, where references to more sophisticated models of molecules were also given.

7. *Model Features*

a) At a constant gas temperature T, in the limit $t \to \infty$, the relaxing system evolves toward equilibrium where the population density of rotational levels is described by the equilibrium Boltzmann distribution

$$N_n = N_0 g_n \exp\left(-\frac{E_n}{kT}\right)$$

where $g_n = (2n+1)$ for linear molecules, and $g_n = (2n+1)^2$ for spherical top molecules; N_0 is the population density of the ground rotational state. For both linear and spherical top molecules, $E_n = Bn(n+1)$, where B is the rotational constant (see Chapter 1 of the first volume).

b) Detailed balance relations have the form

$$g_m k_{mn}^{\mathrm{XY-M}_j} \exp\left(-\frac{E_m}{kT}\right) = g_n k_{mn}^{\mathrm{XY-M}_j} \exp\left(-\frac{E_n}{kT}\right)$$

8. *General and Particular Solutions*

In the general case, the kinetic equations are solved by numerical methods.

9. *Example*

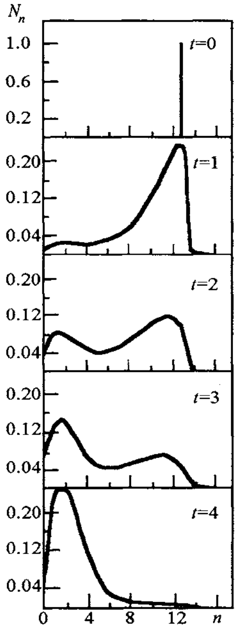

Fig. 3.1

Figure 3.1 illustrates the relaxation of population density distribution N_n normalized by the total number density of HCl molecules and calculated at the moments $t = 0, \ldots, 4$ for an HCl$-$H$_2$ mixture evolving from an initial delta function distribution (see Refs. 1 and 3). The rate constant k_{mn} was calculated with the Polanyi–Woodall model (see model I-R.2). The two intermediate peaks observed in Fig. 3.1 are consistent with the results of infrared (IR) chemiluminescence measurements reported in Ref. 10. Their occurrence is explained by the facts that rotational states are not equidistant, and the spacing between the states increases with n, so that rate constants of rotational transitions between adjacent states $n \to n-1$ in the vicinity of the initial delta distribution are much lower than the transition rate constants in the thermal (low n) energy domain (see description of model I-R.2 ([R.1]).

10. *Comments*

a) The expression in brackets on the right-hand side of the kinetic equation represents rotational–translational energy exchange. When the nonequilibrium specie XY is a low-concentration impurity in a gas of M_i particles, the terms containing k_{mn}^{XY-XY} and k_{nm}^{XY-XY} should be dropped in this expression. The last term on the right-hand side of the kinetic equation represents the RR energy exchange in collisions of relaxing molecules in a single-component gas or in a multicomponent gas with a substantial fraction of nonequilibrium species; this term should be dropped when the concentration of nonequilibrium species is low.

b) Because $(\tau_{RT}/\tau_{TT}) \sim \max\{(m_{XY}/m_{M_j}); (m_{M_j}/m_{XY})\}$ for most pairs XY and M_j, this model cannot be applied when m_{XY} and m_{M_j} are of the same order of magnitude. When $\tau_{RT} \sim \tau_{TT}$, rotational relaxation kinetics can be described by a set of Boltzmann equations for multicomponent mixture where molecules in different rotational states are treated as different species.

Relevant material can be found in Refs. 1–3.

B. Diffusion Approximation for Rotational Relaxation (R.2)

1. *Purpose of the Model*

The model aims at calculation of the energy distribution over rotational levels for test molecules diluted in a gas of structureless particles.

2. *Assumptions*

a) See Assumptions 1–4 in the description of model R.1.
b) A diffusion approximation is assumed to be applicable.
c) A low concentration of rotators XY is contained in a mixture with structureless particles.
d) The velocity distribution of structureless particles is Maxwellian with temperature T.

3. *Restrictions*

a) The diffusion approximation is applicable to slow relaxation processes, if the rotational energy quantization can be neglected, i.e., if $|\Delta E_{n+1,n}| \ll kT$, where $\Delta E_{nn'} = E_n - E_{n'}$ (the notation is explained in the description of model R.1). A process can be treated as slow if the change of a quantity (e.g., energy) in a single elementary collision act is small compared to a typical value of that quantity.

b) Diffusion approximation can be applied to both Rayleigh and Lorentz gases (see definitions in model T.2) under the assumption that the molecules are rigid rotators.

4. *Kinetic Equations*

a) In the general case

$$\frac{\partial f(\varepsilon, t)}{\partial t} = \frac{\partial}{\partial \varepsilon}\left[D(\varepsilon)\left(\frac{\partial f(\varepsilon, t)}{\partial \varepsilon} + \frac{1}{kT} f(\varepsilon, t)\right)\right], \qquad D(\varepsilon) = \frac{\overline{\Delta}^2}{2\tau_0}$$

initial condition

$$f(\varepsilon, 0) = \varphi(\varepsilon)$$

boundary condition

$$\left(\frac{\partial f}{\partial \varepsilon} + \frac{1}{kT} f\right)\Bigg|_{\varepsilon=0} = 0$$

b) For Rayleigh gas (low concentration of heavy molecules in a light gas)

$$\frac{\partial f(\varepsilon, t)}{\partial t} = \frac{\partial}{\partial \varepsilon}\left[b\varepsilon\left(\frac{\partial f(\varepsilon, t)}{\partial \varepsilon} + \frac{1}{kT} f(\varepsilon, t)\right)\right]$$

$$b = \sum_j \frac{32}{3} \frac{m_{\mathrm{M}_j} N^{\mathrm{M}_j}}{m} kT\Omega_{1j}^{(11)}$$

5. *Nomenclature*

a) Quantities calculated with the model:

$f(\varepsilon, t)$ – distribution function of molecules over rotational energy ε

b) Kinetic coefficients:

$D(\varepsilon)$ – diffusion coefficient in the rotational energy space

c) Other quantities:

$\overline{\Delta}^2$ – mean square energy transferred to the rotational degrees of freedom in a collision with a thermal-bath particle
τ_0 – mean free time between collisions of a rotator in a monatomic gas
j – index referring to structureless particles
m – mass of an XY molecule
m_{M_j} – mass of an M_j particle
N^{XY} – number density of XY molecules
N^{M_j} – number density of M_j particles
τ_{RT} – rotational relaxation time
τ_{TT} – translational relaxation time
$P(\varepsilon \to \varepsilon')$ – probability density for $\varepsilon \to \varepsilon'$ rotational transition in a collision, averaged over the Maxwellian velocity distribution
T_R – rotational temperature
$\Omega_{1j}^{(11)}$ – collision integral
R_{0j} – gas kinetic radius

6. *Description of Coefficients and Parameters*

a) $D = \text{const}$:

A constant value of $\bar{\Delta}^2/2\tau_0$ can be used when the probability density $P(\varepsilon, \varepsilon')$ depends only on the transferred energy $|\varepsilon - \varepsilon'|$ and rapidly decreases with increasing $|\varepsilon - \varepsilon'|$, so that $P(\varepsilon - \varepsilon') \gg P(kT)$ if $|\varepsilon - \varepsilon'| \ll kT$. The value of $\bar{\Delta}^2/2\tau_0$ is determined experimentally or calculated (Refs. 11 and 12) as

$$\bar{\Delta}^2 = \int_0^\infty (\varepsilon' - \varepsilon)^2 P(\varepsilon, \varepsilon')\, \mathrm{d}\varepsilon'$$

b) $D = b\varepsilon$:

For the Rayleigh gas, the hard-sphere model with gas kinetic radii R^{XY} (heavy molecules, small admixture) and R^{M_j} (structureless species, the medium of light particles) predicts that

$$b = \sum_j \frac{8}{3} \frac{m_{\mathrm{M}_j}}{m} \frac{kT}{\tau_{TT_j}}$$

$$\tau_{TT_j} = \frac{2N^{\mathrm{M}_j} R_{0j}^2}{\sqrt{2\pi kT/m_{\mathrm{M}_j}}}, \qquad R_{0j} = R^{\mathrm{XY}} + R^{\mathrm{M}_j}$$

This expression for b is valid in the impulsive-collision approximation (when the duration of a collision between a rotating molecule and a structureless particle is short as compared with the rotation period).

7. *Model Features*

The modeled process is canonically invariant in the case of a Rayleigh gas:

$$\text{if} \quad f(\varepsilon, t = 0) = \frac{N^{\mathrm{XY}}}{kT_R(0)} \exp\left[-\frac{\varepsilon}{kT_R(0)}\right]$$

then the solution to the diffusion equation has the form

$$f(\varepsilon, t) = \frac{N^{\mathrm{XY}}}{kT_R(t)} \exp\left[-\frac{\varepsilon}{kT_R(t)}\right]$$

where T_R is found from the equation

$$\frac{\mathrm{d}T_R}{\mathrm{d}t} = -\frac{T_R - T}{\tau_{RT}} \quad \text{with } \tau_{RT} = \frac{kT}{b}$$

8. *General and Particular Solutions*

a) General solution for $D(\varepsilon) = \text{const}$ (Refs. 11 and 12):

$$f(\varepsilon, t) = \int_0^\infty G(\varepsilon, \varepsilon', t) f(\varepsilon', 0)\, \mathrm{d}\varepsilon'$$

where Green's function G is expressed as

$$G(\varepsilon, \varepsilon', t) = \frac{1}{2kT}\left(\frac{\pi t}{\tau_{RT}}\right)^{-1/2}\left\{\exp\left[-\left(\frac{\varepsilon-\varepsilon'}{kT}+\frac{t}{\tau_{RT}}\right)^{2}\frac{\tau_{RT}}{4t}\right]\right.$$

$$\left.+\exp\left[-\left(\frac{\varepsilon+\varepsilon'}{kT}+\frac{t}{\tau_{RT}}\right)^{2}\frac{\tau_{RT}}{4t}\right]\right\}\exp\left(\frac{\varepsilon'}{kT}\right)$$

$$+\frac{1}{2kT}\left\{1-\Phi\left[\left(\frac{\varepsilon+\varepsilon'}{kT}-\frac{t}{\tau_{RT}}\right)\frac{1}{2}\sqrt{\frac{\tau_{RT}}{t}}\right]\right\}\exp\left(-\frac{\varepsilon}{kT}\right)$$

$$\Phi(z) = \frac{2}{\sqrt{\pi}}\int_0^z \exp(-y^2)\,\mathrm{d}y, \qquad \tau_{RT} = \frac{(kT)^2}{D}$$

b) General solution for $D(\varepsilon) = b\varepsilon$:

$$f(\varepsilon, t) = \sum_n c_n \exp\left(-\frac{nt}{\tau_{RT}}\right) L_n\left(\frac{\varepsilon}{kT}\right)\exp\left(-\frac{\varepsilon}{kT}\right)$$

$$c_n = \frac{1}{kT}\int f(\varepsilon, t=0) L_n\left(\frac{\varepsilon}{kT}\right)\mathrm{d}\varepsilon, \quad \tau_{RT} = \frac{kT}{b}$$

where $L_n(x)$ is a Laguerre polynomial.

c) In the case of a Lorentz gas (low concentration of light rotators in a heavy gas), the diffusion equation does not lend itself to a simple solution.

9. *Example*

a) If the delta function $f(\varepsilon, t=0) = N^{XY}\delta(\varepsilon - \varepsilon_0)$ is taken as an initial distribution, and $D(\varepsilon) = \text{const}$, then the solution $f(\varepsilon, t) = N^{XY}G(\varepsilon, \varepsilon_0, t)$ will describe transition of particles from the initial energy domain around ε_0 (first expression in braces in the Green's function G) into the ensemble of particles described by the Boltzmann distribution (second expression in braces in the Green's function). Relaxation starting from a delta function can be graphically represented as a slow spread of the initial sharp distribution at high energies and a fast transformation into the Boltzmann distribution in the low-energy domain. This relaxation pattern is quite general. It provides an explanation for the experimental fact that higher rotational levels are characterized by higher effective temperatures, as compared to lower levels, in expanding jet flows with high stagnation temperatures. Because of the difference in rotational relaxation rates, the high rotational levels are overpopulated, and the low levels are underpopulated. This effect may lead to a population inversion between certain groups of rotational levels (Ref. 1).

b) In highly rarefied gases (for example, in interstellar clouds), radiative transitions between rotational levels of dipole molecules cause the corresponding populations to deviate from the Boltzmann distribution. The effect of radiative transitions on rotational energy distribution was studied in diffusion approximation in (Ref. 13).

10. Comment

For most molecules, the rotational relaxation time is on the order of the mean free time between collisions, $\tau_{RT} \sim \tau_{TT} \approx \tau_0$, except for light diatomic molecules and molecules in highly excited rotational states. In particular, $\tau_{RT}/\tau_0 \sim 4$–6 for N_2 and O_2, and $\tau_{RT}/\tau_0 \sim 100$ for H_2 and D_2.

Relevant material can be found in Refs. 1, 2, 8, and 9.

C. Strong Collision Model (R.3)

1. Purpose of the Model

The model aims at calculation of rotational state population densities in a uniform gas.

2. Assumptions

See the description of model R.1 and Assumption 2 in the description of model T.3.

3. Restrictions

For qualitative description of the relaxation process, there are no restrictions. The most reliable quantitative characterization of relaxation processes (without any additional restrictions) is given by this model for systems close to equilibrium, that is, when

$$|N_n^0 - N_n| \ll N_n^0$$

4. Kinetic Equations

$$\frac{dN_n}{dt} = \nu(N_n^0 - N_n); \qquad N_n^0 = \frac{Ng_n}{Q_r}\exp\left(-\frac{E_n}{kT}\right)$$

5. Nomenclature

a) Quantities calculated with the model:

N_n – population density for the nth rotational level of XY molecules

b) Kinetic coefficients:

ν – empirical parameter

c) Other quantities:

N_n^0 – equilibrium population density for the nth rotational level at a gas temperature T
Q_r – rotational partition function
N – number density of molecules

g_n – statistical weight for the nth rotational level
B – rotational constant
τ_{RT} – characteristic time of rotational relaxation

6. Description of Coefficients and Parameters

The empirical parameter ν cannot be determined within the framework of the model. It is used as an adjustable parameter on the order of the characteristic time τ_{RT} of rotational relaxation.

The values of Q_r for some rigid rotators can be found in the Partition Functions and Integrals section (in Chapter 8 of this volume). The statistical weight g_n is equal to $g_n = (2n + 1)$ for linear molecules, and $g_n = (2n + 1)^2$ for spherical top molecules. The expression for N_n^0 is not valid for spherically symmetrical molecules. Since molecules of this type contain equivalent nuclei, the corresponding statistical weights depend on the values of nuclear spins. For linear and spherical top molecules, $E_n = Bn(n + 1)$, where B is the rotational constant (see Chapter 1 in the first volume of this reference book).

7. Model Features

The model does not provide any explicit description of rotational state-to-state transitions.

8. General and Particular Solutions

The solution for a uniform gas characterized by $\nu = \text{const}$ is

$$N_n(t) = N_n(t = 0)e^{-\nu t} + N_n^0(1 - e^{-\nu t})$$

9. Example

The strong-collision model is used to evaluate the bottleneck effect in calculations of rotational populations for the vibrational states of a molecular gas excited by an infrared laser radiation (see Ref. 14).

10. Comment

The model provides the simplest possible description of rotational relaxation and can be used only in approximate analyses.

Relevant material can be found in Refs. 1–3.

D. Model of Rotational Energy Relaxation (R.4)

1. Purpose of the Model

The model aims at determination of the time dependence of rotational energy for molecules in a relaxing gas.

2. Assumptions

a) The characteristic time τ_{RT} of rotational relaxation is substantially longer than the translational relaxation time τ_{TT}.

b) The governing kinetic equation has the form of a simple relaxation equation. The rotational energy E_R is expressed as either:
  - the sum of the rotational energies corresponding to individual levels (see the description of model R.1),

$$E_R = \sum_n E_n N_n$$

  - or the integral of the energy distribution over rotational levels of a molecule (see the description of model R.2),

$$E_R = \int \varepsilon f(\varepsilon, t), \, \mathrm{d}\varepsilon.$$

3. *Restrictions*

a) The rotational level population densities N_n are close to equilibrium values described by the Boltzmann distribution N_n^0; $|N_n^0 - N_n| \ll N_n^0$ (see the description of model R.3).

b) The model describes the evolution of rotational energy E_R for linear and spherically symmetric molecules
  - in a Rayleigh gas (low concentration of heavy molecules in a mixture with different molecules treated as structureless particles, see the Restrictions in the description of model R.2);
  - in an arbitrary gas near equilibrium, when $|E_R - E_R^0| \ll E_R^0$ and $\tau_{RT} \gg \tau_{TT}$.

4. *Kinetic Equation*

$$\frac{\mathrm{d}E_R}{\mathrm{d}t} = -\frac{E_R - E_R^0}{\tau_{RT}}, \qquad E_R^0 = N^{\mathrm{XY}} kT$$

5. *Nomenclature*

a) Quantity calculated with the model:

E_R – mean rotational energy of molecules

b) Kinetic coefficient:

τ_{RT} – rotational relaxation time

c) Other quantities:

E_R^0 – equilibrium value of rotational energy
N_n – population density for the *n*th rotational level
N_n^0 – equilibrium population density for the *n*th rotational level
N^{XY} – number density of XY molecules
N^{M_j} – number density of M_j particles
T – translational temperature (gas temperature)
E_n – rotational energy of an XY molecule in level *n*

ε – rotational energy of XY molecules in the classical approximation
$f(\varepsilon, t)$ – distribution function for the rotational energy ε
τ_0 – mean free time between collisions for molecules

6. *Description of Coefficients and Parameters*

The rotational relaxation time τ_{RT} for the Rayleigh gas is $\tau_{RT} = kT/b$, where b can be evaluated by using formulas presented in the description of model R.2.

In other cases, experimentally measured results can be invoked (see Refs. 1, 2, 15, 16 and Chapter 6). The rotational relaxation time τ_{RT} is then written in dimensionless form as $Z_{RT} = \tau_{RT}/\tau_0$, where τ_0 is the mean free time between collisions. Thus, Z_{RT} can be interpreted as the number of collisions required to excite the rotational degrees of freedom of a molecule.

a) Examples for hydrogen molecules:

Relaxing molecules	Collision partner	Gas temperature T, K				Reference
		77	90.5	170	293	
		Z_{RT}				
para-H_2	*para*-H_2	715	634	711	—	17
		—	1124	151	122	18
	ortho-H_2	394	—	—	—	17
	H_2	—	—	194	—	
	^4He		369	207		
	Ne		235	140		
	Ar		225	198		
	Kr		—	253		
	Xe			356		
ortho-H_2	*ortho*-H_2			790	530	19

For heavier diatomic molecules, the values of Z_{RT} increase with temperature, approaching unity.

b) Examples for N_2–N_2 collisions:

T, K	Z_{RT}	Reference	T, K	Z_{RT}	Reference
77.1	1.8	20	300	4.3	21
293	5.6	20	700	8.1	21
			1300	11.4	21

For nonpolar molecules, the values of Z_{RT} also increase with temperature. Example for CH_4–CH_4 collisions (spherical top molecules):

$$Z_{RT} = 3.0 \text{ at } T = 77.1\,\text{K}, \quad Z_{RT} = 8.6 \text{ at } T = 293\,\text{K}, \quad \text{and}$$
$$Z_{RT} = 14.8 \text{ at } T = 500\,\text{K (Refs. 22 and 23).}$$

For polar diatomic and polyatomic molecules, the values of Z_{RT} are on the order of unity.

The values of τ_{RT} can also be evaluated by using other expressions, such as Parker formula (see Refs. 3 and 24).

7. *Model Features*

The model cannot be applied when the initial distribution of molecules over rotational levels substantially differs from the Boltzmann distribution. In the case of a Boltzmann initial distribution, the model is not canonically invariant, i.e., the Boltzmann distribution is not preserved (e.g., for hydrogen molecules; see Refs. 11 and 25).

8. *General and Particular Solutions*

The solution of the relaxation equation for τ_{RT} = const is

$$E_R(t) = E_R(0)e^{-t/\tau_{RT}} + E_R^0(1 - e^{-t/\tau_{RT}})$$

9. *Example*

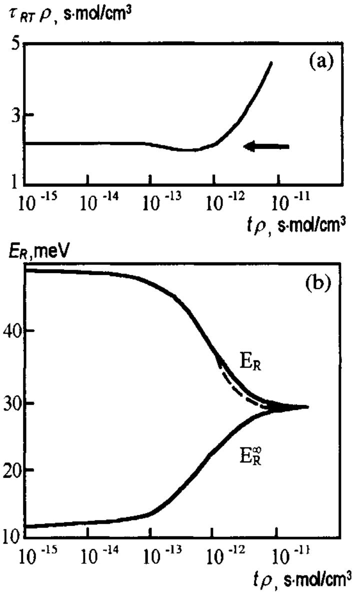

Fig. 3.2

Figure 3.2 (part B) shows the rotational energy E_R for *para*-H_2 molecules as a function of $t\rho$ (ρ is a constant gas density) starting from the initial Boltzmann distribution with rotational temperature $T_R(0) = 600$ K and the translational gas temperature $T(0) = 200$ K obtained with the state-to-state model R.1 (solid curve) (Ref. 25) and with the energy relaxation model R.4 (dashed curve) with the time-independent τ_{RT} shown in the upper plot (see Ref. 26). Here, $\Delta T = T(0) - T_R(0) < 0$. The increase in τ_{RT} because of slow relaxation of high rotational levels has little effect on the rotational energy E_R. Calculations have shown that the value of τ_{RT} remains virtually invariant when $\Delta T > 0$, which confirms the applicability of the model R.4.

10. *Comments*

a) The simple relaxation equation for E_R with $\tau_{RT} = \text{const}$ given by the model R.4 can be used in approximate estimations. A realistic time dependence $E_R(t)$ can be obtained with the simple relaxation equation and τ_{RT} that is a function of E_R. However, this function is not universal, that is, it varies from problem to problem.

b) The characteristic time τ_{RT} of rotational relaxation used in the model is the relaxation time corresponding to the mean rotational energy, i.e., the relaxation time for an equilibrium rotational energy distribution. The relaxation of the high-energy tail of the distribution can be characterized by substantially different relaxation times (Refs. 1 and 3).

c) Investigations of rotational relaxation in expanding supersonic jet and nozzle flows are the main applications of model R.4.

Relevant material can be found in Refs. 1–3.

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Chapter 4

Vibrational Relaxation (V Models)

I. Introduction

ESTABLISHMENT OF equilibrium in the system of the vibrational degrees of freedom (vibrational relaxation) is a relatively slow process. Characteristic vibrational relaxation times are much longer than the translational and rotational relaxation times. For example, vibrational relaxation in pure oxygen takes 10^8 collisions at $T = 288$ K, and 10^3 collisions at $T = 3000$ K.

In an isolated system with arbitrary initial conditions, vibrational relaxation leads to the equilibrium vibrational distribution (Boltzmann distribution), see item 1 of the subsection "Features of the Model" of the model V.1, and item 2 of the same subsection of the model V.3, and also Sec. VI in Chapter 1 of the first volume. In nonisolated (open) systems, which can exchange mass, momentum, and/or energy with the environment, the vibrational distribution of molecules may be substantially different from the Boltzmann one; this occurs, for example, in flows of relaxing gases in nozzles and jets.

Theoretical analysis of the vibrational relaxation with state-specific kinetics (V.1–V.3, V.5, and V.6), mode kinetics (V.7–V.9), and in the diffusion approximation (V.4) is performed for spatially uniform systems, for which the state of the medium varies with time t only. In these models, gas-dynamic variables (such as gas density and mean-mass velocity) are assumed to be constant, and external forces are not considered. When solving gas dynamic problems, the relaxation equations from models V.1–V.9 should be added to the corresponding equations of gas dynamics.

Relaxation equations presented here were formulated assuming that the vibrational frequencies of the molecules are much higher than the mean collision frequency of a molecule. This provides the possibility to operate only with the populations of vibrational levels (diagonal elements of the density matrix, see Ref. 1).

Relaxation processes that cannot be described in terms of populations of vibrational levels (such as polarization and super-radiation) are described in terms of the coherent kinetics (see Ref. 3). Such processes are not considered in this book.

A. Vibrational Relaxation of Diatomic Molecules as a Low-Concentration Impurity in a Gas of Structureless Particles: State-Specific Kinetic Model (V.1)

1. *Purpose of the Model*

The model aims at determination of population densities for vibrational levels of diatomic molecules (in particular, harmonic oscillators) as a low-concentration impurity in a mixture with other molecules treated as structureless particles.

2. *Assumptions*

a) The system consists of diatomic molecules AB as a low-concentration impurity diluted in a gas of other particles $\mathrm{M}_j (j \geq 1)$. The molecules AB participate only in vibrational–translational energy exchange. Collisions between impurity molecules are neglected.

b) The characteristic time of vibrational relaxation is much greater than the translational and rotational relaxation times. Accordingly, the probabilities of vibrational energy exchange are functions of the gas temperature, T.

c) Three-body collisions are ignored, because the product of three-body collision frequency and the probability of vibrational transition induced by a three-body collision is assumed to be substantially smaller than an analogous product for binary collisions.

d) The frequency Z of collisions of AB with other particles is independent of the vibrational state of AB. For harmonic oscillators, this assumption holds if $R_0 \gg (n\hbar/2\mu\omega)^{1/2}$, where R_0 is the gas kinetic radius, $\mu = (m_\mathrm{A} m_\mathrm{B}/(m_\mathrm{A} + m_\mathrm{B}))$ is the reduced mass of an AB molecule (m_A and m_B are the masses of atoms A and B, respectively), ω is the vibrational angular frequency, and n is the vibrational quantum number.

e) For harmonic oscillators, only single-quantum, $n \leftrightarrow n+1$ and $n \leftrightarrow n-1$, transitions are taken into account, and the corresponding VT transition rate constants are expressed as $k_{n,n+1}^{\mathrm{AB-M}_j} = (n+1)k_{01}^{\mathrm{AB-M}_j}$ and $k_{n,n-1}^{\mathrm{AB-M}_j} = nk_{10}^{\mathrm{AB-M}_j}$ (see description of model I-V.7).

3. *Restrictions*

a) The number density N^AB of diatomic molecules must be such that $k_{10}^\mathrm{AB-AB} N^\mathrm{AB} \ll k_{10}^{\mathrm{AB-M}_j} N^{\mathrm{M}_j} (j \geq 1)$. When $k_{10}^\mathrm{AB-AB} \sim k_{10}^{\mathrm{AB-M}_j}$, this restriction reduces to $N^\mathrm{AB} \ll N^{\mathrm{M}_j}$.

b) The particle number densities N^{M_j} must be such that $k_{10}^{\mathrm{AB-M}_j\mathrm{-M}_i} N^{\mathrm{M}_i} \ll k_{10}^{\mathrm{AB-M}_j} (i, j \geq 1)$. Then, three-body collisions can be ignored.

c) The harmonic oscillator approximation can be used to describe vibrational relaxation when the mean vibrational energy per molecule is smaller than, or on the order of, $\hbar\omega$, so that the average number of vibrational quanta per molecule, α, is restricted by the inequality $\alpha = (1/N)\sum nN_n \leq 1$. If $\alpha > 1$, this model can be used to obtain qualitative results or estimates.

4. *Basic Kinetic Equations*

$$\frac{dN_n}{dt} = \sum_j N^{M_j} \sum_m (k_{mn}^{AB-M_j} N_m - k_{nm}^{AB-M_j} N_n), \quad n, m = 0, 1, 2, \ldots$$

5. *Kinetic Equations for Molecules as Harmonic Oscillators*

$$\frac{dN_n}{dt} = \sum_j k_{10}^{AB-M_j} N^{M_j} \left\{ (n+1) N_{n+1} - \left[(n+1) \exp\left(-\frac{0}{T} \right) + n \right] N_n \right.$$
$$\left. + n \exp\left(-\frac{\theta}{T} \right) N_{n-1} \right\} \qquad \theta = \frac{\hbar\omega}{k}, \quad n = 0, 1, 2, \ldots$$

6. *Nomenclature*

a) Quantities calculated with the model:

N_n	population density for the nth vibrational level of AB molecules

b) Kinetic coefficients:

$k_{mn}^{AB-M_j}$	rate constant for the $m \to n$ V–T transitions induced by AB–M_j collisions
k_{mn}^{AB-AB}	rate constant for the $m \to n$ V–T transitions induced by AB–AB collisions

c) Other quantities:

i, j	indices (subscripts) referring to structureless species
T	translational temperature (gas temperature)
T_v	vibrational temperature
ω	vibrational angular frequency for AB molecules
E_n	vibrational energy of AB molecule in level n
$Q_v(T)$	vibrational partition function for AB
N^{AB}	number density of AB molecules
N^{M_j}	number density of M_j particles
θ	characteristic vibrational temperature of AB molecules ($\theta = E_1/k$)
τ_{VT}	vibrational relaxation time
α	average number of vibrational quanta per molecule
$\alpha_0(T)$	equilibrium value of α at a gas temperature T

7. *Description of Coefficients and Parameters*

Expressions for the rate constants $k_{mn}^{AB-M_j}(T)$ of VT energy exchange are presented in Chapter 4 of volume I (models I-V.1–I-V.8).

Dependence of vibrational energy E_n for AB on the number n of a vibrational level for harmonic and simplest anharmonic oscillators was described in Chapter 1 of volume I (including characteristics of species) and supplemented with a list of references to more sophisticated models of molecules. The characteristic vibrational temperature θ is defined as the energy of the first vibrationally excited state of AB and measured in Kelvin.

8. *Features of the Model*

a) When the gas has a constant temperature T, the system evolves toward equilibrium as $t \to \infty$. The equilibrium vibrational level population densities are described by Boltzmann distributions:

– For arbitrary models of molecular oscillators,

$$N_n^0 = \frac{N}{Q_v(T)} \exp\left(\frac{-E_n}{kT}\right); \quad Q_v(T) = \sum_n \exp\left(\frac{-E_n}{kT}\right); \quad N = \sum_n N_n$$

– For molecules treated as harmonic oscillators,

$$N_n^0 = N(1 - e^{-\theta/T})e^{-n(\theta/T)}$$

b) Detailed balance relations:

– For arbitrary models of molecular oscillators,

$$k_{mn}^{\mathrm{AB-M}_j} \exp\left(-\frac{E_m}{kT}\right) = k_{nm}^{\mathrm{AB-M}_j} \exp\left(-\frac{E_n}{kT}\right)$$

– For molecules treated as harmonic oscillators,

$$k_{10}^{\mathrm{AB-M}_j} \exp\left(-\frac{\theta}{T}\right) = k_{01}^{\mathrm{AB-M}_j}$$

c) The model is canonically invariant for molecules treated as harmonic oscillators: the Boltzmann form of the initial distribution, $N_n(t = 0) = N[1 - \exp(-\theta/(T_v(t = 0)))]\exp(-n(\theta/(T_v(t = 0))))$, is preserved in the course of relaxation:

$$N_n(t) = N\left[1 - \exp\left(-\frac{\theta}{T_v(t)}\right)\right] \exp\left(-n\frac{\theta}{T_v(t)}\right)$$

The corresponding variation of vibrational temperature $T_v(t)$ is expressed as

$$\frac{T_v(t)}{\theta} = \left\{ \ln \left[\frac{\exp(-t/\tau_{VT})[1 - \exp(\theta/T - \theta/(T_v(t = 0)))] - \exp(\theta/T)[1 - \exp(-\theta/(T_v(t = 0)))]}{\exp(-t/\tau_{VT})[1 - \exp(\theta/T - \theta/(T_v(t = 0)))] - [1 - \exp(-\theta/(T_v(t = 0)))]} \right] \right\}^{-1}$$

$$\tau_{VT} = \left\{ \sum_j k_{10}^{\mathrm{AB-M}_j} N^{\mathrm{M}_j} [1 - \exp(-\theta/T)] \right\}^{-1}$$

(see descriptions of models I-V.2 and I-V.5).

9. *General and Particular Solutions*

a) In the general case, the analytical solution to the kinetic equations for molecules treated as harmonic oscillators with $\tau_{VT} = \text{const}$ is

$$N_n(t) = \sum_m C_m l_n(m) \exp\left(-\frac{mt}{\tau_{VT}}\right)$$

$$l_n(m) = \exp\left(-n\frac{\theta}{T}\right) \sum_{\nu=0}^{\infty} \left[1 - \exp\left(\frac{\theta}{T}\right)\right]^{\nu} \binom{n}{\nu}\binom{m}{\nu}$$

$$= F\left[-n, m+1, 1; 1 - \exp\left(-\frac{\theta}{T}\right)\right]$$

$$\binom{n}{\nu} = \begin{cases} n!/\nu!(n-\nu)! & \text{if } n \geq \nu \text{ and } \nu > 0 \\ 0 & \text{if } n < \nu \text{ or } \nu < 0 \\ 1 & \text{if } \nu = 0 \end{cases}$$

$$l_n(0) = \exp(-n\theta/T), \qquad l_n(1) = \exp(-n\theta/T)[1 + (1 - \exp\theta/T)n]$$

The orthogonality condition for nonnegative integer m and n,

$$\sum_{\nu=0}^{\infty} \exp(-\nu\theta/T) l_n(\nu) l_m(\nu) = \begin{cases} 0 & n \neq m \\ \exp(-n\theta/T)[1 - \exp(-\theta/T)]^{-1} & n = m \end{cases}$$

$$\sum_{n=0}^{\infty} \exp(n\theta/T) l_n(\nu) l_n(m) = \begin{cases} 0 & n \neq \nu \\ \exp(\nu\theta/T)[1 - \exp(-\theta/T)]^{-1} & n = \nu \end{cases}$$

Here, $l_n(m)$ is Gottlieb's polynomial, $F[-n, m+1, 1; 1 - \exp(-\theta/T)]$ is a hypergeometric function; C_m denotes coefficients determined by the initial level population density $N_n(t = 0)$, which is assumed to be known:

$$C_m = \exp\left(\frac{-m\theta}{T}\right)\left[1 - \exp\left(-\frac{\theta}{T}\right)\right] \sum_{n=0}^{\infty} \exp\left(\frac{n\theta}{T}\right) l_n(m) N_n(t = 0)$$

$$= \left[1 - \exp\left(-\frac{\theta}{T}\right)\right] \sum_{n=0}^{\infty} l_m(n) N_n(t = 0).$$

b) The kinetic equations for molecules treated as harmonic oscillators are solved by means of a generating function. If a function depending on an additional argument z is defined as $G(z, t) = \sum_{n=0}^{\infty} z^n x_n(t)$, then

$$\frac{\partial G}{\partial t} = \sum_j k_{10}^{\mathrm{AB-M}_j} N^{\mathrm{M}_j}(z-1) \exp\left(-\frac{\theta}{T}\right)\left[\frac{\partial G}{\partial z}\left(z - \exp\left(\frac{\theta}{T}\right)\right) + G\right]$$

and

$$G(z, t) = \frac{1 - \exp(\theta/T)}{(z - \exp(\theta/T)) - (z - 1)\exp(-t/\tau_{VT})} G_0(y)$$

$$y = \frac{(z - 1)\exp(-t/\tau_{VT})\exp(\theta/T) - (z - \exp(\theta/T))}{(z - 1)\exp(-t/\tau_{VT}) - (z - \exp(\theta/T))}$$

$$G_0(z) = G(z, 0) = \sum z^n N_n(0)$$

The explicit form of $N_n(t)$ is obtained by representing $G(z, t)$ as a power series in z^n for G_0 determined by the initial conditions (see Ref. 8).

c) An approximate analytical solution to the basic kinetic equations for low gas temperatures ($T < \theta$) and a Boltzmann initial distribution with $T_v(t = 0) < \theta$ was obtained in Ref. 9 by taking into account only single-quantum transitions in molecules treated as anharmonic oscillators.

10. Example

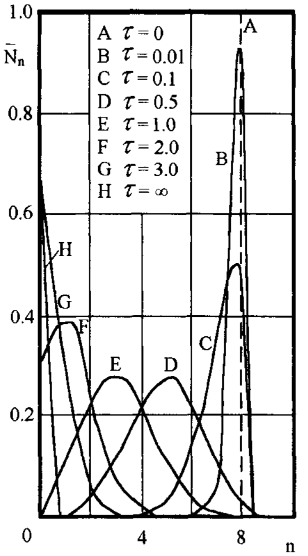

Fig. 4.1

Figure 4.1 shows the time evolution of population densities for various vibrational levels involved in the relaxation of an initial delta distribution (curve *A*) for O_2 at $v = 8$ resulting from the reaction $O + ClO_2 \rightarrow ClO + O_2$ in a nitrogen atmosphere at $T = 288$ K (see Ref. 10). Curve *H* corresponds to the equilibrium distribution. The dimensionless time is defined as $\tau = t/\tau_{VT}$. The level population density $\bar{N}_n$ is measured here in arbitrary units.

11. Comments

a) When a low concentration of molecules treated as harmonic oscillators is added to an inert gas characterized by a non-Maxwellian, steady-state velocity distribution, vibrational relaxation leads to the Boltzmann distribution of molecules over vibrational energy levels with vibrational temperature T_v defined by the condition

$$\exp\left(-\frac{\theta}{T_v}\right) = \frac{k_{01}^*}{k_{10}^*}$$

where k_{10}^* and k_{01}^* are the corresponding rate constants averaged over the non-Maxwellian distribution (Ref. 3).

b) For anharmonic oscillators, the population densities of vibrational levels are characterized by relaxation rates different from those for harmonic oscillators. (The relaxation in a system of harmonic oscillators is canonically invariant; see Refs. 3 and 5). Populations of higher states evolve toward equilibrium faster than those of lower levels do, because the rate constants for transitions between high levels are higher for an anharmonic oscillator as compared to the corresponding harmonic one.

Relevant material can be found in Refs. 2–7.

B. Vibrational Relaxation of a Single-Component Gas of Diatomic Molecules: State-Specific Kinetic Model (V.2)

1. *Purpose of the Model*

The model aims at determination of population densities for vibrational levels of diatomic molecules (in particular, harmonic oscillators) in a single-component system or in a mixture with other molecules treated as structureless particles.

2. *Assumptions*

a) See assumptions 2–4 in the description of model V.1.

b) For harmonic oscillators, only $n \leftrightarrow n+1$ and $n \leftrightarrow n-1$ single-quantum transitions are taken into account, with rate constants $k_{n,n+1}^{\mathrm{AB-M}_j} = (n+1)k_{01}^{\mathrm{AB-M}_j}$, $k_{n,n-1}^{\mathrm{AB-M}_j} = nk_{10}^{\mathrm{AB-M}_j}$, $k_{n+1,n}^{s,s+1} = (n+1)(s+1)k_{10}^{01}$, and $k_{n-1,n}^{s,s-1} = nsk_{01}^{10}$ (see description of model I-V.7).

3. *Restrictions*

See Restrictions 2 and 3 in the description of model V.1. The restrictions concerning three-body collisions also apply to AB–AB, AB–AB–AB, and AB–AB–M$_j$ collisions.

4. *Basic Kinetic Equations*

$$\frac{dN_n}{dt} = \sum_m \left[\left(k_{mn}^{\mathrm{AB-AB}}N + \sum_j k_{mn}^{\mathrm{AB-M}_j}N^{\mathrm{M}_j}\right)N_m - \left(k_{nm}^{\mathrm{AB-AB}}N + \sum_j k_{nm}^{\mathrm{AB-M}_j}N^{\mathrm{M}_j}\right)N_n\right]$$

$$+\sum_{\substack{m,s,l\\ s\neq l}}(k_{mn}^{sl}N_mN_s - k_{nm}^{ls}N_nN_l) \qquad n,\, m,\, s,\, l = 0,\, 1,\, 2, \ldots$$

5. *Kinetic Equations for Molecules as Harmonic Oscillators*

$$
\begin{aligned}
\frac{\mathrm{d}N_n}{\mathrm{d}t} = {}& \left(k_{10}^{\mathrm{AB-AB}}N + \sum_j k_{10}^{\mathrm{AB-M}_j}N^{\mathrm{M}_j}\right)\Bigg\{(n+1)N_{n+1} \\
& -\left[(n+1)\exp\left(-\frac{\theta}{T}\right)+n\right]N_n + n\exp\left(-\frac{\theta}{T}\right)N_{n-1}\Bigg\} \\
& + k_{10}^{01}N\{(n+1)(1+\alpha)N_{n+1} - [(n+1)\alpha + n(1+\alpha)]N_n + n\alpha N_{n-1}\}
\end{aligned}
$$

$$
N = \sum_n N_n; \quad \alpha = \frac{1}{N}\sum nN_n, \quad n = 0, 1, 2, \ldots
$$

6. *Nomenclature*

a) Quantities calculated with the model:

N_n	population density for the *n*th vibrational level of AB molecule

b) Kinetic coefficients:

$k_{mn}^{\mathrm{AB-M}_j}$	rate constant for the $m \to n$ VT transitions induced by AB–M_j collisions
$k_{mn}^{\mathrm{AB-AB}}$	rate constant for the $m \to n$ VT transitions induced by AB–AB collisions
$k_{mn}^{sl}(T)$	rate constant for the VV energy exchange involving an $m \to n$ vibrational transition in one molecule and an $s \to l$ transition in the other

c) Other quantities:

j	indices (subscripts) referring to structureless species
T	translational temperature (gas temperature)
T_v	vibrational temperature
T_1	vibrational temperature of the first vibrational level
ω	vibrational angular frequency
E_n	vibrational energy of an AB molecule in level *n*
$Q_v(T)$	vibrational partition function for AB
N	number density of AB molecules
N^{M_j}	number density of structureless particles of the *j*th species
θ	characteristic vibrational temperature of AB molecules
α	average number of vibrational quanta per molecule
$\alpha_0(T)$	equilibrium value of α at a gas temperature, T
τ_{VT}	VT relaxation time
τ_{VV}	VV relaxation time

7. *Description of Coefficients and Parameters*

See the corresponding subsection in the description of model V.1. Expressions for the rate constants $k_{mn}^{sl}(T)$ of VV energy exchange are presented in Chapter 4 of volume I (models I-V.3, I-V.4, and I-V.6).

8. *Features of the Model*

a) The first term in each basic kinetic equation describes VT exchange processes; the second term describes VV exchange. When the initial state is described by the Boltzmann distribution of vibrational-level population densities with $T_v(t=0) \neq T$, the term representing VV exchange vanishes. VV and VT energy exchange processes can be treated independently if

$$k_{10}^{01} N_0 \gg k_{10}^{\mathrm{AB-AB}} N + \sum_j k_{10}^{\mathrm{AB-M}_j} N^{\mathrm{M}_j}$$

where N_0 is the level population density for $n = 0$.

b) See model property 1 in the description of model V.1.

c) Detailed balance relations:

– For arbitrary models of molecular oscillators,

$$k_{mn}^{\mathrm{AB-M}_j} \exp\left(-\frac{E_m}{kT}\right) = k_{nm}^{\mathrm{AB-M}_j} \exp\left(-\frac{E_n}{kT}\right),$$

$$k_{mn}^{\mathrm{AB-AB}} \exp\left(-\frac{E_m}{kT}\right) = k_{nm}^{\mathrm{AB-AB}} \exp\left(-\frac{E_n}{kT}\right)$$

$$k_{mn}^{sl} \exp\left(-\frac{E_m + E_s}{kT}\right) = k_{nm}^{ls} \exp\left(-\frac{E_n + E_l}{kT}\right)$$

– For harmonic oscillators,

$$k_{10}^{\mathrm{AB-M}_j} \exp\left(-\frac{\theta}{T}\right) = k_{01}^{\mathrm{AB-M}_j}, \quad k_{10}^{\mathrm{AB-AB}} \exp\left(-\frac{\theta}{T}\right) = k_{01}^{\mathrm{AB-AB}} \quad k_{10}^{01} = k_{01}^{10}$$

d) The model is canonically invariant for molecules treated as harmonic oscillators (see model property 3 in the description of model V.1); τ_{VT} is expressed as

$$\tau_{VT} = \left\{\left[k_{10}^{\mathrm{AB-AB}} N + \sum_j k_{10}^{\mathrm{AB-M}_j} N^{\mathrm{M}_j}\right]\left[1 - \exp\left(-\frac{\theta}{T}\right)\right]\right\}^{-1}$$

9. *General and Particular Solutions*

a) Solution of the basic kinetic equations for a single-component gas of relaxing harmonic oscillators

1.1. It is assumed that $k_{10}^{01} \gg k_{10}^{\mathrm{AB-AB}} N + \sum_j k_{10}^{\mathrm{AB-M}_j} N^{\mathrm{M}_j}$; i.e., the rates of VV energy exchange are substantially higher than the rates of VT energy exchange. In this case, vibrational relaxation involves two stages. At the first (fast) stage, characterized by the relaxation time $\tau_{VV} = 1/k_{10}^{01} N(1+\alpha)$, the terms describing VT energy exchange can be neglected. The reduced equations have the form

$$\frac{dN_n}{dt} = k_{10}^{01}N\{(n+1)(1+\alpha)N_{n+1} - [(n+1)\alpha + n(1+\alpha)]N_n + n\alpha N_{n-1}\}$$

The solution for this set of equations is:

$$N_n(t) = \sum C_m l_n(m) e^{-(mt/\tau_{VV})}; \qquad \tau_{VV} = \frac{1}{k_{10}^{01}N(1+\alpha)}$$

where $l_n(m) = F[-n, m+1, 1; 1-\exp(-\theta/T)]$ is Gottlieb's polynomial, F is a hypergeometric function, and C_m denotes coefficients determined by the initial level population density $N_n(t=0)$, which is assumed to be known (see also description of model V.1, Ref. 2).

Single-quantum VV energy exchange leaves the total number of vibrational quanta invariant; therefore, $\alpha = \text{const}$.

The fast stage results in the Boltzmann distribution

$$N_n = N\left[1 - \exp\left(-\frac{\theta}{T_v}\right)\right]\exp\left(-n\frac{\theta}{T_v}\right)$$

with a vibrational temperature, T_v determined by the instantaneous number of vibrational quanta according to the equation

$$\exp\left(-\frac{\theta}{T_v}\right) = \frac{\alpha}{1+\alpha}$$

At the second (slow) stage (characterized by the relaxation time τ_{VT}), the Boltzmann distribution is preserved, and only the vibrational temperature (or the average number of vibrational quanta per molecule) varies as predicted by the equation (see description of model V.1)

$$\frac{d\alpha}{dt} = -\frac{\alpha - \alpha_0}{\tau_{VT}}$$

1.2. The condition $k_{10}^{01}N_0 \gg k_{10}^{\text{AB-AB}}N + \sum_j k_{10}^{\text{AB-M}_j}N^{\text{M}_j}$ does not hold. In the general case, the kinetic equations for level population densities describing simultaneous VT and VV energy exchange processes are solved by numerical methods. The dependencies $\alpha = \alpha(t)$ and $T = T(t)$ must be taken into account. They can be found by using the fact that the sum of translational, rotational, and vibrational energies is a conserved quantity.

b) Solution of the basic kinetic equations for a single-component gas of relaxing anharmonic oscillators

2.1. A steady-state solution to the kinetic equations describing single-quantum VV energy exchange (referred to as the *Treanor distribution*) is

$$N_n\big|_{st} = N_0 \exp\left(-\gamma n - \frac{E_n}{kT}\right)$$

where γ is a parameter determined by the initial number of vibrational quanta.

In practical calculations, a steady state is maintained by keeping population densities constant for one or several vibrational levels. If a steady N_1 or the "vibrational temperature of the first level" T_1 is determined by the equation

$$N_1 = N_0 e^{-E_1/T_1}, \quad \text{then} \quad \gamma = \frac{E_1}{k}\left(\frac{1}{T_1} - \frac{1}{T}\right)$$

If $T_1 < T$ (as in relaxation behind a shock front), then $\gamma > 0$; for $n > 1$, this implies that

$$N_n\big|_{st} < N_n^0 = \frac{N}{Q_v(T)} e^{-E_n/kT}$$

If $T_1 > T$ (as in the case of relaxation in expanding flows or in cases of energy input into vibrational degrees of freedom of molecules), then $\gamma < 0$; for $n > 1$, this implies that

$$N_n\big|_{st} > N_n^0 = \frac{N}{Q_v(T)} e^{-E_n/kT}$$

The minimum point of the Treanor distribution is the integer number closest to

$$n^* = \frac{E_1}{2\Delta E}\frac{T}{T_1} + \frac{1}{2}, \qquad T_1 > T$$

where $E_n = nE_1 - \Delta E n(n-1)$ (ΔE is the anharmonicity of a molecule). For example, $n^* \approx 12$ for CO molecules ($E_1 = 2168\,\text{cm}^{-1}$, $\Delta E = 13\,\text{cm}^{-1}$) at $T = 350\,\text{K}$ and $T_1 = 2500\,\text{K}$. The positively sloped portion of the Treanor distribution (see Fig. 4.2) is not physical in the general case, because $N_0 k_{n+1,n}^{01} \leq N k_{n+1,n}$ in this domain of n, and VV exchange cannot be treated consistently without allowing for VT processes or other mechanisms of dissipation of vibrational quanta. For CO molecules at room temperature, $k_{n+1,n}^{01} \sim k_{n+1,n}$ for $n \sim 20$–30.

2.2. Population densities for vibrational levels in the case of simultaneous VV and VT energy exchange. Specific population densities for vibrational levels are obtained by applying numerical methods to kinetic equations with prescribed rate constants k_{mn}^{sl} and

k_{mn} or, in some cases, by using approximate analytical methods (see Refs. 3 and 5). Specific characteristics of level population densities are determined by the ratios of VV and VT energy exchange probabilities and by the nonequilibrium excess of vibrational energy. At low vibrational levels, kinetics are dominated by VV exchange leading to the Treanor distribution. At high vibrational levels, kinetics are dominated by VT energy exchange leading to the Boltzmann distribution over vibrational energy levels characterized by the translational temperature of the gas. In the intermediate range of vibrational quantum numbers, where VV and VT exchange processes are characterized by comparable probabilities, the Treanor distribution gradually transforms into the Boltzmann distribution. When levels lying above the minimum point of the Treanor distribution are excited to a significant degree, a population-density plateau develops, where a minor inversion may occur.

10. Example

Figure 4.2 shows normalized population densities for vibrational levels of CO molecules at $T_l = 2700$ K and various gas temperatures, T.

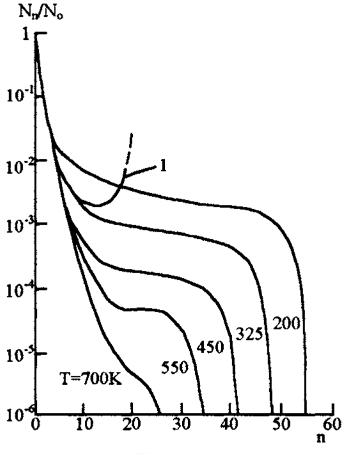

Fig. 4.2

Normalized population densities for vibrational levels of CO molecules at $T_l = 2700$ K and various gas temperatures. Curve 1 corresponds to the Treanor distribution at $T = 325$ K.

The distribution shown here is typical for most diatomic molecules treated as anharmonic oscillators.

11. Comments

a) The distribution of population densities for vibrational levels of anharmonic oscillators discussed in item 2.2 in the General and Particular Solutions subsection is obtained under steady-state conditions when vibrational energy flux toward higher levels is balanced by energy input at lower levels.

b) One version of a state-specific kinetic model is the so-called *energy-flux model*, in which the system of kinetic equations for level population densities of anharmonic oscillators is integrated as a transport equation describing vibrational energy transfer between levels as a flux of vibrational quanta driven by VV and VT processes. The loss of vibrational quanta contained in the highest levels is attributed to a negative source (vibrational energy sink), whereas the input of vibrational energy is treated as a positive source. The energy-flux model can be used to simplify solution of kinetic equations for level population densities (Ref. 8).

c) For an isolated system of harmonic oscillators in a mixture with structureless particles, M_j, the value of T is determined by the equation

$$N\hbar\,\omega\alpha_0(t=0)+\frac{5}{2}NkT(t=0)+T(t=0)\sum_j c_j N^{\mathrm{M}_j}$$
$$=N\hbar\,\omega\alpha(T)+\frac{5}{2}NkT+T\sum_j c_j N^{\mathrm{M}_j}$$

Here, c_j is the specific heat per particle for the jth structureless species; for monatomic particles, $c_j=(3/2)k$ (k is Boltzmann constant).

Relevant material can be found in Refs. 2–6.

C. Vibrational Relaxation in a Binary Mixture of Diatomic Molecules: State-Specific Kinetic Model (V.3)

1. *Purpose of the Model*

The model aims at determination of population densities for vibrational levels of molecules (in particular, harmonic oscillators) in a binary mixture of diatomic gases with possible addition of other molecules treated as structureless particles.

2. *Assumptions*

a) See Assumptions b–d in the description of model V.1 and Assumption b in the description of model V.2.

b) For harmonic oscillators, only $n \leftrightarrow n+1$ and $n \leftrightarrow n-1$ single-quantum transitions are taken into account, and the corresponding VT transition rate constants are expressed as

$$k_{n,n+1}^{\mathrm{AB-M}_j}=(n+1)k_{01}^{\mathrm{AB-M}_j},\quad k_{n,n-1}^{\mathrm{AB-M}_j}=nk_{10}^{\mathrm{AB-M}_j},$$

$$k_{n+1,n}^{s,s+1^{\mathrm{AB-AB}}}=(n+1)(s+1)k_{10}^{01^{\mathrm{AB-AB}}}$$

$$k_{n+1,n}^{s,s+1^{\mathrm{AB-CD}}}=(n+1)(s+1)k_{10}^{01^{\mathrm{AB-CD}}}$$

(relations obtained by simultaneously interchanging AB with CD also apply here; see description of model I-V.7).

3. *Restrictions*

See Restrictions B and C in the description of model V.1. The restrictions concerning three-body collisions also apply to AB–AB, AB–CD, AB–M_j, and CD–M_j, and all three-body collisions involving various combinations of AB, CD, and M_j molecules.

4. *Basic Kinetic Equations*

$$
\begin{aligned}
\frac{\mathrm{d}N_n^{\mathrm{AB}}}{\mathrm{d}t} = \sum_m \Bigg[& \left(k_{mn}^{\mathrm{AB-AB}} N^{\mathrm{AB}} + k_{mn}^{\mathrm{AB-CD}} N^{\mathrm{CD}} + \sum_j k_{mn}^{\mathrm{AB-M}_j} N^{\mathrm{M}_j} \right) N_m^{\mathrm{AB}} \\
& - \left(k_{nm}^{\mathrm{AB-AB}} N^{\mathrm{AB}} + k_{nm}^{\mathrm{AB-CD}} N^{\mathrm{CD}} + \sum_j k_{nm}^{\mathrm{AB-M}_j} N^{\mathrm{M}_j} \right) N_n^{\mathrm{AB}} \Bigg] \\
& + \sum_{\substack{m,s,l \\ s \neq l}} [k_{mn}^{sl^{\mathrm{AB-AB}}} N_m^{\mathrm{AB}} N_s^{\mathrm{AB}} - k_{nm}^{ls^{\mathrm{AB-AB}}} N_n^{\mathrm{AB}} N_l^{\mathrm{AB}}] \\
& + \sum_{\substack{m,s,l \\ s \neq l}} [k_{mn}^{sl^{\mathrm{AB-CD}}} N_m^{\mathrm{AB}} N_s^{\mathrm{CD}} - k_{nm}^{ls^{\mathrm{AB-CD}}} N_n^{\mathrm{AB}} N_l^{\mathrm{CD}}]
\end{aligned}
$$

$$
\begin{aligned}
\frac{\mathrm{d}N_n^{\mathrm{CD}}}{\mathrm{d}t} = \sum_m \Bigg[& \left(k_{mn}^{\mathrm{CD-AB}} N^{\mathrm{AB}} + k_{mn}^{\mathrm{CD-CD}} N^{\mathrm{CD}} + \sum_j k_{mn}^{\mathrm{CD-M}_j} N^{\mathrm{M}_j} \right) N_m^{\mathrm{CD}} \\
& - \left(k_{nm}^{\mathrm{CD-AB}} N^{\mathrm{AB}} + k_{nm}^{\mathrm{CD-CD}} N^{\mathrm{CD}} + \sum_j k_{nm}^{\mathrm{CD-M}_j} N^{\mathrm{M}_j} \right) N_n^{\mathrm{CD}} \Bigg] \\
& + \sum_{\substack{m,s,l \\ s \neq l}} [k_{mn}^{sl^{\mathrm{CD-CD}}} N_m^{\mathrm{CD}} N_s^{\mathrm{CD}} - k_{nm}^{ls^{\mathrm{CD-CD}}} N_n^{\mathrm{CD}} N_l^{\mathrm{CD}}] \\
& + \sum_{\substack{m,s,l \\ s \neq l}} [k_{mn}^{sl^{\mathrm{CD-AB}}} N_m^{\mathrm{CD}} N_s^{\mathrm{AB}} - k_{nm}^{ls^{\mathrm{CD-AB}}} N_n^{\mathrm{CD}} N_l^{\mathrm{AB}}]
\end{aligned}
$$

E. *Kinetic Equations for Molecules as Harmonic Oscillators*

$$
\begin{aligned}
\frac{\mathrm{d}N_n^{\mathrm{AB}}}{\mathrm{d}t} = & \left(k_{10}^{\mathrm{AB-AB}} N^{\mathrm{AB}} + k_{10}^{\mathrm{AB-CD}} N^{\mathrm{CD}} + \sum_j k_{10}^{\mathrm{AB-M}_j} N^{\mathrm{M}_j} \right) \\
& \times \left\{ (n+1) N_{n+1}^{\mathrm{AB}} - \left[(n+1) \exp\left(-\frac{\theta^{\mathrm{AB}}}{T} \right) + n \right] N_n^{\mathrm{AB}} \right. \\
& \left. + n \exp\left(-\frac{\theta^{\mathrm{AB}}}{T} \right) N_{n-1}^{\mathrm{AB}} \right\} \\
& + k_{10}^{01^{\mathrm{AB-AB}}} N^{\mathrm{AB}} \{ (n+1)(1+\alpha^{\mathrm{AB}}) N_{n+1}^{\mathrm{AB}} - [(n+1)\alpha^{\mathrm{AB}} \\
& + n(1+\alpha^{\mathrm{AB}})] N_n^{\mathrm{AB}} + n\alpha^{\mathrm{AB}} N_{n-1}^{\mathrm{AB}} \} \\
& + k_{10}^{01^{\mathrm{AB-CD}}} N^{\mathrm{CD}} \left\{ (n+1)(1+\alpha^{\mathrm{CD}}) \exp\left(\frac{\theta^{\mathrm{AB}}}{T} \right) N_{n+1}^{\mathrm{AB}} \right.
\end{aligned}
$$

$$-\left[(n+1)\alpha^{\mathrm{CD}}\exp\left(\frac{\theta^{\mathrm{CD}}}{T}\right)+n(1+\alpha^{\mathrm{CD}})\exp\left(\frac{\theta^{\mathrm{AB}}}{T}\right)\right]N_n^{\mathrm{AB}}$$

$$\left.+\,n\alpha^{\mathrm{CD}}\exp\left(\frac{\theta^{\mathrm{CD}}}{T}\right)N_{n-1}^{\mathrm{AB}}\right\}$$

$$\frac{\mathrm{d}N_n^{\mathrm{CD}}}{\mathrm{d}t}=\left(k_{10}^{\mathrm{CD-CD}}N^{\mathrm{CD}}+k_{10}^{\mathrm{CD-AB}}N^{\mathrm{AB}}+\sum_j k_{10}^{\mathrm{CD-M}_j}N^{\mathrm{M}_j}\right)$$

$$\times\left\{(n+1)N_{n+1}^{\mathrm{CD}}-\left[(n+1)\exp\left(-\frac{\theta^{\mathrm{CD}}}{T}\right)+n\right]N_n^{\mathrm{CD}}\right.$$

$$\left.+n\exp\left(-\frac{\theta^{\mathrm{CD}}}{T}\right)N_{n-1}^{\mathrm{CD}}\right\}+k_{10}^{01^{\mathrm{CD-CD}}}N^{\mathrm{CD}}\{(n+1)(1+\alpha^{\mathrm{CD}})N_{n+1}^{\mathrm{CD}}$$

$$-\,[(n+1)\alpha^{\mathrm{CD}}+n(1+\alpha^{\mathrm{CD}})]N_n^{\mathrm{CD}}+n\alpha^{\mathrm{CD}}N_{n-1}^{\mathrm{CD}}\}$$

$$+\,k_{10}^{01^{\mathrm{CD-AB}}}N^{\mathrm{AB}}\left\{(n+1)(1+\alpha^{\mathrm{AB}})\exp\left(\frac{\theta^{\mathrm{CD}}}{T}\right)N_{n+1}^{\mathrm{CD}}\right.$$

$$-\left[(n+1)\alpha^{\mathrm{AB}}\exp\left(\frac{\theta^{\mathrm{AB}}}{T}\right)+n(1+\alpha^{\mathrm{AB}})\exp\left(\frac{\theta^{\mathrm{CD}}}{T}\right)\right]N_n^{\mathrm{CD}}$$

$$\left.+\,n\alpha^{\mathrm{AB}}\exp\left(\frac{\theta^{\mathrm{AB}}}{T}\right)N_{n-1}^{\mathrm{CD}}\right\}$$

$$\alpha^{\mathrm{AB}}=\frac{1}{N^{\mathrm{AB}}}\sum nN_n^{\mathrm{AB}};\qquad \alpha^{\mathrm{CD}}=\frac{1}{N^{\mathrm{CD}}}\sum nN_n^{\mathrm{CD}}$$

$$N^{\mathrm{AB}}=\sum N_n^{\mathrm{AB}};\qquad N^{\mathrm{CD}}=\sum N_n^{\mathrm{CD}};\quad n=0,1,2,\ldots$$

6. Nomenclature

a) Quantities calculated with the model:

N_n^{AB}	population density for the *n*th vibrational level of AB
N_n^{CD}	population density for the *n*th vibrational level of CD

b) Kinetic coefficients:

$k_{mn}^{\mathrm{AB-M}_j}$	rate constant for the $m \to n$ VT transitions in AB molecules induced by AB–M_j collisions
$k_{mn}^{\mathrm{CD-M}_j}$	rate constant for the $m \to n$ VT transitions in CD molecules induced by CD–M_j collisions
$k_{mn}^{\mathrm{AB-AB}}$	rate constant for the $m \to n$ VT transitions induced by AB–AB collisions
$k_{mn}^{\mathrm{AB-CD}}$	rate constant for the $m \to n$ VT transitions in AB molecules induced by AB–CD collisions

$k_{mn}^{\text{CD-CD}}$	rate constant for the $m \to n$ VT transitions induced by CD–CD collisions
$k_{mn}^{\text{CD-AB}}$	rate constant for the $m \to n$ VT transitions in CD molecules induced by CD–AB collisions
$k_{mn}^{sl\,\text{AB-AB}}(T)$	rate constant for the VV energy exchange between AB molecules involving an $m \to n$ vibrational transition in one molecule and an $s \to l$ transition in the other
$k_{mn}^{sl\,\text{CD-CD}}(T)$	rate constant for the VV energy exchange between CD molecules involving an $m \to n$ vibrational transition in one molecule and an $s \to l$ transition in the other
$k_{mn}^{sl\,\text{AB-CD}}(T)$	rate constant for the VV′ energy exchange in collisions of AB and CD molecules involving $m \to n$ vibrational transitions in AB molecules and $s \to l$ transitions in CD molecules
$k_{mn}^{sl\,\text{CD-AB}}(T)$	rate constant for the VV′ energy exchange in collisions of AB and CD molecules involving $m \to n$ vibrational transitions in CD molecules and $s \to l$ transitions in AB molecules

c) Other quantities:

j	indices (subscripts) referring to structureless species
T	translational temperature (gas temperature)
ω^{AB}	vibrational angular frequency for an AB molecule
ω^{CD}	vibrational angular frequency for a CD molecule
E_n^{AB}	vibrational energy of an AB molecule in level n
E_n^{CD}	vibrational energy of a CD molecule in level n
Q_v^{AB}	vibrational partition function for AB
Q_v^{CD}	vibrational partition function for CD
N^{AB}	number density of AB molecules
N^{CD}	number density of CD molecules
N^{M_j}	number density of structureless particles of the jth species
c_j	specific heat per particle for the jth structureless species
θ^{AB}	characteristic vibrational temperature of AB molecules
θ^{CD}	characteristic vibrational temperature of CD molecules
α^{AB}	average number of vibrational quanta per AB molecule
α^{CD}	average number of vibrational quanta per CD molecule
$\alpha_0^{\text{AB}}(T)$	equilibrium value of α^{AB} at a gas temperature T
$\alpha_0^{\text{CD}}(T)$	equilibrium value of α^{CD} at a gas temperature T
τ_{VT}^{AB}	VT relaxation time for AB molecules
τ_{VT}^{CD}	VT relaxation time for CD molecules
τ_{VV}^{AB}	VV relaxation time for AB molecules
τ_{VV}^{CD}	VV relaxation time for CD molecules
$\tau_{VV'}$	VV′ relaxation time for energy transfer between AB and CD molecules

7. *Description of Coefficients and Parameters*

For a description, see the corresponding subsections in the description of models V.1 and V.2. Expressions for the rate constant $k_{mn}^{sl\,\text{AB-CD}}$ of VV′

energy exchange, as well as for other rate constants with AB changed to CD and vice versa, are presented in Chapter 4 of the first volume (models I-V.3 and I-V.6).

8. *Features of the Model*

a) The first, second, and third terms in the basic kinetic equations represent VT, VV, and VV′ energy exchange processes, respectively. VV′, VV, and VT energy exchange processes can be treated independently if

$$k_{10}^{01^{\text{AB-AB}}} n^{\text{AB}}, \quad k_{10}^{01^{\text{CD-CD}}} N^{\text{CD}} \gg k_{10}^{01^{\text{AB-CD}}} N^{\text{CD}} \gg k_{10}^{\text{AB-AB}} N^{\text{AB}} + k_{10}^{\text{AB-CD}} N^{\text{CD}}$$
$$+ \sum_j k_{10}^{\text{AB-M}_j} N^{\text{M}_j}, \quad k_{10}^{\text{CD-CD}} N^{\text{CD}} + k_{10}^{\text{CD-AB}} N^{\text{AB}} + \sum_j k_{10}^{\text{CD-M}_j} N^{\text{M}_j}$$

and if they are characterized by vastly different time scales. More precisely, the fastest processes are those of energy exchange within individual modes. They are followed by energy exchange between modes, and the final stage is that of VT relaxation.

b) As $t \to \infty$, the system evolves toward equilibrium. The equilibrium vibrational-level population densities are described by Boltzmann distributions:

– For arbitrary models of molecular oscillators,

$$(N_n^0)^{\text{AB}} = \frac{N^{\text{AB}}}{Q_v^{\text{AB}}(T)} e^{-E_n^{\text{AB}}/kT}, \qquad (N_n^0)^{\text{CD}} = \frac{N^{\text{CD}}}{Q_v^{\text{CD}}(T)} e^{-E_n^{\text{CD}}/kT}$$

$$Q_v^{\text{AB}} = \sum_n \exp\left(\frac{-E_n^{\text{AB}}}{kT}\right), \qquad Q_v^{\text{CD}} = \sum_n \exp\left(\frac{-E_n^{\text{CD}}}{kT}\right)$$

– For molecules treated as harmonic oscillators,

$$(N_n^0)^{\text{AB}} = N^{\text{AB}}\left[1 - \exp\left(-\frac{\theta^{\text{AB}}}{T}\right)\right]\exp\left(-n\frac{\theta^{\text{AB}}}{T}\right), \quad N^{\text{AB}} = \sum_n N_n^{\text{AB}}$$

$$(N_n^0)^{\text{CD}} = N^{\text{CD}}\left[1 - \exp\left(-\frac{\theta^{\text{CD}}}{T}\right)\right]\exp\left(-n\frac{\theta^{\text{CD}}}{T}\right)$$

c) Detailed balance relations:

– For arbitrary models of molecular oscillators,

$$k_{mn}^{\text{AB-M}_j} \exp\left(-\frac{E_m^{\text{AB}}}{kT}\right) = k_{nm}^{\text{AB-M}_j} \exp\left(-\frac{E_n^{\text{AB}}}{kT}\right)$$

$$k_{mn}^{\text{AB-AB}} \exp\left(-\frac{E_m^{\text{AB}}}{kT}\right) = k_{nm}^{\text{AB-AB}} \exp\left(-\frac{E_n^{\text{AB}}}{kT}\right)$$

$$k_{mn}^{\mathrm{AB-CD}} \exp\left(-\frac{E_m^{\mathrm{AB}}}{kT}\right) = k_{nm}^{\mathrm{AB-CD}} \exp\left(-\frac{E_n^{\mathrm{AB}}}{kT}\right)$$

$$k_{mn}^{sl^{\mathrm{AB-AB}}} \exp\left(-\frac{E_m^{\mathrm{AB}} + E_s^{\mathrm{AB}}}{kT}\right) = k_{nm}^{ls^{\mathrm{AB-AB}}} \exp\left(-\frac{E_n^{\mathrm{AB}} + E_l^{\mathrm{AB}}}{kT}\right)$$

$$k_{mn}^{sl^{\mathrm{AB-CD}}} \exp\left(-\frac{E_m^{\mathrm{AB}} + E_s^{\mathrm{CD}}}{kT}\right) = k_{nm}^{ls^{\mathrm{AB-CD}}} \exp\left(-\frac{E_n^{\mathrm{AB}} + E_l^{\mathrm{CD}}}{kT}\right)$$

Additional relations are obtained by interchanging AB with CD.
– For molecules treated as harmonic oscillators,

$$k_{10}^{\mathrm{AB-M}_j} \exp\left(-\frac{\theta^{\mathrm{AB}}}{T}\right) = k_{01}^{\mathrm{AB-M}_j}; \qquad k_{10}^{\mathrm{AB-AB}} \exp\left(-\frac{\theta^{\mathrm{AB}}}{T}\right) = k_{01}^{\mathrm{AB-AB}}$$

$$k_{10}^{\mathrm{AB-CD}} \exp\left(-\frac{\theta^{\mathrm{AB}}}{T}\right) = k_{01}^{\mathrm{AB-CD}}, \qquad \theta^{\mathrm{AB}} = \frac{\hbar\omega^{\mathrm{AB}}}{k}, \qquad \theta^{\mathrm{CD}} = \frac{\hbar\omega^{\mathrm{CD}}}{k}$$

$$k_{10}^{01^{\mathrm{AB-AB}}} = k_{01}^{10^{\mathrm{AB-AB}}}, \qquad k_{10}^{01^{\mathrm{AB-CD}}} \exp\left(-\frac{\theta^{\mathrm{AB}}}{T}\right) = k_{01}^{10^{\mathrm{AB-CD}}} \exp\left(-\frac{\theta^{\mathrm{CD}}}{T}\right)$$

Additional relations are obtained by interchanging AB with CD.

9. *General and Particular Solutions*

1. Solution of the basic kinetic equations for a binary gaseous mixture of relaxing harmonic oscillators subject to the condition $\tau_{VT}^{\mathrm{AB}}, \tau_{VT}^{\mathrm{CD}} \gg \tau_{VV'} \gg \tau_{VV}^{\mathrm{AB}}, \tau_{VV}^{\mathrm{CD}}$, where

$$\tau_{VT}^{\mathrm{AB}} = \left\{\left[k_{10}^{\mathrm{AB-AB}} N^{\mathrm{AB}} + k_{10}^{\mathrm{AB-CD}} N^{\mathrm{CD}} + \sum_j k_{10}^{\mathrm{AB-M}_j} N^{\mathrm{M}_j}\right]\left[1 - \exp\left(-\frac{\theta^{\mathrm{AB}}}{T}\right)\right]\right\}^{-1}$$

$$\tau_{VT}^{\mathrm{CD}} = \left\{\left[k_{10}^{\mathrm{CD-CD}} N^{\mathrm{CD}} + k_{10}^{\mathrm{CD-AB}} N^{\mathrm{AB}} + \sum_j k_{10}^{\mathrm{CD-M}_j} N^{\mathrm{M}_j}\right]\left[1 - \exp\left(-\frac{\theta^{\mathrm{CD}}}{T}\right)\right]\right\}^{-1}$$

$$\tau_{VV}^{\mathrm{AB}} = [k_{10}^{01^{\mathrm{AB-AB}}} N^{\mathrm{AB}}(1 + \alpha^{\mathrm{AB}})]^{-1}; \qquad \tau_{VV}^{\mathrm{CD}} = [k_{10}^{01^{\mathrm{CD-CD}}} N^{\mathrm{CD}}(1 + \alpha^{\mathrm{CD}})]^{-1}$$

$$\tau_{VV'}^{\mathrm{AB-CD}} = [k_{10}^{01^{\mathrm{AB-CD}}} N^{\mathrm{CD}}]^{-1}; \qquad \tau_{VV'}^{\mathrm{CD}} = [k_{10}^{01^{\mathrm{CD-AB}}} N^{\mathrm{AB}}]^{-1}$$

Under these conditions for relaxation times, the fastest processes are those of energy exchange within individual modes. They are followed by energy exchange between modes, and the final stage is that of V–T relaxation.

When these inequalities are satisfied, vibrational relaxation consists of three stages:

- At the first stage, when $t \le \tau_{VV}^{\mathrm{AB}}, \tau_{VV}^{\mathrm{CD}}$,

$$N_n^{\mathrm{AB}}(t) = \sum C_m^{\mathrm{AB}} l_n(m) \exp\left(-\frac{mt}{\tau_{VV}^{\mathrm{AB}}}\right), \quad N_n^{\mathrm{CD}}(t) = \sum C_m^{\mathrm{CD}} l_n(m) \exp\left(-\frac{mt}{\tau_{VV}^{\mathrm{CD}}}\right)$$

where $l_n(m)$ is Gottlieb's polynomial (see description of model V.2), and C_m^{AB} and C_m^{CD} denote coefficients determined by the initial level population densities $N_n^{\mathrm{AB}}(t=0)$ and $N_n^{\mathrm{CD}}(t=0)$, respectively, that are assumed to be known (see also description of model V.1).

At the first stage (characterized by relaxation times τ_{VV}^{AB} and τ_{VV}^{CD}), both AB and CD subsystems evolve toward respective Boltzmann distributions with temperatures T_v^{AB} and T_v^{CD}, determined by the available number of AB and CD vibrational quanta. At this stage, the vibrational relaxation is similar to single-component vibrational relaxation dominated by VV exchange, because VV′ and VT energy exchanges are negligible on time scales $t \le \tau_{VV}^{\mathrm{AB}}, \tau_{VV}^{\mathrm{CD}}$.

- At the second stage, which is characterized by a relaxation time $\tau_{VV'}$ ($\tau_{VV}^{\mathrm{AB}}, \tau_{VV}^{\mathrm{CD}} \ll t \ll \tau_{VT}^{\mathrm{AB}}, \tau_{VT}^{\mathrm{CD}}$), the system evolves toward a state with correlated vibrational temperatures T_v^{AB} and T_v^{CD}. The Boltzmann distribution corresponding to each component retains its form, while the evolution of vibrational temperatures results in a state characterized, when dominated by single-quantum transitions, by the relation (E_1 is the first-level vibrational energy)

$$\frac{E_1^{\mathrm{AB}}}{kT_v^{\mathrm{AB}}} - \frac{E_1^{\mathrm{CD}}}{kT_v^{\mathrm{CD}}} = \frac{E_1^{\mathrm{AB}} - E_1^{\mathrm{CD}}}{kT}$$

or, when dominated by multiquantum transitions (p vibrational quanta of AB transform into q vibrational quanta of CD), by the relation

$$\frac{pE_1^{\mathrm{AB}}}{kT_v^{\mathrm{AB}}} - \frac{qE_1^{\mathrm{CD}}}{kT_v^{\mathrm{CD}}} = \frac{pE_1^{\mathrm{AB}} - qE_1^{\mathrm{CD}}}{kT}$$

The values of T_v^{AB}, T_v^{CD}, and T are determined by two additional equations. For example, when the system is isolated, this relation is supplemented with a conservation condition for the total number of vibrational quanta (when V−V′ energy transfer is dominated by single-quantum transitions),

$$N^{\mathrm{AB}}\alpha^{\mathrm{AB}}(t=0) + N^{\mathrm{CD}}\alpha^{\mathrm{CD}}(t=0) = N^{\mathrm{AB}}\alpha^{\mathrm{AB}} + N^{\mathrm{CD}}\alpha^{\mathrm{CD}}$$

and energy conservation,

$$\begin{aligned}&\frac{5}{2}kT(t=0)(N^{\mathrm{AB}}+N^{\mathrm{CD}}) + N^{\mathrm{AB}}\alpha^{\mathrm{AB}}(t=0)E_1^{\mathrm{AB}} + N^{\mathrm{CD}}\alpha^{\mathrm{CD}}(t=0)E_1^{\mathrm{CD}}\\ &\quad + T(t=0)\sum_j c_j N^{\mathrm{M}_j} = \frac{5}{2}kT(N^{\mathrm{AB}}+N^{\mathrm{CD}}) + N^{\mathrm{AB}}\alpha^{\mathrm{AB}}E_1^{\mathrm{AB}}\\ &\quad + N^{\mathrm{CD}}\alpha^{\mathrm{CD}}E_1^{\mathrm{CD}} + T\sum_j c_j N^{\mathrm{M}_j}\end{aligned}$$

When controlled by single-quantum VV′ energy exchange, the time dependence of T_v^{AB}, T_v^{CD}, and T for $\tau_{VV}^{\mathrm{AB}}, \tau_{VV}^{\mathrm{CD}} \ll t \le \tau_{VV'}^{\mathrm{AB}}$ and $\tau_{VV'}^{\mathrm{CD}} \ll \tau_{VT}^{\mathrm{AB}}$, τ_{VT}^{CD} is determined by solving the equation

$$\frac{\mathrm{d}\alpha^{\mathrm{AB}}}{\mathrm{d}t} = k_{10}^{01\,\mathrm{AB\text{-}CD}} N^{\mathrm{CD}}\left[\alpha^{\mathrm{CD}}(1+\alpha^{\mathrm{AB}})\exp\left(\frac{E_1^{\mathrm{CD}}}{kT}\right) - \alpha^{\mathrm{AB}}(1+\alpha^{\mathrm{CD}})\exp\left(\frac{E_1^{\mathrm{AB}}}{kT}\right)\right]$$

combined with the conservation equations for total number of quanta and energy.

- At the third stage, when $\tau_{VV'}^{\mathrm{AB-CD}} \ll t \sim \tau_{VT}^{\mathrm{AB,CD}}$,

$$N_n^{\mathrm{AB}}(t) = N^{\mathrm{AB}}\left[1 - \exp\left(-\frac{E_1^{\mathrm{AB}}}{kT_v^{\mathrm{AB}}(t)}\right)\right]\exp\left(-n\frac{E_1^{\mathrm{AB}}}{kT_v^{\mathrm{AB}}(t)}\right)$$

$$N_n^{\mathrm{CD}}(t) = N^{\mathrm{CD}}\left[1 - \exp\left(-\frac{E_1^{\mathrm{CD}}}{kT_v^{\mathrm{CD}}(t)}\right)\right]\exp\left(-n\frac{E_1^{\mathrm{CD}}}{kT_v^{\mathrm{CD}}(t)}\right)$$

$$\frac{E_1^{\mathrm{AB}}}{kT_v^{\mathrm{AB}}} - \frac{E_1^{\mathrm{CD}}}{kT_v^{\mathrm{CD}}} = \frac{E_1^{\mathrm{AB}} - E_1^{\mathrm{CD}}}{kT}$$

(predominantly single-quantum transitions) and the temperatures T_v^{AB}, T_v^{CD}, and T equalize.

The time dependence of T_v^{AB}, T_v^{CD}, and T in the interval $\tau_{VV'}^{\mathrm{AB-CD}} \ll t \leq \tau_{VT}^{\mathrm{AB,CD}}$ is determined by energy conservation and one of the VT relaxation equations

$$\frac{\mathrm{d}\alpha^{\mathrm{AB}}}{\mathrm{d}t} = -\frac{\alpha^{\mathrm{AB}} - \alpha_0^{\mathrm{AB}}}{\tau_{VT}^{\mathrm{AB}}}, \qquad \frac{\mathrm{d}\alpha^{\mathrm{CD}}}{\mathrm{d}t} = -\frac{\alpha^{\mathrm{CD}} - \alpha_0^{\mathrm{CD}}}{\tau_{VT}^{\mathrm{CD}}}$$

$$\alpha_0^{\mathrm{AB}}(T) = \frac{1}{\exp(\theta^{\mathrm{AB}}/T) - 1}, \qquad \alpha_0^{\mathrm{CD}}(T) = \frac{1}{\exp(\theta^{\mathrm{CD}}/T) - 1}$$

More precisely, the governing equation is that for which the value of τ_{VT} is smaller.

2. Solution of the basic kinetic equations for a binary mixture of relaxing anharmonic oscillators.

The kinetic equations describing vibrational relaxation in a binary mixture of anharmonic oscillators AB and CD are solved by numerical methods. As in the case of a single-component gas of anharmonic oscillators, it is impossible to single out a process that dominates the evolution of all vibrational levels. For this reason, the vibrational spectrum is divided into ranges dominated by specific processes. At low vibrational levels, kinetics is dominated by single-quantum VV′ transitions leading to Treanor distributions in both species, with constants γ^{AB} and γ^{CD} determined by their respective pools of vibrational quanta. In VV′ transitions, the vibrational quanta pool is redistributed among the components, and the values of γ^{AB} and γ^{CD} equalize (see definition of the Treanor distribution parameter γ in the description of model V.2). At high vibrational levels, kinetics is dominated by VT energy exchange leading to the Boltzmann distribution of vibrational energy characterized by the translational temperature of the gas. In the intermediate range of vibrational energies, the distribution is sensitive to gas temperature, vibrational quanta pool, and other characteristics of the mixture.

10. Example

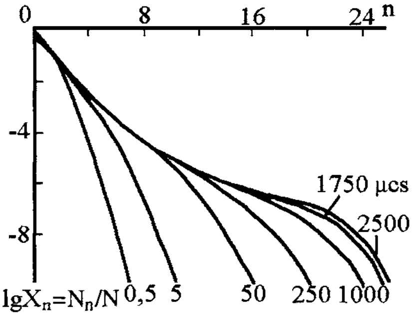

Fig. 4.3

Figure 4.3 illustrates the evolution of level population densities for nitrogen molecules after the normalized population density of the first vibrational level is instantly increased by 30% ($x_1 = x_1^0 + 0.3$, $x_1 = N_1/N$, where N_1 is the number density of the first vibrational level, N is the total number density of these molecules, x_1^0 is the initial Boltzmann distribution, see Ref. 11) at the gas temperature $T = 300$ K and pressure of 1 atm; time is measured in milliseconds. The figure demonstrates that the vibrational-level population density approaches a quasi-steady distribution at $t \geq 2500$ μs. The instant increase in level population density can be induced, e.g., by a nonlinear interaction with laser radiation, as in two-photon Raman excitation (see Ref. 12).

11. Comments

a) For a binary isolated system of harmonic oscillators in a mixture with structureless particles, M_j, the temperature T at $\tau_{VV'}^{\mathrm{AB-CD}} < t \leq \tau_{VT}^{\mathrm{AB}}, \tau_{VT}^{\mathrm{CD}}$ is determined by solving the equation

$$N^{\mathrm{AB}}\hbar\,\omega^{\mathrm{AB}}\alpha^{\mathrm{AB}}(t=0) + N^{\mathrm{CD}}\hbar\,\omega^{\mathrm{CD}}\alpha^{\mathrm{CD}}(t=0) + \frac{5}{2}(N^{\mathrm{AB}} + N^{\mathrm{CD}})$$

$$\times\, kT(t=0) + T(t=0)\sum_j c_j N^{\mathrm{M}_j} = N^{\mathrm{AB}}\hbar\,\omega^{\mathrm{AB}}\alpha^{\mathrm{AB}}$$

$$+\, N^{\mathrm{CD}}\hbar\,\omega^{\mathrm{CD}}\alpha^{\mathrm{CD}} + \frac{5}{2}(N^{\mathrm{AB}} + N^{\mathrm{CD}})kT + T\sum_j c_j N^{\mathrm{M}_j}$$

When $\theta^{\mathrm{AB}} > \theta^{\mathrm{CD}}$, the gas cools down if $\alpha^{\mathrm{CD}}(t=0) > \alpha^{\mathrm{CD}}(t)$: $T(t) < T(t=0)$ (Ref. 4).

b) The results of approximate analytical calculations of vibrational-level population densities for a highly nonequilibrium binary mixture of diatomic molecules treated as anharmonic oscillators were reviewed in

Ref. 13. It was shown that when the distribution of vibrational energy in the component with the smaller vibrational quantum has a plateau-like portion, the distribution of the other component can exhibit two negatively sloped Treanor branches and two plateau regions.

Relevant material can be found in Refs. 2–6.

D. Vibrational Relaxation of Diatomic Molecules: Diffusion Approximation (V.4)

1. *Purpose of the Model*

The model aims at determination of the vibrational energy distribution for diatomic molecules of various gaseous species.

2. *Assumptions*

a) Vibrational relaxation is represented as diffusion in the vibrational energy space. The vibrational energy of diatomic molecules is treated in the classical approximation (quantization is ignored).

b) The change in the vibrational energy of a molecule induced by a collision is assumed to be small as compared to the thermal energy per molecule: $(\overline{\Delta\varepsilon^2})^{1/2} \ll kT$.

3. *Restrictions*

a) Because vibrational energy quantization is ignored, the model can only be applied to describe processes that take place at high temperatures $(T \gg \theta)$.

b) In analyzing the vibrational relaxation of molecules of a low-concentration impurity in a gas of structureless particles, the number densities of the molecules and particles are subject to Restrictions a and b in the description of model V.1.

c) For harmonic oscillator approximation, see Restriction c in the description of model V.1.

4. *Basic Kinetic Equation*

- For diatomic molecules as a low-concentration impurity in a gas of structureless particles,

$$\frac{\partial f(\varepsilon, t)}{\partial t} = \frac{\partial}{\partial \varepsilon}\left[D_{VT}\left(\frac{\partial f}{\partial \varepsilon} + \frac{1}{kT} f\right)\right]$$

$$D_{VT} = \frac{1}{2}\frac{\overline{\Delta\varepsilon^2}}{\tau_0}, \qquad \overline{\Delta\varepsilon^2} = \int (\varepsilon' - \varepsilon)^2 P(\varepsilon, \varepsilon')\mathrm{d}\varepsilon'$$

$D_{VT} = b_{VT}\varepsilon$, $b_{VT} = k\theta k_{01}N$ for harmonic oscillator approximation with single-quantum transitions.

- For a single-component gas of diatomic molecules,

$$\frac{\partial f(\varepsilon, t)}{\partial t} = \frac{\partial}{\partial \varepsilon}\left[D_{VT}\left(\frac{\partial f}{\partial \varepsilon} + \frac{1}{kT}f\right)\right] + \frac{\partial}{\partial \varepsilon}\left[D_{VV}\left(\frac{\partial f}{\partial \varepsilon} + \frac{1}{kT_v}f\right)\right]$$

$$\left.\begin{aligned} D_{VT} &= b_{VT}\varepsilon, \quad b_{VT} = k\theta k_{01}N, \\ D_{VV} &= b_{VV}\varepsilon, \quad b_{VV} = k\theta k_{10}^{01}N(1+\alpha), \end{aligned}\right\} \text{for harmonic oscillator approximation}$$

$$\alpha N = \frac{1}{k\theta}\int_0^\infty \varepsilon f(\varepsilon)\mathrm{d}\varepsilon, \qquad \frac{\alpha}{\alpha+1} = \exp\left(-\frac{\theta}{T_v}\right).$$

5. *Nomenclature*

a) Quantity calculated with the model:

$f(\varepsilon, t)$	vibrational energy distribution function

b) Kinetic coefficients:

D, D_{VT}, D_{VV}	diffusion coefficients in the vibrational energy space

c) Other quantities:

ε'	energy of a molecule after a collision
$P(\varepsilon, \varepsilon')$	probability density of an $\varepsilon \to \varepsilon'$ transition induced by a collision
$\overline{\Delta\varepsilon^2}$	mean square energy transferred to a molecule in a collision
T	translational temperature
T_v	vibrational temperature
θ	characteristic vibrational temperature of a molecule
N	number density of molecules
k_{01}	rate constant for the $0 \to 1$ VT energy exchange induced by a collision of molecules
$k_{10}^{01}(T)$	rate constant for the VV energy exchange in a collision involving the $1 \to 0$ vibrational transition in one of the colliding molecules and the $0 \to 1$ transition in the other
α	average number of vibrational quanta per molecule
τ_{VT}	vibrational relaxation time
τ_0	mean free time between collisions for a molecule

6. *Description of Coefficients and Parameters*

Expressions for the rate constants of VT and VV energy exchange, k_{01} and $k_{10}^{01}(T)$, and the vibrational relaxation time, τ_{VT}, were given in Chapter 4 of the first volume (see models I-V.1–I-V.6).

7. *Features of the Model*

a) In the case of VT energy exchange in a system of diatomic molecules treated as harmonic oscillators, the solution is

$$f(\varepsilon, t) = \sum_{m=0} C_m \exp\left(-\frac{\varepsilon}{kT}\right) L_m\left(\frac{\varepsilon}{kT}\right) \exp\left(-\frac{mt}{\tau_{VT}}\right)$$

$$C_m = \frac{1}{kT}\int_0^\infty f(\varepsilon, 0) L_m\left(\frac{\varepsilon}{kT}\right) d\varepsilon, \quad \tau_{VT} = \frac{kT}{b_{VT}}$$

where $L_m(y)$ is a Laguerre polynomial.

The coefficients C_m are related to the mth and lower-order moments of the initial distribution function. The solution demonstrates that higher-order moments decay at faster rates with time. As $t \to \infty$, only the equilibrium term (with $m = 0$) remains finite in the sum.

b) The model is canonically invariant: under the initial condition

$$f(\varepsilon, 0) = \frac{N}{kT_0}\exp\left(-\frac{\varepsilon}{kT_0}\right), \qquad T_0 = T_v(t = 0)$$

the solution to the diffusion equation is

$$f(\varepsilon, t) = \frac{N}{kT_v(t)}\exp\left(-\frac{\varepsilon}{kT_v(t)}\right)$$

where T_v is determined by solving the equation $dT_v/dt = -(T_v - T)/\tau_{VT}$.

c) In the case of a single-component gas, the first and second terms in the kinetic equation represent the vibrational relaxation processes because of VT and VV energy exchange, respectively. When $b_{VV} \gg b_{VT}$, vibrational relaxation proceeds in two stages. At the first (fast) stage, characterized by a time scale $t \sim \tau_{VV} = kT_v/b_{VV}$, the solution is

$$f(\varepsilon, t) = \sum_{m=0} C_m \exp\left(-\frac{\varepsilon}{kT_v}\right) L_m\left(\frac{\varepsilon}{kT_v}\right) \exp\left(-\frac{mt}{\tau_{VV}}\right)$$

This stage results in the Boltzmann distribution with vibrational temperature T_v, corresponding to the instantaneous vibrational energy pool. When the initial distribution has Boltzmann form, VV energy exchange processes can be ignored because they do not affect the form of the Boltzmann distribution and the value of T_v. At the second (slow) stage, the Boltzmann form of the distribution is preserved. Only VT energy exchange plays an essential role as a factor that makes T_v approach T. The resulting formulas are similar to those obtained for a low-concentration impurity, but the variation of T_v affects the value of T in this case.

8. *General and Particular Solutions*

In the case of diatomic molecules as a low-concentration impurity, the basic kinetic equation admits an analytical solution when $D_{VT} = \text{const}$ (see description of model R.2).

9. *Example*

Consider vibrational energy distribution in a system with a source creating a small population of vibrationally excited molecules with energy, ε_0, as an impurity in an inert gas diluent. In this system, vibrational relaxation is described by the equation

$$\frac{\partial f}{\partial \tau} = \frac{\partial}{\partial x}\left(xf + x\frac{\partial f}{\partial x}\right) + \eta\delta(x - x_0)$$

where $x = \varepsilon/kT$, $x_0 = \varepsilon_0/kT$, $\tau = t/\tau_{VT}$, and η is the dimensionless source intensity. At $\tau \gg 1$, this equation has a quasi-steady-state solution of the form (see Ref. 10)

$$f(x, \tau) = e^{-x}\left(\int_0^\infty \varphi(\xi)d\xi + \eta\tau\right) + \eta e^{-x}\sum_{\nu=1}\frac{1}{\nu}L_\nu(x_0)L_\nu(x)$$

where $f(x, 0) = \varphi(x)$. The first term in this expression represents the addition of particles supplied by the source to the vibrational reservoir described by the Boltzmann distribution. This energy is carried by the molecules that have already thermalized at $t \gg \tau_{VT}$. The second term describes the steady-state distribution of relaxing molecules. At $x > x_0 \gg 1$, this distribution has the form of a decreasing exponential: $\eta\exp[-(x - x_0)]/x_0$. At $x_0 > x \gg 1$, it behaves as η/x, exhibiting a plateau-like dependence.

10. Comment

a) The vibrational energy distributions predicted by models based on state-specific kinetics (see models V.1–V.3) and diffusion approximation (model V.4) are qualitatively similar. In certain cases, the diffusion approximation should be recommended because it leads to a single equation, rather than many equations for individual level population densities.
b) The diffusion approximation is more general than the single-quantum transition model because it allows for multiquantum transitions.
c) A diffusion model of vibrational relaxation for anharmonic molecules as a low-concentration impurity in an inert gas was presented in Ref. 17; for a binary mixture of harmonic and anharmonic oscillators, analogous models were developed in Ref. 18.

Relevant material can be found in Refs. 4, 14–16.

E. Vibrational Relaxation in a Gas of Polyatomic Molecules: State-Specific Kinetic Model (V.5)

1. Purpose of the Model

The model aims at the calculation of the population densities for vibrational modes in polyatomic molecules in gaseous mixtures.

2. Assumptions

a) See Assumptions 2 and 3 in the description of model V.1.
b) The frequency Z of collisions of molecules with one another and with other particles is independent of the vibrational state of the molecules.

c) The ith mode vibrations of polyatomic molecules are modeled in the harmonic oscillator approximation characterized by a set of vibrational quantum numbers, v_i.
d) Each kinetic equation describes the vibrational energy exchange in a mode ξ via a single channel defined by specifying a pair $\{l_i, l_j\}$ of quantum numbers. In the case of energy exchange via several channels, the right-hand side of the corresponding kinetic equation is the sum over all the pairs $\{l_i, l_j\}$ involved in the process.

3. *Restrictions*

a) In analyzing the vibrational relaxation of polyatomic molecules as a low-concentration impurity in a gas of structureless particles, the number density N^{XY} of polyatomic molecules must be such that

$$k^{\mathrm{XY-XY}}\begin{Bmatrix} l_i \to 0 \\ 0 \to l_j \end{Bmatrix} N^{\mathrm{XY}} \ll k^{\mathrm{XY-M}_q}\begin{Bmatrix} l_i \to 0 \\ 0 \to l_j \end{Bmatrix} N^{\mathrm{M}_q}$$

b) Because three-body collisions are ignored, the number densities of XY, M_q, and $\mathrm{M}_{q'}$ must satisfy the condition

$$k^{\mathrm{XY-M}_q\mathrm{-M}_{q'}}\begin{Bmatrix} l_i \to 0 \\ 0 \to l_j \end{Bmatrix} N^{\mathrm{M}_{q'}} \ll k^{\mathrm{XY-M}_q}\begin{Bmatrix} l_i \to 0 \\ 0 \to l_j \end{Bmatrix}$$

as well as analogous conditions with symbol M_q or $\mathrm{M}_{q'}$ replaced by XY.
c) The vibrational state of a polyatomic molecule can be modeled by a set of mutually independent harmonic oscillators only when the degree of vibrational excitation is low. As a consequence, the scope of the model is restricted to a few low-energy vibrational levels in each mode of molecule.

4. *Basic Kinetic Equations*

a) For polyatomic molecules XY as a low-concentration impurity in a gas of structureless particles, M_q:

$$\frac{\mathrm{d}N^{\mathrm{XY}}(v_\xi)}{\mathrm{d}t} = \sum_q N^{\mathrm{M}_q} \times \sum_{v_i, v_j \neq v_\xi} \left[k^{\mathrm{XY-M}_q}\begin{Bmatrix} v_i - l_i \to v_i \\ v_j + l_j \to v_j \end{Bmatrix} \times N^{\mathrm{XY}}(v_i - l_i, v_j + l_j) \right.$$
$$\left. - k^{\mathrm{XY-M}_q}\begin{Bmatrix} v_i \to v_i - l_i \\ v_j \to +l_j \end{Bmatrix} \times N^{\mathrm{XY}}(v_i, v_j) \right]$$

b) For a mixture of a single polyatomic species XY with structureless particles M_q, similar terms are added to the right-hand sides of the equations, with symbol M_q replaced by XY.
c) For a mixture of two polyatomic species, XY and ZW, with structureless particles M_q, similar terms are added to the right-hand sides of the equations, with symbol M_q replaced by XY, and XY replaced by ZW.

5. *Nomenclature*

a) Quantities calculated with the model:

$N^{XY}(v_\xi)$	population density for the vibrational level v_ξ in the mode ξ of XY molecules

b) Kinetic coefficients:

$k^{XY-M_q}\left\{\begin{matrix} v_i \to v_i - l_i \\ v_j \to v_j + l_j \end{matrix}\right\}$	rate constant for VV energy transfer of the following type induced by an XY–M_q collision:

$$(v_1,\ldots,v_k;\, v_{k+1},\ldots,v_L) \equiv \{v_i,v_j\} \to (v_1 \pm l_1,\ldots,v_k \pm l_k;\, v_{k+1} \mp l_{k+1},\ldots,v_L \mp l_L) \equiv \{v_i \pm l_i;\, v_j \mp l_j\}$$

$k^{XY-XY}\left\{\begin{matrix} v_i \to v_i - l_i \\ v_j \to v_j + l_j \end{matrix}\right\}$	analogous rate constant for VV energy transfer induced by an XY–XY collision
$k^{XY-ZW}\left\{\begin{matrix} v_i \to v_i - l_i \\ v_j \to v_j + l_j \end{matrix}\right\}$	analogous rate constant for VV energy transfer induced by an XY–ZW collision
$k_{SSH}^{XY-M_q}\left\{\begin{matrix} v_i \to v_i - l_i \\ v_j \to v_j + l_j \end{matrix}\right\}$	analogous rate constant calculated by applying the Schwartz–Slawsky–Herzfeld (SSH) theory to XY–M_q collisions
$k_{SSH}^{XY-XY}\left\{\begin{matrix} v_i \to v_i - l_i \\ v_j \to v_j + l_j \end{matrix}\right\}$	analogous rate constant calculated by applying the Schwartz–Slawsky–Herzfeld (SSH) theory to XY–XY collisions
$k_{SSH}^{XY-ZW}\left\{\begin{matrix} v_i \to v_i - l_i \\ v_j \to v_j + l_j \end{matrix}\right\}$	rate constant calculated by applying the SSH theory to XY–ZW collisions

c) Other quantities:

ξ	symbol referring to the vibrational mode under analysis
i, j	indices of the modes involved in vibrational energy transfer
v_i, v_j, v_s	vibrational states with *i*th, *j*th, and *s*th number
L	total number of vibrational modes in the colliding molecules
k	total number of vibrational modes that lose quanta
l_i	the number of quanta lost in the *i*th mode ($i = 1,\ldots,k$)
l_j	the number of quanta gained in the *j*th mode ($j = k+1,\ldots,L$)
N	number density of molecules
$N^{XY}(v_i, v_j)$	number density of XY molecules at a particular vibrational state (v_i, v_j) in modes *i* and *j*; for ZW molecules, the symbol XY is replaced by ZW
N^{M_q}, $N^{M_{q'}}$	number densities of M_q and $M_{q'}$ molecules
$g(v_i, v_j)$	statistical weight (multiplicity) of the vibrational state $\{v_i, v_j\}$
$g(v_s)$	statistical weight (multiplicity) of the vibrational state $\{v_s\}$
θ_i	characteristic temperature of the *i*th vibrational mode of XY molecules (for ZW molecules, the corresponding symbol is used)

r_i	degeneracy of the ith mode of XY molecules (for ZW molecules, the corresponding symbol is used)
q, q'	indices denoting structureless particles
$N^{CO_2}_{12^l3}$	number density of CO_2 molecules with populations of symmetric $(i, j = 1)$, bending $(i, j = 2)$, and asymmetric $(i, j = 3)$ modes; l is the quantum number describing the projection of the momentum of bending vibrations onto the axis of molecule with $r_2 = 2$

6. *Description of Coefficients and Parameters*

The rate constants for VT and VV energy transfers induced by collisions involving different polyatomic molecules can be found in Refs. 20–25. Some examples are (from Ref. 20):

	k (cm^3/mol · s) $= \exp(A + BT^{-1/3} + CT^{-2/3})$		
Process	A	B	C
VT: CO_2—CO_2			
$(01^10) \rightarrow (00^00)$	38.3	−177	451
$(03^10, 11^10) \rightarrow (03^00)$	37.2	−89.3	227
$(04^40) \rightarrow (03^10, 01^10)$	30.1	−171	264
VT: H_2O—H_2O			
$(010) \rightarrow (000)$	52.8	−363	1462
$(001) \rightarrow (000)$	55.1	−522	1999
$(100) \rightarrow (000)$	58.6	−541	2084
VT: H_2O—N_2, O_2, CO			
$(100) \rightarrow (000)$	55.3	−435	1079
VV′: $CO_2(00^01) + CO(v = 0) \rightarrow CO_2(01^10) + CO(v = 1)$	28.7	0	−153

The rate constants for VT and VV energy transfer can be estimated by using generalizations of the SSH theory developed to describe energy exchange in a gas of diatomic molecules (see formulas presented in model I-V.3 and references cited therein). In such an analysis, each mode should be considered as a separate oscillator, without taking into account its degeneracy and the structure of the particular polyatomic molecule that has this mode. Note that the actual rates of VV energy transfer may be substantially higher than those predicted by the SSH theory because of intermode anharmonicity and Coriolis interactions.

Recursive relations for rate constants:

$$k^{XY-M_q}\begin{Bmatrix} l_i \rightarrow 0 \\ 0 \rightarrow l_j \end{Bmatrix} = k_{SSH}^{XY-M_q}\begin{Bmatrix} l_i \rightarrow 0 \\ 0 \rightarrow l_j \end{Bmatrix} \prod_{i=1}^{k} r_i^{l_i} \prod_{j=k+1}^{L} r_j^{l_j} \left[\prod_{i=1}^{k} \binom{l_i + r_i - 1}{l_i}\right]^{-1}$$

$$k^{XY-XY}\begin{Bmatrix} l_i \rightarrow 0 \\ 0 \rightarrow l_j \end{Bmatrix} = k_{SSH}^{XY-XY}\begin{Bmatrix} l_i \rightarrow 0 \\ 0 \rightarrow l_j \end{Bmatrix} \prod_{i=1}^{k} (2r_i)^{l_i} \prod_{j=k+1}^{L} (2r_j)^{l_j} \left[\prod_{i=1}^{k} \binom{l_i + r_i - 1}{l_i}\right]^{-1}$$

$$k^{\mathrm{XY\text{-}ZW}}\left\{\begin{matrix} l_i \to 0 \\ 0 \to l_j \end{matrix}\right\} = k^{\mathrm{XY\text{-}ZW}}_{\mathrm{SSH}}\left\{\begin{matrix} l_i \to 0 \\ 0 \to l_j \end{matrix}\right\} \prod_{i=1}^{k} r_i^{l_i} \prod_{j=k+1}^{L} r_j^{l_j} \left[\prod_{i=1}^{k}\binom{l_i + r_i - 1}{l_i}\right]^{-1}$$

The last two relations hold when the symbols XY and ZW are interchanged.

For collisions of XY molecules with structureless particles, the total number of vibrational modes, L, is set equal to the number of modes in an XY molecule. In the case of interaction between two identical or different molecules, L is set equal to the total number of vibrational modes in both molecules.

7. *Features of the Model*

Detailed balance relations:

$$k^{\mathrm{XY\text{-}M}_q}\left\{\begin{matrix} v_i - l_i \to v_i \\ v_j + l_j \to v_j \end{matrix}\right\} = \frac{g\{v_i, v_j\}}{g\{v_i - l_i, v_j + l_j\}} \prod_{i=1}^{k} \beta_i^{l_i}$$
$$\times \prod_{j=k+1}^{L} \beta_j^{-l_j} k^{\mathrm{XY\text{-}M}_q}\left\{\begin{matrix} v_i \to v_i - l_i \\ v_j \to v_j + l_j \end{matrix}\right\}$$

$$g\{v_i, v_j\} = \prod_{s=1}^{L} g(v_s) = \prod_{s=1}^{L}\binom{v_s + r_s - 1}{v_s}; \quad \beta_s = \exp\left(-\frac{\theta_s}{T}\right), \quad s = 1, \ldots, L$$

Here

$$\binom{p}{n} = \frac{(p(p-1) \times \cdots \times (p - n + 1))}{n!}.$$

A similar relation holds with the symbol M_q replaced by XY, with replacing r_s by $2r_s$ in the appropriate expression for $g\{v_i, v_j\}$.

8. *General and Particular Solutions*

No analytical solution is available, and the system of governing equations must be solved by a numerical method.

9. *Example*

Results concerning the state-specific vibrational kinetics in the relaxation zone behind a shock wave in the mixture of $\mathrm{CO_2}$ and M molecules are presented in Ref. 24. The $\mathrm{CO_2}$ molecule consists of three modes (symmetric—v_1, $r_1 = 1$, bending—v_2, $r_2 = 2$, and asymmetric—v_3, $r_3 = 1$ modes—see subsection Nomenclature), and M molecule does not change its internal state. Among VT and intramode VV processes, only the single-quantum transitions are taken into account as the more probable ones. Intermode VV processes include:

- near-resonant, two-quantum VV($v_1 \rightleftarrows v_2$) exchange between the symmetric and bending modes,
- three-quantum VV($v_2 \rightleftarrows v_3$) exchange between the asymmetric and bending modes,
- VV($v_1 \rightleftarrows v_2 \rightleftarrows v_3$) exchange between all three vibrational modes.

The required rate constants have been calculated using the SSH theory (see Ref. 27 and descriptions of models I-V.2 and I-V.3).

The probabilities of intramode VV exchange and intermode VV($v_1 \rightleftarrows v_2$) exchange are much higher than the probabilities of other vibrational energy exchange. It leads to a rapid establishment of three-temperature vibrational distributions, and CO_2 vibrational populations $N_{12^l3}^{CO_2}$ are expressed in terms of the gas temperature T, the temperature of the first vibrational level of the asymmetric mode T_3, and the vibrational temperature T_{12} that characterizes the symmetric and bending modes coupled because of their rapid exchange (see Refs. 26 and 28):

$$N_{12^l3}^{CO_2} = \frac{Ng_v}{Q_v} \exp\left[-\frac{(2v_1 + v_2)E_{01^10}}{kT_{12}} - \frac{v_3 E_{00^01}}{kT_3} - \frac{E_{12/3} - (2v_1 + v_2)E_{01^10} - v_3 E_{00^01}}{kT} \right]$$

Here g_v is the statistical weight (multiplicity), Q_v is the vibrational partition function, $E_{12/3}$ is the vibrational energy of level v_1, v_2, v_3, with degeneracy of level l ($l = 0$ or $l = 1$ for v_2).

The following free stream conditions for one-dimensional stationary CO_2 flow in Euler approximation have been considered: $T_0 = 293$ K, $p_0 = 100$ Pa, M_0 (Mach number) = 4. The vibrational distributions in the free stream are assumed to be equilibrium Boltzmann distributions with the gas temperature T_0 and remain the same just behind the shock ($x = 0$) because the vibrational energy transitions in the shock front are frozen. The vibrational levels possessing the total energy less than $D_0/4$ (D_0 is the dissociation energy) have been taken into account. This corresponds to the maximum values $v_1 = 6$, $v_2 = 12$, $v_3 = 3$. Figure 4.4 shows reduced (relative) level populations of the combined mode as functions of energy $E_{12/3}/k$, K, where curve $1 - x = 0.07$ mm; $2 - x = 2$ mm; $3 - x = 2$ cm.

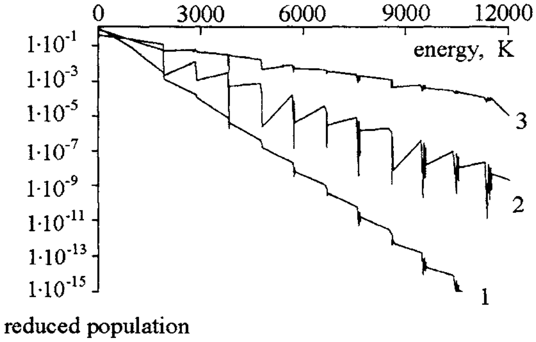

Fig. 4.4

The process of vibrational excitation in the relaxation zone is shown in Fig. 4.4, where the populations in the combined mode with the vibrational number $v = 2v_1 + v_2$ and $v_3 = 0$ are given as functions of the vibrational energy $E_{12/3}/k$ for different distances x from the front. One can notice a sawtooth behavior of the vibrational distribution for the location close to the front (at

$x = 2$ mm). Approaching equilibrium, the distributions become smoother. Similar distributions have been obtained in Ref. 28 in the three-temperature approximation, in the case of very high storage of vibrational energy in the combined mode ($T_{12}/T \sim 10$).

10. Comment

The system of kinetic equations previously described provides the most general description of vibrational relaxation of a polyatomic molecule represented as a system of harmonic oscillators. The harmonic oscillator model can be applied only to polyatomic molecules characterized by relatively low degrees of vibrational excitation. In the case of an anharmonic molecule, interactions between vibrational modes, as well as effects because of degeneracy, rotational splitting, and complex rotational structure, make it possible to treat the vibrational spectrum of a polyatomic molecule as a quasi-continuum (characterized by a high density of vibrational states), except for a few low levels. For example, the lower boundary of the quasi-continuum is close to 3000–4000 cm^{-1} for SF_6, which corresponds to the energy of 3 to 4 vibrational quanta (Refs. 29 and 30). For triatomic molecules, qualitatively correct results can be obtained by using the harmonic oscillator approximation up to the dissociation limit (Ref. 31). See also Comments in the description of model V.8.

Relevant material can be found in Ref. 19.

F. Vibrational Relaxation in Chemically Reacting Gas: State-Specific Kinetic Model (V.6)

1. Purpose of the Model

The model aims at the determination of population densities of vibrational levels of molecules during simultaneous processes of vibrational energy exchange and chemical reactions.

2. Assumptions

a) The characteristic time of vibrational relaxation is much greater than the translational and rotational relaxation times and is comparable with the characteristic time of chemical reaction. The equilibrium Maxwell–Boltzmann distribution of particles over translational and rotational energies with common temperature T is preserved.

b) Three-body collisions in the absence of recombination are ignored as less probable in comparison with binary collisions.

c) The population densities N_m for vibrational levels m of XY molecules in reacting gas mixture are considered. XY molecules are involved in VT, VV, and VV′ energy exchange processes in collisions without the change of chemical composition (see description of models V.I–V.3, and V.5), and also in chemical transformation, altogether in l processes and reactions. The reactions with XY molecules are conventionally classified into direct (d,f) for reagents and reverse (r,b) for reaction products (see subsection "Nomenclature").

3. *Restrictions*

The restrictions on the calculation of the population density of vibrational levels as a result of vibrational energy exchange are indicated in descriptions of models V.1–V.3 and V.5 in accordance to the problems being solved.

4. *Basic Kinetic Equation*

For change of vibrational states $m \rightleftarrows m', n \rightleftarrows n'$ of components i, j, i', j' in reactions $l(i \rightleftarrows i', j \rightleftarrows j')$ in binary collisions:

$$\frac{\mathrm{d}N_m^{\mathrm{XY}}}{\mathrm{d}t} = \sum_l \left\{ \sum_{m,m',n'} k_{m'ml}^{n'n} N_{m'}^{i'} N_{n'}^{j'} - \sum_{n,m',n'} k_{mm'l}^{nn'} N_m^i N_n^j \right\}$$

If any vibrational state is not specified (simplified state-specific kinetics) or is absent (as an example, for atoms), the corresponding notation of state is omitted, and is not considered in the equation. The description of vibrational energy exchange without chemical transformation is included in the equation formally with $l = 0$: $i \rightleftarrows i, j \rightleftarrows j$).

5. *Kinetic Equations for Particular Types of Reactions*

For dissociation of diatomic molecules AB, A_2, and B_2, and for recombination of atoms A, B with formation of diatomic molecules, assuming that particle M_s state does not change:

$$\mathrm{AB}(m) + \mathrm{M}_s \rightleftarrows \mathrm{A} + \mathrm{B} + \mathrm{M}_s \quad (\text{for } \mathrm{A}_2 \text{ and } \mathrm{B}_2\text{–similarly})$$

$$\frac{\mathrm{d}N_m^{\mathrm{AB}}}{\mathrm{d}t} = \left(\frac{\mathrm{d}N_m^{\mathrm{AB}}}{\mathrm{d}t}\right)_{VT,VV} - \sum_s k_{dm}^{\mathrm{AB-M}_s} N_m^{\mathrm{AB}} N^{\mathrm{M}_s} + \sum_s k_{rm}^{\mathrm{A-B-M}_s} N^{\mathrm{A}} N^{\mathrm{B}} N^{\mathrm{M}_s}$$

For reactions of decomposition and formation of polyatomic molecules, assuming that particle M_s state does not change:

$$\mathrm{XYZ}(\xi m) + \mathrm{M}_s \rightleftarrows \mathrm{XY} + \mathrm{Z} + \mathrm{M}_s$$

$$\frac{\mathrm{d}N_{\xi m}^{\mathrm{XYZ}}}{\mathrm{d}t} = \left(\frac{\mathrm{d}N_{\xi m}^{\mathrm{XYZ}}}{\mathrm{d}t}\right)_{VT,VV,VV'} - \sum_s k_{d\xi m}^{\mathrm{XYZ-M}_s} N_{\xi m}^{\mathrm{XYZ}} N^{\mathrm{M}_s} + \sum_s k_{r\xi m}^{\mathrm{XY-Z-M}_s} N^{\mathrm{XY}} N^{\mathrm{Z}} N^{\mathrm{M}_s}$$

For reactions of a simple exchange with diatomic molecules:

$$\mathrm{AB}(m) + \mathrm{C} \rightleftarrows \mathrm{AC}(m') + \mathrm{B}$$

$$\frac{\mathrm{d}N_m^{\mathrm{AB}}}{\mathrm{d}t} = \left(\frac{\mathrm{d}N_m^{\mathrm{AB}}}{\mathrm{d}t}\right)_{VT,VV,VV'} - \sum_{m'} k_{fmm'}^{\mathrm{AB-C}} N_m^{\mathrm{AB}} N^{\mathrm{C}} + \sum_{m'} k_{bmm'}^{\mathrm{AC-B}} N_{m'}^{\mathrm{AC}} N^{\mathrm{B}}$$

For reactions of a double exchange with diatomic molecules:

$$\mathrm{AB}(m) + \mathrm{CD}(n) \rightleftarrows \mathrm{AC}(m') + \mathrm{BD}(n')$$

$$\frac{\mathrm{d}N_m^{\mathrm{AB}}}{\mathrm{d}t} = \left(\frac{\mathrm{d}N_m^{\mathrm{AB}}}{\mathrm{d}t}\right)_{VT,VV,VV'} - \sum_{n,m'n'} k_{fmn,m'n'}^{\mathrm{AB-C}} N_m^{\mathrm{AB}} N_n^{\mathrm{CD}} + \sum_{n,m'n'} k_{bmn,m'n'}^{\mathrm{AC-BD}} N_{m'}^{\mathrm{AC}} N_{n'}^{\mathrm{BD}}$$

If any vibrational state is not specified, the corresponding notation of state is omitted and is not considered in the equation.

The formulas for rate of population density change for *m*th vibrational level as a result of vibrational energy exchange $(\mathrm{d}N_m^{\mathrm{AB}}/\mathrm{d}t)_{VT,VV}$ and $(\mathrm{d}N_{\xi m}^{\mathrm{XZY}}/\mathrm{d}t)_{VT,VV,VV'}$ are determined by the relations presented in the descriptions of models V.1 – V.3 and V.5, with assumptions and restrictions accepted there. Note that the processes of VT and VV′ exchange with reaction products and other chemical components must be taken into account. The role of VV and VV′ energy exchange processes is negligibly small if $N^{\mathrm{AB}} \ll N_s$, $N^{\mathrm{XYZ}} \ll N_s$.

6. *Nomenclature*

a) Quantities calculated with the model:

N_m^{XY}, N_m^i	population density for the *m*th vibrational level of XY and M_i molecules
N_n^j	population density for the *n*th vibrational level of N_i molecules
N_m^{AB}	population density for the *m*th vibrational level of AB molecules
$N_{\xi m}^{\mathrm{XYZ}}$	population density for the *m*th vibrational level in the mode ξ of XYZ molecules

b) Kinetic coefficients:

$k_{mm'l}^{nn'}$, $k_{m'ml}^{n'n}$	rate constants for transitions $m \Leftrightarrow m', n \Leftrightarrow n'$ in *l*th reaction
$k_{dm}^{\mathrm{AB-M}_s}$	rate constant for dissociation of AB molecule from the *m*th vibrational level induced by AB–M_s collisions
$k_{rm}^{\mathrm{A-B-M}_s}$	rate constant for recombination of A and B atoms with formation of AB molecule in the *m*th vibrational level induced by A–B–M_s collisions
$k_{d\xi m}^{\mathrm{XYZ-M}_s}$, $k_{r\xi m}^{\mathrm{XY-Z-M}_s}$	analogous rate constants for decomposition and formation of polyatomic XYZ molecules in the mode ξ
$k_{fmm'}^{\mathrm{AB-C}}$, $k_{bm'm}^{\mathrm{AC-B}}$	rate constants for reactions of a simple exchange $\mathrm{AB} + \mathrm{C} \rightleftarrows \mathrm{AC} + \mathrm{B}$ in forward (*f*) and back (*b*) directions with decomposition and formation of AB molecule in the *m*th vibrational level and with formation and decomposition of AC molecule in the *m*th level
$k_{fmn,m'n'}^{\mathrm{AB-CD}}$, $k_{bm'n'mn}^{\mathrm{AC-BD}}$	rate constants for a double exchange $\mathrm{AB} + \mathrm{CD} \rightleftarrows \mathrm{AC} + \mathrm{BD}$ in forward (*f*) and back (*b*) directions with decomposition and formation of AB molecule in the *m*th level, of CD molecule in the *n*th level, and AC, BD, molecules in the *m*th and *n*th levels, correspondingly

c) Superscripts denote chemical components participated in reactions

d) Subscripts

d, r	reactions of dissociation (decomposition) and recombination (formation), correspondingly
f, b	forward and back reactions, correspondingly
m, n	vibrational states in d, f reactions
m', n'	vibrational states in r, b reactions
i, j	mixture components participating in d, f reactions
i', j'	mixture components participating in r, b reactions
ξ	vibrational mode of polyatomic molecule under analysis

e) Other quantities:

$(\mathrm{d}N_m^{\mathrm{AB}}/\mathrm{d}t)_{VT,VV}$	rate of population density change for mth vibrational level of AB molecules as a result of VT and VV energy exchange
$(\mathrm{d}N_{\xi m}^{\mathrm{XYZ}}/\mathrm{d}t)_{VT,VV,VV'}$	rate of population density change for mth vibrational level of XYZ molecules in the mode ξ as a result of VT, VV, and VV′ energy exchange
$N_n^{\mathrm{CD}}, N_{m'}^{\mathrm{AC}}, N_{n'}^{\mathrm{BD}}$	population density for vibrational levels indicated by subscripts, and for molecules, indicated by superscripts
$N^{\mathrm{A}}, N^{\mathrm{B}}, N^{\mathrm{C}}, N^{\mathrm{AB}}, N^{\mathrm{AC}}, N^{\mathrm{BD}}, N^{\mathrm{XY}}, N^{\mathrm{M}_s}$	number densities of species indicated by superscripts
$E_m, E_m^{\mathrm{AB}}, E_{\xi m}^{\mathrm{XYZ}}$	vibrational energy of mth vibrational level, for AB and XYZ molecules (in the mode ξ), in particular
D_0, D^0	dissociation energy of diatomic molecule and chemical bond energy for decomposition of polyatomic molecule, correspondingly
E_a	activation energy in chemical exchange reactions
$k_d^0(T)$	thermally equilibrium rate constant of dissociation
$K_p(T)$	constant of chemical equilibrium in terms of partial pressures
$Q_v, Q_v^{\mathrm{AB}}, Q_{v\xi}^{\mathrm{XYZ}}, Q_v^{\mathrm{AC}}, Q_v^{\mathrm{BD}}, Q_v^{\mathrm{CD}}$	partition functions over vibrational states, for molecules indicated by superscripts, in particular
$\sigma_0(T)$	averaged cross section for elastic collisions
m_i, m_j	mass of particles i, j
μ	reduced mass of colliding particles
α	the efficiency of vibrational energy in activation of reaction (see description of model I-C.19)
α	average number of vibrational quanta per molecule (in subsection "General and Particular Solution")
Z	gas kinetic collision frequency per unit number density
R_0	gas kinetic radius
W_d	dissociation rate

Q_{10}^{01}	probability of resonant VV exchange in collisions of identical molecules (vibrational transfers 1 → 0, 0 → 1)

7. *Coefficients and Parameters*

The state-specific rate constants of chemical reactions depend on vibrational state of molecules-reactants and/or reaction products, and also on specifics of these molecules and reactions in which they participate.

For dissociation of diatomic molecules, Marrone–Treanor model (see Ref. 32 and also Refs. 33–35) leads to

$$k_{dm}(T) = k_d^0(T)\left\{\frac{Q_v(T)}{Q_v(-U)}\exp\left[\frac{E_m}{k}\left(\frac{1}{T}+\frac{1}{U}\right)\right]\right\}$$

The values of parameter U are presented in the description of model I-C.21. The expressions for thermally equilibrium rate constant k_d^0 for dissociation of molecules O_2, N_2, NO, CO, CN, and C_2 at temperatures from 300 up to 40,000 K are presented in Ref. 36 (see also descriptions of models I-C.11, I-C.12).

According to the ladder model of dissociation, only single-quantum transitions between vibrational levels take place in collisions, and the molecules dissociate only in transitions from the uppermost vibrational level $m = m_{\max}$ to continuum spectrum (free state). The probability of dissociation per appearance of a molecule in the uppermost level $m = m_{\max}$ is equal to one, so that

$$k_{dm}(T) = 0 \qquad \text{for } m < m_{\max}$$

$$k_{dm}(T) = \left(\frac{8kT}{\pi\mu}\right)^{1/2}\sigma_0(T) \quad \text{for } m = m_{\max}$$

$$\mu = \frac{m_i m_j}{m_i + m_j}.$$

The values of average cross sections for elastic collisions $\sigma_0(T)$ of the particles i–j are reviewed in the descriptions of models I-T.I–I-T.3 (for model of hard spheres, $\sigma_0(T) = \pi R_0^2$).

More complex versions of the ladder model (Refs. 31, 37 and 38) find applications in the problems of polyatomic molecules decomposition. In this case, the state-specific rate constants for decomposition of polyatomic molecules in vibrational states $E_m < D^0$ (D^0 is the energy of breaking bond of polyatomic molecule) are determined by the same expressions as in reactions of dissociation of diatomic molecules (in particular, with the Marrone–Treanor model). Spontaneous unimolecular decomposition of molecules whose energy state is higher than the threshold D^0 is modeled by state-specific rate constants in accordance with Ref. 39 see the description of model I-C.13. The results of the solution of this problem and calculations of the state-specific rate constants of decomposition of CO_2 molecules are presented in Ref. 40.

Assuming 100%-efficiency of translational energy of reactants in overcoming the activation barrier E_a (see the description of model I-C.19 and Ref. 41), the state-specific rate constants of exchange reactions are:

$$k_{fm}(T) = A(T)\cdot\exp\left[-\frac{E_a - \alpha E_m}{kT}\cdot\bar{\theta}(E_a - \alpha E_m)\right]$$

where α is the efficiency of vibrational energy E_m utilization in activation of the reaction, and $\bar{\theta}$ is the Heaviside function:

$$\bar{\theta}(x) = 1 \quad \text{for } x \geq 0$$
$$\bar{\theta}(x) = 0 \quad \text{for } x < 0$$

The values of the coefficient α are indicated in the description of model I-C.19. The pre-exponential factor $A(T)$ is close to the value of rate constant for gas-kinetic collisions or to the collision frequency per unit number density of particles $Z = \pi R_0^2(8kT/\pi\mu)^{1/2}$.

Calculations from Ref. 42 on the basis of the model of chemically active collisions in Ref. 43 show that for some exchange reactions:

$$k_{fm}(T) = C(m+1) \cdot T^{\beta} \exp\left[-\frac{E_a - E_m}{kT} \cdot \bar{\theta}(E_a - E_m)\right]$$

where $C = 4.17 \times 10^{12}$, $\beta = 0$ for reaction $N_2(m) + O \rightarrow NO + N$, and $C = 1.15 \times 10^9$, $\beta = 1.0$ for reaction $O_2(m) + N \rightarrow NO + O$ (k_{fm} is in units of $cm^3/(mol \cdot s)$).

Experimental results for reaction $H_2(m) + OH \rightarrow H_2O + H$ are approximated by the formula (Ref. 43)

$$k_{fm=0} = 5.6 \times 10^{12} \exp\left(\frac{-2165}{T}\right) cm^3/(mol \cdot s)$$

The Macheret formulas (Ref. 44) for state-specific rate constants of endothermic reactions of simple exchange (see the description of model I-C.20) are presented on page 176 of Ref. 6. The results for vibrational energy disposal (distribution) in products of many exothermic reactions are listed in the review (see Ref. 45).

Comprehensive data on state-specific kinetics in chemically reacting gases can be obtained by numerical solutions of dynamic problems of molecular collisions and the use of the Monte-Carlo method (see Refs. 46–53). In such a manner, state-specific rate constants for a number of exchange reactions were computed. The results of calculations can be approximated by various expressions. The examples follow.

When the results of calculation (in Ref. 47) are approximated by the expression

$$k_{fm}(T) = A \cdot \exp\left[-\frac{E_a - \gamma E_m}{\beta kT} \cdot \bar{\theta}(E_a - \gamma E_m)\right]$$

the values of approximation parameters for some reactions are the following:

Reaction	E_a, eV	β	γ
$H_2(m) + O \rightarrow OH + H$	0.41	0.72	0.21
$N_2(m) + O \rightarrow NO + N$	3.20	0.90	0.52
$O_2(m) + N \rightarrow NO + O$	0.33	0.46	0.12

Here, β, γ are the parameters describing participation of translational and vibrational energies in reactions, and $A \approx \pi R_0^2 (8kT/\pi\mu)^{1/2}$.

The results of calculation in Ref. 54 for reaction $N_2(m) + O \rightarrow NO + N$ are approximated by the expression $\log k_{fm} = b_0 + b_1 E_m + b_2 E_m^2 + b_3 E_m^3$ (k_{fm} is in $cm^3/(mol \cdot s)$, and E_m is in eV) with parameters that depend on temperature:

T	b_0	b_1	b_2	b_3
7000	1.099×10	7.809×10^{-1}	-6.605×10^{-2}	1.672×10^{-3}
10,000	1.193×10	5.496×10^{-1}	-4.512×10^{-2}	1.257×10^{-3}
14,000	1.258×10	3.919×10^{-1}	-2.978×10^{-2}	7.670×10^{-4}

More complete state-to-state kinetics, with transitions between specified vibrational states of reactants and products $m \rightarrow m'$ are considered in Ref. 54 for the reaction $N_2(m) + O \rightarrow NO(m') + N$ (see Fig. 9 on page 2832 of Ref. 54), and in Ref. 55 for the reaction of unimolecular decomposition of N_2O.

8. *Features of the Model*

Relations of detailed balance for state-specific rate constants are:

a) For reactions of dissociation and recombination of diatomic molecules

$$\frac{k_{dm}^{\mathrm{AB-M}_s}}{k_{rm}^{\mathrm{A-B-M}_s}} = \frac{Q_v^{\mathrm{AB}}(T)}{\exp(-E_m^{\mathrm{AB}}/kT)} \times \begin{cases} \dfrac{K_p(T)}{kT} & (1) \\ \left(\dfrac{N^{\mathrm{A}} N^{\mathrm{B}}}{N^{\mathrm{AB}}}\right)_{eq} & (2) \end{cases}$$

b) For reactions of decomposition and formation of polyatomic molecules (disregarding degeneracy of mode ξ)

$$\frac{k_{d\xi m}^{\mathrm{XYZ-M}_s}}{k_{r\xi m}^{\mathrm{XY-Z-M}_s}} = \frac{Q_{v\xi}^{\mathrm{XYZ}}(T)}{\exp(-E_{\xi m}/kT)} \times \begin{cases} \dfrac{K_p(T)}{kT} & (1) \\ \left(\dfrac{N^{\mathrm{XY}} N^{\mathrm{Z}}}{N^{\mathrm{XYZ}}}\right)_{eq} & (2) \end{cases}$$

c) For reactions of simple exchange ($m \rightleftarrows m'$)

$$\frac{k_{fmm'}^{\mathrm{AB-C}}}{k_{bmm'}^{\mathrm{AC-B}}} = \frac{Q_v^{\mathrm{AB}}}{\exp(-E_m^{\mathrm{AB}}/kT)} \times \begin{cases} K_p(T) & (1) \\ \left(\dfrac{N^{\mathrm{XY}} N^{\mathrm{Z}}}{N^{\mathrm{XYZ}}}\right)_{eq} & (2) \end{cases}$$

d) For reactions of double exchange ($mn \rightleftarrows m'n'$)

$$\frac{k_{fmn,m'n'}^{\mathrm{AB-CD}}}{k_{bm'n',mn}^{\mathrm{AC-BD}}} = \frac{Q_v^{\mathrm{AB}} Q_v^{\mathrm{CD}}}{Q_v^{\mathrm{AC}} Q_v^{\mathrm{BD}}} \frac{\exp\left[-(E_{m'}^{\mathrm{AC}} + E_{n'}^{\mathrm{BD}})/kT\right]}{\exp\left[-(E_m^{\mathrm{AB}} + E_n^{\mathrm{CD}})/kT\right]} \times \begin{cases} K_p(T) & (1) \\ \left(\dfrac{N^{\mathrm{AC}} N^{\mathrm{BD}}}{N^{\mathrm{AB}} N^{\mathrm{CD}}}\right)_{eq} & (2) \end{cases}$$

(1) for reactions in simple gases, with no components other than those participating in the reactions under analysis;
(2) for reactions in complex mixtures with other components.

The value of an equilibrium constant of chemical reactions $K_p(T)$ in terms of partial pressures of reacting components for reactions in simple gases is discussed in the section Calculation of Thermodynamic Characteristics in Chapter 8 of this book. The values with subscripts "*eq*" correspond to equilibrium number densities of components in complex mixtures.

9. *General and Particular Solutions*

The system of equations of state-specific kinetics in chemically reacting gas is solved by numerical methods (Refs. 46 and 47).

For diatomic molecules modeled as truncated harmonic oscillators with fast VV exchange, assuming that only single-quantum vibrational transitions occur and that dissociation occurs only from the vibrational level $m_{\max}$ closest to the dissociation energy D_0, the approximate analytical solution for the initial stage of dissociation (in the absence of a noticeable recombination) is (Ref. 56):

$$N_m = N_m^0 \left[1 - \frac{W_d \exp(-m\theta/T_v)}{k_{10}^{01}(1+\alpha)N^{\mathrm{AB}}} \sum_{n=1}^{m} \frac{\exp(n\theta/T_v) - 1}{n} \right] \quad (m \le m_{\max})$$

where $W_d = (\mathrm{d}N^{\mathrm{AB}}/\mathrm{d}t)_d$ is the dissociation rate, $\alpha = \sum_n^{m_{\max}} nN_n^{\mathrm{AB}}/N^{\mathrm{AB}}$, $\exp(-\theta/T_v) = \alpha/(1+\alpha)$, $N_m^0 = N^{\mathrm{AB}}[1 - \exp(-\theta/T_v)] \cdot \exp(-m\theta/T_v)$, R_0 is gas kinetic radius of elastic collisions, T_v is the vibrational temperature, and θ is the characteristic vibrational temperature. In this case, the derivations used the conservation law for total (translational plus rotational plus vibrational) energy in the following form:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{5}{2}\frac{T}{\theta} + \alpha \sum_{k=0}^{m_d} N_m\right) = -m_{\max} W_d$$

The solution indicates that a noticeable deviation from Boltzmann distribution occurs near the dissociation level $m = m_{\max}$.

10. *Example*

The calculation results from Ref. 42 for distributions of population density of vibrational levels (expressed in molar fractions) for O_2 molecule behind a shock wave front in air are shown in Fig. 4.5; the initial temperature of air immediately behind the normal shock front in this example is equal to 22,000 K, the pressure before the front is equal to 0.02 Torr.

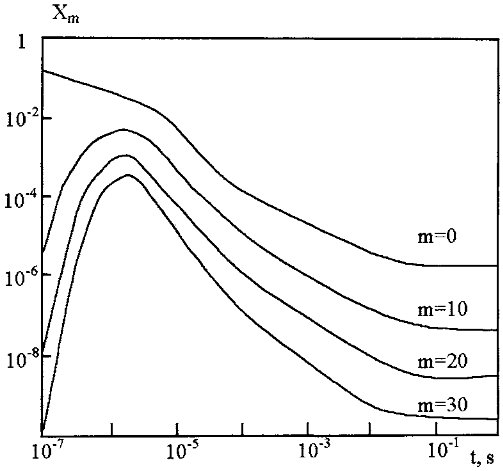

Fig. 4.5

The values of state-specific rate constants for dissociation, according to Ref. 42, are taken as $k_{dm} = C(m+1)T^{\beta}\exp[-(D_0 - E_m)/kT]$ $\text{cm}^3/(\text{mol}\cdot\text{s})$, where $C = 2 \times 10^{13}$ and $\beta = 0$ for dissociation of O_2, and $C = 1.14 \times 10^{15}$ and $\beta = -0.6$ for dissociation of N_2; for exchange reactions, the values of k_{fm} are previously discussed in the subsection Description of Coefficients and Parameters, with the reference to Ref. 42. When solving the equations of vibrational kinetics in Ref. 42, the rate constants for single-quantum VT and VV transitions were those calculated in Ref. 5. As seen in Fig. 4.5, the populations of excited vibrational levels grow initially (up until about 2×10^{-6} s) because of vibrational energy exchange, and then they decrease because of chemical reactions. The steady-state equilibrium distribution of molecules O_2 over vibrational levels corresponds to the temperature of 5810 K.

Examples of solutions of state-specific kinetic problems in chemically reacting gases are given in Refs. 55 and 57–59 for flows in shock waves, in Refs. 60 and 61 for nozzle flows, and in Refs. 62 and 63 for boundary layers.

11. Comments

State-specific kinetics of processes that take place in collisions of molecules with electrons is considered in Ref. 5.

Relevant material can be found in Refs. 5, 6, and 46.

G. Vibrational Energy Relaxation in Diatomic Molecules: Mode Kinetics Model (V.7)

1. Purpose of the Model

The model aims at calculation of the vibrational energy of diatomic molecules as a function of time in gas mixtures.

2. *Assumptions*

a) See Assumptions b–d in the description of model V.1 and Assumption 2 in the description of model V.2.

b) The course of vibrational relaxation processes is characterized by a single variable: the mean vibrational energy ε per molecule. The value of ε and the average number of vibrational quanta α per molecule are calculated in the harmonic oscillator approximation. Accordingly, $\varepsilon = \theta \cdot \alpha$, where θ is the characteristic vibrational temperature and ε is measured in Kelvin. The anharmonicity of molecular vibrations is taken into account by introducing corrections to the vibrational relaxation time τ.

c) When the model parameters are represented as functions of vibrational temperature, it is assumed that the rates of intramode VV exchange are substantially higher than the rates of VT processes and energy exchange between modes ($\tau_{VV} \ll \tau_{VT}, \tau_{VV'}$). This ensures Boltzmann distributions characterized by well-defined vibrational temperatures, at least for the lowest vibrational levels, whose population densities determine the total vibrational energy. Accordingly, it can be assumed that the dependence of vibrational energy on vibrational temperature (T_v) can be represented in the harmonic oscillator approximation:

$$\varepsilon(T_v) = \frac{\theta}{\exp(\theta/T_v) - 1}$$

where ε is measured in Kelvin.

3. *Restrictions*

See Restrictions a and c in the description of model V.1.

4. *Relaxation Equations*

a) For diatomic molecules in a gaseous mixture of a low concentration impurity with structureless particles, and for single-component gas of diatomic molecules,

$$\frac{d\alpha}{dt} = -\frac{\alpha - \alpha_0}{\tau_{VT}}, \qquad \alpha_0 = \left[\exp\left(\frac{\theta}{T}\right) - 1\right]^{-1}$$

b) For a binary mixture of diatomic molecules,

$$\frac{d\alpha^{AB}}{dt} = -\frac{\alpha^{AB} - \alpha_0^{AB}}{\tau_{VT}^{AB}} + \frac{\alpha^{CD}(1+\alpha^{AB})\exp(\theta^{CD}/T) - \alpha^{AB}(1+\alpha^{CD})\exp(\theta^{AB}/T)}{\tau_{VV'}}$$

$$\frac{d\alpha^{CD}}{dt} = -\frac{\alpha^{CD} - \alpha_0^{CD}}{\tau_{VT}^{CD}} + \frac{\alpha^{AB}(1+\alpha^{CD})\exp(\theta^{AB}/T) - \alpha^{CD}(1+\alpha^{AB})\exp(\theta^{CD}/T)}{\tau_{VV'}}$$

$$\alpha_0^{AB} = \left[\exp\left(\frac{\theta^{AB}}{T}\right) - 1\right]^{-1}; \qquad \alpha_0^{CD} = \left[\exp\left(\frac{\theta^{CD}}{T}\right) - 1\right]^{-1}$$

5. *Nomenclature*

a) Quantities calculated with the model:

α, α^{AB}	average number of vibrational quanta per AB molecule
α^{CD}	average number of vibrational quanta per CD molecule

b) Kinetic coefficients:

τ_{VT}, τ_{VT}^{AB}	VT relaxation time for AB molecules
τ_{VT}^{CD}	VT relaxation time for CD molecules
$\tau_{VV'}$	characteristic time of VV′ energy exchange between AB and CD molecules

c) Other quantities:

$k_{10}^{\mathrm{AB-M}_j}$	rate constant for the 1 → 0 vibrational transition in AB molecules associated with VT energy exchange induced by its collision with M_j particles
$k_{10}^{\mathrm{CD-M}_j}$	rate constant for the 1 → 0 vibrational transition in CD molecules associated with VT energy exchange induced by its collision with M_j particles
$k_{10}^{\mathrm{AB-AB}}$	rate constant for the 1 → 0 vibrational transition in an AB molecule associated with VT energy exchange induced by an AB–AB collision
$k_{10}^{\mathrm{AB-CD}}$	rate constant for the 1 → 0 vibrational transition in an AB molecule associated with VT energy exchange induced by an AB–CD collision
$k_{10}^{\mathrm{CD-CD}}$	rate constant for the 1 → 0 vibrational transition in a CD molecule associated with VT energy exchange induced by a CD–CD collision
$k_{10}^{\mathrm{CD-AB}}$	rate constant for the 1 → 0 vibrational transition in a CD molecule associated with VT energy exchange induced by a CD–AB collision
$k_{10}^{01^{\mathrm{AB-AB}}}$	rate constant for the VV′ energy exchange in an AB molecule induced by an AB–AB collision involving the 1 → 0 vibrational transition in one molecule and the 0 → 1 vibrational transition in the other
$k_{10}^{01^{\mathrm{CD-CD}}}$	rate constant for the VV′ energy exchange in a CD molecule induced by a CD–CD collision involving the 1 → 0 vibrational transition in one molecule and the 0 → 1 vibrational transition in the other
$k_{10}^{01^{\mathrm{AB-CD}}}$	rate constant for the VV′ energy exchange in an AB molecule induced by an AB–CD collision involving the 1 → 0 vibrational transition in the AB molecule and the 0 → 1 vibrational transition in the CD molecule
$k_{10}^{01^{\mathrm{CD-AB}}}$	rate constant for the VV′ energy exchange in a CD molecule induced by a CD–AB collision involving the 1 → 0 vibrational transition in the CD molecule and the 0 → 1 vibrational transition in the AB molecule

θ^{AB}	characteristic vibrational temperature of AB molecules
θ^{CD}	characteristic vibrational temperature of CD molecules
$\alpha_0^{\mathrm{AB}}(T)$	equilibrium value of α^{AB} corresponding to translational temperature T
$\alpha_0^{\mathrm{CD}}(T)$	equilibrium value of α^{CD} corresponding to translational temperature T
τ_{VV}	characteristic time of intramode energy exchange
N_n, N_n^{AB}	population density in the nth vibrational level of AB molecules
N_n^{CD}	population density in the nth vibrational level of CD molecules
E_1	vibrational energy of an AB molecule excited to the level with $v = 1$
ω	vibrational angular frequency of AB molecule
m_{AB}	mass of an AB molecule
m_{M_j}	mass of an M_j particle
α_p	parameter of the Born–Mayer potential (see model I-T.3)
D_0	dissociation energy of a molecule
T	translational temperature (gas temperature)
T_v,T_v^{AB}	vibrational temperature of AB molecules
T_v^{CD}	vibrational temperature of CD molecules
T_1	vibrational temperature of the first excited level
N^{AB}	number density of AB molecules
N^{CD}	number density of CD molecules
N^{M_j}	number density of M_j particles

6. *Description of Coefficients and Parameters*

Vibrational relaxation times for molecules treated as harmonic oscillators are related to the VT and VV energy exchange rate constants by the following relations:

$$\tau_{VT}^{\mathrm{AB}} = \left\{\left[k_{10}^{\mathrm{AB\text{-}AB}} N^{\mathrm{AB}} + k_{10}^{\mathrm{AB\text{-}CD}} N^{\mathrm{CD}} + \sum_j k_{10}^{\mathrm{AB\text{-}M}_j} N^{\mathrm{M}_j}\right]\left[1 - \exp\left(-\frac{\theta^{\mathrm{AB}}}{T}\right)\right]\right\}^{-1}$$

$$\tau_{VT}^{\mathrm{CD}} = \left\{\left[k_{10}^{\mathrm{CD\text{-}CD}} N^{\mathrm{CD}} + k_{10}^{\mathrm{CD\text{-}AB}} N^{\mathrm{AB}} + \sum_j k_{10}^{\mathrm{CD\text{-}M}_j} N^{\mathrm{M}_j}\right]\left[1 - \exp\left(-\frac{\theta^{\mathrm{CD}}}{T}\right)\right]\right\}^{-1}$$

$$\tau_{VV'} = [k_{10}^{01^{\mathrm{AB\text{-}CD}}} N^{\mathrm{CD}}]^{-1} = [k_{10}^{01^{\mathrm{CD\text{-}AB}}} N^{\mathrm{AB}}]^{-1}$$

The VT and VV′ energy exchange rate constants for the indicated transitions between vibrational levels can be evaluated with various models presented in Chapter 4 of the first volume in this series.

To allow for anharmonicity effects on VT energy exchange, a correction factor, K_a, is introduced into the expression for the vibrational relaxation time τ_{VT}: $\tau_{VT}^a = K_a \tau_{VT}$ (τ_{VT}^a is the vibrational relaxation time for an anharmonic oscillator). Formulas and estimates for K_a can be found in Refs. 3, 9, and 64. In the approximation developed in Ref. 64,

$$K_a = \left[\frac{1 - \gamma(T) \cdot \exp(-\theta/T_v)}{1 - \exp(-\theta/T_v)}\right]^2$$

$$\gamma = \exp\left(\frac{\chi\theta}{2D_0}\right), \quad \chi = \left(\frac{\theta_{LT}}{T}\right)^{1/3}, \quad \theta_{LT} = \frac{\pi^2 \mu \omega^2}{2\alpha_p^2 k}, \quad \mu = \frac{m_{\mathrm{AB}} \cdot m_{\mathrm{M}_j}}{m_{\mathrm{AB}} + m_{\mathrm{M}_j}}$$

for small deviations from equilibrium; for gaseous N_2 and O_2, this leads to $\gamma = \exp(1.277 \cdot T^{-1/3})$ and $\gamma = \exp(1.478 \cdot T^{-1/3})$, respectively. Here, the Morse model is used as the simplest anharmonic oscillator model. It is assumed that the Boltzmann distribution over energy levels characterized by a vibrational temperature, T_v, is preserved in the course of vibrational relaxation via single-quantum transitions. The interaction between colliding particles is described here by the Born–Mayer potential characterized by the inverse radius α_p of interaction (see model I-T.3). In calculating the transition probabilities $P_{n+1/n}$ for transition $n + 1 \to n$, only the fact that Morse oscillator levels are not energy-equidistant is taken into account, which leads to $P_{n+1/n} = (n+1)P_{10}\gamma^n$ according to Ref. 65. This approximation of K_a is applicable if $T_v \leq \theta \cdot \ln \gamma$. A refined version of this approximation allowing for deviation of population densities at high vibrational levels from the Boltzmann distribution is:

$$K_a = \left[\frac{1 - \exp(-\theta/T_1 + \delta_{VT})}{1 - \exp(-\theta/T_1)}\right]^2$$

where $T_1 = (E_1/k)\ln(N_0/N_1)$ is the temperature of the first vibrational level and δ_{VT} is the anharmonicity factor specified in model I-V.8; this formula is valid if $T_1 \leq \theta/\delta_{VT}$.

When $T \geq \theta$, the following approximation proposed in Ref. 9 can be applied:

$$K_a = \left[\frac{1 - \exp(-\theta/T_1)}{1 - \exp(-\theta/T_1)/[2\exp(\delta_{VT}) - 1]}\right]^2$$

This formula allows for anharmonicity effects on both the vibrational energy distribution function and the probabilities of vibrational transitions.

In any case, for example, the value of K_a calculated for O_2–Ar at $T = 8000$ K decreases from 0.98 at $T_v = 300$ K to 0.264 at $T_v = 8000$ K.

Additional information about the effects of anharmonicity on vibrational relaxation rates for various types of deviation from equilibrium can be found in Refs. 3, 5 and 6.

7. *Features of the Model*

In a binary mixture of diatomic molecules AB and CD treated as harmonic oscillators for which $\tau_{VV'}^{\mathrm{AB}}, \tau_{VV'}^{\mathrm{CD}} \ll \tau_{VT}^{\mathrm{AB}}, \tau_{VT}^{\mathrm{CD}}$, the evolution of vibrational energy involves two stages. At the first stage ($t \geq \tau_{VV'}$), the following correlation between α^{AB} and α^{CD} develops:

$$\alpha^{\mathrm{AB}}(1 + \alpha^{\mathrm{CD}})\exp(\theta^{\mathrm{AB}}/T) - \alpha^{\mathrm{CD}}(1 + \alpha^{\mathrm{AB}})\exp(\theta^{\mathrm{CD}}/T) = 0$$

which is equivalent to

$$\frac{\theta^{\mathrm{AB}} - \theta^{\mathrm{CD}}}{T} = \frac{\theta^{\mathrm{AB}}}{T_v^{\mathrm{AB}}} - \frac{\theta^{\mathrm{CD}}}{T_v^{\mathrm{CD}}}$$

At the second stage ($t \sim \tau_{VT}^{\mathrm{AB}}, \tau_{VT}^{\mathrm{CD}}$), VT energy is transferred as predicted by the relation above combined with one of the equations below, namely, the one having the lower value of τ_{VT}:

$$\frac{\mathrm{d}\alpha^{\mathrm{AB}}}{\mathrm{d}t} = -\frac{\alpha^{\mathrm{AB}} - \alpha_0^{\mathrm{AB}}}{\tau_{VT}^{\mathrm{AB}}}, \qquad \frac{\mathrm{d}\alpha^{\mathrm{CD}}}{\mathrm{d}t} = -\frac{\alpha^{\mathrm{CD}} - \alpha_0^{\mathrm{CD}}}{\tau_{VT}^{\mathrm{CD}}}$$

When $\tau_{VT}^{\mathrm{AB}} \ll \tau_{VT}^{\mathrm{CD}}$, the resulting relaxation equation is

$$\frac{\mathrm{d}\alpha^{\mathrm{AB}}}{\mathrm{d}t} = -\frac{\alpha^{\mathrm{AB}} - \alpha_0^{\mathrm{AB}}}{\tau_{VT}^{*}}, \quad \text{where } \tau_{VT}^{*} = \tau_{VT}^{\mathrm{AB}}\left(1 + \frac{N^{\mathrm{CD}}}{N^{\mathrm{AB}}} \cdot \frac{\mathrm{d}\alpha^{\mathrm{AB}}}{\mathrm{d}\alpha^{\mathrm{CD}}}\right).$$

This shows that vibrational relaxation in an AB–CD mixture is characterized by an effective time τ_{VT}^{*} that is greater than τ_{VT}^{AB} because the vibrational energy of AB molecules can be increased via VV′ exchange induced by collisions with CD molecules.

8. *General and Particular Solutions*

When diatomic molecules treated as harmonic oscillators constitute either a low-concentration impurity in a diluent or a single-component gas, the variation of vibrational energy at $T = \text{const}$ can be described by the expression

$$\alpha(t) = \alpha(0) + \alpha_0\left[1 - \exp\left(\frac{-t}{\tau_{\mathrm{VT}}}\right)\right]$$

9. *Example*

As an example of vibrational relaxation in a gaseous mixture, consider vibrational relaxation in air behind a shock front. Figure 4.6 shows the profiles of

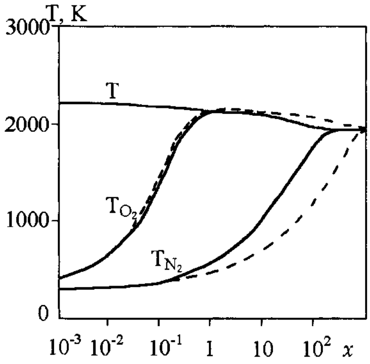

Fig. 4.6

translational temperature T and vibrational temperatures of oxygen and nitrogen, T_{O_2} and T_{N_2}, calculated in the harmonic oscillator approximation with and without allowing for VV′ energy exchange (solid and dotted curves, respectively) for the shock velocity $V = 2$ km/s and initial pressure $p_1 = 1$ Torr, as functions of the distance x (cm) from the shock front.

Figure 4.6 reveals a difference between the effects of VV′ energy exchange on the relaxation of nitrogen and oxygen. The relaxation time of N_2 is substantially reduced by VV′ energy exchange, whereas the relaxation time of O_2 is only slightly increased. When O_2 molecules are excited, N_2 molecules remain largely unexcited, and the vibrational energy transferred from N_2 to O_2 is negligible. The vibrational energy transfer from O_2 to N_2 only slightly increases the relaxation time for O_2, because the rate of O_2 excitation via TV energy exchange is higher than the rate of deactivation of O_2 via VV′ exchange from O_2 to N_2. On the other hand, N_2 molecules are excited in the presence of already excited O_2 molecules. Under these conditions, the rate of vibrational energy transfer from O_2 to N_2 can be substantially higher than the rate of N_2 excitation via direct TV exchange. Accordingly, the effective N_2 relaxation time is much shorter than in the absence of VV′ energy exchange. Calculations show that the effects because of V–V′ energy transfer are weaker for higher shockwave velocities. This is explained by the more rapid increase in the rate of direct VT excitation with temperature, as compared to the increase in the rate of VV′ energy exchange. At high temperatures, the difference between these rates is insignificant, and the effects because of VV′ energy exchange can be ignored.

10. Comment

Vibrational relaxation in a mixture of anharmonic oscillators with α^{AB}, $\alpha^{CD} \geq 1$ can be described in the mode kinetics approximation by using the formulas obtained for harmonic oscillators and introducing a correction factor K_a into the value of τ_{VT}. When $\alpha^{AB}, \alpha^{CD} \gg 1$ vibrational relaxation of anharmonic oscillators cannot be modeled in the framework of mode kinetics, and the vibrational energy must be evaluated by combining the equations of state-specific kinetics with the relation

$$\varepsilon = \frac{1}{N} \sum_n N_n \cdot E_n$$

where E_n is the energy of the nth vibrational level.

Quasi-steady-state approximation for the kinetics of anharmonic oscillators was discussed in Ref. 66; diffusion approximation was discussed in Ref. 67.

Relevant material can be found in Refs. 3–6.

H. Vibrational Energy Relaxation in Polyatomic Molecules: Mode Kinetics Model (V.8)

1. Purpose of the Model

The model aims at calculation of vibrational energy of polyatomic molecules as a function of time in gaseous mixtures.

2. *Assumptions*

a) See Assumptions b and c in the description of model V.1.

b) Each vibrational mode of polyatomic molecules is modeled in the harmonic oscillator approximation and characterized by Boltzmann distribution over vibrational levels of energy with temperatures T_i, T_j for ith and jth modes.

3. *Restrictions*

a) See Restriction c in the description of model V.1 and Restrictions a and b in the description of model V.5.

b) The times of processes under consideration are vastly longer than the characteristic time of intramode VV energy exchange $\tau_{VV} = (k_{10}^{01}N)^{-1}$. This imposes a constraint on number density N, because for a fast formation of Boltzmann distribution within each vibrational mode with corresponding vibrational temperatures, the time of intramode energy exchange must be far shorter than the time of intermode energy exchange:

$$k_{10}^{01}N^{\mathrm{XY}} \gg \max_{v_i,v_j,q}\left[k^{\mathrm{XY-M}_q}\begin{Bmatrix} v_i \to v_i - 1 \\ v_j \to v_j + 1 \end{Bmatrix}N^{\mathrm{M}_q}\right]$$

4. *Relaxation Equations*

a) For polyatomic molecules XY as a low-concentration impurity in a gas of structureless particles M_q:

$$\frac{\mathrm{d}\alpha_\xi}{\mathrm{d}t} = \left(\sum_q k^{\mathrm{XY-M}q}\begin{Bmatrix} l_i \to 0 \\ 0 \to l_j \end{Bmatrix}N^{\mathrm{M}q}\right) l_\xi \prod_{i=1}^{k}\binom{l_i + r_i - 1}{l_i}[r_i(r_i + \alpha_i^0)]^{-l_i}$$

$$\times \prod_{j=k+1}^{L}(r_j\alpha_j^0)^{-l_j}\left\{\prod_{i=1}^{k}[\alpha_i^0(r_i + \alpha_i)]^{l_i}\prod_{j=k+1}^{L}[\alpha_j(r_j + \alpha_j^0)]^{l_j}\right.$$

$$\left. - \prod_{i=1}^{k}[\alpha_i(r_i + \alpha_i^0)]^{l_i}\prod_{j=k+1}^{L}[\alpha_j^0(r_j + \alpha_j)]^{l_j}\right\}$$

$$\alpha_s^0 = r_s \exp\left(-\frac{\theta_s}{T}\right)\left[1 - \exp\left(-\frac{\theta_s}{T}\right)\right]^{-1} \qquad s = i, j$$

b) For a mixture of a single polyatomic species XY with structureless particles M_q:

$$\frac{\mathrm{d}\alpha_\xi}{\mathrm{d}t} = \left(\frac{1}{2}k^{\mathrm{XY-XY}}\begin{Bmatrix} l_i \to 0 \\ 0 \to l_j \end{Bmatrix}N^{\mathrm{XY}} l_\xi \prod_{i=1}^{k}\binom{l_i + 2r_i - 1}{l_i}[r_i(r_i + \alpha_i^0)]^{-l_i}\right.$$

$$
\begin{aligned}
&\times \prod_{j=k+1}^{L} (r_j\alpha_j^0)^{-l_j} \left\{ \prod_{i=1}^{k} [\alpha_i^0(r_i+\alpha_i)]^{l_i} \prod_{j=k+1}^{L} [\alpha_j(r_j+\alpha_j^0)]^{l_j} \right. \\
&\left. - \prod_{i=1}^{k} [\alpha_i(r_i+\alpha_i^0)]^{l_i} \prod_{j=k+1}^{L} [\alpha_j^0(r_j+\alpha_j)]^{l_j} \right\} \\
&+ \sum_q k^{\mathrm{XY\text{-}M}_q} \begin{Bmatrix} l_i \to 0 \\ 0 \to l_j \end{Bmatrix} N^{\mathrm{M}_q} \Bigg) \\
&\times l_\xi \prod_{i=1}^{k} \binom{l_i - r_i - 1}{l_i} [r_i(r_i+\alpha_i^0)]^{-l_i} \prod_{j=k+1}^{L} (r_j\alpha_j^0)^{-l_j} \\
&\times \left\{ \prod_{i=1}^{k} [\alpha_i^0(r_i+\alpha_i)]^{l_i} \prod_{j=k+1}^{L} [\alpha_j(r_j+\alpha_j^0)]^{l_j} \right. \\
&\left. - \prod_{i=1}^{k} [\alpha_i(r_i+\alpha_i^0)]^{l_i} \prod_{j=k+1}^{L} [\alpha_j^0(r_j+\alpha_j)]^{l_j} \right\}
\end{aligned}
$$

$$
\alpha_s^0 = r_s \exp\left(-\frac{\theta_s}{T}\right)\left[1 - \exp\left(-\frac{\theta_s}{T}\right)\right]^{-1} \qquad s = i, j
$$

c) For a mixture of two polyatomic species, XY and ZW, with structureless particles M_q:

$$
\begin{aligned}
\frac{\mathrm{d}\alpha_\xi}{\mathrm{d}t} = &\left(\frac{1}{2} k^{\mathrm{XY\text{-}XY}} \begin{Bmatrix} l_i \to 0 \\ 0 \to l_j \end{Bmatrix} N^{\mathrm{XY}} l_\xi \prod_{i=1}^{k} \binom{l_i + 2r_i - 1}{l_i} [r_i(r_i+\alpha_i^0)]^{-l_i} \right. \\
&\times \prod_{j=k+1}^{L} (r_j\alpha_j^0)^{-l_j} \left\{ \prod_{i=1}^{k} [\alpha_i^0(r_i+\alpha_i)]^{l_i} \prod_{j=k+1}^{L} [\alpha_j(r_j+\alpha_j^0)]^{l_j} \right. \\
&\left. - \prod_{i=1}^{k} [\alpha_i(r_i+\alpha_i^0)]^{l_i} \prod_{j=k+1}^{L} [\alpha_j^0(r_j+\alpha_j)]^{l_j} \right\} + k^{\mathrm{XY\text{-}ZW}} \begin{Bmatrix} l'_i \to 0 \\ 0 \to l'_j \end{Bmatrix} \\
&\times N^{\mathrm{ZW}} l'_\xi \prod_{i=1}^{k'} \binom{l'_i + r_i - 1}{l'_i} [r_i(r_i+\alpha_i^0)]^{-l'_i} \prod_{j=k'+1}^{L'} (r_j\alpha_j^0)^{-l'_j} \\
&\times \left\{ \prod_{i=1}^{k'} [\alpha_i^0(r_i+\alpha_i)]^{l'_i} \prod_{j=k'+1}^{L'} [\alpha_j(r_j+\alpha_j^0)]^{l'_j} - \prod_{i=1}^{k'} [\alpha_i(r_i+\alpha_i^0)]^{l'_i} \right.
\end{aligned}
$$

$$\left.\times \prod_{j=k'+1}^{L'} [\alpha_j^0(r_j+\alpha_j)]^{l'_j}\right\} + \sum_q k^{\mathrm{XY-M}_q} \left\{\begin{matrix} l_i \to 0 \\ 0 \to l_j \end{matrix}\right\} N^{\mathrm{M}_q} \Bigg)$$

$$\times\, l_\xi \prod_{i=1}^{k} \binom{l_i - r_i - 1}{l_i} [r_i(r_i+\alpha_i^0)]^{-l_i} \prod_{j=k+1}^{L} (r_j \alpha_j^0)^{-l_j}$$

$$\times \left\{ \prod_{i=1}^{k} [\alpha_i^0(r_i+\alpha_i)]^{l_i} \prod_{j=k+1}^{L} [\alpha_j(r_j+\alpha_j^0)]^{l_j} \right.$$

$$\left. - \prod_{i=1}^{k} [\alpha_i(r_i+\alpha_i^0)]^{l_i} \prod_{j=k'+1}^{L} [\alpha_j^0(r_j+\alpha_j)]^{l_j} \right\}$$

$$\alpha_s^0 = r_s \exp\left(-\frac{\theta_s}{T}\right)\left[1 - \exp\left(-\frac{\theta_s}{T}\right)\right]^{-1} \qquad s = i, j$$

Here

$$\binom{p}{n} = \frac{p(p-1)\cdots(p-n+1)}{n!}.$$

5. *Nomenclature*

a) Quantities calculated with the model:

α_ξ	average number of vibrational quanta in the mode ξ of XY molecules

b) Kinetic coefficients:

$k^{\mathrm{XY-M}_q}\left\{\begin{matrix} v_i \to v_i - l_i \\ v_j \to v_j + l_j \end{matrix}\right\}$	rate constant for VV energy transfer induced by XY–M_q collisions (see the nomenclature for XY–XY and XY–ZW collisions in the description of model V.5)

c) Subscripts:

ξ	vibrational mode of XY molecule involved in XY–M_q and XY–XY collisions
ξ'	vibrational mode of XY molecule involved in XY–ZW collisions
i, j	modes involved in vibrational energy transfer
q, q'	structureless particles in XY–M_q, XY–XY and XY–ZW collisions

d) Other quantities:

α_i, α_j	average number of vibrational quanta in the ith and jth modes of XY, ZW molecules
α_i^0, α_j^0	equilibrium values of α_i, α_j at a gas temperature T
L	total number of vibrational modes in XY molecule involved in XY–M_q and XY–XY collisions

L'	total number of vibrational modes in XY molecule involved in XY–ZW collisions
k	total number of vibrational modes in which quanta are lost
l_i	the number of quanta lost in the ith mode ($i = 1, \dots, k$) as a result of XY–M_q, XY–XY collisions
l'_i	the same for XY–ZW collisions ($i = 1, \dots, k'$)
l_j	the number of quanta gained in the jth mode ($j = k + 1, \dots, L$) as a result of XY–ZW collisions
l'_j	the same for XY–ZW collisions ($j = k' + 1, \dots, L'$)
N	number density of molecules
$N^{XY}(v_i, v_j)$	number density of XY molecules in a specified vibrational mode state (v_i, v_j); for ZW molecules the symbol XY is replaced by ZY
N^{M_q}, $N^{M_{q'}}$	number densities of M_q and $M_{q'}$ molecules
k_{10}^{01}	rate constant for intramode VV energy transfer in a collision involving the 1 → 0 vibrational transition in one of the colliding molecules and the 0 → 1 transition in the other
τ_{VV}	characteristic time of intramode VV relaxation
T_i, T_j	temperatures of ith and jth modes in molecules
θ_i, θ_j	characteristic vibrational temperatures of ith and jth modes in molecules
r_i, r_j	degeneracy of ith and jth modes in molecules

6. *Description of Coefficients and Parameters*

See the description of model V.5.

7. *Features of the Model*

a) The kinetic equations describe the change of the average number of vibrational quanta per molecule, α_ξ, in a mode ξ of XY molecule via a single channel that is defined by specifying a pair (l_i, l_j) of quantum numbers:

$$\begin{aligned} (v_1, \dots, v_k; v_{k+1}, \dots, v_L) &\equiv \{v_i, v_j\} \\ &\rightarrow (v_1 - l_1, \dots, v_k - l_k; v_{k+1} + l_{k+1}, \dots, v_L + l_L) \\ &\equiv \{v_i - l_i; v_j + l_j\} \quad i = 1, \dots, k; \ j = k + 1, \dots, L \end{aligned}$$

Similarly, a channel (l'_i, l'_j) is defined for a change of $\alpha_{\xi'}$ in a mode ξ' of XY molecule in XY–ZW collisions. In the presence of multiple relaxation channels, the right-hand side of the kinetic equation needs to be summed over all the values l_i, l_j and l'_i, l'_j. With $q = 0$, processes in gases XY, ZW without other components are modeled.

b) For detailed balance relations, see the appropriate subsection in the description of model V.5.

c) In the absence of VT energy exchange, when $\tau_{VV} \ll t \ll \tau_{VT}$, the quasi-stationary state takes place in binary mixtures of polyatomic molecules. In this quasi-stationary state, there is a relation between the temperatures T_i and T_j of vibrational modes in molecules XY, ZW. Specifically, if a specific relaxation channel (l_i, l_j) plays a dominant role for any mode ξ in collisions XY–ZW, the vibrational temperatures T_i and T_j of the appropriate modes are related by:

$$\sum_{i=1}^{k'} \frac{l'_i\theta_i}{T_i} - \sum_{j=k'+1}^{L'} \frac{l'_j\theta_j}{T_j} = \frac{\left(\sum_{i=1}^{k'} l'_i\theta_i - \sum_{j=k'+1}^{L'} l'_j\theta_j\right)}{T}$$

Analogous relations, with other channels (l'_i, l'_j), occur at the quasi-stationary state for energy relaxation in other modes. The complete set of these relations for L' vibrational temperatures T_i, T_j presents a system of linear equations for values $1/T_i$, $1/T_j$. If the determinant of this system differs from zero, this system has a single trivial solution $T_i = T_j = T$, suggesting that non-equilibrium quasi-stationary distribution is absent. If the number of independent equations is less than L', then the solution for temperatures T_i, $T_j \neq T$ exists, and it determines the relation between vibrational temperatures of different modes in the process of VT relaxation. The rate of the latter process is mostly determined by the rate of VT energy exchange for vibrational mode with the lowest characteristic temperature θ, because the rate constant of VT exchange for this mode usually is much higher than the analogous rate constants for other modes with higher values of θ.

8. *Example*

The mode kinetics of vibrational energy exchange in the mixture of molecules CO_2–N_2 follows.

a) Nomenclature and values of parameters:

Molecule	Mode	Index	Characteristic temperature, K	Mode degeneracy
CO_2	Symmetric	1	$\theta_1 = 2000$	$r_1 = 1$
CO_2	Bending	2	$\theta_2 = 960$	$r_2 = 2$
CO_2	Asymmetric	3	$\theta_3 = 3380$	$r_3 = 1$
N_2	Vibrational	4	$\theta_4 = 3354$	$r_4 = 1$

b) The principal relaxation channels for transitions between the lowest vibrational levels and the appropriate nomenclature of the rate constants follow.

$$N_2(v=1) + CO_2(00^00) = N_2(v=0) + CO_2(00^01) \qquad k(4 \to 3)$$

$$N_2(v=1) + CO_2(00^00) = \begin{cases} N_2(v=0) + CO_2(11^10) & k(4 \to 1,2) \\ N_2(v=0) + CO_2(03^10) & k(4 \to 2) \end{cases}$$

$$CO_2(00^01)+M=\begin{cases} CO_2(11^10)+M & k_M(3\to 1,2)\\ CO_2(03^10)+M & k_M(3\to 2)\end{cases}$$

$$CO_2(10^00)+M=CO_2(02^00)+M \quad k_M(1\to 2)$$

$$CO_2(01^10)+M=CO_2(00^00)+M \quad k_M(2\to 0)$$

$$M=CO_2,\ N_2$$

c) Vibrational relaxation equations for the average numbers of vibrational quanta α_i, α_j in modes 1–4 for CO_2–N_2 mixture follow.

$$\frac{d\alpha_4}{dt}=k(4\to 3)N^{CO_2}(\alpha_3-\alpha_4)+k(4\to\Sigma)N^{CO_2}$$
$$\times\left[\exp\left(-\frac{500}{T}\right)\left(\frac{\alpha_2}{2}\right)^3(1+\alpha_4)-\alpha_4\left(1+\frac{\alpha_2}{2}\right)^3\right]$$

$$\frac{d\alpha_3}{dt}=-k(4\to 3)N^{N_2}(\alpha_3-\alpha_4)+[k(3\to\Sigma)N^{CO_2}+k(3\to\Sigma)N^{N_2}]$$
$$\times\left[\exp\left(-\frac{500}{T}\right)\left(\frac{\alpha_2}{2}\right)^3(1+\alpha_3)-\alpha_3\left(1+\frac{\alpha_2}{2}\right)^3\right]$$

$$\frac{d(\alpha_2+2\alpha_1)}{dt}=-3[k(3\to\Sigma)N^{CO_2}+k(3\to\Sigma)N^{N_2}]$$
$$\times\left[e^{-500/T}\left(\frac{\alpha_2}{2}\right)^3(1+\alpha_3)-\alpha_3\left(1+\frac{\alpha_2}{2}\right)^3\right]$$
$$-k(4\to\Sigma)N^{N_2}\left[e^{-500/T}\left(\frac{\alpha_2}{2}\right)^3(1+\alpha_4)-\alpha_4\left(1+\frac{\alpha_2}{2}\right)^3\right]$$
$$+[k(2\to 0)N^{CO_2}+k(2\to 0)N^{N_2}](1-\beta_2)(\alpha_{02}-\alpha_2)$$

$$k(4\to\Sigma)=k(4\to 1,2)+k(4\to 2);\quad k(3\to\Sigma)$$
$$=k(3\to 1,2)+k(3\to 2)$$

These kinetic equations are written on the assumptions that $\theta_1=2\theta_2$, $\theta_3=\theta_4$, $T_1=T_2$.

The values of rate constants for mixture of molecules CO_2–N_2 are listed in Ref. 25 (see also corresponding subsection in the description of model V.5).

The simulation of vibrational energy exchange in CO_2–N_2 mixture serves as a basis for the description of processes in CO_2 lasers (Refs. 25, 68 and 69).

9. *Comments*

a) Collections of experimental data on vibrational relaxation times of triatomic molecules can be found in Refs. 21, 22, and 70–75. These data can be useful in calculations with other types of relaxation equations and for approximate estimates.

b) Anharmonicity of vibrations of polyatomic molecules affects the mechanism of the intermode vibrational energy exchange, which determines the channels of the VV′ energy exchange. In a polyatomic molecule, the quantum of one vibrational mode can be a multiple of the quantum of another mode. In this case, the Fermi resonance arises between different vibrational levels of the same symmetry, and anharmonic intermode coupling leads to the mixing of the energetically degenerate states. As a result, shift and splitting of the energy levels takes place. Fermi resonance between the bending and symmetric vibrational modes is observed in CO_2, CS_2, N_2O, and other molecules. The Fermi resonance in CO_2 provides fast deactivation of the lower laser level 10^00 in the CO_2 laser operating on the transition $00^01 \rightarrow 10^00$.

Anharmonic inter-mode coupling leads to the coupling of the vibrational distributions in different vibrational modes. Therefore, vibrational relaxation of polyatomic molecules is to be considered in the space of the vibrational numbers of several vibrational modes (Ref. 3).

See also comments in the description of model V.5.

Relevant material can be found in Refs. 3, 4, 5, 6, and 19.

I. Vibrational Relaxation in Chemically Reacting Gases: Mode Kinetics Model (V.9)

1. *Purpose of Model*

The model aims at the determination of the mean vibrational energy of diatomic and polyatomic molecules as a function of time in chemically reacting gases.

2. *Assumptions*

a) See Assumption a in the description of model V.6.

b) The course of vibrational relaxation processes and chemical reactions is characterized by a single variable—the mean vibrational energy ε per molecule. Different types (modes) i of vibrations in molecules s are considered in chemically reacting mixture with distinct molecules, including polyatomic molecules. In this mixture, different vibrational temperatures T_i for ith types of vibrations can exist.

c) The Gulberg–Waage mass action law is obeyed in reacting mixtures with simple reversible chemical reactions (see also the description of model C.2 in Chapter 6 in this volume).

3. *Restrictions*

a) The characteristic time of chemical reactions τ_c is much greater than the characteristic time of intramode VV energy exchange $\tau_{VV} = (k_{10}^{01}N)^{-1}$: $\tau_c \gg \tau_{VV}$.

b) For harmonic oscillator approximation, see Restriction c in the description of model V.1.

4. *Relaxation Equations*

a) For vibrational energy of *i*th type (mode) of vibration in molecules *s* with *l* chemical reactions:

$$\frac{\mathrm{d}\varepsilon_i}{\mathrm{d}t} = \left(\frac{\mathrm{d}\varepsilon_i}{\mathrm{d}t}\right)_{VT,VV'}\Bigg|_s + \frac{1}{N_s}\sum_l (E_{il}^* - \varepsilon_i)(\nu_{sl}^- - \nu_{sl}^+)\cdot W_l$$

$$W_l = k_l^+ \prod_s N_s^{\nu_{sl}^+} - k_l^- \prod_s N_s^{\nu_{sl}^-}$$

b) For vibrational energy of diatomic AB molecules treated as harmonic oscillators, comprising a low-concentration impurity in a gas of particles $M(N^{AB} \ll N^{M})$, and experiencing VT exchange and reactions of dissociation and recombination:

$$\frac{\mathrm{d}\varepsilon^{AB}}{\mathrm{d}t} = \frac{\varepsilon_0^{AB} - \varepsilon^{AB}}{\tau_{VT}} - (E_d^* - \varepsilon^{AB})\frac{1}{N^{AB}}\left(\frac{\mathrm{d}N^{AB}}{\mathrm{d}t}\right)_d + (E_r^* - \varepsilon^{AB})\frac{1}{N^{AB}}\left(\frac{\mathrm{d}N^{AB}}{\mathrm{d}t}\right)_r$$

$$\left(\frac{\mathrm{d}N^{AB}}{\mathrm{d}t}\right)_d = k_d N^{AB} N^{M} \qquad \left(\frac{\mathrm{d}N^{AB}}{\mathrm{d}t}\right)_r = k_r N^{A} N^{B} N^{M}$$

5. *Nomenclature*

a) Quantities calculated with the model:

ε_i	mean vibrational energy of *i*th type (mode) per molecule
ε^{AB}	mean vibrational energy per molecule for AB molecule

b) Kinetic coefficients:

k_l^+, k_l^-	rate constants of *l*th reaction in forward and back directions
k_d, k_r	rate constants for dissociation and recombination, correspondingly
τ_{VT}	vibrational relaxation time

c) Other quantities:

$(\mathrm{d}\varepsilon_i/\mathrm{d}t)_{VT,VV'}\vert_s$	rate of vibrational energy change for *i*th mode of molecule *s* as a result of VT and VV′ energy exchange in accordance with models V.7 and V.8

$\varepsilon_0^{\mathrm{AB}}$	equilibrium value of $\varepsilon^{\mathrm{AB}}$ (at $T_v = T$)
T_v	vibrational temperature
N_s, N^{AB}, N^{M}, N^{A}, N^{B}	number densities for molecules s, AB, particles M, and atoms A and B, respectively
E_{il}^*	average vibrational energy per molecule lost or gained in the ith type of vibration (mode) in each act of reaction l
E_d^*, E_r^*	analogously in reactions of dissociation (d) and recombination (r), respectively
W_l	rate of reaction l
$(\mathrm{d}N^{\mathrm{AB}}/\mathrm{d}t)_d$, $(\mathrm{d}N^{\mathrm{AB}}/\mathrm{d}t)_r$	analogously for reaction of dissociation (d) and recombination (r)
ν_{sl}^+, ν_{sl}^-	stoichiometric coefficients for component s in the lth reaction in forward and back directions
m	number of vibrational level
N_m	population density in the mth vibrational level
E_m	vibrational energy of molecule in the mth level
k_{lm}, k_{dm}, k_{rm}	rate constants for lth reaction, dissociation (d) and recombination (r), respectively, for molecules in the mth level
P_m	probability of chemical transformation of molecule in the mth level
θ, θ_v	characteristic vibrational temperature
D_0	dissociation energy
E_a	activation energy
$k_{10}^{\mathrm{AB-M}_s}$	rate constants for vibrational VT transfer 1 → 0 induced by collisions of AB molecules with M_s particles
τ_{VV}, τ_{VT}	time of VV and VT relaxation, respectively
τ_c, τ_d	characteristic time of relaxation to chemical equilibrium (c), and dissociation equilibrium (d) in particular

6. *Description of Coefficients and Parameters*

Evaluation of rate constants of chemical reactions is considered in the Chapter 6 of the first volume. In nonequilibrium gases, rate constants k_i, k_d depend not only on translational temperature, but also on vibrational temperature of the ith vibrational mode (see models I-C.19–I-C.28).

The time of VT relaxation of the molecules AB in collisions with particles M_s (here, $\mathrm{M}_s = \mathrm{AB}$, A_2, B_2, A, or B) is given by the formula:

$$\tau_{VT} = \left\{ \left(\sum_s k_{10}^{\mathrm{AB-M}_s} N_s \right) [1 - \exp(-\theta^{\mathrm{AB}}/T)] \right\}^{-1}$$

Rate constants k_{10} are evaluated using the formulas from the models I-V.2 and I-V.5. For the gas mixtures, $\tau_{VT}^{-1} = \sum_s (\xi^{\mathrm{M}_s}/\tau_{VT}^{\mathrm{AB-M}_s})$, where $\xi^{\mathrm{M}_s} = N_s/\sum_s N_s$ is the relative concentration (mole fraction) of the particles M_s.

The value of the basic parameter E^*_{il} (in particular, E^*_d and E^*_r) of this model is determined by the state-specific kinetics of chemical reaction (see the description of model V.6):

$$E^*_{il} = \left.\frac{\sum_m N_m E_m k_{lm}}{\sum_m N_m k_{lm}}\right|_i, \quad E^*_d = \frac{\sum_m N_m E_m k_{dm}}{\sum_m N_m k_{dm}}, \quad E^*_r = \frac{\sum_m N_m E_m k_{rm}}{\sum_m N_m k_{rm}}$$

State-specific rate constants k_{lm}, k_{dm}, k_{rm} of the chemical reactions that enter these expressions can be replaced by the probabilities P_m.

In the models of distributed probability of thermally nonequilibrium reactions (see models I-C.21, I-C.26 and the literature cited there), where the molecules are modeled as truncated harmonic oscillators, P_m depends parametrically on the number m of vibrational level. Thus, for $T_v \le T$ in the Marrone–Treanor model (I-C.21) of dissociation of diatomic molecules and recombination of atoms:

- mean vibrational energy lost (in K)

$$E^*_d = \frac{\theta}{\exp(\theta/T_F)} - \frac{D_0}{\exp(D_0/T_F) - 1}, \quad T_F = \left(\frac{1}{T_v} - \frac{1}{T} - \frac{1}{U}\right)^{-1}$$

- mean vibrational energy gained (in K)

$$E^*_r = \frac{\theta}{\exp(\theta/U) - 1} - \frac{D_0}{\exp(D_0/U) - 1}$$

Possible values of the parameter U that characterizes distribution of the dissociation probabilities from different vibrational levels are considered in the description of the model I-C.21.

Assumption that dissociation takes place predominantly from high vibrational levels of molecule leads to the values of E^*_d close to D_0. If dissociation from low-lying levels is taken into account, E^*_d decreases. Estimation in Ref. 67, p.108, gives $E^*_d \approx 0.3D_0$.

The mean vibrational energy lost and gained in the exchange reactions, dissociation and recombination reactions, and associative ionization, can be calculated within the generalized CVCV Marrone–Treanor model (I-C.26). Corresponding formulas are given in Ref. 77.

In gas dynamic problems, the following values of E^*_d, E^*_r, E^*_{il} can be used as zero-order estimates in many cases:

$E^*_d \approx E^*_r \approx 0.5D_0$	for dissociation of diatomic molecules, decomposition of polyatomic molecules, and recombination reactions;
$E^*_{il} \approx 0.7E_a$	for exchange chemical reactions.

7. *Features of the Model*

At sufficiently high temperatures, $T > \theta$, it may be supposed that the following relations between characteristic times of the different processes proceeding in the gas take place: $\tau_{VT} \sim \tau_c(\tau_v \sim \tau_d)$, $\tau_{VV} \ll \tau_{VT}$. Under such conditions, several stages are necessary for the establishment of complete equilibrium. During the first, fast, stage, quasi-stationary Boltzmann vibrational distribution with the temperature T_v (different from the translational temperature T) is established because of VV energy transfer. At the second stage, VT energy transfer leads to equilibration between T_v and T. Finally, at the last stage, the role of recombination reaction increases, and chemical equilibrium is established.

An important feature of vibrational relaxation in high-temperature nonequilibrium chemically reacting gases is a coupling between the vibrational relaxation and chemical reactions. This vibration-chemistry (in particular, vibration-dissociation) coupling can result in a quasi-stationary state of the gas, when the increase of molecular vibrational energy because of VT energy exchange is balanced by its decrease in chemical reactions. This quasi-stationary state is observed distinctly in dissociation of diatomic molecules in the absence of recombination (i.e., at the second stage previously mentioned) when the vibrational energy ε^{AB} is determined by the balance between vibrational excitation in VT energy exchange and the loss of vibrational energy in molecular dissociation:

$$\frac{d\varepsilon^{AB}}{dt} = 0, \qquad \frac{\varepsilon_0^{AB} - \varepsilon^{AB}}{\tau_{VT}} = (E_d^* - \varepsilon^{AB}) \sum_s k_{ds}(T, T_v) N_s$$

where k_{ds} is the rate constant of dissociation of AB molecules in collisions with particles s (AB, A_2, A, B, etc.), τ_{VT} is the VT relaxation time in the mixture (see subsection Description of Coefficients and Parameters). This formula, viewed as an implicit transcendental equation, allows one to determine the dependence of vibrational temperature T_v on translational temperature T at the quasi-stationary stage of the dissociation process. The function $T_v = f(T)$ is determined by the model of nonequilibrium dissociation that gives the values of E_d^* (see above), and by the dissociation rate constants $k_d(T, T_v)$ (see the corresponding section in Chapter 6 of the first volume). Examples of T_v dependence on T at quasi-stationary stage of O_2 and N_2 dissociation at different number densities are given in Ref. 78.

8. *General and Particular Solutions*

In the general case, the system of kinetic equations given above is solved numerically.

9. *Example*

An example of calculated profiles of translational temperature T and vibrational temperatures of oxygen (T_{O_2}) and nitrogen (T_{N_2}) behind a shock front in air ($T = 300$ K, $p = 5.3 \times 10^{-5}$ atm) is presented in Fig. 4.7. In this figure, x is a distance from the shock front, solid curves correspond to the Marrone–Treanor model (I-C.21), and dashed curves are the results of calculations with $E_d^* = 0.6D_0$.

Other examples of solution of the vibrational relaxation equations in chemically reacting gases can be found in Refs. 46 and 76–80.

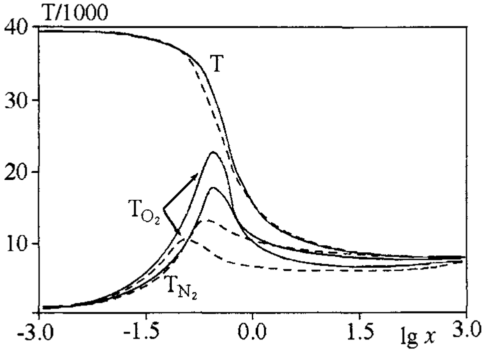

Fig. 4.7

10. *Comments*

a) Effect of anharmonicity on vibrational relaxation of various modes in chemically reacting gases at different degrees of deviation from equilibrium is considered in Refs. 3 and 6.

b) If anharmonicity is taken into account, the Marrone–Treanor model gives the following general expressions for the mean vibrational energy lost (E_d^*) and mean vibrational energy gained (E_r^*):

$$E_d^* = \frac{\sum_m E_m \exp(-E_m/T_F)}{\sum_m \exp(-E_m/T_F)}, \qquad E_r^* = \frac{\sum_m E_m \exp(-E_m/U)}{\sum_m \exp(-E_m/U)}$$

where $T_F = (1/T_v - 1/T - 1/U)^{-1}$, and U is a parameter of the Marrone–Treanor model (I-C.21). Dependence of the vibrational energy E_m on the number m of the level is determined by the model of the molecular oscillator (see p. 12 in Chapter 1 of the first volume with the notation $U \equiv m$).

Relevant material can be found in Refs. 2, 6, 46, 67 and 76.

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Chapter 5

Electronic Relaxation (E Models)

I. Introduction

ELECTRONIC KINETICS deals with the description of processes occurring during transitions between electronic states of atoms and molecules below the ionization limit. This field of kinetics lies at the junction with plasma processes, cluster kinetics, chemical reactions, and vibrational kinetics. The boundaries of this field are defined by the following conditions:

1. Collisions with free electrons do not play any significant part in electronic relaxation;
2. Clusters exist only in an unstable state;
3. Chemical reactions are treated as a constituent part of the process of electronic relaxation; and
4. The processes of vibrational energy exchange are treated as related to their interaction with electronic transitions.

Electronic kinetics of plasma processes involving collisions with electrons is the subject of Chapter 7 (see models P.9, P.10, P.11 in this volume).

A unified system of molecules plus atoms is treated in the case of electronic kinetics of atomic-molecular gas. The electronic terms of polyatomic molecules represent a system of multidimensional energy surfaces in the space of energy and of normal coordinates of molecules. The terms are divided into bonding and antibonding (repulsive) ones; they are characterized by the presence or absence of a potential well. Each bonding term has a certain number of vibrational and rotational levels associated with it. New molecules may be formed in the course of electronic relaxation, new relaxation channels may arise, and chemical reactions may proceed. Many of the processes are sensitive to minor impurities and changes of conditions. In solving the problems of electronic kinetics, three main approximations are used.

A. Adiabatic Approximation

In the adiabatic approximation, the motion of atoms and molecules is treated independently of the motion of electrons and, because of the large difference between the characteristic times, the electron and nuclear motions may be described separately (Born–Oppenheimer approximation, see Ref. 1). Additionally, electronic transition frequencies $|E_m - E_n|/\hbar$ exceeds considerably molecular vibrational frequencies. Within this approximation, the molecular energy E may be represented as a sum of electronic, E_e, vibrational, E_v, and rotational, E_r, energies, or $E = E_e + E_v + E_r$, and the wave function may be represented as the product of the respective wave functions, $\Psi = \Psi_e \times \Psi_v \times \Psi_r$.

In this approximation, the energy terms and the wave functions of atoms and molecules are calculated. For polyatomic molecules, the wave function is constructed from the wave functions of hydrogen-like atoms, such as atomic orbitals (AO). The interaction of each electron with all other electrons is taken into account in the form of interaction with the averaged field produced by the nucleus and the remaining electrons. The wave function for molecules is constructed by the method of molecular orbitals (MO) from the functions describing the behavior of individual electrons in the field produced by the remaining electrons and by all atomic nuclei that form the molecular core. The descriptions of the AO and MO methods, as well as of their applications, are given in Refs. 1–3. These methods serve as the basis for the theory of structure of molecules and their reactivity.

For nondegenerate electronic states, calculations in the adiabatic approximation bring about insignificant errors in calculating the total energy. For degenerate electronic states, this approximation is invalid.

B. Nonadiabatic Approximation for Vibronic Interactions

When the adiabatic approximation is violated, one must take into account the coupling between electron and nuclear motion. This coupling is referred to as vibronic interaction. As a result, the single-electron states of molecules calculated by the MO method partially lose their individuality and are mixed.

The vibronic effects are important in analyzing the processes of activation of chemical reactions and of formation of excited states of various particles. The vibronic approach and its applications are described in Refs. 4–7.

C. Nonadiabatic Semiempirical Approximation

The adiabatic and vibronic approximations provide a general basis for the analysis of kinetic phenomena. However, when solving specific problems, a semiempirical approach is required in most cases. Because of the mixing of electronic states, nonadiabatic processes are characterized by the presence of multiple channels. The states of products are often not identified; a number of channels of the processes, as well as their cross sections as functions of the parameters that determine the mixing of electronic states and the interaction with the collision partner, also remain unknown. Experimental data are required for the calculation in most cases of practical interest.

Fast resonant and quasiresonant processes play a critical role in the population kinetics of electronic states of atoms and molecules in nonequilibrium media. The identification of fast and slow processes and the determination of the hierarchy of characteristic times enable one to develop a qualitative pattern of kinetics (see Chapter 1).

The details of the semiempirical approach are treated in Refs. 8–10.

The theory of electronic relaxation can be divided into three qualitatively distinct parts, namely, kinetics of simple media consisting of a single element, kinetics of binary and multicomponent media, and kinetics of media with structural transformations.

1. Media of Simple Chemical Composition

The electronic relaxation of simple atomic-molecular media containing molecules, atoms, and ions of a single element has its own specific features and serves as a basis for the analysis of more complex systems. A great part in the kinetics of simple media is played by metastable electronically excited states of atoms and diatomic molecules, which have very long radiative lifetimes ($\tau \sim 0.1-10\,\mathrm{s}$) and small quenching cross sections in collisions with particles having a closed electron shell (see Refs. 9, 10, 12, and 46). Because of the long radiative lifetime and low rate of quenching, lower metastable states of homonuclear diatomic molecules (N_2, O_2) represent a bottleneck of electronic relaxation. This leads to high concentrations (typical number density $n \sim 10^{12}-10^{16}\,\mathrm{cm}^{-3}$) of metastable particles that carry considerable energy ($E \sim 1-6\,\mathrm{eV}$); therefore, these particles can be used as a reservoir of electronic excitation energy.

The kinetic pattern of processes occurring in media of simple chemical composition is largely determined by the magnitude of energy or power loading of the medium. In the case of low energy loading, analysis of processes for electronic states of molecules below the dissociation limit is sufficient (model E.1). For higher energy loading, kinetics of an atomic-molecular medium is used (model E.2).

2. Binary and Multicomponent Media

For multicomponent atomic-molecular media, the electronic kinetics are complex and cannot be described by a universal model. In constructing particular models, metastable electronic states of particles of the medium are usually identified, and balance equations are written for their populations. Models of binary systems containing two chemical elements have been developed in detail, with special attention given to models based on the mixing of simple single-element media. The mixing processes serve as regulators of kinetics; in particular, they make it possible to store energy in certain states, which is favorable to the development of laser media. The characteristic features of the kinetics of binary media in chemically reacting gases are treated in model E.3.

3. Kinetics of Media with Structural Transformations

As the energy or power loading of the matter increase, along with the emergence of free atoms, molecules and radicals containing an ever-increasing number of particles are formed. Chains of structural transformations arise, whose rates may reach values corresponding to the gas-kinetic cross sections. This leads to a coupled electronic–structural kinetics. An example is provided by the combustion kinetics, where the transformation of molecules proceeds via series of intermediate particles whose qualitative and quantitative composition largely remains uncertain. When a large number of reactions occur simultaneously, the possibility of error in determining the mechanism of the processes is quite large. One can be guided to a certain extent by the statistical model (see Ref. 11) that describes a gas of radicals and free atoms interacting with one another to form ever more complex radicals. Here, two characteristic times may be identified for elementary processes, namely, that for radical–molecule collisions (analog of the VT process), and that for radical–radical collisions (analog of the VV process).

Investigation of electronic–structural relaxation lies at the junction of electronic kinetics, chemical kinetics, and the cluster theory. Model E.4 for polymerization processes is an example of models of electronic-structural transformations.

D. Atomic-Molecular Kinetics of a Medium of Simple Composition (E.1)

1. Purpose of the Model

The purpose of the model is the calculation of populations of the electronic states of atoms and molecules at a given energy loading.

2. Assumptions

The relaxation channels that do not involve metastable particles are ignored.

3. Restrictions

The energy loading of the medium should not exceed a certain level at which significant numbers of free electrons appear in the medium. The electrons start playing an important part in the kinetics at a degree of ionization of about 10^{-8}.

4. Kinetic Equations

$$\frac{\mathrm{d}N_n}{\mathrm{d}t} = \sum_m k_{mn}N_m - \sum_m k_{nm}N_n + \sum_m \sum_l L_{ml,n}N_mN_l - \sum_m \sum_l L_{mn,l}N_mN_n$$

5. Nomenclature

a) Quantities calculated with the model:

N_n	population density (population) for nth electronic term

b) Kinetic coefficients:

k_{mn}, k_{nm}	rate constants for the transitions $m \to n$ and $n \to m$, respectively
$k_{ml,n}, L_{mn,l}$	rate constants for the transitions $m,l \to n$ and $m,n \to l$, respectively

c) Other quantities:

n, m, l	indices (subscripts) denoting electronic terms

6. *Description of Coefficients and Parameters*

The values of rate constants are determined both theoretically and experimentally. For relations between rate constants and probabilities, see appropriate subsection in the description of model E.2. Data on the probabilities of processes in O_2–O and N_2–N systems are available in Refs. 12–21.

7. *Typical Values and Examples*

The general set of kinetic equations previously described is used to describe electronic processes in oxygen (O_2–O system) for energy states up to the ionization limit; in particular, the beginning of thermal ionization, at the stage of formation of primary electrons, can be analyzed. When heated, a molecular gas starts to dissociate because of growing vibrational excitation of molecules. Atoms in the ground electronic state are formed. As a result of nonadiabatic transitions from the repulsive to bound terms, atoms may compose a molecule in a higher excited electronic state. This molecule may dissociate as well, but with the formation of atoms in excited states. Gradually formed are bound molecular terms with an ever-higher energy, up to the ionization limit.

The set of kinetic equations for the populations of 14 terms of molecules, atoms, and ions of the O_2–O system is given in Ref. 16. These equations describe the following states:

$$^3\Sigma_g^-,\ ^1\Delta_g,\ ^1\Sigma_g^+,\ ^3\Sigma_u^-,\ ^1\Delta_u,\ ^1\Sigma_u^+,\ ^3\Sigma_u^+,\ ^1\Sigma_u^-,\ ^3\Delta_u,\ \mathrm{O}(^1D),\ \mathrm{O}(^3P),\ \mathrm{O}(^1S),$$

$$\mathrm{O}_2^+(X^2\Pi_g),\ \mathrm{O}_2^-,\ \mathrm{O}^-(^2P^0),\ \mathrm{O}^+(^4S^0)$$

Altogether, 91 elementary processes are covered by these equations. The results of calculation of the initial stage of thermal ionization have demonstrated that, under shock-wave conditions at $t = 10^{-6}$ s, $N = 10^{19}$ cm^{-3}, and $T = 4000$ K, the degree of ionization is approximately 10^{-6}.

8. *Error of the Model*

The model gives results correct within an order of magnitude, and its error is determined by the error of the probabilities (rate constants) of electronic transitions.

9. *Comments*

Applications of the model to new systems (that is, systems not previously studied) must be preceded by an analysis of the system of terms.

Relevant material can be found in Ref. 16.

E. Model of Electronic Excitation Exchange (E.2)

1. *Purpose of the Model*

The model aims at calculations of the populations of metastable states in an atomic-molecular system, and an estimation of the energy stored in the metastable states.

2. *Assumptions*

EE exchange processes between metastable states are assumed to dominate the population kinetics. Moreover, single-quantum EE exchange is assumed to be predominant.

3. *Restrictions*

The calculated distributions of metastable states of atoms and molecules, which arise due to EE exchange, are valid during time intervals substantially shorter than the electronic-translational relaxation (dissipation) time. That such an interval exists is due to the hierarchy of the characteristic times of EE exchange and the electronic energy dissipation: $\tau_{EE} \ll \tau_{ET}$.

4. *Kinetic Equations*

$$\frac{\mathrm{d}N_n}{\mathrm{d}t} = \sum_{m,s,l} k^{sl}_{mn} N_s N_m - \sum_{m,s,l} k^{ls}_{nm} N_l N_n + \sum_{n} k_{mn} N_m - \sum_{m} k_{nm} N_n$$

5. *Nomenclature*

a) Quantities calculated with the model:

N_n	population density (population) for the nth metastable state of atoms and molecules

b) Kinetic coefficients:

k^{sl}_{mn}	rate constants for transitions $m \to n$ in one particle and $s \to l$ in the other
k^{ls}_{nm}	analogous rate constants for transitions $n \to m$ and $l \to s$
k_{mn}, k_{nm}	rate constants for transitions $m \to n$ and $n \to m$, respectively, due to collisional and radiative processes

c) Other quantities:

n, m, l, s	indices (subscripts and superscripts) denoting electronic terms
Z	gas kinetic collision frequency per unit number density
R_0	gas kinetic collision radius (see Chapters 1 and 2 in the first volume)
μ	(reduced mass of colliding particles (see Chapters 1 and 2 in the first volume)
m_X, m_Y	masses of particles X and Y

6. *Description of Coefficients and Parameters*

The rate constants k_{mn}, k_{nm}, k^{sl}_{mn}, k^{ls}_{nm} are determined by the corresponding values of probabilities P_{mn}, P_{nm}, Q^{sl}_{mn}, so that $k_{mn} = ZP_{mn}$, etc., where $Z = \pi R_0^2 (8kT/\pi\mu)^{1/2}$ and $\mu = m_X m_Y/(m_X + m_Y)$. The values of probabilities are treated in the first volume of this handbook.

A number of papers are devoted to methods for calculations of specific coefficients (for example, see Refs. 12–21).

7. *Typical Values and Examples*

The model is used to analyze kinetic processes in nitrogen plasmas. For the conditions of glow discharge, a strong coupling exists between the terms $N_2(A^3\Sigma_u^+)$, $N_2(B^3\Pi_g)$, and $N_2(C^3\Pi_u)$, even at relatively low excitation levels. The fastest processes of electronic excitation transfer are the EE exchange between the N_2 molecular terms,

$$N_2(A) + N_2(A) \rightleftarrows N_2(B) + N_2(X)$$

$$N_2(A) + N_2(B) \rightleftarrows N_2(C) + N_2(X)$$

and the electronic energy exchange between molecules and atoms (EE′ exchange),

$$N_2(A) + N(^4S) \rightleftarrows N_2(X) + N_2(^2P)$$

These processes of EE exchange approximately conserve the total amount of electronic energy. The loss of electronic energy is determined by the rate of quenching of molecules and atoms in collisions with heavy particles and electrons; the characteristic time is of the order of 10^{-5} s. A quasistationary distribution of populations, similar to the Treanor distribution for vibrational levels, was obtained in Ref. 22.

8. *Error of the Model*

The model gives results valid within an order of magnitude.

9. *Comments*

a) Along with the N_2–N system, the distribution functions for populations of electronic molecular terms were obtained for the O_2–O, Cl_2–Cl, and S_2–S systems. The results obtained with this model were compared with the experimental data, in particular, for recombination of chlorine atoms in supersonic flows (see Ref. 23).

b) The form of the set of kinetic equations coincides with that of equations of vibrational kinetics (see Chapter 4 of this volume).

Relevant material can be found in Refs. 16 and 24.

F. Electronic Energy Exchange in Chemically Reacting Gases: A Kinetic Model of Oxygen–Iodine Medium (E.3)

1. *Purpose of the Model*

The model aims at the calculation of the populations of electronic states in an atomic–molecular system where electronic energy exchange and chemical reactions occur simultaneously. An example is the calculation of the populations of lower terms of oxygen molecules and iodine atoms at various parameters of the oxygen–iodine medium.

2. *Assumptions*

a) See the assumptions of model V.6 and substitute vibrational relaxation processes by electronic energy exchange (VT, VV → ET, EE, and so on).
b) The electronic relaxation channels not related to metastable states are ignored. The overall kinetic mechanism of population of excited states of oxygen and iodine is defined by the reactions of electronic energy exchange, quenching, and by the chemical reactions of formation of atomic iodine.

3. *Restrictions*

The model includes a kinetic scheme for the electronic states of a binary mixture of molecular oxygen and atomic iodine. Only the lower energy terms are taken into account. The electronic states of molecule I_2 are not considered. Real systems such as the active medium of an oxygen–iodine laser contain impurities (H_2O_2, H_2O, Cl_2) whose effect can only be estimated.

4. *Master Kinetic Equation*

The kinetic equation for the population of an electronic state, taking into account changes of electronic states $m \rightleftarrows m'$, $n \rightleftarrows n'$ of components i, j, i', j' in binary–collision reactions l $(i \rightleftarrows i', j \rightleftarrows j')$ is:

$$\frac{\mathrm{d}N_m}{\mathrm{d}t} = \sum_l \left\{ \sum_{m,m',n'} k^{n'n}_{m'ml} N^{i'}_{m'} N^{j'}_{n'} - \sum_{n,m',n'} k^{nn'}_{mm'l} N^{i}_{m} N^{j}_{n} \right\}$$

If an electronic state is not specified or is absent, the corresponding notation of state is omitted and is not considered in the equation. The equation describes electronic energy exchange without chemical transformation; formally, if $l = 0$, then $i \rightleftarrows i, j \rightleftarrows j$.

5. *Kinetic Equations for Oxygen–Iodine Medium*

The set of balance (master) equations for the populations of electronic states is written on the basis of the kinetic scheme including the following transitions between electronic states:

1. $O_2(a^1\Delta_g) + I(^2P_{3/2}) \rightleftarrows O_2(X^3\Sigma_g^-) + I(^2P_{1/2})$
2. $O_2(a^1\Delta_g) + O_2(a^1\Delta_g) \rightarrow O_2(X^3\Sigma_g^-) + O_2(b^1\Sigma_g^+)$
3. $O_2(a^1\Delta_g) + I(^2P_{1/2}) \rightarrow O_2(b^1\Sigma_g^+) + I(^2P_{3/2})$
4. $O_2(b^1\Sigma_g^+) + M \rightarrow O_2(a^1\Delta_g) + M$
5. $O_2(a^1\Delta_g) + M \rightarrow O_2(X^3\Sigma_g^-) + M$
6. $I(^2P_{1/2}) + M \rightarrow I(^2P_{3/2}) + M$
7. $O_2(b^1\Sigma_g^+) + I_2 \rightarrow O_2(X^3\Sigma_g^-) + 2I(^2P_{3/2})$
8. $O_2(a^1\Delta_g) + I_2 \rightarrow O_2(X^3\Sigma_g^-) + I_2(20 \le v \le 40)$
9. $I(^2P_{1/2}) + I_2 \rightarrow I(^2P_{3/2}) + I_2(20 \le v \le 40)$
10. $O_2(a^1\Delta_g) + I_2(20 \le v \le 40) \rightarrow O_2(X^3\Sigma_g^-) + 2I(^2P_{3/2})$

11. $I(^2P_{1/2}) + I_2(20 \leq v \leq 40) \rightarrow (I_3) \rightarrow 3I(^2P_{3/2})$
12. $2I(^2P_{3/2}) + M \rightarrow I_2 + M$
13. $O_2(b^1\Sigma_g^+) + W \rightarrow O_2(X^3\Sigma_g^-) + W$
14. $O_2(a^1\Delta_g) + W \rightarrow O_2(X^3\Sigma_g^-) + W$
15. $I(^2P_{1/2}) + W \rightarrow I(^2P_3) + W$

An example of the balance equation for the population of oxygen molecules in the electronic state $O_2(b^1\Sigma_g^+)$ is:

$$\frac{dN_b}{dt} = k_2N_a^2 + k_3N_aN_{I'} - k_4N_bN_M - k_7N_bN_{I_2} + k_{-7}N_xN_{I''} - k_{13}N_b$$

6. *Nomenclature*

a) Quantities calculated with the model:

N_m	population density (population) for the *m*th electronic state (term)
N_b	population density (population) for the oxygen molecules in the electronic state $O_2(b^1\Sigma_g^+)$

b) Kinetic coefficients:

$k_{mm'l}^{nn'}$, $k_{m'ml}^{n'n}$	rate constants for transitions $m \Leftrightarrow m'$, $n \Leftrightarrow n'$ in *l*th reaction
k_l, k_{-l}	rate constant for direct and reverse *l*th reaction, respectively, in accordance with the numbering of reactions (see above)

c) Subscripts:

m, n	electronic states in direct reactions
m', n'	electronic states in reverse reactions
i, j	mixture components participating in direct reactions
i', j'	mixture components participating in reverse reactions
l	reaction number
b, a, x, I′, I″	states notation: b is for $O_2(b^1\Sigma_g^+)$, a is for $O_2(a^1\Delta_g)$, x is for $O_2(X^3\Sigma_g^-)$, I′ is for $I(^2P_{1/2})$, I″ is for $I(^2P_{3/2})$

d) Other quantities:

M	nonreacting particle as a collision partner
W	collision partner for collisions with a wall or a surface
$N_n, N_{m'}, N_{n'}$, $N_a, N_x, N_{I'}, N_{I''}$	population density (population) for electronic states indicated by subscripts
N_M	number density of nonreacting particle (collision partners)

7. *Description of Coefficients and Parameters*

A summary of data for coefficients, as well as a comparative analysis of the procedures and accuracy of measurements, are given in Refs. 25 and 26.

8. *Typical Values and Examples*

The model of electronic kinetics of an oxygen–iodine medium, in conjunction with gas dynamic equations, was used to calculate the operating modes and energy characteristics of oxygen–iodine lasers (see Refs. 24–26). The principle of its operation is based on near-resonant energy transfer from metastable oxygen to an iodine atom that is a radiating component. The main advantages of the laser include a high specific energy extraction, high uniformity of the medium in the resonator, a short radiation wavelength $\lambda = 1.315$ micron that lies within the atmospheric transparency window, the relative simplicity of design, and a lower (compared with an HF laser) toxicity of the reactants. In typical oxygen–iodine lasers, the temperature of the gas mixture is usually lower than room temperature, the oxygen pressure is several Torr, the singlet oxygen concentration is $[O_2(a^1\Delta_g)]/\{[O_2(a^1\Delta_g)] + [O_2(X^3\Sigma_g^-)]\} > 40\%$, the molar fraction of injected iodine is $[I_2]/[O_2] < 2\%$ and the molar fraction of water vapor is $[H_2O]/[O_2] < 5\%$.

9. *Error of the Model*

The model gives results with an accuracy within a factor of 2–3.

10. *Comments*

a) A simplified kinetic mechanism for this model can be reduced to a single equation for molar fraction of excited oxygen, see Ref. 25.

b) A comprehensive list of references pertaining to oxygen–iodine lasers and to the kinetics of processes occurring in their active media is given in the review paper (Ref. 27). A bibliography on sources of singlet oxygen can be found in Ref. 26. Experimental investigations of the Na_3–Br binary system were performed in Refs. 34 and 35.

c) A model of electronic energy exchange in chemically reacting gases was used to analyze H_2–F–NF_2 and H_2–F–HN_3 flames (see Ref. 36, also Refs. 37–39). In these flames, metastable states of NF(a, b) and N_2(A) are efficiently produced, which may be used for developing a laser in the visible spectral range. The kinetic scheme of this model contains 15 reactions with seven electronic states of NF and N_2 molecules and vibrationally excited NF(v) molecules. Specific values of rate constant for these reactions are given in Refs. 40–42.

Relevant material can be found in Refs. 24–33.

G. Model of Photochemical Polymerization Wave (E.4)

1. *Purpose of the Model*

The model aims at the calculation of the polymerization kinetics and at determination of the size distribution function of polymer molecules.

2. *Assumptions*

a) The original reactant in the process of polymerization is an A=B monomer molecule possessing at least one double bond. As a result of absorption of radiation with a certain quantum $h\nu$, a monomer molecule, after the rupture of one bond, makes a transition to excited state and may react with the original monomer to form an —A—B—A—B— active dimer radical. This radical, in turn, interacts with an A=B monomer and forms a trimer, and so on. The following kinetic scheme corresponds to such a chain mechanism:

$$
\begin{aligned}
&1.\quad (\mathrm{AB})_1 + h\nu \to (\mathrm{AB})_{1^*}\\
&2.\quad (\mathrm{AB})_{1^*} + (\mathrm{AB})_1 \to (\mathrm{AB})_{2^*}\\
&3.\quad (\mathrm{AB})_{2^*} + (\mathrm{AB})_1 \to (\mathrm{AB})_{3^*}\\
&4.\quad (\mathrm{AB})_{3^*} + (\mathrm{AB})_1 \to (\mathrm{AB})_{4^*}
\end{aligned}
$$

b) The spectral absorption band of the original monomer does not coincide with the bands of intermediate (polymer) fragments of the chain process.

3. *Restrictions*

The model is sensitive to the presence of side reactions; impurities may bring about a break in the chain. New side channels of the type

$$(\mathrm{AB})_{i^*} + (\mathrm{AB})_{k^*} \to (\mathrm{AB})_{i+k^*}$$

may arise as a result of considerable decrease in the monomer concentration.

4. *Kinetic Equations*

$$\left(\frac{1}{c}\frac{\partial}{\partial t}+\frac{\partial}{\partial x}\right)I = -\sigma I N_1$$

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = -\sigma I N_1 - N_1\sum_{i=1}^{\infty} k_i N_i'$$

$$\frac{\mathrm{d}N_1'}{\mathrm{d}t} = \sigma I N_1 - k_1 N_1' N_1$$

$$\frac{\mathrm{d}N_i'}{\mathrm{d}t} = k_{i-1}N_{i-1}'N_1 - k_i N_i' N_i \qquad i \geq 2$$

5. *Nomenclature*

c	speed of light
I	electromagnetic radiation flux
σ	photoabsorption cross section for process 1
k_i	rate constant for respective elementary processes (k_1, k_2, k_3 for processes 2, 3, 4)
N_1, N_1', N_2', N_3'	number densities of the reactants $(\mathrm{AB})_1$, $(\mathrm{AB})_{1^*}$, $(\mathrm{AB})_{2^*}$, $(\mathrm{AB})_{3^*}$ respectively

6. *Description of Coefficients and Parameters*

The coefficients and parameters of the model are treated in Refs. 43–45.

7. *Typical Values and Examples*

At $\sigma = 10^{-19}\,\mathrm{cm}^2$, $I = 10^{21}$ photon/(cm$^2 \cdot$ s), $N_0 = 1018\,\mathrm{cm}^{-3}$, and $k_i = 10^{-13}\,\mathrm{cm}^3/\mathrm{s}$, the velocity of the polymerization wave front is $D \approx 10^4\,\mathrm{cm/s}$.

8. *Error of the Model*

The model gives results with accuracy within a factor of 2–3.

9. *Comment*

As follows from the solution of the set of kinetic equations, one can change the chemical composition of the mixture behind the polymerization wave front by varying the intensity of the external radiation flux and, accordingly, the wave velocity. Because the final composition depends considerably on the initial conditions, the possibility arises of controlling the process to obtain products with desired properties, for example, with the aid of short-wavelength irradiation, electron beams, and lasers. The possibilities of controlling the processes of synthesis of substances during combustion were considered in Ref. 11.

Relevant material can be found in Refs. 11 and 45.

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Chapter 6

Chemical Kinetics (C Models)

OBJECTS of chemical kinetics are chemical reactions, that is, processes of transformation of some chemical species into others, taking place in chemically reacting media. The process of chemical transformation is described by the stoichiometric and kinetic laws.

Chemical kinetics studies:

1. temporal dynamics of a chemical process; relations between the concentrations of reactants, rate of the process, and conditions of its realization (temperature, pressure, etc.); and
2. mechanism of chemical process: what elementary stages it consists of, how these stages are related to each other, and what intermediate species participate in the process.

Kinetics and mechanisms of chemical processes in ideal gases are considered in this chapter. In such gases, the duration of interaction between the reacting particles is negligible in comparison with the time of their free motion (see Chapter 9, Equations of State, in this volume).

I. Introduction and Definitions

A. Chemical System

Chemically reacting system (*medium*) is a system, particles of which undergo chemical conversion during their interactions with each other.

Open chemical system is a system that exchanges matter and energy with environment.

Closed chemical system is a system that may exchange energy, but does not exchange matter with environment.

Adiabatic chemical system is a system that does not exchange energy with environment.

Isolated chemical system is a closed adiabatic system, that is, a chemical system that exchanges neither matter nor energy with environment.

Homogeneous chemical system is a system consisting of one phase. Inside such a system, there are no phase interfaces or any other surfaces that would separate parts of a system having properties different from each other.

Thermally equilibrium chemical system is a system in which deviations from equilibrium between internal (vibrational, rotational, electronic) and translational degrees of freedom of molecules are negligible.

Thermally nonequilibrium chemical system is a system in which molecular translational degrees of freedom have Maxwellian energy distribution, and internal (vibrational and/or rotational and/or electronic) degrees of freedom have a Boltzmann one, but the temperature(s) of internal degrees of freedom is (are) notably different from the translational temperature.

B. Components (species) of Chemically Reacting Mixture

Component of chemically reacting mixture is a group of particles that have identical elemental compositions and structures. In some problems of gas dynamics, the components (species) of a mixture can differ from each other by the energy state of particles, for example, groups of molecules with a certain vibrational quantum state can be viewed as different components (species), see description of model V.6 in Chapter 4, Vibrational Relaxation.

Initial substances (*reactants*) are components of a mixture entering into chemical transformations.

Reaction products are components of a mixture that are generated as a result of chemical transformations.

Intermediates are components (species) that are generated in some reactions and consumed in other reactions. Reactivity of intermediates varies, depending on chemical nature and conditions of the reaction process. Alongside with stable intermediates, as, for example, H_2 and CO generated during hydrocarbon combustion, or those less stable, as the aldehydes and hydrogen peroxide present in the same combustion reaction, extremely unstable (labile) intermediates, such as free atoms and radicals, are observed.

Labile intermediates are components of a mixture that are not present in a chemical system in quantities commeasurable with quantities of reactants and reaction products.

Inert substances are components of a mixture that are not consumed in chemical reactions.

Catalysts are components of a mixture that initiate or accelerate chemical reactions without being substantially consumed in the reaction.

Inhibitors are components of a mixture that, while having concentrations much lower than those of reactants, slow down the reaction.

C. Measurement Units of Chemical Composition

Chemical composition of a mixture indicates a proportion between the amounts of individual substances present in the mixture. Relative quantity of an ith component in a chemically reacting mixture are measured:

1. by the number of particles in 1 cm^3, 1 liter, 1 m^3, etc. (*number density* n_i [particles/unit volume]);
2. by the number of moles in 1 cm^3, 1 liter, 1 m^3, etc. (*molar–volume concentration* y_i [moles/unit volume]);

3. by the number of moles in 1 g, 1 kg, etc., of a reacting mixture (*molar–mass concentration* c_i [mole/unit mass]);
4. by the mass (grams, kilograms, etc.) in 1 cm^3, 1 liter, 1 m^3, etc. (*partial density* ρ_i [mass unit/unit volume]);
5. by the ratio of the number of moles of the component to the total number of moles of the mixture (*molar fraction*, or *volume fraction* ξ_i [dimensionless]);
6. by the ratio of the mass of component i to the total mass of matter in 1 cm^3 (*mass fraction*, or *relative density* α_i [dimensionless]); and/or
7. by the value of *molar–mass* concentration of an ith component c_i in the given region of a chemical system multiplied by the molar mass μ_∞ of a mixture in another region of this system (*normalized molar–mass concentration* γ_i [dimensionless]).

Relations between the different quantities expressing chemical composition of a mixture of chemical components i ($n = \sum_i n_i$, $\rho = \sum_i \rho_i$, $\mu = \rho \cdot N_\text{A}/n$):

$$\rho_i = m_i \cdot n_i$$

$$y_i = \frac{n_i}{N_\text{A}} = \frac{\rho_i}{\mu_i} = \xi_i \cdot \frac{n}{N_\text{A}} = \gamma_i \cdot \left(\frac{n_\infty}{N_\text{A}}\right) \cdot \left(\frac{\rho}{\rho_\infty}\right)$$

$$c_i = \frac{y_i}{\rho} = \frac{\rho_i}{\mu_i} \cdot \rho = \frac{\alpha_i}{\mu_i}$$

$$\alpha_i = \frac{\rho_i}{\rho} = m_i \cdot n_i \Big/ \sum_i m_i \cdot n_i = c_i \cdot \mu_i = y_i \cdot \frac{\mu_i}{\rho},$$

$$\xi_i = \frac{n_i}{n} = c_i \Big/ \sum_i c = \gamma_i \Big/ \sum_i \gamma_i = \alpha_i \Big/ \left[\mu_i \cdot \sum_i (\alpha_i/\mu_i)\right],$$

$$\gamma_i = c_i \cdot \mu_\infty = \xi_i \cdot \frac{\mu_\infty}{\mu} = \left(\frac{n_i}{n_\infty}\right) \cdot \left(\frac{\rho_\infty}{\rho}\right).$$

Molar weight (that is, the weight of one mole, or molecular weight) of a mixture is equal to

$$\mu = \sum_i \xi_i \cdot \mu_i = \sum_i \mu_i \cdot y_i \Big/ \sum_i y_i = \sum_i \mu_i \cdot y_i \Big/ \sum_i n_i$$

$$= \sum_i \gamma_i \cdot \mu_i \Big/ \sum_i \gamma_i = 1 \Big/ \sum_i c_i = 1 \Big/ \sum_i (a_i/\mu_i).$$

The values marked here by the subscript ∞ refer to those regions of the medium where they are assumed to be known, according to the problem formulation. The quantity γ_i is used for the description of chemically reacting mixtures in flowing media.

Partial pressure p_i is the pressure produced by a gas of component i in the volume occupied by the entire gas mixture at the given temperature. The partial pressure p_i is equal to $p_i = n_i kT$ for an ideal gas.

D. Nomenclature

$N_A = 6.0221 \times 10^{23}$ mole^{-1} is the Avogadro number (the number of particles in one mole of matter)

μ_i	molar weight (molecular weight) of a component i (g/mole)
m_i	mass of a particle of a component i (g)
ρ	gas density (g/cm^3)
n	number density of a gas mixture (cm^{-3})

Generalized nomenclature of particles as components of chemically reacting mixtures is presented in the introduction to Chapter 1 of the first volume in this series.

E. Comments

1. In this book, the usage of chemical kinetics terms is as close as possible to the recommendations of the International Union of Pure and Applied Chemistry (IUPAC) and the Committee on Data for Scientific Unions (CODATA). The measurement units are used in accordance with the current practice of chemical kinetics and computer simulation research. In some cases, the nomenclature varies from that used in other books.
2. At high pressures and low temperatures, the notion of fugacity (Refs. 1 and 2) is used instead of concentration for accurate evaluations of chemical composition.

F. Chemical Reactions

Elementary chemical process (*act*) is a chemical transformation of components of a system happening at one collision, when interacting particles of reactants transform directly to reaction products, without intermediates. Two or three particles interact in elementary chemical reaction because the probability of simultaneous collision of four and more particles in the gas phase is negligible.

Simple chemical reaction (*or single-step reaction*) is a set of identical elementary chemical processes that take place in the system under consideration. A simple reaction proceeds without catalyst, and is not slowed down by inhibitors. A simple chemical reaction can be a stage in a complex reaction.

Irreversible chemical reaction is a reaction that runs in only one direction under the given conditions.

Reversible chemical reaction is a reaction that runs in both direct (*forward reaction*) and reverse (*backward, or reverse, reaction*) directions.

Stage of complex chemical reaction (*chemical stage*) is one or more simple chemical reactions that constitute a part of a complex chemical process.

Elementary stage of complex chemical reaction is a simple reversible reaction that is a stage of a complex chemical process.

Complex chemical reaction is a set of simple chemical reactions interrelated with one another through their reactants or products. One of the features, and also a criterion, of complexity of a chemical reaction is the formation of intermediates during the reaction. Intermediates are products of one of the chemical stages and serve as reactants for other stages. The presence of intermediates during chemical reaction indicates its complexity, that is, a presence of multiple chemical stages.

Consecutive stages of complex chemical reaction are two or more stages of a complex chemical reaction in which a chemical component generated at one stage is a reactant for another stage.

Parallel stages of complex chemical reaction are two or more stages of a chemical reaction in which the same chemical species is a reactant for all stages.

Consecutive-parallel stages of complex chemical reaction are two or more stages of a complex chemical reaction, which are consecutive with respect to one of the components, and are parallel with respect to other components participating in these stages.

Thermal reaction proceeds under the impact of heat, when the reactants are activated only because of the thermal motion of molecules.

Endothermic reaction is a thermal reaction during which energy is consumed. For endothermic reaction, the numerical value of thermal effect of chemical reaction (the difference between the sum of enthalpies of reaction products and the sum of enthalpies of reactants) is positive, $\Delta H_r^0 > 0$ (see the details in Chapter 8, Thermodynamics of Gases and Plasmas, of this book).

Exothermic reaction is a thermal reaction during which energy is released. For exothermic reaction, the numerical value of thermal effect of chemical reaction (difference between the sum of enthalpies of reaction products and the sum of enthalpies of reactants) is negative, $\Delta H_r^0 < 0$ (see the details in Chapter 8, Thermodynamics of Gases and Plasmas, of this book).

Reaction space is an internal volume of a phase or an area of phase interface where chemical reaction occurs.

Homogeneous chemical reaction is a reaction that runs within one phase. (For example, any reaction in the bulk of a gas mixture). A reaction space is the liquid, gaseous, solid, or plasma phase of a system.

Heterogeneous chemical reaction is a reaction that runs at a phase interface. (For example, any reaction on a surface of solid catalyst).

Homogeneous–heterogeneous reaction is a reaction in which some stages are homogeneous, and others are heterogeneous (for example, reactions between gases, some stages of which occur on the walls of the reaction vessel). Homogeneous–heterogeneous reaction can be a complex, multistage process only.

Homo-phase chemical reaction is a process in which reactants, stable intermediates, and reaction products are within one phase.

Hetero-phase chemical reaction is a process in which reactants, stable intermediates, and reaction products form more than one phase.

The notions of homo- and hetero-phase reactions are independent from the notions of homo- and heterogeneous reactions. For example, neutralization of an acid by an alkali is a homogeneous homo-phase process, but hydrogenation of ethylene $C_2H_4 + H_2 \rightarrow C_2H_6$ in the presence of metallic nickel proceeds on the surface of the metal and represents homo-phase heterogeneous process. Oxidation of hydrocarbons in liquid phase by gaseous oxygen represents homogeneous hetero-phase process. Lime slaking $CaO + H_2O \rightarrow Ca(OH)_2$, when all three components form separate phases and the process proceeds at the interface between liquid water and solid CaO, is a heterogeneous hetero-phase process.

Homogeneous elementary reactions can be distinguished by the number of particles participating in the elementary chemical process.

Molecularity of a simple reaction characterizes the number of particles (atoms, molecules, ions, or free radicals) undergoing chemical transformation during one elementary act of the reaction:

- in *unimolecular reaction*, one particle undergoes transformation;
- in *bimolecular reaction*, two particles undergo transformation;
- in *termolecular reaction*, three particles undergo transformation.

Molecular formula (*equation*) of an elementary chemical act (simple chemical reaction) is as follows:

$$\sum X_i \text{ [reactants]} \rightarrow \sum X_i \text{ [products]}$$

where X denotes a particle of any atomic composition, and the arrow indicates a direction of the elementary act (from reactants to products).

For example:

$$N_2 + O_2 \rightarrow NO + NO, \qquad N_2 + N \rightarrow N + N + N$$

In a formula (equation) of an elementary act or simple reaction such as $AB + M \rightarrow A + B + M$, where M is any particle, it is implied that the density (or concentration) of M is equal to the sum of densities (or concentrations) of all (or of a certain part of) components of the mixture. Usage of stoichiometric coefficients is possible in the molecular formula (equation) of an elementary act or simple reaction (see Chemical Reaction Stoichiometry).

Mechanism of a simple chemical reaction is an actual set of processes descriptive of reallocation of the atoms, electrons, and bonds in reactants during their transformation into reaction products in one stage.

Mechanism of a complex chemical reaction is an actual set of coupled simple reactions or elementary acts of which a complex reaction consists.

Kinetic scheme of a complex chemical reaction is a model of the actual chemical process reflecting its basic kinetic features (dependence of the rate of chemical reaction on concentrations of reactants and temperature). Kinetic scheme includes a set of elementary stages together with the values of the corresponding kinetic parameters (reaction rate constants of forward and reverse reactions and orders of reactions).

Detailed (*comprehensive*) *kinetic scheme* of a chemical reaction is a model of the chemical process, including the complete set of all initial reactants, intermediates, and reaction products that are possible in the chemical system under consideration, and complete list of elementary chemical stages, in which each elementary stage and its relation with other stages of the overall chemical process is known and justified. Values of kinetic parameters of the comprehensive model (such as reaction rate constants of forward and reverse reactions and orders of reactions) are defined for each stage.

Reduced (*compact*) *kinetic scheme of a chemical reaction* is a simplified kinetic scheme of a chemical process that adequately describes time behavior of various quantities (such as temperature and concentrations of components).

Global kinetic scheme of a chemical reaction is an extremely simplified model of a chemical process that adequately describes the main transformations of initial reactants into reaction products with minimum number of intermediates and stages. For example, the global scheme of complete combustion of methane in oxygen is described by the following two main stages that couple five basic species: two initial reactants (CH_4, O_2), one intermediate (CO), and two products (CO_2, H_2O):

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$$
$$2CO + O_2 \rightarrow 2CO_2$$

The detailed kinetic scheme of this process includes about a hundred elementary stages and dozens of reactants (Refs. 3 and 4).

Relevant material can be found in Refs. 5–24.

II. Chemical Reaction Stoichiometry

The stoichiometry of chemical reactions determines quantitative relations between components of a chemical system. Being one of the forms of the matter conservation law, the stoichiometric relations allow one to establish some general features of a complex chemical process without data on the rates of elementary stages.

A. Basic Definitions

Stoichiometric coefficients ν_{ij} are numbers of particles of a component X_i ($i = 1, 2, \ldots, N$) participating in a reversible chemical reaction (jth elementary stage of a complex reaction); ν_{ij}^{+} are stoichiometric coefficients for reactants, and ν_{ij}^{-} are those for reaction product.

Stoichiometric equation of the jth elementary stage of a complex reaction is a phenomenological relation between the molar fractions of reactants (shown on the left side of stoichiometric equations) and those of reaction products (shown on the right side of stoichiometric equations), with the use of the stoichiometric coefficients. A stoichiometric equation may use a sign of equality or double arrows (an arrow indicates the direction of the reaction):

$$\sum_{i=1}^{N} \nu_{ij}^{+} \cdot \mathrm{X}_i = \sum_{i=1}^{N} \nu_{ij}^{-} \cdot \mathrm{X}_i; \qquad \sum_{i=1}^{N} \nu_{ij}^{+} \cdot \mathrm{X}_i \rightleftarrows \sum_{i=1}^{N} \nu_{ij}^{-} \cdot \mathrm{X}_i$$

Here, N is the number of components participating in a simple reversible reaction.

Homogeneous form of a stoichiometric equation is as follows:

$$\sum_{i=1}^{N} \nu_{ij} \cdot \mathrm{X}_i = 0$$

where ν_{ij} are the stoichiometric coefficients, negative for reactants and positive for reaction products.

B. Example

Stoichiometric equation: $N_2 + O_2 \rightleftarrows 2NO$

Homogeneous form of the equation: $-N_2 - O_2 + 2NO = 0$

Stoichiometric vector $\vec{\nu}_j$ is the well-ordered finite set of the stoichiometric coefficients $\nu_{ij} = \nu_{ij}^{-} - \nu_{ij}^{+}$ for the *j*th stage of a complex reaction:

$$\vec{\nu}_j = \begin{bmatrix} \nu_{1j} \\ \cdots \\ \nu_{Nj} \end{bmatrix}$$

Stoichiometric matrix $\bar{\Gamma}$ of a complex chemical reaction is a matrix, *j*th column of which is a stoichiometric vector of *j*th stage complex for given reaction:

$$\bar{\Gamma} = \|\nu_{ij}\| = \begin{bmatrix} \nu_{1j} & \cdots & \nu_{1S} \\ \cdots & \cdots & \cdots \\ \nu_{Nj} & \cdots & \nu_{NS} \end{bmatrix}, \qquad j = 1, 2, \ldots, S$$

Here, S is the number of stages of a complex chemical reaction.

Elements of the matrix $\bar{\Gamma}$ are positive and negative integers.

The element matrix $\bar{X}$ is a matrix with elements x_{ik} equal to the number of atoms of the *k*th chemical element in the molecule X_i:

$$\bar{X} = \|x_{ik}\| = \begin{bmatrix} x_{11} & \cdots & x_{1L} \\ \cdots & \cdots & \cdots \\ x_{N1} & \cdots & x_{NL} \end{bmatrix}$$

Here, L is the total number of chemical elements.

Vector of chemical components

$$\vec{X} = |X_i| = \begin{bmatrix} X_1 \\ X_2 \\ \cdots \\ X_N \end{bmatrix}$$

where X_i is the *i*th component of a reacting system.

Vector of molar masses of components

$$\vec{\mu} = |\mu_i| = \begin{bmatrix} \mu_1 \\ \mu_2 \\ \cdots \\ \mu_N \end{bmatrix}$$

Here, μ_i is the molar mass (the mass of one mole, or molecular weight) of the component X_i of the chemical reaction.

Vector of charges of components

$$\vec{z} = |z_i| = \begin{bmatrix} z_1 \\ z_2 \\ \dots \\ z_N \end{bmatrix}$$

Here, z_i is the electric charge of component of the chemical reaction.

Stoichiometric equation of a complex reaction is a phenomenological relation between reactants, intermediates and reaction products written in the form of a system of stoichiometric equations describing all the stages of the complex reaction:

$$\sum_{i=1}^{N} \nu_{i1}^{+} X_i = \sum_{i=1}^{N} \nu_{i1}^{-} X_i \quad \text{or} \quad \sum_{i=1}^{N} \nu_{i1}^{+} X_i \rightleftarrows \sum_{i=1}^{N} \nu_{i1}^{-} X_i$$

$$\sum_{i=1}^{N} \nu_{i2}^{+} X_i = \sum_{i=1}^{N} \nu_{i2}^{-} X_i \quad \text{or} \quad \sum_{i=1}^{N} \nu_{i2}^{+} X_i \rightleftarrows \sum_{i=1}^{N} \nu_{i2}^{-} X_i$$

$$\dots\dots$$

$$\sum_{i=1}^{N} \nu_{iS}^{+} X_i = \sum_{i=1}^{N} \nu_{iS}^{-} X_i \quad \text{or} \quad \sum_{i=1}^{N} \nu_{iS}^{+} X_i \rightleftarrows \sum_{i=1}^{N} \nu_{iS}^{-} X_i$$

where N is the number of components participating in the complex reaction that consists of S stages.

Global stoichiometric equation of a complex chemical reaction is a simplified stoichiometric equation of a process adequately reflecting transformation of initial substances to the reaction products, or most important stages of this transformation, without specifying separate stages. Both integer and fractional stoichiometric coefficients can be used in a global stoichiometric equation.

For example, the global stoichiometric equation of the water formation reaction can be written in the form $2H_2 + O_2 = 2H_2O$. Then the stoichiometric coefficients of hydrogen, oxygen and water will be as follows: $\nu_{H_2} = 2$, $\nu_{O_2} = 1$, $\nu_{H_2O} = 2$. If the equation of this reaction is written in the form $H_2 + 1/2O_2 = H_2O$, one would get another set of values of stoichiometric coefficients, namely $\nu_{H_2} = 1$, $\nu_{O_2} = 1/2$, $\nu_{H_2O} = 1$.

Application of the global stoichiometric equations is a matter of importance in a number of practical cases, when detailed kinetic mechanism of a complex chemical reaction cannot be included in the computational scheme of the gas dynamic problem under consideration because of:

a) hardware and software constraints: limitations of computer memory, processor speed, and/or other computer characteristics;
b) an absence of sufficiently developed and experimentally verified detailed kinetic schemes.

C. Example

The global stoichiometric equation of a complex reaction of ethylene chlorination can be written as $C_2H_4 + Cl_2 = C_2H_4Cl_2$. The mechanism of this complex reaction consists of six stages; therefore, the global stoichiometric equation can be replaced by six equations written for each reversible simple chemical reactions:

1. $Cl_2 = 2Cl$
2. $C_2H_4 + Cl_2 = C_2H_4Cl + Cl$
3. $C_2H_4 + Cl = C_2H_4Cl$
4. $C_2H_4Cl + Cl_2 = C_2H_4Cl_2 + Cl$
5. $C_2H_4Cl + C_2H_4Cl = C_4H_8Cl_2$
6. $C_2H_4Cl + Cl = C_2H_4Cl_2$

$$X_1 = Cl_2, \quad X_2 = C_2H_4, \quad X_3 = Cl, \quad X_4 = C_2H_4Cl,$$
$$X_5 = C_2H_4Cl_2, \quad X_6 = C_4H_8Cl_2$$

Chemical elements of the system are as follows:

$$E_1 = Cl, \quad E_2 = C, \quad E_3 = H$$

Correspondingly, the stoichiometric and element matrices have the forms:

$$\begin{array}{cc} & \text{reactions} \\ \text{components} & \bar{\Gamma} = \begin{bmatrix} -1 & -1 & 0 & -1 & 0 & 0 \\ 0 & -1 & -1 & 0 & 0 & 0 \\ 2 & 1 & -1 & 1 & 0 & -1 \\ 0 & 1 & 1 & -1 & -2 & -1 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix} \end{array}, \quad \begin{array}{cc} & \text{elements} \\ \text{components} & \bar{X} = \begin{bmatrix} 2 & 0 & 0 \\ 0 & 2 & 4 \\ 1 & 0 & 0 \\ 1 & 2 & 4 \\ 2 & 2 & 4 \\ 2 & 4 & 8 \end{bmatrix} \end{array}$$

D. Stoichiometric Conservation Laws

1. *conservation law for number of particles of chemical elements* in stages (orthogonality relation):
   - in matrix form: $\bar{\Gamma}^{T}\bar{X} = 0$, where $\bar{\Gamma}^{T}$ is the transposed matrix;
   - in coordinate form: $\sum_{i=1}^{N} \nu_{ij} \cdot x_{ik} = 0$.
2. *mass conservation law* in stages:
   - in matrix form: $\mu \cdot \bar{\Gamma} = 0$;
   - in coordinate form: $\sum_{i=1}^{N} \mu_i \cdot \nu_{ij} = 0$.
3. *charge conservation law* in stages:
   - in matrix form: $z \cdot \bar{\Gamma} = 0$;
   - in coordinate form: $\sum_{i=1}^{N} z_i \cdot \nu_{ij} = 0$.

Stoichiometric mixture is a mixture containing molar quantities of initial substances in proportion equal to the ratio of their stoichiometric coefficients. In a stoichiometric mixture, a practically complete transformation of the initial substances to reaction products is possible. An example is a hydrogen–oxygen mixture where one mole of oxygen is present for two moles of hydrogen,

$H_2:O_2 = 2:1$. In mixtures with a nonstoichiometric composition, the relative concentrations change nonproportionally to each other in the course of the reaction. The reaction terminates when the component that is deficient is consumed completely.

Stoichiometric concentrations are the initial concentrations of reactants in a stoichiometric mixture.

Stoichiometric order of the *j*th stage of a complex reaction in the forward and reverse directions is determined by the sum of the appropriate stoichiometric coefficients: $\nu_{fj} = \sum_{i=1}^{N} \nu_{ij}^{+}$, $\nu_{bj} = \sum_{i=1}^{N} \nu_{ij}^{-}$.

The stoichiometric order of the *j*th stage (simple reversible chemical reaction) of a complex reaction in the forward direction may not coincide with the stoichiometric order of the same reaction in the reverse direction, generally, $\nu_{fj} \neq \nu_{bj}$. For example, for a recombination of atoms producing a molecule AB, $A + B + M = AB + M$, the values ν_f and ν_b are, correspondingly, $\nu_f = 3$ and $\nu_b = 2$.

Key components are the components of chemical system that correlate with linearly independent lines of the stoichiometric matrix. The set of key components is invariant with respect to an addition of stoichiometric linearly dependent equations.

Relevant material can be found in Refs. 1, 11, 14, 23, and 25.

III. Chemical Reaction Rates

A. Rate of Simple Chemical Reaction

Rate of simple chemical reaction, w, is the number of elementary chemical acts occurring per unit time in unit volume for homogeneous reactions, or at unit surface for the heterogeneous reactions. Chemical reaction rate is expressed as a function of chemical composition of reagents and the thermodynamic parameters of system (for example, temperature).

Rate of formation (or consumption) of ith reagent of simple chemical reaction in closed system $R_i = \pm(\mathrm{d}N_i/\Omega \mathrm{d}t)$ is an increase (sign "+") or decrease (sign "−") of quantity of *i*th reagent, expressed in moles ($\mathrm{d}N_i$), per unit time in unit reaction space (Ω). For homogeneous reactions, $\Omega = V$, where V is the volume of reacting system; for heterogeneous reactions, $\Omega = S$, where S is the surface area of phase interface at which the $\tilde{\nu}_i$ reaction takes place.

In a closed system, a change in the quantity of a substance with time occurs because of chemical reactions only. The changes in quantities of each reagent are not independent of each other, but are related by the stoichiometric proportions. A quantity of substance reacting per unit time is proportional to the magnitude of reaction space, that is, to the volume of a phase or to the surface area of phase interface. For example, for reaction $\sum_{i=1}^{N} \nu_i^{+} \cdot X_i = \sum_{i=1}^{N} \nu_i^{-} \cdot X_i$ the following relation holds true:

$$(\nu_1^{+})^{-1}\mathrm{d}N_1 = (\nu_2^{+})^{-1}\mathrm{d}N_2 = \cdots = (\nu_N^{-})^{-1}\mathrm{d}N_N = \mathrm{d}\xi$$

where $\mathrm{d}\xi$ is the differential reaction run, as a number of elementary chemical acts performed during time period $\mathrm{d}t$, and ν_i^{+} и ν_k^{-} are the stoichiometric coefficients of the initial substances and the reaction products, respectively (the rule for algebraic signs of the stoichiometric coefficients in the homogeneous form of stoichiometric equation is explained above).

Chemical reaction rate w and the rates of consumption (or formation) of reagents R_i in closed systems are related by the following condition:

$$w = -\frac{1}{\nu_1^+} \cdot \frac{dN_1}{\Omega dt} = -\frac{1}{\nu_2^+} \cdot \frac{dN_2}{\Omega dt} = \cdots = \frac{1}{\nu_1^-} \cdot \frac{dN_1}{\Omega dt} = \frac{1}{\nu_n^-} \cdot \frac{dN_n}{\Omega dt} = \cdots = \frac{d\xi}{\Omega dt}$$

Reaction rate value is always positive.

In a particular case when the magnitude of a reaction space does not change during the reaction ($\Omega = \text{const}$), the reaction rate is determined by the formula:

$$w = -\frac{1}{\nu_i^+} \cdot \frac{dy_i}{dt} = \cdots = \frac{1}{\nu_k^-} \cdot \frac{dy_k}{dt}$$

where $y_i = N_i/\Omega$ is the molar–volume or molar–surface concentration of the initial ith reagent, and $y_k = N_k/\Omega$ is the molar–volume or molar–surface concentration of the kth product of chemical reaction.

Rate of simple chemical reaction in an open system is a change of reacting substance quantity with time because of both chemical reactions and the matter exchange with environment. Definition of a chemical reaction rate in an open system depends on the open system model (see the section Models of Chemical Reactors).

Kinetic function is a function that determines the magnitude of chemical reaction rate depending on component concentrations, temperature, and, possibly, other parameters of the reacting medium.

Kinetic equation of reaction is an equation that links chemical reaction rate (left-hand side of equation) and the kinetic function (right-hand side of equation).

Kinetic order of the reaction with respect to a given reactant is the exponent with which the reactant concentration (for example, y_i) appears in the kinetic equation for reaction rate written in polynomial form $w = k \cdot y_i^{\tilde{\nu}_i} \cdot y_j^{\tilde{\nu}_j}$. For simple reactions, the kinetic order of reaction with respect to a given reactant is equal to the number of reactant particles participating in an elementary act, and it coincides with the reaction molecularity. For example, for reaction $2NO + Cl_2 \rightarrow 2NOCl$, the kinetic order of reaction with respect to Cl_2 is equal to 1, and with respect to NO it is equal to 2. Note that polynomial representation of kinetic function is not applicable for some heterogeneous reactions.

Overall kinetic order of reaction $\tilde{\nu} = \sum_{i=1}^{N} \tilde{\nu}_i$ is the sum of kinetic orders of all reactants that are included in the kinetic equation for reaction rate. For a simple reaction, the overall kinetic order of reaction is equal to the number of all particles participating in the elementary act. It is always a positive integer number. For example, for reaction $2NO + Cl_2 \rightarrow 2NOCl$, the overall order of reaction is equal to 3. Kinetic order of a complex chemical reaction with respect to ith reacting component is not always equal to its stoichiometric coefficient in the chemical equation of the complex reaction. The necessary condition for the coincidence of the stoichiometric order of reaction, and the overall kinetic order of the reaction is that the chemical reaction is simple. Overall kinetic order of reaction can be integer, fractional, and negative (for autocatalytic and chain auto-initiated reactions, see details in Refs. 5 and 9), and can vary with initial conditions. Kinetic order of a complex reaction is determined by the mechanism of the chemical process. Discrepancy between experimentally observed kinetic orders with respect to components and the appropriate stoichiometric coefficients is evidence that the chemical reaction is complex.

Kinetic curve is a plot of concentration of reacting substance (initial reactant or reaction product) versus time.

Equation of kinetic curve is a mathematical expression describing a reacting substance concentration variation with time, for example, kinetic curve expressed in analytical form.

Law of mass action (Guldberg and Waage law): the rate of a simple chemical reaction in one direction at any moment of time is directly proportional to the product of the current concentrations of the reacting substances taken with the exponents of power equal to the stoichiometric coefficients. The coefficient of proportionality in the expression for reaction rate is called the *reaction rate constant* or *specific reaction rate*, or the rate for unit concentration of each of the reacting substances.

Kinetically ideal chemical system is a system the kinetic functions of which obey the law of mass action.

Thermodynamic analysis of equations of chemical kinetics is discussed in Refs. 23 and 24.

B. Units of Measurement of Chemical Reaction Rates

The rate of a homogeneous chemical reaction is measured by:

a) the number of moles (quantity of matter) reacting in unit volume (1 m^3, 1 liter, 1 cm^3, etc.) per unit time (such as second, or hour), or
b) the number of particles reacting in unit volume per unit time.

The coefficients of conversion between the units:

$$1\,\mathrm{mol/(l \cdot s)} = 10^{-3}\,\mathrm{mol/(cm^3 \cdot s)} = 6.02 \times 10^{20}\,\mathrm{particles/(cm^3 \cdot s)}.$$

C. Kinetic Model of Simple Irreversible Chemical Reaction (Mass Action Law) (C.1)

1. *Purpose of the Model*

The model aims at the evaluation of the rate of a simple irreversible chemical reaction.

2. *Assumptions*

a) An ideal chemically reacting gas is considered.
b) The reaction does not distort the equilibrium (Maxwell–Boltzmann) energy distribution over translational and rotational degrees of freedom of the reacting particles.
c) The reactants are uniformly distributed over the reactor volume.
d) Changes in reactant concentration do not affect the properties of medium.
e) The chemical system is assumed to be kinetically ideal.
f) The stoichiometric coefficients and the reaction rate constant are known.

3. *Restrictions*

a) The reaction time scale is much longer than the time of relaxation to equilibrium in the translational and rotational degrees of freedom of the reactants.
b) The reaction time is much shorter than the time for mass transport processes such as diffusion and convection.

4. *Rate of a Simple Irreversible Chemical Reaction*

$$\sum_{i=1}^{N} \nu_i^+ \cdot \mathrm{X}_i \rightarrow \sum_{i=1}^{N} \nu_i^- \cdot \mathrm{X}_i$$

- for molar–volume concentrations of components:

$$w = k_f \prod_{i=1}^{N} y_i^{\nu_i^+}$$

- for number densities of components:

$$w = k_f \prod_{i=1}^{N} \left(\frac{n_i}{N_\mathrm{A}}\right)^{\nu_i^+} = k_f \left(\frac{1}{N_\mathrm{A}}\right)^{\sum_i \nu_i^+} \prod_{i=1}^{N} (n_i)^{\nu_i^+}$$

- for molar–mass concentrations of components:

$$w = k_f \prod_{i=1}^{N} (c_i \rho)^{\nu_i^+} = k_f (\rho)^{\sum_i \nu_i^+} \prod_{i=1}^{N} (c_i)^{\nu_i^+}$$

5. *Nomenclature*

k_f	irreversible reaction rate constant
ν_i^+	stoichiometric coefficient for a reagent X_i
y_i, n_i, c_i	concentration of component i in different units of measurements (see above)
N	number of the reacting components

6. *Description of Coefficients and Parameters*

The chemical reaction rate constant k is a function of temperature, and for some types of the reactions (for example, for unimolecular decomposition at high pressures), it is also a function of pressure. For liquid-phase reactions, k can depend on the medium (solvent). The simplest and commonly used dependence of reaction rate constant on temperature is given by the *Arrhenius formula* $k_f(T) = \mathrm{A}\exp(-E_a/RT)$ and its generalization $k_f(T) = \mathrm{A}'T^n \exp(-E_a/RT)$, $k_f(T) = A''(T/298)^n \exp(-E_a/RT)$, where A, A′, and A″ are constant pre-exponential factors, n is the dimensionless exponent in the temperature cofactor of the pre-exponential factor, E_a is the activation energy of an elementary reaction, and R is the universal gas constant (see details in the description of model I-C.1 in the first volume). According to the Arrhenius formula, temperature dependence $k(T)$ is a straight line in coordinates $\log k$, $1/T$ (the Arrhenius coordinates); the line slope is determined by the activation energy. The generalized Arrhenius formula takes into account more complex dependence of reaction rate constant on temperature. Numerical values of the quantities A, A′, A″, n, E_a are evaluated empirically or with quantum chemistry calculations. The units of pre-exponential factor are determined by the kinetic order of reaction and are dependent on units of measurement of concentration. For example, for concentrations expressed in the traditional for chemical kinetics units mol/cm^3, the units of reaction rate constant k_f are the following:

s^{-1}	for reactions of first order with respect to substance i $$\frac{dy_i}{dt} = -k_f y_i,$$
$cm^3/(mol \cdot s)$	for reactions of second order with respect to substance i $$\frac{dy_i}{dt} = -k_f y_i^2,$$
$cm^6/(mol^2 \cdot s)$	for the reactions of third order with respect to substance i $$\frac{dy_i}{dt} = -k_f y_i^3.$$

Model I-C.1 in the first volume is devoted to the calculation of the rate of a simple chemical reaction in a thermally equilibrium gas using Arrhenius formula; the activation energy E_a can be evaluated with models I-C.2–C.4; the pre-exponential factor can be evaluated using models I-C.5–C.8. For unimolecular decomposition reactions, the rate constant k_f is dependent on pressure (see descriptions of the models I-C.15, I-C.16 and Refs. 26 and 27). Results of experimental and theoretical work on estimation of the numerical values of reaction rate constants are summarized in monographs, handbooks, and reviews (see, for example Refs. 6 and 28–34), and publications in the Journal of Physical and Chemical Reference Data).

In a thermally nonequilibrium gas that is characterized by an absence of equilibrium between the translational and vibrational degrees of freedom of the reacting molecules and is described by two different temperatures, translational T and vibrational T_v, the dependence of a reaction rate constant on temperature is determined by the expression

$$k(T, T_v) = Z(T, T_v) \cdot k^0(T)$$

where $Z(T, T_v)$ is a nonequilibrium factor, $k^0(T)$ is the thermally equilibrium reaction rate constant. Models I-C.19–I-C.28 in the first volume are devoted to calculations of the nonequilibrium factor.

7. *Features of the Model*

For simple reactions of different orders, running at constant temperature in constant-volume gas, expressions for the reaction rate w, the current concentrations of species (for example, molar–volume concentration y_i), and the half-life time $\tau_{1/2}$ (the time during which half of the initial quantity of reactant is converted) have the following forms (y_{X0} is the initial concentration of component X):

Reaction order reaction formula	First $X \rightarrow$ products	Second $X + Y \rightarrow$ products
w	$-\frac{dy_X}{dt} = k \cdot y_X$	$-\frac{dy_X}{dt} = -\frac{dy_Y}{dt} = k \cdot y_X \cdot y_Y$
y_i	$y_X = y_{X0} \exp(-kt)$	$y_X = y_{X0} \frac{(y_{Y0} - y_{X0}) \exp[-(y_{Y0} - y_{X0})kt]}{y_{Y0} - y_{X0} \exp[-(y_{Y0} - y_{X0})kt]}$ $y_Y = y_{Y0} \frac{y_{Y0} - y_{X0}}{y_{Y0} - y_{X0} \exp[-(y_{Y0} - y_{X0})kt]}$
$\tau_{1/2}$	$\ln 2/k$	see $\tau_{1/2}$ for reaction $X + X \rightarrow$ products

Reaction order reaction formula	Second $X + X \rightarrow$ products	Third* $X + Y + Z \rightarrow$ products (at $y_X = y_Y = y_Z = y$) $X + 2Y \rightarrow$ products (at $y_Y = y$, $y_X = y/2$)
w	$-\frac{dy_X}{dt} = 2ky_X^2$	$-\frac{dy_X}{dt} = -\frac{dy_Y}{2dt} = ky_X y_Y^2$
y_i	$y_X = \frac{y_{X0}}{1 + 2y_{X0}kt}$	$y = y_0(1 + 2y_0^2 kt)^{-1/2}$
$\tau_{1/2}$	$2/ky_{X0}$	$3/2ky_0^2$

*In the general case, with arbitrary ratio of the concentrations y_X, y_Y, y_Z, simple analytical expressions for y_i cannot be derived.

8. *Example*

The reaction of thermal dissociation of molecular oxygen can be written as (the arrow indicates the direction of the reaction):

$$O_2 + M \rightarrow 2O + M$$

where M is an arbitrary particle. If particles M of all species have the same effectiveness of reaction in their collisions with O_2 molecules, then the reaction rate:

$$w = k_f y_{O_2} y_M$$

where y_{O_2} and y_M are the concentrations of O_2 and particles M, respectively.

9. *Comment*

The mass action law of Guldberg and Waage is the basis of the theory of formal kinetics of chemical reactions. As a part of chemical kinetics, formal kinetics is devoted to studies of reaction rate dependence on the reactant concentrations. The objectives of formal kinetics are to establish the mechanisms of complex chemical reactions and to ascertain quantitative relations between reaction rates and reagent concentrations in the form of a set of differential and/or algebraic equations.

Relevant material can be found in Refs. 6, 8, and 9.

D. Kinetic Model of Simple Reversible Chemical Reaction (C.2)

1. *Purpose of the Model*

The model aims at evaluation of the rate of a simple reversible chemical reaction (or *j*th stage of a complex chemical reaction) w_j.

2. *Assumptions*

a) See assumptions a–f in the description of model C.1.
b) The simple reversible reaction can be an elementary stage in a complex chemical reaction.

3. *Restrictions*

See the appropriate section in the description of model C.1.

4. *Rate of a Simple Reversible Chemical Reaction*

$$\sum_{i=1}^{N} \nu_{ij}^{+} \mathrm{X}_i \rightleftarrows \sum_{i=1}^{N} \nu_{ij}^{-} \mathrm{X}_i \qquad \text{or} \qquad \sum_{i=1}^{N} \nu_{ij}^{+} \mathrm{X}_i = \sum_{i=1}^{N} \nu_{ij}^{-} \mathrm{X}_i$$

- for molar–volume concentrations of components:

$$w_j = w_j^{+} - w_j^{-} = k_{fj} \prod_{i=1}^{N} y_i^{\nu_{ij}^{+}} - k_{bj} \prod_{i=1}^{N} y_i^{\nu_{ij}^{-}}$$

- for number densities of components:

$$w_j = k_{fj} \left(\frac{1}{N_{\mathrm{A}}}\right)^{\sum_i \nu_{ij}^{+}} \prod_{i=1}^{N} (n_i)^{\nu_{ij}^{+}} - k_{bj} \left(\frac{1}{N_{\mathrm{A}}}\right)^{\sum_i \nu_{ij}^{-}} \prod_{i=1}^{N} (n_i)^{\nu_{ij}^{-}}$$

- for molar–mass concentrations of components:

$$w_j = k_{fj} (\rho)^{\sum_i \nu_{ij}^{+}} \prod_{i=1}^{N} (c_i)^{\nu_{ij}^{+}} - k_{bj} (\rho)^{\sum_i \nu_{ij}^{-}} \prod_{i=1}^{N} (c_i)^{\nu_{ij}^{-}}$$

5. *Nomenclature*

k_{fj}, k_{bj}	reaction rate constants in the forward and reverse directions, respectively
ν_{ij}^+, ν_{ij}^-	stoichiometric coefficients for the initial reactants and reaction products
y_i	molar–volume concentration of component i
n_i	number density of substance i
c_i	molar–mass concentration of species i
N	number of the substances participating in reaction

6. *Description of Coefficients and Parameters*

See appropriate subsection in the description of model C.1.

7. *Features of the Model*

In the early stages, when mostly the initial reactants are present in the system, the reaction runs mainly in the forward direction. With accumulation of the reaction products, the rate of a simple reversible reaction (or jth elementary stage of a complex chemical reaction) slows down, and at the *chemical equilibrium state*, the reaction rate becomes zero because the rate of forward reaction is equal to the rate of the reverse ones (*kinetic condition for chemical equilibrium*):

$$w_{fj}^0 = w_{bj}^0 \qquad \text{or} \qquad k_{fj}\prod_{i=1}^{N}\bar{y}_i^{\nu_{ij}^+} = k_{bj}\prod_{i=1}^{N}\bar{y}_i^{\nu_{ij}^-}$$

where the equilibrium values are marked by the top bars and superscript 0. From this, the relation between the rates of forward and reverse reactions, referred to as the *detailed equilibrium* (*balance*) *principle* (Refs. 1 and 5), follows:

$$K_{cj}(T) = \frac{k_{fj}(T)}{k_{bj}(T)} = \frac{\prod_{i=1}^{N}\bar{y}_i^{\nu_{ij}^-}}{\prod_{i=1}^{N}\bar{y}_i^{\nu_{ij}^+}}$$

The quantity $K_{cj}(T)$ is called the *concentration equilibrium constant* for reaction j. The equilibrium constant, expressed in terms of partial pressures p_i of the components, has the following form:

$$K_{pj}(T) = \frac{\prod_{i=1}^{N}\bar{p}_i^{\nu_{ij}^-}}{\prod_{i=1}^{N}\bar{p}_i^{\nu_{ij}^+}} = (RT)^{-\Delta\nu_{ij}}\cdot\frac{\prod_{i=1}^{N}\bar{y}_i^{\nu_{ij}^-}}{\prod_{i=1}^{N}\bar{y}_i^{\nu_{ij}^+}} = (RT)^{-\Delta\nu_{ij}}\cdot K_{cj}(T)$$

where $\Delta\nu_{ij} = \sum\nu_{ij}^+ - \sum\nu_{ij}^-$ (see also Chapter 8, Thermodynamics of Gases and Plasmas in this volume). Numerical value of the equilibrium constant depends on temperature.

In thermally nonequilibrium gases, the equilibrium constant $K_{cj}(T)$ is determined by the relation $K_{cj} = K_{fj}^0(T)/k_{bj}^0(T)$, where $k_{fj}^0(T)$ and $k_{bj}^0(T)$ are the thermally equilibrium rate constants (see description of model C.1).

8. *Example*

The reversible reaction of the thermal dissociation–recombination of molecular oxygen can be written as (the arrows indicate the possible directions of the reaction)

$$O_2 + M \rightleftarrows 2O + M$$

where M is an arbitrary particle. If particles M of all species have the same effectiveness of reaction in their collisions with O_2 molecules, then the reaction rate:

$$w = k^+ \cdot y_{O_2} \cdot y_M - k^- \cdot y_O^2 \cdot y_M$$

where y_{O_2}, y_O and y_M are the concentrations of O_2, O, and particles M, respectively.

9. *Comment*

Equilibrium constant for a reversible reaction is of interest to chemical kinetics as a quantity that defines the limit for variations of the concentrations of reacting components under the given conditions. Also, based on known values of equilibrium constant and the forward reaction rate constant, the rate constant of the reverse reaction can be calculated.

Relevant material can be found in Refs. 6, 8, and 9.

IV. Rates of Complex Chemical Reactions

Rate of complex chemical reaction $\vec{w}$ is a set of rates of the chemical stages that determine the change of composition of chemically reacting system per unit time in a unit of reaction space in accordance with the kinetic scheme of the complex reaction under consideration. The magnitude of the complex reaction rate is defined by the vector of rates that characterize the separate elementary chemical stages ($j = 1, 2, \dots, S$):

$$\vec{w} = |w_i| = \begin{bmatrix} w_1 \\ w_2 \\ \dots \\ w_S \end{bmatrix}$$

Principle of kinetic independence of simple reactions is defined as following. The separate simple reactions that constitute a complex chemical reaction proceed independently from each other, so that the kinetic functions (that is, the simple reaction rates as functions of concentrations and temperature) are not changed when the other reactions run in the given system. The principle of independence of complex reaction stages is justified when the separate reactions, expressed in the form of stoichiometric equations, are consistent with the elementary acts of chemical conversion, that is, the stoichiometric scheme represents the actual mechanism of the complex reaction correctly. The principle of independence of simple reactions is applicable to the principal types of complex reactions: parallel (concurrent), consecutive, and chain ones. For those complex reactions in which some simple reactions substantially affect the others, as, for example, in conjugated reactions, the principle of independence is not applicable. The principle of independence of complex reaction stages is only satisfied in thermally equilibrium gas, when the Maxwell–Boltzmann distribution takes place in all degrees of freedom. Under extreme conditions and in fast processes, such as those in shock waves and hypersonic flows, electric discharges, combustion and explosions, in gas lasers, and in gases subjected to a laser or some other powerful radiation, a substantial deviation from thermal equilibrium is possible. This nonequilibrium results in acceleration or retardation of some chemical reactions. For example, super-thermal vibrational excitation, when the vibrational temperature T_v is higher then the translational temperature T, accelerates endothermic reactions substantially (sometimes, by orders of magnitude). The principle of independence of elementary stages is violated under nonequilibrium conditions. The description of models of thermally nonequilibrium chemical reactions can be found in I-C.19–I-C.28.

Kinetic vector-function of complex chemical reaction is a vector of the kinetic functions for separate elementary stages of complex chemical reaction

$$\vec{f}(\vec{y}, T) = |f(y_1, y_2, \ldots, y_N, T)_i| = \begin{bmatrix} f_1(y_1, y_2 \ldots, y_N, T) \\ f_2(y_1, y_2, \ldots, y_N, T) \\ \ldots \\ f_S(y_1, y_2, \ldots, y_N, T) \end{bmatrix}$$

A representation of kinetic function of a complex chemical reaction as a vector is valid if the principle of independence of elementary stages of the complex reaction is satisfied.

A. Kinetic Model of Complex Chemical Reactions (C.3)

1. *Purpose of the Model*

The model aims at evaluation of a complex (multistep) chemical reaction rate.

2. *Assumptions*

a) See assumptions a and b in the description of model C.1.
b) It is assumed that the principle of independence of stages of complex chemical reaction is obeyed.
c) The kinetic scheme of a complex chemical reaction, the stoichiometric coefficients, and the rate constants for the forward and backward directions of elementary stages are known.

3. *Restrictions*

See appropriate restrictions in the description of model C.1.

4. *Rate of Change of the* i*th Component Concentration Because of Complex Chemical Reaction*

- in coordinate form:

$$R_i = \sum_{j=1}^{S} (\nu_{ij}^{-} - \nu_{ij}^{+}) w_j = \sum_{j=1}^{S} (\nu_{ij}^{-} - \nu_{ij}^{+}) \cdot k_{fj}^{+} \prod_{k=1}^{N} y_k^{\nu_{kj}^{+}}$$

$$+ \sum_{j=1}^{S} (\nu_{ij}^{+} - \nu_{ij}^{-}) \cdot k_{bj}^{-} \prod_{k=1}^{N} y_k^{\nu_{kj}^{-}} \quad i = 1, 2, \ldots, N, \; j = 1, 2, \ldots, S, \; w_j$$

(see the description of model C.2)

- in matrix form: $\vec{R} = \bar{\Gamma} \cdot \vec{w}$.

5. *Nomenclature*

w_i	rate of change of the ith component concentration
i, j	subscripts referring to reacting components and stages of complex chemical reaction, respectively
N, S	number of reacting components and stages of complex chemical reaction, respectively
k_{fj}, k_{bj}	reaction rate constants in forward and backward directions, respectively
$\nu_{ij}^{+}, \nu_{ij}^{-}$	stoichiometric coefficients for the reactants and products of reactions for stages of complex chemical reaction under consideration
w_j	rate of the jth stage of complex chemical reaction

Nomenclature of other symbols is shown in the appropriate subsection in the description of model C.2.

6. *Description of Coefficients and Parameters*

See the appropriate section of the model C.1 description.

7. *Features of the Model*

As time goes on, the reacting system comes to chemical equilibrium state, when the concentration change rates for all components become zero in closed systems, and become equal to reactant supply rate for open systems.

8. *Example*

In the combustion of hydrocarbon fuels, partial oxidation of nitrogen occurs, and the combustion products can contain substantial amounts of nitrogen monoxide NO. The mechanism of NO formation is determined by the stoichiometric equations:

1. $N_2 + O = NO + N$
2. $O_2 + N = NO + O$
3. $OH + N = NO + H$

which constitute the extended Zel'dovich mechanism. The rate of NO formation:

$$\begin{aligned}
R_{NO} &= w_1 + w_2 + w_3 \\
w_1 &= k_{f1} y_{N_2} y_O - k_{b1} y_{NO} y_N \\
w_2 &= k_{f2} y_{O_2} y_N - k_{b2} y_{NO} y_O \\
w_3 &= k_{f3} y_N y_{OH} - k_{b3} y_{NO} y_H
\end{aligned}$$

9. Comment

The rate of change of concentration vector $\vec{y} = |y_i|$ is defined as the vector $d\vec{y}/dt$. In closed system with constant volume, where concentration changes occur because of chemical reactions only, the kinetic equation is written as $d\vec{y}/dt = \bar{\Gamma} \cdot \vec{w}$, where $\bar{\Gamma}$ is the stoichiometric matrix (see Chemical Reaction Stoichiometry). The kinetic equation for closed systems with variable volume is presented in model C.9. Kinetic equations for open systems, where concentration change rate is dependent on reactant flow parameters, are presented in models C.10–C.11.

Relevant material can be found in Refs. 5–10 and 13–22.

V. Empirical Correlations for Overall Rates of Complex Chemical Reactions

Overall rate of complex chemical reaction is the rate of conversion of the initial reactants into reaction products, attributed to the slowest stage (either of the reactants consumption or products formation) of a complex chemical reaction. For the majority of complex chemical reactions, *a priori* theoretical predictions of the overall rate cannot be made because of insufficient knowledge of kinetic mechanisms and of the rate constants for elementary stages. In those cases, empirical correlations are widely used for practically important chemical reactions. The correlations are inferred from specific experiments.

Example

For processes of hydrocarbon (fuel) combustion in oxygen (oxidizer) according to global stoichiometric equation

$$C_nH_mO_r + \left(n + \frac{m}{4} - \frac{r}{2}\right)O_2 \rightarrow nCO_2 + \left(\frac{m}{2}\right)H_2O$$

the overall rate of combustion are approximated by the formula

$$\bar{R} = \bar{A}\exp\left(-\frac{\bar{E}}{RT}\right) \cdot N_1^{\nu_1} \cdot$$

where

N_1, ν_1	concentration and kinetic parameter for fuel (hydrocarbon $C_nH_mO_r$)
N_2, ν_2	concentration and kinetic parameter for oxidizer (oxygen O_2)
$\bar{A}$	effective (empiric) per-exponential factor
$\bar{E}$	effective (empiric) activation energy
n, m, r	numbers of atoms of carbon, hydrogen and oxygen in hydrocarbon molecule accordingly
R	universal gas constant

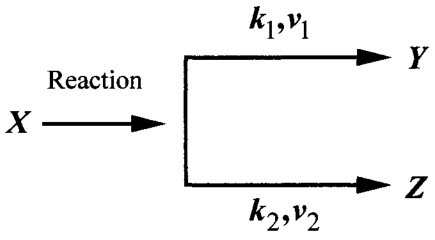
The numerical values for $\bar{A}$, $\bar{E}$, ν_1 and ν_2 are shown in the following table (according to the data from Refs. 4, 35 and 36); the units of measurement: $\bar{A}$, $(\mathrm{cm}^3/\mathrm{mol})^{\nu_1+\nu_2-1} \cdot \mathrm{s}^{-1}$; $\bar{E}$, kcal/mol; N_1, N_2, mol/cm^3.

Fuel	$\bar{A}$	$\bar{E}$	ν_1	ν_2	Fuel	$\bar{A}$	$\bar{E}$	ν_1	ν_2
CH_4	1.3×10^8	48.4	−0.3	1.3	C_9H_{20}	4.2×10^{11}	30.0	0.25	1.5
CH_4	8.3×10^5	30.0	−0.3	1.3	$C_{10}H_{22}$	3.8×10^{11}	30.0	0.25	1.5
C_2H_6	1.1×10^{12}	30.0	0.1	1.65	CH_3OH	3.2×10^{12}	30.0	0.25	1.5
C_3H_8	8.6×10^{12}	30.0	0.1	1.65	C_2H_5OH	1.5×10^{12}	30.0	0.15	1.6
C_4H_{10}	7.4×10^{11}	30.0	0.15	1.6	C_6H_6	2.0×10^{11}	30.0	−0.1	1.85
C_5H_{12}	6.4×10^{11}	30.0	0.25	1.5	C_7H_8	1.6×10^{11}	30.0	−0.1	1.85
C_6H_{14}	5.7×10^{11}	30.0	0.25	1.5	C_2H_4	2.0×10^{12}	30.0	0.1	1.65
C_7H_{16}	5.1×10^{11}	30.0	0.25	1.5	C_3H_6	4.2×10^{11}	30.0	−0.1	1.85
C_8H_{18}	4.6×10^{11}	30.0	0.25	1.5	C_2H_2	6.5×10^{12}	30.0	0.5	1.25
C_8H_{18}	7.2×10^{11}	40.0	0.25	1.5					

VI. Kinetic Behavior of Complex Reactions

A. Parallel Reactions

Parallel reactions are two or more stages of a complex chemical reaction, when the same component participates in all the stages as an initial reactant.



k_1, k_2	rate constants of the stages 1 and 2
ν_1, ν_2	stoichiometric coefficients of reagents in the stages 1 and 2

Kinetic equations:

$$-\frac{dn_X}{dt} = k_1 n_X^{\nu_1} + k_2 n_X^{\nu_2}, \qquad \frac{dn_Y}{dt} = k_1 n_X^{\nu_1}, \qquad \frac{dn_X}{dt} = k_2 n_X^{\nu_2}$$

Particular solutions for the initial conditions $n_X = a_0$, $n_Y = n_Z = 0$ at $t = 0$

1. $\nu_1 = \nu_2 = \nu$,
   for $\nu = 1$: $n_X = a_0 e^{-(k_1+k_2)\cdot t}$,
   for $\nu \neq 1$:

$$\frac{1}{n_X^{\nu-1}} - \frac{1}{a_0^{\nu-1}} = (k_1 + k_2)\cdot a_0^{\nu-1}\cdot t, \qquad \frac{n_Y}{n_Z} = \frac{k_1}{k_2}, \qquad n_Y = \frac{k_1}{k_1+k_2}(n_X - a_0)$$

2. $\nu_1 = 0$, $\nu_2 = 1$ and $\delta = k_1/(k_2 a_0)$:

$$n_X = a_0[(\delta + 1)e^{-k_2 t} - \delta], \qquad n_Y = a_0 \delta \ln\left(\frac{1+\delta}{\delta + n_X}\right)$$

3. $\nu_1 = 1$, $\nu_2 = 2$, and $\delta = k_1/(k + 2a_0)$:

$$\ln\left[\frac{\delta + (n_X/a_0)}{(n_X/a_0)(1+\delta)}\right] = a_0 k_2 t \delta$$

4. $\nu_1 = 1$, $\nu_2 - 3$, and $\beta = (k_1/k_2)^{1/2}$:

$$n_Y = \beta \cdot [\arctan\,(a_0/\beta) - \arctan\,(n_X/\beta)]$$

B. Consecutive Reactions

Consecutive reactions are two or more stages of a complex chemical reaction, when a component that is formed in one stage is an initial reactant for another stage.

Reaction $X \xrightarrow{k_1,\,\nu_1} Y \xrightarrow{k_2,\,\nu_2} Z$, $k_1, k_2; \nu_1, \nu_2$ (see above)

Kinetic equations:

$$-\frac{dn_X}{dt} = k_1 n_X^{\nu_1}, \qquad \frac{dn_Y}{dt} = k_1 n_X^{\nu_1} - k_2 n_X^{\nu_2}, \qquad \frac{dn_Z}{dt} = k_2 n_Y^{\nu_2}$$

1. $\nu_1 = \nu_2 = 1$, $X \xrightarrow{k_1} Y$; $Y \xrightarrow{k_2} Z$
   Solutions for the initial conditions $n_X = a_0$, $n_Y = n_Z = 0$ at $t = 0$:

$$n_X = a_0 e^{-k_1 t}, \qquad n_Y = \frac{k_1 a_0}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}),$$

$$n_Z = a_0\left(1 - \frac{k_2}{k_2 - k_1}e^{-k_1 t} + \frac{k_1}{k_2 - k_1}e^{-k_2 t}\right)$$

Here, n_X exponentially decays, n_Z monotonically increases, tending to a_0, and n_Y has a maximum:

$$n_{Y\max} = a_0\left(\frac{k_2}{k_1}\right)^{-k_2/(k_2-k_1)} \qquad \text{for } t_{\max} = \frac{\ln(k_2/k_1)}{k_2 - k_1}$$

For $k_2 \gg k_1$, $n_{Y\max} \rightarrow 0$; for $k_2 \ll k_1$, $n_{Y\max} \rightarrow a_0$. The rate of formation of species Z for $k_2 \gg k_1$, $w_Z \approx a_0 k_1 \exp(-k_1 t)$, is determined by the rate of the slow first reaction; for $k_2 \ll k_1$, $w_Z \approx a_0 k_2 \exp(-k_2 t)$ is determined by the rate of the slow second reaction.

2. $\nu_1 = 2$, $\nu_2 = 1$, $2X \xrightarrow{k_1} Y$; $Y \xrightarrow{k_2} Z$

Kinetic equations:

$$-\frac{dn_X}{dt} = k_1 n_X^2, \qquad \frac{dn_Y}{dt} = k_1 n_X^2 - k_2 n_Y, \qquad \frac{dn_Z}{dt} = k_2 n_Y$$

Solution:

$$n_Y = \frac{a_0}{2\delta\tau}\left[(\alpha+1) - 2\alpha\left(1 + \frac{\alpha-1}{\alpha+1}\tau\alpha\right)\right], \quad n_{Y\max} = a_0\tau_{\max}(1/2\delta)^{1/2}$$

$$\delta = \frac{k_1}{k_2}, \qquad \tau = 1 + a_0 k_1 t, \qquad \alpha = (1 + 2\delta)^{1/2}.$$

Rate determining (*rate-controlling*) *step* is a reaction with the rate constant that is much slower than all the other stages in a series of consecutive reactions; this slowest reaction determines the overall rate of complex reaction.

If one of the consecutive stages controls the dynamics of a complex reaction (has the slowest rate), then the kinetic order of the complex reaction is equal to the kinetic order of the rate-controlling stage.

C. Conjugated Reactions

Chemical induction is a process when a spontaneously occurring reaction induces or accelerates another reaction that would occur very slowly in the absence of the former reaction.

Conjugated reactions are two reactions, one of which induces the other reaction.

Chemical induction phenomenon is possible only in a case when both conjugated reactions are complex. Elementary reaction cannot be induced by another reaction because of the principle of kinetic independence of elementary stages of complex chemical reactions.

Inductor is a component of chemical system, the reaction of which with one of the initial reactants induces transformation of other initial reactants.

Actor is an initial substance reacting with the inductor.

Acceptor is an initial substance, the transformation of which in a chemical system is possible only with chemical induction between actor and inductor.

Induction factor is a measure of chemical induction effectiveness, equal to the ratio of acceptor consumption rate to the inductor consumption rate. Induction factor can vary from zero to 1.

D. Simplest Kinetic Scheme of Two Conjugated Reactions:

$$\begin{aligned} &\mathrm{A} + 1 \rightarrow \mathrm{R} \\ &\mathrm{R} + m\mathrm{I} \rightarrow m\mathrm{B} \\ &\mathrm{R} + \mathrm{C} \rightarrow \mathrm{D} \end{aligned}$$

where A is an actor, I is an inductor, B is the product of inductor transformation, C is the acceptor, D is the product of acceptor transformation, R is a common intermediate product, *m* is the number of inductor molecules consumed in reaction with the intermediate product.

E. Example

Reaction of carbon monoxide oxidation $2CO + O_2 = 2CO_2$ proceeds at high temperatures only. With H_2 present, joint oxidation of hydrogen $2H_2 + O_2 = 2H_2O$ and carbon monoxide occurs at lower temperatures. Induction is caused by formation of OH radicals in chain reaction of hydrogen oxidation. The OH radicals oxidize CO: $OH + CO = CO_2 + H$. Here, O_2 is the actor, H_2 is the inductor, and CO is the acceptor.

Relevant material can be found in Refs. 5–9.

VII. Photochemical Reactions

Photochemical reactions are conjugated chemical reactions induced by visible light (wavelength between 400 and 800 nm), near ultraviolet (100–400 nm) or infrared radiation (0.8–1.5 μm). The photons (quanta of light) are the inductors.

Gershell–Draper law: photochemical transformation occurs because of the light absorbed by reactant; the amount of product of photochemical reaction is proportional to the intensity of incident light and to the time of its impact.

Einstein–Stark law (*photochemical equivalence law*) every absorbed photon excites only one molecule of the reactive substance. However, with a very intense radiation (for example, in a powerful laser beam), multiquantum absorption becomes possible, when more then one photon per molecule can be absorbed.

Primary photochemical processes are processes that result in formation of active intermediate (vibrationally or electronically excited) particles because of exposure of reactants to light. Deactivation of the electronically or vibrationally excited particles occurs in one of the deactivation channels: 1) molecule dissociation into atoms or radicals, 2) molecule ionization with formation of molecular ion and electron, 3) light emission by the excited molecule (fluorescence), 4) excitation quenching because of collisions with other molecules. Rates of primary photochemical processes are independent on temperature. Temperature dependence of photochemical reaction rate points to a complex chemical mechanism of the process and to a substantial influence of secondary chemical reactions on the overall process rate.

Example

Photochemical explosion of gas mixture of hydrogen with chlorine:

$$Cl_2 + h\nu \rightarrow Cl + Cl$$
$$Cl + H_2 \rightarrow HCl + H$$
$$H + Cl_2 \rightarrow HCl + Cl$$

Here the first reaction describes the primary photochemical process (chlorine atoms formation), and the second and third reactions are the secondary reactions.

Photolysis is a chemical process in which absorption of a photon results in the breakup of a chemical bond.

Quantum photochemical yield $\phi_{\lambda,i}$ is a number of the transformed (disintegrated or formed) molecules per unit volume of reacting medium divided by the number of absorbed quanta of light with wavelength λ. Quantum yield is a dimensionless quantity. It characterizes both primary photochemical process effectiveness and a contribution of the secondary chemical reactions. The value of quantum yield greater than 1 implies that secondary reactions are important. The quantum yield value greater than 2 indicates chain branching mechanism of the chemical process.

Secondary photochemical processes are thermal and nonequilibrium reactions of the atoms and radicals formed in primary photochemical processes. In secondary reactions, the atoms and radicals react with each other or with reactants that do not absorb light.

Lambert's law: the amount of light absorbed is determined by the thickness of the absorbing layer. Specifically, in homogeneous optically thin (weak absorption) medium the intensity of monochromatic (wavelength λ) light I_λ (the number of photons passed per time unit though a unit surface area) remaining after the light has passed the path length l, is equal to $I_\lambda = I_{\lambda 0} e^{-\varepsilon_\lambda l}$, where ε_λ is the absorption coefficient (cm^{-1}) (Refs. 6 and 8).

Beer's law: the amount of light absorbed is determined by the concentration of the photo-absorbing species. The intensity of light is decreased exponentially with substance concentration: $I = I_0 e^{-\varepsilon_{\lambda,i} \cdot l \cdot y_i}$, where $\varepsilon_{\lambda,i}$ is the specific absorption coefficient for ith photo-absorbing species, and y_i is the molar–volume concentration of the species.

A. Kinetic Model of Photochemical Reactions

1. Purpose of the Model

The model aims at the evaluation of photochemical reaction rates and dynamics of chemical composition of reacting systems exposed to photo-radiation.

2. Assumptions

a) An ideal, chemically reacting gas is considered.
b) The reactants are uniformly distributed in space.
c) The chemical system is assumed kinetically ideal.

d) The quantum photochemical yields of the photoactive reactants, the stoichiometric coefficients, and the rate constants for secondary chemical reactions are known.
e) Light radiation absorption occurs uniformly in space.

3. *Restrictions*

The optical thickness should be small $D_\lambda = \varepsilon_{\lambda,i} \cdot l \cdot y_i \ll 1$, so that the main system parameters (temperature, pressure, and gas density) are practically undisturbed.

4. *Kinetic Equation*

Rate of change of the *i*th component concentration because of photochemical reaction:

$$\frac{\mathrm{d}y_i}{\mathrm{d}t} = w_{phi} + R_i = \sum_\lambda w_{phi,\lambda} + \sum_{j=1}^{S} (\nu_{ij}^- - \nu_{ij}^+) w_j$$

$$= \sum_\lambda w_{phi,\lambda} + \sum_{j=1}^{S} (\nu_{ij}^- - \nu_{ij}^+) k_{fj} \prod_{k=1}^{N} y_k^{\nu_{kj}^+} + \prod_{j=1}^{S} (\nu_{ij}^+ - \nu_{ij}^-) k_{fj} \prod_{k=1}^{N} y_k^{\nu_{kj}^-}$$

$$i = 1, 2, \ldots, N, \qquad j = 1, 2, \ldots, S$$

$w_{phi,\lambda} = \nu_{ph} \cdot \phi_{\lambda,i} \cdot \varepsilon_{\lambda,i} \cdot l \cdot I_\lambda \cdot y_i$ is the rate of primary photochemical reaction between photo-absorbing component *i* and photon with wavelength λ.

5. *Nomenclature*

y_i	molar–volume concentration of component *i*
ν_{phi}	stoichiometric coefficient for component *i* formation in primary photochemical reaction
w_i	rate of the *i*th component concentration change because of the secondary chemical reactions (see description of model C.3)
I_λ	number of photons with wavelength λ absorbed in unit volume per unit time
$\phi_{\lambda,i}$	quantum photochemical yield for component *i* induced by light with wavelength λ
$\varepsilon_{\lambda,i}$	specific absorption coefficient for the *i*th photo-absorbing species and light with wavelength λ

6. *Description of Coefficients and Parameters*

Numerical values of the quantum yield are determined in photochemical experiments and are tabulated (see, for example, Refs. 6 and 37). Typical magnitudes of the quantum yield for some gas-phase photochemical reactions are shown in the following table:

Reaction	ϕ	λ(Å)
$CH_3CHO \rightarrow CH_4 + CO$	0.3	3130–2380
$2HI \rightarrow H_2 + I_2$	2.0	300–1800
$3O_2 \rightarrow 2O_3$	2.0	1900–1300
$N_2O \rightarrow N_2 + 1/2O_2$	1.44	1840–1470
$2NOCl \rightarrow 2NO + Cl_2$	2.0	6350–3650

7. *Features of the Model*

The kinetic equation permits one to evaluate, taking into account specific features of the problem under consideration, temporal behavior of the reactant concentration for arbitrary time-dependent intensity of photo-radiation.

8. *Example*

a) *Photodissociation of hydrogen peroxide*

In the presence of carbon monoxide, photodissociation of hydrogen peroxide is described by the following kinetic scheme:

$$H_2O_2 + h\nu \rightarrow 2OH$$

$$OH + CO \xrightarrow{k_1} CO_2H$$

$$CO_2H + H_2O_2 \xrightarrow{k_2} CO_2 + H_2O + OH$$

$$H_2O_2 + OH \xrightarrow{k_3} H_2O + HO_2$$

$$2HO_2 \xrightarrow{k_4} O_2 + H_2O_2$$

and by the set of kinetic equations:

$$\frac{d[H_2O_2]}{dt} = -\phi \cdot I_\lambda[H_2O_2] - k_2[H_2O_2] \cdot [CO_2H] - k_3[H_2O_2] \cdot [OH] + k_4[HO_2]^2$$

$$\frac{d[OH]}{dt} = +2 \cdot \phi \cdot I_\lambda[H_2O_2] - k_1[OH] \cdot [CO] + k_2[H_2O_2] \cdot [CO_2H]$$

$$- k_3[H_2O_2] \cdot [OH]$$

$$\frac{d[CO_2H]}{dt} = k_1[OH] \cdot [CO] - k_2[H_2O_2] \cdot [CO_2H]$$

$$\frac{d[HO_2]}{dt} = k_1[OH] \cdot [CO] - k_2[HO_2]^2$$

b) Photochemical smog

Air pollution in large cities due to automobile exhaust gases results, under certain conditions, in photochemical smog (Ref. 38). Photodissociation of nitrogen dioxide causes smog formation. Nitrogen dioxide absorbs light in the entire range of the visible and ultraviolet spectrum. Absorption of light with wavelength shorter than 395 nm results in photo-dissociation into NO and O: $NO_2 + h\nu \to NO + O(^3P)$. According to Beer's law, the rate of photolysis of molecules X is defined by the expression $\mathrm{d}y_X/\mathrm{d}t = -k_\Sigma \cdot y_X$, where k_Σ is the photolysis rate constant (1/s). Given the intensity of sunlight at sea level and the small zenith angles of the Sun, the integration over the wavelength range 290–400 nm yields the value $k_\Sigma = 7.8 \times 10^{-3}\ \mathrm{s}^{-1}$ for photodissociation rate constant.

Relevant material can be found in Refs. 6, 7, 37, and 38.

VIII. Radiative-Chemical Reactions

Radiative-chemical (*radiation-induced*) reactions are chemical reactions induced by ionizing radiation, for example, by high-energy particles (such as electrons, protons, α-particles, or neutrons) or by electromagnetic radiation (γ or X-ray quanta) with energy in the range 10^3–10^7 eV.

Primary radiative-chemical processes are physico-chemical processes of excitation and ionization of reactants, radical formation, and formation of negative ions due to capture of electrons by atoms and molecules, under the impact of high-energy particles or photons on chemical systems.

Secondary radiative-chemical processes are complex chemical reactions between the secondary electrons (so-called δ-electrons), radicals, and excited atoms or molecules that are formed during ionization and excitation of atoms and molecules by the primary high-energy particles or photons, and the neutral reactants of reacting medium.

Radiation yield G_{ij} is the number of particles (molecules, atoms, radicals, or ions) of type j, formed or consumed during absorption of 100 eV of radiation energy by the reactant of type i. For gaseous mixture composed of N components, the radiation yield of reactant j is defined by the expression

$$G_j = \frac{\sum_{i=1}^{N} G_{ij} x_i z_i}{\sum_{i=1}^{N} x_i z_i}$$

where x_i is the molar fraction of component i, and z_i is a weight factor. The magnitudes of radiation yields and weight factors z_i are determined in radiation-chemical experiments and are tabulated (see, for example, Refs. 39 and 40).

Absorbed dose is the ionizing radiation energy absorbed per unit mass of irradiated substance. Units of measurement of absorbed dose: 1 gray = 1 J/kg = 10^{-3} J/g = 0.1 rad.

Power (*rate*) *of absorbed dose* is the ionizing radiation dose absorbed per unit time.

A. Kinetic Model of Radiative-Chemical Reactions (C.5)

1. *Purpose of Model*

Model aims at the evaluation of radiative-chemical reaction rates and temporal dynamics of chemical composition of systems exposed to ionizing radiation.

2. *Assumptions*

a) An ideal, chemically reacting gas is considered.
b) The reactants are uniformly distributed in space.
c) The chemical system is assumed to be kinetically ideal.
d) The quantum radiation yields of the reactants, the stoichiometric coefficients, and rate constants for secondary chemical reactions are known.
e) Ionizing radiation absorption occurs uniformly in space.

3. *Restrictions*

The magnitude of absorbed dose is small $D \ll c_v T$ (here, c_v is the specific heat and T is the temperature of absorbing substance), so that the main parameters of the medium (temperature, pressure, and gas density) are practically unchanged.

4. *Kinetic Equation of Radiative-Chemical Reaction*

$$-G_{ii} \cdot \mathrm{X}_i \rightarrow \sum_{j=1}^{N} G_{ij} \mathrm{X}_j$$

for molar–volume concentration of components:

$$\frac{\mathrm{d}y_i}{\mathrm{d}t} = \sum_{j=1}^{N} k_{ij} y_j + w_i$$

$$k_{ij} = 1.036 \times 10^{-7} \cdot I \cdot z_i \cdot G_{ij} \frac{\sum_{k=1}^{N} x_k \mu_k}{\sum_{k=1}^{N} x_k z_k}$$

5. *Nomenclature*

y_i	molar–volume concentration of component i
k_{ij}	rate constant of component j formation because of the radiation impact on component i (s^{-1})
w_i	rate of change of concentration of the ith component because of secondary reactions
I	power of absorbed dose (kgray)
z_i	weight factor for component i
G_{ij}	radiation yield for component j under radiation impact on component i (particles/100 eV)
x_i	molar fraction of particles of type i in the gas
μ_i	molar mass (molecular weight) of particles of type i
N	number of reacting components

6. Description of Coefficients and Parameters

For some common gases, the magnitudes of quantity z_i are:

$z(\mathrm{He}) = 2.24$ $z(\mathrm{H_2}) = 3.08$ $z(\mathrm{Ar}) = 6.60$ $z(\mathrm{O_2}) = 6.24$
$z(\mathrm{N_2}) = 7.02$ $z(\mathrm{NO}) = 7.91$ $z(\mathrm{CO}) = 8.39$ $z(\mathrm{CH_4}) = 10.0$
$z(\mathrm{CO_2}) = 10.9$ $z(\mathrm{C_2H_2}) = 14.7$ $z(\mathrm{Xe}) = 14.9$ $z(\mathrm{C_6H_6}) = 16.5$

7. Features of the Model

The kinetic equation permits one to evaluate, taking into account specific features of the problem under consideration, temporal behavior of the reactant concentration for arbitrary time-dependent intensity of radiation.

8. Example: Electron-Beam Cleaning of Exhaust Gases

The radiative-chemical effects in gases play a key role in technological facilities for electron-beam purification of the exhaust gases in industrial facilities and power plants (Ref. 41). For key air components, reactions of formation of active components have the following form (Ref. 42):

$$\begin{aligned}4.43\mathrm{N_2} \rightarrow\ & 0.29\mathrm{N_2^*} + 0.89\mathrm{N(^2D)} + 0.29\mathrm{N(^2P)} + 1.87\mathrm{N(^4S)} + 2.27\mathrm{N_2^+}\\ & + 0.69\mathrm{N^+} + 2.96\mathrm{e^-}\end{aligned}$$

$$\begin{aligned}5.38\mathrm{O_2} \rightarrow\ & 0.08\mathrm{O_2^*} + 2.25\mathrm{O(^1D)} + 2.80\mathrm{O(^3P)} + 0.18\mathrm{O^*} + 2.07\mathrm{O_2^+}\\ & + 1.23\mathrm{O^+} + 3.30\mathrm{e^-}\end{aligned}$$

$$\begin{aligned}7.33\mathrm{H_2O} \rightarrow\ & 0.51\mathrm{H_2} + 0.46\mathrm{O(^3P)} + 4.25\mathrm{OH} + 4.15\mathrm{H} + 1.99\mathrm{H_2O^+} + 0.01\mathrm{H_2^+}\\ & + 0.57\mathrm{OH^+} + 0.67\mathrm{H^+} + 0.06\mathrm{O^+} + 3.30\mathrm{e^-}\end{aligned}$$

$$\begin{aligned}7.54\mathrm{CO_2} \rightarrow\ & 4.72\mathrm{CO} + 5.16\mathrm{O(^3P)} + 2.24\mathrm{CO_2^+} + 0.51\mathrm{CO^+} + 0.07\mathrm{C^+}\\ & + 0.21\mathrm{O^+} + 3.03\mathrm{e^-}\end{aligned}$$

Relevant material can be found in Refs. 39, 40, and 42.

IX. Oscillatory Chemical Reactions

Oscillatory chemical reaction is a complex chemical reaction in which concentrations of intermediates and/or catalyst oscillate in time. The origin of oscillatory process is related to the decrease of Gibbs free energy in the reaction in a chemical system far from thermodynamic equilibrium. Under certain conditions, oscillatory chemical reactions can be accompanied by diffusion processes, resulting in the generation of *traveling waves of reactivity*.

Gas-phase oscillatory chemical reactions are subdivided into *isothermal* and *thermo-kinetic* reactions. The most extensively studied isothermal oscillatory reaction is the reaction of oscillatory oxidation of carbon monoxide. Oxidation of hydrocarbons at subatmospheric pressures (*cool flames*) is a typical example of thermo-kinetic oscillatory reactions. The basic feature of thermo-kinetic reactions is the coupling of thermal and kinetic factors. The balance between heat production and its dissipation in environment during temperature changes in reaction are important conditions of realization of oscillatory reactions.

Example

Two types of behavior are observed for reactions in stoichiometric mixture of H_2 and O_2 in an open system at subatmospheric pressures:

a) reaction proceeds at a sufficiently low rate, providing a stationary yield of the reaction products;
b) reaction proceeds as a series of pronounced pulses of ignition. Each pulse can be accompanied by complete consumption of the reactant (H_2) and by 400 K temperature rise.

However, the nonisothermal effects are not the reason of oscillatory behavior of chemically reacting media. During intervals between the pulses, the system is filled with fresh reactants. Transition to oscillatory ignition can happen either when temperature in the reactor is increased at constant pressure, or when pressure is changed at constant temperature.

Relevant material can be found in Refs. 43–46.

X. Catalytic Reactions

Catalytic reactions are reactions that are selectively accelerated at the presence of a foreign substance, called the catalyst. A catalyst forms an intermediate component with some of the reactants. The intermediate component, in turn, reacts with other reactants to create the desired products and to regenerate the catalyst. The quantity of the catalyst and its state remain virtually unchanged by the end of the process. This quasi-invariance distinguishes a *catalyst* from an *inductor* (in conjugated reactions) or *initiator* (in chain reactions), which are not regenerated at the end of the process.

Each catalyst is capable of catalyzing only certain particular chemical reactions or classes of reactions. The term “catalyst” with reference to any substance is not meaningful in separation from the reactions which it catalyzes.

If catalyst and reactant are in the same phase, *homogeneous catalysis* takes place, as distinct from a *heterogeneous catalysis*, when chemical reaction proceeds at a phase interface between the catalyst and the reactant. Heterogeneous catalytic reactions are a subject of one of the subsequent volumes.

In many reactions, the role of homogeneous catalyst is reduced to initiation of the reaction, that is, to create chemically active intermediates. The catalyst not only accelerates the reaction, but can also change its direction, causing preferential formation of a certain product.

In some cases, a catalyst is created during the reaction, being one of its products. Accumulation of this product during the reaction causes self-acceleration (*autocatalysis*) of the reaction. Catalytic and autocatalytic triggers and oscillators in models of critical chemical phenomena are considered in Ref. 47.

Example

- Addition of 0.24% NO_2 to a mixture $2H_2 + O_2$ results in 100 K decrease of the ignition temperature in this mixture. The accelerating action of NO_2 is connected with chemical reactions $2NO_2 = 2NO + O_2$, $HO_2 + NO = NO_2 + OH$ (see Chain Reactions).
- Thermal dissociation of hydrogen takes place in the reaction $H_2 + M \rightarrow H + H + M$, where M is any particle. Since the efficiency of atomic hydrogen as a particle M is an order of magnitude higher than the efficiency of H_2, the former can be considered as the catalyst accelerating this dissociation reaction.

Relevant material can be found in Refs. 5–8 and 48.

XI. Chain Reactions

Chain reactions are complex chemical reactions, where the transformation of initial substances into products takes place by repetitive cycles of interdependent (that is, coupled with each other) consecutive reactions that include the *active centers.*

Active center (or *chain carrier*) is an active intermediate particle (free radical with unpaired electron, ion, neutral atom or molecule, or a cluster with excited internal degrees of freedom), generation, consumption, and reproduction of which in a chemical system provides the chain mechanism of a chemical reaction. The chain carriers' concentrations are typically at a trace level.

Chemical chain is a sequence of one or several elementary reactions with the participation of active centers, which repeats in time and thereby constitutes the chain process. Within each cycle of a chemical chain, the product of each elementary reaction is a reactant of the subsequent reaction. Each chemical chain cycle either conserves or increases the number of active centers.

The kinetic mechanism of a chain reaction includes three main stages: initiation, propagation, and termination of a chain.

Initiation of a chain $X \rightarrow R$ is a stage of chain reaction, in which the chain carriers, R, are formed from the chemically stable reactants, X. The participation of these intermediates, R, in the subsequent stages of chain reaction results in consumption of reactants and formation of chemically stable products, P. In contrast to catalysts in conventional catalytic reactions, the chain carriers are irreversibly consumed during chain reaction. The formation of active centers is a *necessary condition of the beginning of chain reaction.* The following principal mechanisms of active particle generation in chain reactions exist:

- *Thermal mechanism*: active centers are produced in unimolecular decay of initial molecules ($H_2 \rightarrow 2H$) or in bimolecular reactions, as the reactive mixture is heated, as, for example, in the case of oxidation of hydrogen by oxygen ($H_2 + O_2 \rightarrow H + HO_2$);
- *Chemical mechanism*: chain carriers are generated by introduction to a system of external *initiators* (species that can easily form radicals and thereby accelerate chain process while being consumed in it), for example, hydrogen peroxide that easily decomposes into two OH radicals: $H_2O_2 \rightarrow 2OH$;

- *Radiative-chemical mechanism*: active centers are generated by an external radiation (such as X-rays, electron beams and protons);
- *Photochemical mechanism*: effect of the photons in the visible or ultraviolet spectral range, as, for example, photochemical initiation of chain reaction of hydrogen with chlorine: $Cl_2 + h\nu \rightarrow Cl_2^* \rightarrow 2Cl$;
- *Catalytic mechanism*: introduction into a chemical system of catalyst promoting appearance of active centers;
- *Mechanochemical mechanism*: generation of active particles as a result of a mechanical effect on a system;
- *Electrochemical mechanism*: conduction of electrical current in a system resulting in appearance of chain carriers;
- *Sonochemical* (*acoustic*) *mechanism*: effect of ultrasonic waves on a reacting mixture.

Chain propagation is a stage in a chain reaction, where the *primary chain carriers*, R, either reproduce themselves or give birth to new *secondary active centers*, $R_1, R_2, \ldots, R_m$. In first case, the average number of active centers per chain propagation cycle is conserved; in the second case, that number is increased. During the chain propagation, active centers can interact chemically or energetically with reactants, with one another, with walls of the reaction vessel, or with external factors (such as heat and radiation). Chain propagation stage can consist of several elementary reactions.

Cycle of chain propagation $R \xrightarrow[1]{} R_1 \cdots \xrightarrow[m]{} \varepsilon \cdot R + P$ is a sequence of m elementary reactions of chain propagation, beginning and ending with a *primary active center*,

$$Br + H_2 \rightarrow HBr + H, \qquad H + Br_2 \rightarrow HBr + Br.$$

Here, the primary chain carrier (initiator), Br, causes the formation of secondary chain carrier, H, during the first reaction. In the second reaction of chain propagation cycle, the secondary active particle induces reproduction of primary active center, Br.

The *average number of active centers* $\varepsilon \geq 1$ produced in the basic cycle (link) of a chemical chain, can differ from unity. The case $\varepsilon = 1$ corresponds to *simple* (*non-branched*) chain reactions.

The following types of reactions take place in chain propagation:

- *chain propagation reactions*, in which the number of chain carriers is conserved, $\varepsilon = 1$ (for example, $Cl + H_2 \rightarrow HCl + H$, chemical chain starts from one chain carrier, Cl, and is continued by generation of another active center, H);
- *chain branching reactions*, when the number of active centers increases, $\varepsilon > 1$. For example, in the sequence $H + O_2 \rightarrow OH + O$, $O + H_2 \rightarrow OH + H$, one carrier H results in formation of three carriers: one H and two OH.

Chain branching is a kind of chain propagation, during which the average number of active centers produced in the chain propagation cycle becomes greater than unity. For example, in elementary reactions $H + H_2O \rightarrow H + H + OH$ or $H_2 + H \rightarrow H + H + H$, atom H plays the roles of both initial reactant and product. Atoms H are also active centers whose number increases in each of these two reactions. In this example of autocatalysis, the self-reproduction of chain carriers and self-acceleration of reaction rate occur.

The quantity $\delta = \varepsilon - 1$ is the *probability of branching in one chain link.* It characterizes the *branched chain reactions.* If $\delta > 0$, a *branched chain reaction* takes place, when *branching* occurs in separate chain links from time to time, i.e., instead of one, two chains start to develop. In the limiting case $\delta = 1$, a *completely branched chain reaction* takes place, where branching happens in each chain link.

Chain termination $\mathrm{R} \xrightarrow[t]{} \mathrm{P}$ is a stage of a chain reaction where an intermediate active particle is lost. Chain carrier disappearance occurs either in the bulk of the reacting medium (*homogeneous chain termination*) or at a surface: the surface of the reaction vessel or the surface of liquid or solid aerosol particles, if they are present in the reaction zone (*heterogeneous chain termination*).

For the majority of chain reactions at normal and elevated pressures (about 1 atm and higher), homogenous chain termination in gas-phase reactions of recombination of atoms and radicals dominates.

At low gas pressures, heterogeneous processes of recombination and deactivation of active centers start to play a leading role. If the rate of chain termination is limited by diffusion of active centers to the surface, the chain reaction is referred to as proceeding in a *diffusion regime.* A reaction proceeds in a *kinetic regime* if the chain termination is limited by elementary chemical reaction of active centers at or with a surface (Refs. 5 and 6). In the kinetic regime, the concentration of active centers at the surface is practically equal to their concentration in the bulk of gas mixture.

The following chain termination mechanisms are distinguished:

- *linear chain termination in the bulk,* when the rate of loss of chain carriers is proportional to their concentration in the bulk of reaction vessel, $\mathrm{H} + \mathrm{O_2} + \mathrm{M} \rightarrow \mathrm{HO_2} + \mathrm{M}$;
- *linear chain termination at the wall* because of adsorption of chain carriers with their subsequent loss, $\mathrm{Cl}(vol) \xrightarrow[adsorp]{} \mathrm{Cl}(surf)$, $\mathrm{Cl}(surf) + \mathrm{Cl}(surf) \xrightarrow[recomb]{} \mathrm{Cl_2}$;
- *quadratic chain termination in the bulk,* when the rate of chain carrier deactivation is proportional to the square of concentration (e.g., $\mathrm{Cl} + \mathrm{Cl} + \mathrm{M} \rightarrow \mathrm{Cl_2} + \mathrm{M}$) or to the product of concentrations of two active centers ($\mathrm{Cl} + \mathrm{CCl_3} + \mathrm{M} \rightarrow \mathrm{CCl_4} + \mathrm{M}$).

Chain length ν is the average number of chain links which are realized upon appearance of one active center in the system. If the probability of chain propagation in each link is α, and the probability of chain termination in each link is $\beta = 1 - \alpha$, then the probability that a chain will include s links is $P_s = \alpha^s \cdot (1 - \alpha)$ and the average number of links per chain is (Refs. 6 and 49)

$$\nu = \sum_{s=1}^{\infty} s \cdot \mathrm{P} = \sum_{s=1}^{\infty} s \cdot \alpha^s (1 - \alpha) = (1 - \alpha)(\alpha + 2\alpha^2 + 3\alpha^3 + \cdots) = \frac{\alpha}{1 - \alpha} = \frac{\alpha}{\beta}$$

That is, the chain length is equal to the ratio of probabilities of chain propagation and breaking in one link. If the probability of termination is low, $\beta \ll 1$, the chain length is large, $\nu \approx 1/\beta \gg 1$.
The numerical value of chain length can be estimated from:

- $\nu = w_p/w_i$, the ratio of generation rate w_p of product, P, (the rate of chain propagation) to the generation rate w_i of the primary carriers, R;
- $\nu = w_p/w_{tn}$, the ratio of generation rate w_p of product, P, to the rate w_{tn} of loss of one of the active particles, R.

In contrast to conventional catalytic reactions, the value of ν in chain reactions depends not only on the nature of reactants, but also on the external conditions at which the reaction proceeds. Product generation rate that exceeds the rate of active center generation ($\nu \gg 1$) is the main feature of chain reactions.

Inhibitor: In is a specie that reacts with chain carriers and causes termination of a chain, but does not react with molecules of reactants. Inhibitor can either be introduced from outside of the chemical system or be present as an impurity in the reaction vessel. An example of inhibitor is oxygen that slows down the reaction $H_2 + Cl_2 = 2HCl$. The reason of the inhibiting action of O_2 is its interaction with the chain carriers.

Reaction of inhibition: $\mathrm{In} + \mathrm{R} \rightarrow \mathrm{InR}$ is a sort of termination reaction, when chemical interaction of chain carrier R with inhibitor In leads to formation of inactive or near-inactive intermediate products InR that do not participate in chain propagation reactions (Refs. 6 and 50).

Lifetime of an active center (or *time of chain development*) is the mean time interval from the moment of appearance of primary active center in the initiation reaction to the moment of its loss in a termination reaction.

Interaction of chains is *positive* if more than two active centers are formed because of elementary reaction between two chain carriers. *Interaction of chains* is *negative* if a chain termination takes place because of reaction between two active centers (so called *cross-termination of chains*).

Empirical specific features of chain reactions:

- reaction product yield (the number of product particles per each absorbed energy quantum) for radiation or photochemical initiation exceeds unity;
- reaction rate has a threshold dependence on the ratio of the surface area of a reaction vessel to its volume, on the rate of heat removal, and on the values of thermodynamic parameters such as temperature and pressure;
- reaction rate is sensitive to contamination of reactants;
- introduction of initiators accelerates the reaction. When initiator is added to reactants, the reaction may start only after an induction period rather than immediately;
- introduction of small amounts of inhibitors decreases the reaction rate (sometimes down to zero).

Nonbranched chain reaction is a sort of chain reaction in which average number of active centers in a cycle of the chemical chain propagation is preserved (chain branching reactions are absent). Typical example is given by the reaction of hydrogen with chlorine (see Ref. 6).

Branched chain reaction is a sort of chain reaction in which the average number of chain carriers increases in each link of the chemical chain, leading to avalanche growth of concentration of active particles. The *chemical critical phenomena* (such as ignition and detonation) are specific examples of branched chain reactions (see Combustion Reactions).

Chain reaction with degenerate branching is a sort of branched chain reaction in which the formation of active centers and the start of new chains happen with the participation of sufficiently stable products of the chain reaction. Chain reactions with degenerate branching occur in oxidation of a number of hydrocarbon and related compounds by oxygen, and also in slow oxidation of hydrogen sulfide (see Refs. 5–7).

Branched chain reactions can proceed in either *stationary regime* or *nonstationary, self-accelerating regime.* Phenomenological manifestations of nonstationary regime of chain reactions are *chemical* (*chain*) and *thermal explosions.* During explosion, a fast self-acceleration (see model C.6 and Combustion Reactions) of reaction happens in a short period of time (typically, shorter than 10^{-3} s).

Branched chain reactions are classified according to the leading physical or chemical mechanism that determines the overall rate of the chain reaction. Branched chain reactions with *kinetic* (also referred to as *chemical* or *radical*), *thermal, energy* (through vibrational or electronic excitation) and *mixed* (for example, *kinetic–thermal*) *type of branching* are distinguished.

An example of radical chain reaction in which branching through self-reproduction of radicals occurs is given by combustion of hydrogen in oxygen:

$$\mathrm{H} + \mathrm{O_2} \to \mathrm{OH} + \mathrm{O}, \qquad \mathrm{O} + \mathrm{H_2} \to \mathrm{OH} + \mathrm{H}$$

Reaction between hydrogen and fluorine with participation of vibrationally excited molecules $\mathrm{H_2}(v)$ and $\mathrm{F_2}(v)$ is an example of energy chain branching, which is important for chemical gas lasers:

$$\mathrm{H} + \mathrm{F_2} \to \mathrm{HF}(v) + \mathrm{F}; \qquad \mathrm{H} + \mathrm{F_2}(v) \to \mathrm{HF}(v) + \mathrm{F};$$
$$\mathrm{H_2}(v) + \mathrm{F_2} \to \mathrm{HF} + \mathrm{F} + \mathrm{H}$$

A. Semenov's Kinetic Model of Chain Reactions (C.6)

1. Purpose of the Model

The model aims at the determination of the change rate of concentrations of active intermediates in a chain reaction.

2. Assumptions

a) The assumptions adopted for the model C.3 are accepted.
b) Each of the stages is formally represented by one simple reaction and is characterized by a generalized parameter equal to the rate (characteristic frequency) of the stage.
c) The system is under isothermal conditions.
d) Consumption of initial reactants during the reaction is negligible.

e) The initiation of primary active particles, R, happens in a homogeneous space. The rate of generation of primary chain carriers does not depend on time and is determined by the characteristics of a steady process of initiation such as intensity of a beam of photons or radioactive particles and concentrations of the initiator or catalyst.
f) The basic chain link is represented by one simple reaction.
g) The loss of chain carriers takes place in the bulk of gas and/or at the walls of a reaction vessel.

3. *Restrictions*

a) See appropriate restrictions in model C.3.
b) The rate of chain termination with participation of one of the active centers substantially exceeds the rates of chain termination with participation of other chain carriers.

4. *Three-Stage Scheme and Kinetic Equations*

$$\mathrm{X} \xrightarrow[w_i]{} \mathrm{R} \qquad (i)$$

$$\mathrm{R} \xrightarrow[w_p]{} \varepsilon \cdot \mathrm{R} + \mathrm{P} \qquad (p)$$

$$\mathrm{R} \xrightarrow[w_t]{} \mathrm{P}' \qquad (t)$$

$$\frac{\mathrm{d}n_\mathrm{R}}{\mathrm{d}t} = w_i - w_p n_\mathrm{R} + \varepsilon \cdot w_p n_\mathrm{R} - w_t n_\mathrm{R} = w_i - (w_p + w_t) \cdot (1 - \varepsilon\alpha) \cdot n_\mathrm{R}$$

$$\bar{w}_p = \frac{\mathrm{d}n_\mathrm{P}}{\mathrm{d}t} = w_p n_\mathrm{R}, \qquad \alpha = \frac{w_p}{w_p + w_t}$$

5. *Nomenclature*

i	stage of initiation of active centers, R, from stable reactants, X
p	stage of chain propagation resulting in formation of the product, P, and regeneration of active centers, R
t	stage of chain termination
ε	average number of active centers arising in the basic chain link
α	probability of chain propagation
n_R	number density of primary active centers
w_i	rate of initiation of primary active centers
w_p	rate of chain propagation
w_t	rate of chain termination
$\bar{w}_p$	rate of generation of the product of chain reaction
n_P	number density of the reaction product

6. *Description of Coefficients and Parameters*

The characteristic reaction rate $w_p = \tau_p^{-1}$ of the chain propagation stage isequal to the number of acts of interaction of an active center with initialreactants X_i per 1 s (Ref. 3). Generally, $w_p = \tau_p^{-1}\sum_{i=1}^{\mathrm{I}} k_{p,i} n_{\mathrm{R},i}$, where τ_p (s) is the characteristic time of chain propagation stage, $k_{p,i}$ (cm^3/s) is the rateconstant of elementary reaction of active center with a reactant of the sort i, and $n_{\mathrm{R},i}$ (particles/cm^3) is the number density of the ith reactant.

The characteristic rate (frequency) $w_t = \tau_t^{-1}$ of the chain termination stage is equal to the number of acts of loss of an active center per 1 s in elementary reactions of recombination (deactivation).

For homogeneous reactions:

1. with linear termination, $\tau_t^{-1} = k_{t1}$, where τ_t (s) is the characteristic time of chain termination stage, and k_{t1} (s^{-1}) is the rate constant of first-order recombination;
2. with quadratic chain termination, $\tau_p^{-1} = k_{t2} n_\mathrm{R} + \sum_{n=1}^{N} k_{t2,n} n_{\mathrm{R}_n}$, where k_{t2} (cm^3/s) and $k_{t2,n}$ (cm^3/s) are the rate constants of second-order recombination, corresponding to quadratic and cross-termination, respectively, and n_{R_n} is the number density of secondary active centers of a sort n.

In heterogeneous regimes, $\tau_t = 1/k_{tg} = 1/k_{t\,dif} + 1/k_{t\,kin}$, where $k_{t\,dif}$ is the diffusion termination rate constant, and $k_{t\,kin}$ is the kinetic termination rate constant.

7. *Restrictions*

See the description of model C.1.

8. *Features of the Model*

Depending on the ratio w_p/w_t of rates of chain propagation and termination, and on specific features of kinetics of chain reaction (quantity ε), the model describes both stationary and nonstationary regimes of chain reactions.

9. *Particular Cases*

a) *Behavior of active centers in nonchain reactions*

If the product is not formed ($w_p = 0$), then

$$\frac{\mathrm{d}n_\mathrm{R}}{\mathrm{d}t} = w_i - w_t n_\mathrm{R}$$

The analytical solution for $n_\mathrm{R}(t = 0) = n_0$ is

$$n_\mathrm{R}(\tau) = \overline{n_\mathrm{R}}(1 - e^{-t/\tau_t}) + n_0 e^{-t/\tau_t}$$

Establishment of the stationary concentration (number density) $\overline{n_\mathrm{R}} = w_i \tau_t$ of active centers takes place at times $t \gg \tau_t$, much longer than the characteristic lifetime $\tau_{cc} = \tau_t$ of the active center. In a nonbranched chain reaction ($w_p \neq 0$, $\varepsilon = 0$),

$$\frac{\mathrm{d}n_\mathrm{R}}{\mathrm{d}t} = w_i - (w_p + w_t) n_\mathrm{R}, \qquad \bar{w}_p = \frac{\mathrm{d}n_\mathrm{P}}{\mathrm{d}t} = w_p n_\mathrm{R}$$

The increase of number density of active centers is given by the expression

$$n_\mathrm{R}(t) = \frac{w_i}{w_p + w_t}(1 - e^{-(w_p + w_t)t}) + n_0 e^{-(w_p + w_t)t}$$

In the case under consideration, the lifetime of an active center is equal to $\tau_{cc}^r = \tau_p \tau_t/(\tau_p + \tau_t)$. After a time period significantly longer than the lifetime of an active center, the stationary concentration (number density) $\overline{n_{\mathrm{A}}^{r}} = w_i \tau_p \tau_t/(\tau_p + \tau_t)$ is reached. Rate of the stationary non-chain reaction is $\bar{w}_p^r = w_i \tau_t/(\tau_p + \tau_t) = w_i \alpha$.

b) Behavior of active centers in chain reactions

Nonbranched chain reactions ($w_p \neq 0$, $\varepsilon > 0$, $\varepsilon \cdot \alpha < 1$).

c) Increase in the number of active centers

If the chain reaction starts at time instant $t = 0$, when the initial concentration of active centers is equal to zero,

$$\frac{\mathrm{d}n_{\mathrm{R}}}{\mathrm{d}t} = w_i - (w_p + w_t)(1 - \varepsilon \cdot \alpha) \cdot n_{\mathrm{R}}, \qquad \bar{w}_p = \frac{\mathrm{d}n_{\mathrm{P}}}{\mathrm{d}t} = w_p n_{\mathrm{R}}$$

Increase of the number density of active centers is described by the expression

$$n_{\mathrm{R}}(t) = \frac{w_i}{(w_p + w_{tp})(1 - \varepsilon \cdot \alpha)}\left(1 - e^{-(w_p + w_{tp})(1-\varepsilon\cdot\alpha)t}\right)$$

which at time t much longer than the lifetime $\tau_{cc}^{cr} = \tau_p \tau_t/[(\tau_p + \tau_t)(1 - \varepsilon \cdot \alpha)]$ of an active center leads to the stationary number density of active centers $\overline{n_{\mathrm{R}}^{cr}} = w_i \tau_p \tau_t/[(\tau_p + \tau_t)(1 - \varepsilon \cdot \alpha)]$. The rate of stationary chain reaction is equal to

$$\overline{w_p^{cr}} = \frac{w_i \tau_t}{(\tau_p + \tau_t)(1 - \varepsilon \cdot \alpha)]} = \frac{w_i \alpha}{1 - \varepsilon \cdot \alpha} = w_i \nu$$

where $\nu = \alpha/(1 - \varepsilon \cdot \alpha)$ is the average chain length. At large chain length $\nu = \alpha/(1 - \varepsilon \cdot \alpha) \gg 1$, the stationary rate $\overline{w_p^{cr}} = w_i \nu$ of the chain reaction is higher than the rate of nonchain reaction $\overline{w_p^r} = w_i \alpha$. Because τ_p characterizes the time of development of one chain link, then the lifetime of an active center in the chain reaction ($\tau_{cc}^{cr} = \tau_p \alpha/\,(1 - \varepsilon \cdot \alpha) = \tau_p \nu$) is equal to the time of development of one link (τ_p) multiplied by the number of links (ν). In other words, in a nonbranched chain reaction, the total lifetime of an active center is the sum of individual lifetimes (τ_p) of all the chain carriers participating in the development of one chain link.

d) Decay of active centers

If a stationary chain reaction stops at time instant $t = 0$ ($w_i = 0$), when the number density of active centers is $n_{\mathrm{R}}(t = 0) = w_i \tau_{cc}^{cr}$, then

$$\frac{\mathrm{d}n_{\mathrm{R}}}{\mathrm{d}t} = -(w_p + w_t)(1 - \varepsilon \cdot \alpha) n_{\mathrm{R}} = \frac{n_{\mathrm{R}}}{\tau_{cc}^{cr}}, \qquad \bar{w}_p = \frac{\mathrm{d}n_{\mathrm{P}}}{\mathrm{d}t} = w_p n_{\mathrm{R}}$$

The decreases of the number density and reaction rate with time from the initial stationary values are described by the following expressions:

$$n_{\mathrm{R}}(t) = w_i \cdot \tau_{cc}^{cr} e^{-t/\tau_{cc}^{cr}}, \qquad \overline{w_p^{cr}}(t) = w_i \left(\frac{\tau_{cc}^{cr}}{\tau_p}\right) e^{-t/\tau_{cc}^{cr}} = w_i \cdot \nu \cdot e^{-t/\tau_{cc}^{cr}}$$

e) Branched chain reactions ($w_p \neq 0$, $\varepsilon > 0$, $\varepsilon \cdot \alpha > 1$)

$$\frac{\mathrm{d}n_{\mathrm{R}}}{\mathrm{d}t} = w_i + \frac{\varepsilon - 1}{\tau_p} n_{\mathrm{R}} - \frac{1}{\tau_t} n_{\mathrm{R}} = w_i + f n_{\mathrm{R}} - g n_{\mathrm{R}} = w_i + \varphi \cdot n_{\mathrm{R}}$$

Here $f = (\varepsilon - 1)/\tau_p$ is the generalized (characteristic) chain branching rate constant, $q = 1/\tau_t$ is the generalized (characteristic) chain termination rate constant, and $\varphi = f - g$ is the Semenov factor of chain branching.

f) Stationary regime of branched chain reactions $[(\varepsilon - 1) < \tau_p/\tau_t]$

When the factor of chain branching is negative ($\varphi < 0$), establishment of the stationary number density of active centers and of the rate of chain reaction, proportional to it, are described by the expressions:

$$n_{\mathrm{R}}(t) = \frac{w_i}{g-f}(1 - e^{-(g-f)t}), \qquad \bar{w}_p(t) = \frac{w_i w_p}{g-f}(1 - e^{-(g-f)t})$$

g) Nonstationary regime of branched chain reactions $[(\varepsilon - 1) > \tau_p/\tau_t]$

When the factor of chain branching is positive ($\varphi > 0$), the unlimited growth of number density of active centers is described by the Semenov equation:

$$n_{\mathrm{R}}(t) = \frac{w_i}{f-g}(e^{(f-g)t} - 1) = \frac{w_i}{\varphi}(e^{\varphi t} - 1)$$

An avalanche autocatalytic acceleration of the branched chain reaction takes place:

$$\bar{w}_p(t) = \frac{w_i w_p(\varepsilon - 1)}{\varphi}(e^{\varphi t} - 1)$$

During a finite time (*induction period*) t_{ind}, the rate of the branched chain reaction reaches the minimal experimentally observable value, $w_{\min}$. Because for the majority of the chain reactions w_i is much lower than $w_{\min}$, then at $t > t_{ind}$, the rate can be approximated with adequate accuracy as $\bar{w}_p(t) \approx w_i w_p(\varepsilon - 1) \cdot e^{\varphi t}/\varphi$, and the induction time can be described by the expression

$$t_{ind} \approx \frac{1}{\varphi}\ln\frac{w_{\min}\varphi}{(\varepsilon - 1)w_i w_p}$$

10. Example

For the reaction of hydrogen with oxygen, the rate of production of chain carriers (hydrogen atoms) is described by the equation $d[\mathrm{H}]/dt = w_i + \varphi \cdot [\mathrm{H}]$, where $\varphi = -k_2[\mathrm{O_2}] - k_4 - k_5[\mathrm{O_2}] \cdot [\mathrm{M}]$, k_2 is the rate constant of elementary chain branching reaction $\mathrm{H + O_2 \xrightarrow{k_2} HO + O}$, k_4 is the rate constant of chain termination on a wall $\mathrm{H} + wall \xrightarrow{k_4} 1/2\mathrm{H_2}$, and k_5 is the rate constant of chain termination in the bulk $\mathrm{H + O_2 + M \xrightarrow{k_5} HO_2 + M}$. The Semenov's equation previously given describes satisfactorily the first and second limits of explosion of hydrogen–oxygen mixtures (see Refs. 6, 7 and 51 and Fig. 6.1).

11. Comments

a) The model demonstrates qualitatively different behavior of active centers in nonbranched and branched chain reactions, and gives the definition of a characteristic lifetime of active centers.

b) Pressure dependence of the explosion limit of hydrogen–oxygen mixture has a particular Z shape with three alternating branches, where the ignition temperature decreases, increases, and decreases again with increasing pressure (see Fig. 6.1). Similar Z-shaped ignition curve have been obtained in premixed flames, in diffusion flames Ref. 52, and in the continuously stirred tank reactors Ref. 53. In all those chemical systems, the first (low pressures) and second (intermediate pressures) ignition branches have been shown to be controlled by kinetic factors, that is, by chain carrier generation and loss. The third ignition branch (high pressures) is determined by thermal factors. Ignition behavior of hydrogen is relatively well studied. Ignition behavior of other widespread fuels, such as methane, butane, and other hydrocarbons that are used as reactants for both chemical synthesis and energy production, is more complex (Refs. 4 and 36).

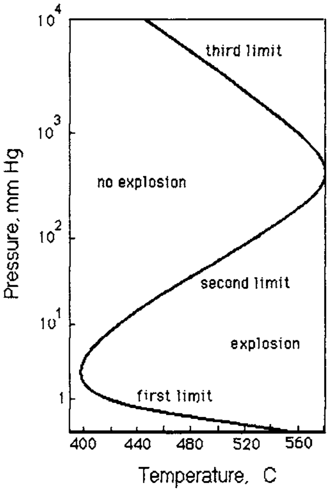


Fig. 6.1

Relevant material can be found in Refs. 5–9 and 51.

XII. Combustion Reactions

Combustion reactions (*auto-accelerating exothermic reactions*) are complex chemical reactions, for which, at certain values of parameters such as temperature, concentration, pressure, dimensions of a vessel, etc., transition to nonstationary auto-accelerating regime (*explosion*) is characterized by the *time (period) of induction*, and the reaction proceeds in space as *propagating* or *standing wave(s) of chemical reactions*.

The main specific feature of combustion reactions is the existence of critical conditions in a chemical system, when the reaction rate and concentrations of active intermediate particles sharply change from a situation of slow process (when the reaction cannot be detected by measuring instruments), to a situation where the formation of noticeable concentrations of reaction products and heat release occur practically instantaneously. During the course of an exothermic combustion reaction, chemical critical phenomena and the time of induction are coupled with heating of the reaction mixture because of chemical reaction heat released in the course of chemical transformation.

Chemical critical phenomena are caused by sharp variation of the reaction rate with minor changes of any of the parameters of a chemical system (mixture composition, temperature, pressure, and parameters of mass or heat transfer). Chemical critical phenomena are specific features of branched-chain, autocatalytic, and combustion reactions (see Refs. 5–7, 51 and 54).

Induction time (*induction period*) *of a combustion reaction* is a period of latent (for a spectator that operates measuring instruments of fixed resolution) proceeding of the reaction between the moment of the beginning of reaction (typically upon heating or mixing of the reactants) and the moment of appearance of visible manifestations (such as flashes and sound effects). The length of the induction period is sensitive to the state of the chemical system (elemental composition of reactive mixture, thermodynamic parameters such as pressure and temperature, and heat and mass transfer parameters) and is determined by the nature of processes taking place in the reacting mixture during the induction period. The notion of induction period is applied most often to the two main types of chemical critical phenomena—*chain explosions* and *thermal explosions*.

Explosion is a regime of very rapid proceeding of a combustion reaction upon achievement by a chemical system of critical conditions. The following types of explosions are distinguished: *chain explosions*, *thermal explosions*, and *chain-thermal explosions*. An explosive regime is determined by the kinetic mechanism of chemical reactions and by the nature of processes that are responsible for transition to explosion.

Propagating waves of explosive chemical reactions is a process of successive ignition of the adjacent layers in a reaction mixture due to the transport of active particles and/or heat. Depending on the velocity of propagating wave of explosive reactions, *waves of combustion* (*deflagration*), or *flames*, and *detonation* waves are distinguished.

Flame (*wave of combustion* or *deflagration*) is a wave of propagation of explosive reactions in space as a result of heat conduction and/or diffusion of active centers with velocity lower than the speed of sound.

Detonation wave is a wave of propagation of explosive reactions in space as a result of ignition by a shock wave with velocity higher than the speed of sound.

Ignition is a transition from normal (quasistationary) to explosive chemical transformation of a reaction mixture under critical conditions.

Chain (*isothermal*) *explosion* is a transition to an auto-accelerating regime of a branched chain reaction at constant temperature. The auto-acceleration is coupled with accumulation of the active centers. Isothermal explosion is a type of chain reactions with *kinetic chain branching*. Chain ignition usually happens at low pressures and temperatures. An example of chain explosion is the combustion of a stoichiometric mixture of hydrogen and oxygen (detonating gas) at temperature $T \leq 800$ K and pressure $p \approx 1$ Torr (see Refs. 6 and 51 and Fig. 6.1).

Thermal explosion is a regime of ignition of auto-accelerating combustion reactions, the rate of which is determined by thermal heating of the mixture because of chemical heat production. The necessary conditions for a chain reaction with thermal branching are exothermicity of the process and high sensitivity of the reaction rate constant to temperature variations. An example of thermal explosion is the combustion reaction of hydrogen with oxygen at pressures higher than 400 Torr (above the third limit of ignition, see Fig. 6.1) and temperatures above approximately 900 K. The following types of thermal explosion are distinguished—*spontaneous combustion, ignition, adiabatic thermal explosion,* and *dynamic thermal explosion.* The type of thermal explosion is determined by the conditions of heat exchange between the reaction mixture and the vessel walls.

Spontaneous ignition (or self-ignition) is a regime of ignition as a result of heating, when the heat is supplied to the chemical system so slowly that the whole system warms up uniformly, and the ignition starts in the core of reactive mixture practically simultaneously throughout the vessel volume.

Forced ignition (or external ignition) is a regime of ignition, when heat is supplied to the system so rapidly that the layer of a reacting mixture near the wall is heated stronger than in the bulk. The ignition starts near the boundary surface (wall), and propagates to the middle of the vessel as deflagration wave.

Adiabatic explosion is a regime of combustion, when heat exchange of the reacting mixture with environment is small, and all the heat produced during the reaction is used for heating of the system.

Dynamic thermal explosion is a regime of combustion under conditions of continuous heating of the reacting system by an external power source.

Explosion initiation is the creation of conditions at which a slow reaction turns into explosion. Initiation of chain explosions can be carried out by heating and light. Initiation of thermal explosions can be done by varying parameters of heat exchange of reacting mixture with the vessel walls or by abrupt change of thermodynamic parameters (temperature and/or pressure) of the mixture, as occurs, for example, in shock waves.

Comment

In engineering practice, chemical composition of combustible mixtures is characterized by:

- *fuel/oxidizer ratio F/O* is the ratio of fuel mass to the oxidizer mass in 1 kilogram of the mixture;
- *equivalence ratio $\phi = (F/O)/(F/O)_{st}$* (or *fuel excess ratio*) is the ratio of a fuel/oxidizer ratio in the mixture under consideration to the fuel/oxidizer ratio under stoichiometric conditions. The case $0 < \phi < 1$ corresponds to *lean mixtures* (oxidizer is in excess), the case $\phi = 1$ corresponds to *stoichiometric mixtures*, and the case $1 < \phi < \infty$ corresponds to *rich mixtures* (fuel is in excess).

Under stoichiometric conditions, all the initial reactants are spent completely during the reaction, and all products are in their most thermodynamically stable form. For example, in oxidation of methane by oxygen under stoichiometric conditions, complete oxidation $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ is realized when at the initial instant of time two molecules of oxygen are present in a mixture per one molecule of methane (fuel/oxidizer ratio $(F/O)_{st} = 1 \cdot (1 \cdot 12 + 4 \cdot 1)/[2 \cdot (2 \cdot 16)] =$

$16/64 = 1/4$). The reactants (methane and oxygen) are transformed completely to products (carbon dioxide and water) that cannot be further oxidized. If at an initial time instant three molecules of oxygen are present per two molecules of methane (fuel/oxidizer ratio $(F/O) = 1 \cdot (1 \cdot 12 + 4 \cdot 1)/[(3/2) \cdot (2 \cdot 16)] = 32/96 = 1/3$), the *reaction of partial oxidation* of methane by oxygen $CH_4 + 3/2O_2 \rightarrow CO + 2H_2O$ will take place under non-stoichiometric conditions ($\phi = (32/96)/(16/64) = 4/3 > 1$, fuel-rich mixture). Here, generated carbon monoxide is thermodynamically unstable and can react further with oxygen forming carbon dioxide that is a thermodynamically stable reaction product.

Relevant material can be found in Refs. 2 and 55–58.

XIII. Models of Chemical Reactors

Reactors, as devices in which the chemical processes occur, are classified according to the way the process takes place. *Batch reactors* work periodically in time. Before chemical process, the reactants are supplied into the reactor. During the reaction course, no substances are fed into or removed from batch reactor. After reaction is finished, the products are extracted from batch reactor. *Continuous* (or *flow*) *reactors* provide a simultaneous and continuous feeding of reactants and extraction of the reaction products. Reactors are also classified according to their design features (such as *tank*, *tubular*, *tower*, *fluidized-bed*, and *slurry-phase reactor*, Refs. 1, 16, 59 and 60).

Batch reactors represent, in most cases, closed chemically reacting systems. Models of chemical reactions widely used for description of chemical reaction kinetics in batch reactors are shown below (see models C.7–C.9). Most of the basic kinetic data for reactor design, process safety, and autoignition characteristics are obtained in reactors of this type. In such studies, a calorimetric bomb (constant volume) reactor is used along with a batch reactor.

Continuous reactors represent a particular type of open reactive systems. Realization of a chemical process in a continuous reactor provides the process continuity and high efficiency in reactor volume utilization, and facilitates a process control. A major feature of processes occurring in continuous reactors at constant flow rate of reacting mixture is the establishment of steady conditions, for which the reactive mixture component concentrations cease to change. Continuous reactors, and their subcategory (semicontinuous reactors, Refs. 16 and 59), have extensive applications in large scale plants.

Continuous reactors are classified according to the modes, or regimes, in which the chemical reaction proceeds. The modes differ from each other by the structure of reactive flows. In the models of chemical reactors described below, it is assumed that the chemical process results in a change of chemical composition of the system, but does not affect fluid dynamics. The limiting regimes in the continuous reactors are the following:

- *plug flow regime* is a one-dimensional steady reacting fluid flow with fluid velocity $u(x)$ in x axis direction, where transverse mixing of reacting components is perfect, and longitudinal mixing is absent (see model C.10);

- *well-stirred* (or *back-mix*, or *perfectly stirred*) *flow regime* is a chemically reactive, open system, where the incoming flow of initial reactants immediately reaches its final composition because of perfect mixing. The concentrations of reactants and the reaction rate do not vary in time and have the same magnitudes in each internal point of the reactor volume (see model C.11).

In all the models described, the fluids are treated as ideal gases (see Chapter 9, Equations of State, in this volume, and also the description of model C.7).

In practical reactors, deviations from the aforementioned ideal flow patterns often occur. Models for cases where chemical reactions substantially affect fluid dynamics, or where coupling between kinetics and mass and heat transfer processes is high, will be described in the subsequent volumes of this series.

The numerical examples below use stoichiometric hydrogen–oxygen gas mixture as a model chemical kinetics system.

A. Model of Isothermal Reaction at Constant Density (C.7)

1. *Purpose of the Model*

The model aims at the determination of the concentrations of chemical components and pressure as functions of time in a closed, isothermal system at constant density (constant volume of the reactor).

2. *Assumptions*

a) The chemical system is assumed to be closed, single-phase, uniform, and homogeneous (isothermal batch reactor).
b) Temperature T and density ρ (or volume) of the system are constant.
c) See the description of model C.3 for other assumptions.

3. *Restrictions*

See the appropriate section in the description of model C.1.

4. *Set of Equations of the Model*

$$\rho\frac{\mathrm{d}c_i}{\mathrm{d}t} = R_i, \quad T = \text{const}, \quad \rho = \text{const}, \quad p = \rho RT\sum_{i=1}^{N} c_i$$

$$R_i = \sum_{j=1}^{S}(\nu_{ij}^{-} - \nu_{ij}^{+})w_j, \quad w_j = k_{fj}\prod_{k=1}^{N}(\rho c_k)^{\nu_{kj}^{+}} - k_{bj}\prod_{k=1}^{N}(\rho c_k)^{\nu_{kj}^{-}}$$

5. *Nomenclature*

ρ	mass density of gas mixture
c_i	molar–mass concentration of component i
p	pressure

R	universal gas constant
R_i	rate of change of concentration of component i
$\nu_{ij}^{+}, \nu_{ij}^{-}$	stoichiometric coefficients for reagents (+) and products (–) of stage j of chemical reaction
k_{fj}	rate constant of stage j of chemical reaction in forward (f) direction
k_{bj}	rate constant of stage j of chemical reaction in backward (b) direction
N	number of chemical components in reacting system
S	number of elementary stages in complex chemical reaction

6. Description of Coefficients and Parameters

Reaction rate constants k_{fj} and k_{bj} depend, in general, on temperature and pressure. Experimental data, as well as semi-empirical and theoretical models for calculation of rate constants are shown in descriptions of models in Chapter 6 of the first volume of this series, and also in other handbooks, reviews, and monographs (Refs. 20–25). Also see the bibliographic references in the description of model C.1. See models I-C.15–I-C.16 in the first volume of this series and also Refs. 26 and 27 for the description of rate constant dependence on pressure for unimolecular reactions.

7. Features of the Model

In this model, gas pressure p is the only gas dynamic variable. A decrease or increase of the sum of concentrations of components $c = \sum_i c_i$ leads to decrease or increase of the magnitude of p during the course of reaction.

8. Example

The model of isothermal reaction at constant density is used for simulation of chain ignition of stoichiometric mixture of hydrogen with oxygen (the so-called detonating gas mixture) at initial temperature $T = 800$ K and initial pressure $p = 2$ Torr. In the vicinity of the first explosion limit (see Fig. 6.1), the rate of homogeneous exothermal reaction in the volume of gas mixture is low, and the overall thermal heating is negligible. The main channel of radical recombination is heterogeneous recombination at the walls of the reactor. Reaction starts under practically isothermal conditions, if the reactor walls have a good thermal conductance, and the reactor is placed in a thermal bath (reservoir). Because the system is closed (mass exchange with the environment is absent, and the total mass of reactants in the gas mixture is conserved) and its volume is constant, then reaction proceeds under constant density of the mixture. Kinetic curves for concentrations of reactants (H_2, O_2), chain carriers (H, O, OH), and the reaction product (H_2O) are shown in Fig. 6.2.

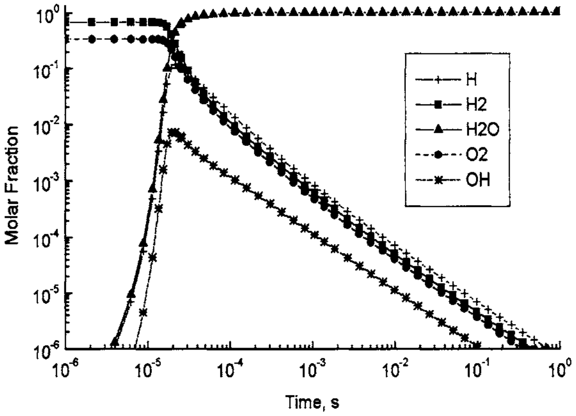


Fig. 6.2

9. *Comments*

The model is convenient for simulation of kinetic processes during isothermal chain ignition in a closed vessel with fixed volume. If the vessel walls conduct heat well, and the vessel is placed in a thermostat (heat bath), then temperature inside the reactor remains constant. These conditions are close to those in experiments on chain ignition, when a mixture is injected into the vessel, quickly heats up to the temperature T of the vessel walls, and develops a self-accelerating chain or chain-branched reaction (Refs. 6 and 51). Effects of inhibitors or promoters on flame behavior and on polymerization processes at constant temperature and constant density are considered in Ref. 50.

Relevant material can be found in Refs. 6 and 51.

B. Model of Adiabatic Reaction at Constant Density (C.8)

1. *Purpose of the Model*

The model aims at the determination of time evolution of the concentrations of chemical components, temperature, and pressure in a closed, thermally insulated reactor at constant density.

2. *Assumptions*

a) The chemical system is assumed to be closed, adiabatic, single-phase, uniform, and homogeneous (adiabatic batch reactor).
b) Density ρ of the system (or the reactor volume) is constant.
c) See the description of model C.3 for other assumptions.

3. *Restrictions*

See the appropriate section in the description of model C.1.

4. *Set of Equations of the Model*

$$\frac{\rho \mathrm{d}c_i}{\mathrm{d}t} = R_i, \qquad \rho = \text{const}, \qquad p = \rho RT \sum_{i=1}^{N} c_i$$

$$(\rho c_p T - p) \cdot \frac{\mathrm{d}T}{\mathrm{d}t} = RT^2 \sum_{i=1}^{N} R_i - T \sum_{i=1}^{N} H_i^0 R_i$$

$$R_i = \sum_{j=1}^{S} (\nu_{ij}^- - \nu_{ij}^+) w_j, \qquad w_j = k_{fj} \prod_{k=1}^{N} (\rho c_k)^{\nu_{kj}^+} - k_{bj} \prod_{k=1}^{N} (\rho c_k)^{\nu_{kj}^-}$$

$$c_{pi} = \frac{\mathrm{d}H_j^0(T)}{\mathrm{d}T}, \qquad c_p = \sum_{i=1}^{N} c_{pi} c_i$$

5. *Nomenclature*

c_p	specific heat at constant pressure
c_{pi}	specific heat of component i at constant pressure
H_i^0	enthalpy of component i

Other symbols are defined in the description of model C.7.

6. *Description of Coefficients and Parameters*

See the description of model C.7 and cited references.

The enthalpies of components H_i^0 depend only on gas temperature, T. For numerical simulation, two basic methods of representation of thermodynamic data are used: 1) tables [see, for example, thermodynamic tables of Gurvich et al. (Ref. 61) or JANAF tables (Ref. 62)] or 2) polynomial interpolation formulas [see, for example Refs. 63 and 64].

7. *Features of the Model*

Chemical reaction is assumed to run in a closed system (system mass $M = \text{const}$) at constant volume; thus, the reaction occurs at constant density $\rho = M/V$. Heat generated in the course of reaction under adiabatic conditions results in temperature increase.

8. *Example*

The model of adiabatic reaction at constant density can be used for simulation of thermal ignition of stoichiometric mixture of hydrogen with oxygen at the initial temperature $T = 1200$ K, and the initial pressure $p = 1$ atm. In the vicinity of the third explosion limit (see Fig. 6.1), self-heating of the gaseous mixture is determined by the rates of exothermal reactions of chain propagation

$$\mathrm{HO_2 + H = OH + OH + 37\,kcal/mol}, \qquad \mathrm{HO_2 + H = H_2O + O + 54\,kcal/mol}$$

and of homogeneous reactions of recombination in the gas volume

$$H + H = H_2 + 103\ \text{kcal/mol}, \qquad O + O = O_2 + 54\ \text{kcal/mol},$$
$$H + OH = H_2O + 32\ \text{kcal/mol}$$

Ignition of the mixture occurs in non-isothermal conditions. The kinetic curves, that is, the concentrations of reactants (H_2, O_2), chain carriers (H, O, OH), and the reaction product (H_2O), as functions of time, are shown in Fig. 6.3.

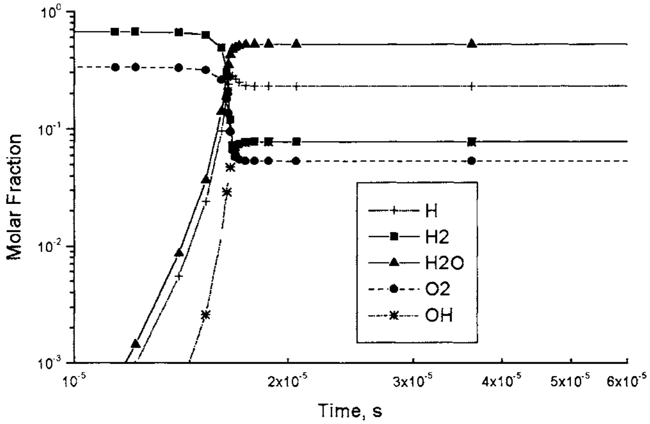


Fig. 6.3

9. *Comments*

a) The model is well suited for a chemical system contained in a closed vessel with thermally insulated walls. Such a system, referred to as calorimetric bomb, is a widespread tool for thermochemical and kinetic research.

b) During the induction period, ignition of fuel-air mixtures in internal combustion engines (ICE) corresponds to idealized model of adiabatic reaction at constant density (constant volume). In Ref. 65 the model of adiabatic reaction (Shell model of gasoline combustion) is used for simulation of self-ignition of hydrocarbon fuels at constant density for initial temperature range 800–1200 K and for initial pressures 10–30 atm. The model of adiabatic reaction with detailed kinetic scheme of gasoline-air gas mixtures was applied to investigation of "knocking" phenomenon in ICE (Ref. 66).

Relevant material can be found in Refs. 6 and 51.

C. Model of Adiabatic Reaction at Constant Pressure (C.9)

1. Purpose of the Model

The model aims at the determination of chemical components concentrations, temperature, and pressure, as functions of time in a closed, adiabatic system at constant pressure.

2. Assumptions

a) The chemical system is assumed to be closed, thermally insulated, single-phase, uniform, and homogeneous (adiabatic batch reactor).
b) Pressure p in the system is constant.
c) See other assumptions in the description of model C.3.

3. Restrictions

See the appropriate section in the description of model C.1.

4. Set of Equations of the Model

$$\frac{\rho \mathrm{d}c_i}{\mathrm{d}t} = R_i, \quad \rho = \text{const}, \quad p = \rho RT \sum_{i=1}^{N} c_i, \quad c_{pi} = \frac{\mathrm{d}H_j^0(T)}{\mathrm{d}T}, \quad c_p = \sum_{i=1}^{N} c_{pi} c_i$$

$$\rho c_p \frac{\mathrm{d}T}{\mathrm{d}t} = -\sum_{i=1}^{N} H_i^0 R_i$$

$$R_i = \sum_{j=1}^{S} (\nu_{ij}^- - \nu_{ij}^+) w_j, \quad w_j = k_{fj} \prod_{k=1}^{N} (\rho c_k)^{\nu_{kj}^+} - k_{bj} \prod_{k=1}^{N} (\rho c_k)^{\nu_{kj}^-}$$

5. Nomenclature

See the appropriate sections in the description of models C.7 and C.8.

6. Description of Coefficients and Parameters

See the description of models C.7 and C.8.

7. Features of the Model

The rate of change for concentration of *i*th component in closed system with variable volume V is defined as an increment of the amount of this component N_i (in mol) per time $\mathrm{d}t$ in unit volume:

$$R_i = \frac{\mathrm{d}N_i}{V\mathrm{d}t} = \frac{\mathrm{d}(y_i V)}{V\mathrm{d}t}$$

If molar–mass concentrations c_i are used instead of N_i, then the expression for R_i for chemical reactions in a closed system with variable volume V is written as:

$$R_i = \frac{\mathrm{d}(\rho c_i V)}{V\mathrm{d}t} = \frac{\mathrm{d}(c_i M)}{V\mathrm{d}t} = \frac{\rho \mathrm{d}c_i}{\mathrm{d}t}$$

This expression does not contain the variable V. Here, $M = \text{const}$ is the mass of the system.

8. Example

The model of adiabatic reaction at constant pressure is used here for simulation of hydrogen combustion in stoichiometric gas mixture with oxygen at the initial temperature $T = 1200\,\text{K}$, and the initial pressure $p = 1\,\text{atm}$. The concentrations of reactants (H_2, O_2), chain carriers (H, O, OH), and the reaction product (H_2O) as functions of time are shown in Fig. 6.4.

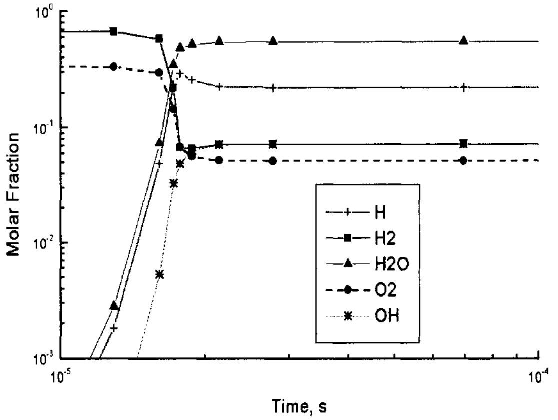


Fig. 6.4

9. Comments

The model is intended for the simulation of chemical systems where pressure is constant and volume is changed because of the reaction. Combustion of nonpremixed gas mixtures in diffusion flames, and premixed fuel-air combustion process (except the ignition stage) in internal combustion engines, are practical examples of adiabatic reactions at constant pressure (see Refs. 34 and 67). In these cases, temperature increase is smaller in comparison with that in reactions running at constant volume because of volume expansion of the mixture.

Relevant material can be found in Refs. 6 and 34.

D. Models of Plug Flow Reactor (C.10)

1. Purpose of the Model

The model aims at the the determination of the spatial profiles of the concentrations of chemical components, temperature, and pressure in a steady flow of chemically reacting gas, where transverse mixing of components is perfect, and longitudinal mixing is absent.

2. *Assumptions*

a) One-dimensional, stationary gas flow in a straight channel with constant cross section and adiabatic walls is considered.
b) Effects of molecular transport in the direction of gas flow are not taken into account.
c) Low-speed flows, where kinetic energy of the gas is small in comparison with the total energy, $u^2/2 \ll \sum_i^N H_i^0 c_i$, are considered.
d) See other assumptions in the description of model C.3.

3. *Restrictions*

The model is applicable for flows in channels with negligible longitudinal mixing: $D\partial(y_i/y)/\partial x \ll u$, where D is the diffusion coefficient (see the third volume of this series).

4. *Set of Equations of the Model*

$$\rho \cdot u \cdot \frac{\mathrm{d}c_i}{\mathrm{d}x} = R_i, \quad \rho \cdot c_p \cdot u \cdot \frac{\mathrm{d}T}{\mathrm{d}x} = -\sum_{i=1}^{N} R_i \cdot H_i^0$$

$$(p - \rho \cdot u^2) \cdot u \cdot \frac{\mathrm{d}\rho}{\mathrm{d}x} = \rho R c_p^{-1} \sum_{i=1}^{N} c_i \sum_{i=1}^{N} H_i^0 R_i - \rho RT \sum_{i=1}^{N} R_i$$

$$\rho u_0 = \text{const}, \quad \rho u^2 + p = \text{const}, \quad c_{pi} = \frac{\mathrm{d}H_i^0(T)}{\mathrm{d}T}, \quad c_p = \sum_{i=1}^{N} c_{pi} c_i$$

$$R_i = \sum_{j=1}^{S} (\nu_{ij}^- - \nu_{ij}^+) w_j, \quad w_j = k_{fj} \prod_{k=1}^{N} (\rho c_k)^{\nu_{kj}^+} - k_{bj} \prod_{k=1}^{N} (\rho c_k)^{\nu_{kj}^-}$$

5. *Nomenclature*

x	coordinate along the flow direction
u	gas velocity

See the definitions of other symbols in the descriptions of models C.7 and C.8.

6. *Description of Coefficients and Parameters*

See the description of models C.7 and C.8.

7. *Features of the Model*

a) The rate of change of concentration of ith component, R_i, in a steady open system operating in plug flow regime is:

$$R_i = \frac{\mathrm{d}l_i}{F\mathrm{d}x} = \frac{\mathrm{d}(u \cdot y_i)}{\mathrm{d}x}$$

where l_i is the molar flux of component i, F is the area of cross section of the reactor, and y_i is the molar–volume concentration of ith component.

Dependence of R_i on concentrations of components is determined by the Guldberg–Waage law (see the description of model C.1). If molar–mass concentrations c_i are used instead of y_i, then the expression for R_i for chemical reactions in plug flow reactor is written as:

$$R_i = \frac{\mathrm{d}(\rho u c_i)}{\mathrm{d}x} = \frac{\rho u \mathrm{d}c_i}{\mathrm{d}x}, \quad \text{since } \rho u = \text{const}$$

b) In a sufficiently long plug flow reactor, a spatially uniform state is established, where the first derivatives of the gas dynamic variables with respect to x become zero.

8. *Example*

The plug flow reactor model is used here for the simulation of combustion of stoichiometric hydrogen–air gas mixture. At the inlet cross section, the reacting gas mixture is characterizing by the molar ratio $H_2 : O_2 : N_2 = 2 : 1 : 4$, the initial temperature $T = 1200$ K, the initial pressure $p = 1$ atm, the gas mixture velocity $u_0 = 1$, m/s. The profiles of concentrations of reactants (H_2, O_2), chain carriers (H, O, OH), and the reaction product (H_2O) along the gas flow are shown in Fig. 6.5.

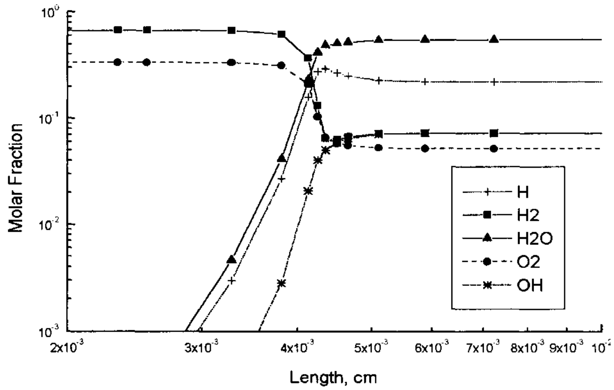


Fig. 6.5

9. *Comments*

a) Assumption 3 is not critical, and was introduced for simplicity of the model equations in cases when influence of heat generation on gas dynamics of reactive mixtures can be neglected. In the general case, when the magnitude of heat released during reaction is comparable with the kinetic energy of gas flow, it is necessary to use a complete energy equation. The complete energy equation has the following integral form: $\sum_i H_i^0 c_i + u^2/2 = \text{const}$. With the chemical heat release, so-called thermal crisis of flow is possible (see Ref. 68). Detailed description of thermal crisis of flow requires a joint solution of equations of chemical kinetics and gas dynamics.

b) If a gas flow passes through a reaction chamber where conditions necessary for the reaction (for example, high temperature or presence of a catalyst) are created, then, in the absence of longitudinal mixing, each volume of the reactive mixture can be regarded as a closed system shifted in space. Plug flow regime of reactions is widely used in research work and in the industry (see Refs. 6 and 16).

c) Tubular ovens in which a chemical process takes place in long tubes with small cross section, embedded in a combustion chamber, are examples of plug flow reactors. Fuel burning in the combustion chamber provides the necessary temperature regime for the chemical reaction in the tubes. Tubular reactors are widely used for hydrocarbon cracking for olephines or gasoline production (Ref. 59).

Relevant material can be found in Refs. 1 and 16.

E. Model of Well-Stirred Reactor

1. *Purpose of the Model*

Model aims at the determination of the parameters (density, temperature, and reactant concentrations) of reactive medium in a reactor where the initial reactants are supplied at a given flow rate, and the reaction products are removed simultaneously with the same mass flow rate.

2. *Assumptions*

a) In a well-stirred (also referred to as a perfectly mixed, back-mix, or stirred-tank) reactor, the chemical reaction runs in a constant volume V at constant pressure p. The reactants entering the reactor instantaneously assume a final, uniform throughout the reactor, chemical composition because of perfect mixing. Thus, the outlet stream has the same chemical composition as that within the reactor.

b) The initial reactive mixture is supplied into reactor with constant mass flow rate G, temperature T_0, and mole-mass concentrations of the components c_{i0}.

c) Heat losses through the reactor walls are constant.

d) See other assumptions in the description of model C.3.

3. *Restrictions*

Applicability of the model is restricted to reactors where uniformity of chemical composition of the reactive mixture throughout the reactor volume is provided by intensive mixing.

4. *Set of Equations of the Model*

$$\frac{\rho \mathrm{d}c_i}{\mathrm{d}t} = -\frac{\rho(c_i - c_{i0})}{\tau} + R_i, \quad \tau = \frac{\rho V}{G}$$

$$\rho c_p \cdot \frac{\mathrm{d}T}{\mathrm{d}t} = \rho \sum_{i=1}^{N} c_{i0} \frac{H_i^0(T_0) - H_i^0(T)}{\tau} - \frac{\sum_{i=1}^{N} H_i^0 R_i Q}{V}$$

$$V = \text{const}, \quad p = \text{const}, \quad \rho = \frac{p}{RT \sum_{i=1}^{N} C_i}$$

$$R_i = \sum_{j=1}^{S} (\nu_{ij}^- - \nu_{ij}^+) w_j, \quad w_j = k_{fj} \prod_{k=1}^{N} (\rho c_k)^{\nu_{kj}^+} - k_{bj} \prod_{k=1}^{N} (\rho c_k)^{\nu_{kj}^-}$$

$$c_{pi} = \frac{\mathrm{d}H_j^0(T)}{\mathrm{d}T}, \quad c_p = \sum_{i=1}^{N} c_{pi} c_i$$

5. *Nomenclature*

G	mass flow rate of reactants
V	reactor volume
τ	residence time in the reactor
Q	heat lost in the reactor to the walls per unit time

See the definitions of other symbols and description of coefficients in the descriptions of models C.7 and C.8.

6. *Features of the Model*

The main feature of the processes occurring in a well-stirred reactor at constant flow rate is the establishment of a steady-state regime under which a chemical reaction rate R_i is determined by the expression:

$$R_i = \frac{l_i - l_{i0}}{V} = \rho \frac{c_i - c_{i0}}{\tau}$$

where l_i is the molar flow rate of component i.

7. *Example*

The model of well-stirred reactor is used for simulation of stoichiometric hydrogen–oxygen combustion. At the inlet of a well-stirred reactor, the gas mixture has the initial temperature $T = 1200$ K and the initial pressure $p = 1$ atm. The average residence time of the mixture in the reactor is $\tau = 1$ s. The stationary values of concentrations of reactants (H_2, O_2), chain carriers (H, O, OH), and the reaction product (H_2O) are shown in Fig. 6.6.

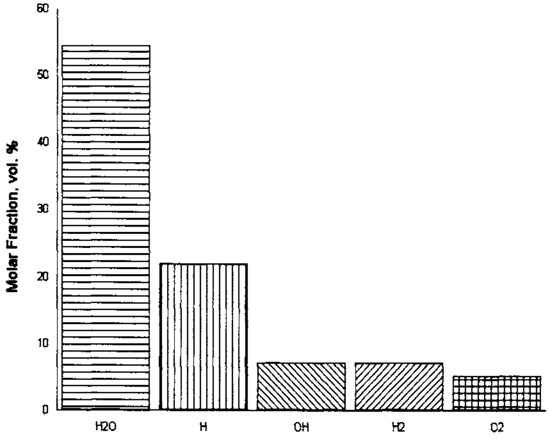


Fig. 6.6

8. *Comments*

a) For sufficiently complex chemical processes that include simple chemical reactions of the second and higher orders, a set of algebraic equations obtained by equating the derivatives of gas dynamic variables to zero can have multiple solutions. This means that for given model parameters, different stationary regimes exist. In such a case, one or the other regime will be realized depending on the initial values of gas dynamic variables. Each stationary regime has a corresponding range of initial values of gas dynamic variables for which the stationary regime can be attained.

b) Well-stirred reactors are used in both industry and research studies. For example, in Ref. 69, a well-stirred reactor is used for the investigation of mechanism of nitrogen oxide formation during methane combustion in air. The necessary degree of mixing was achieved by using a special jet injection of reactants into reactor. The main reason for the use of this type of reactor is the need to exclude the influence of diffusion processes on chemical reaction kinetics.

Relevant material can be found in Refs. 1 and 16.

XIV. Mathematical Modeling in Chemical Kinetics

Mathematical models are used in chemical kinetics for solution of the following basic kinetics problems:

1. *direct kinetic problem*: to calculate time dependencies of component concentrations (kinetic curves) and thermochemical parameters of a chemical system with a given mechanism of complex chemical reaction, known reaction rate constants, and defined initial conditions;

2. *inverse kinetic problem*: to determine rate constants of separate stages of reaction mechanism on the basis of comparison of simulation results and experimental data;
3. *problem of analysis of complex chemical reaction mechanism*: to determine the sensitivity of kinetic curves to the parameters of separate stages of the process, and to build an hierarchy of separate stages according to some criteria.

Solution of chemical kinetics problems is carried out with both *analytical* (mainly asymptotic) and *numerical methods.*

A. Direct Kinetic Problem

Direct kinetic problem in formal representation is a system of ordinary differential equations (ODEs) of first order with specified initial conditions (Cauchy mathematical problem)

$$\frac{\mathrm{d}y_i}{\mathrm{d}t} = f_i(y_1, \ldots, y_n), \quad y_i(0) = y_{i0}, \quad i = 1, \ldots, N$$

where $0 < t < t_{\max}$, and Y_{i0} are the initial conditions for reactant concentrations. The peculiarity of solution of the chemical kinetics equations is that the time scales of different variables (concentrations of reactants, intermediates, and products) have substantially different magnitudes. In a typical reacting system, *fast* and *slow changing variables* exist simultaneously. The values of fast variables adjust practically instantly to the changes in the values of slow variables. This peculiarity permits application of asymptotic analytical methods such as the *method of quasi-stationary concentrations* and the method of *quasi-equilibrium concentrations* to solution of chemical kinetics problems (Refs. 1, 5, 9, 11, 12, 23 and 49).

Stiff ordinary differential equations are differential equations that describe behavior of chemical processes with vastly different time scales. The stiffness of a problem is revealed during investigation of local (in the sense of small deviation from the actual solution) behavior of a set of chemical kinetic equations. The original set of chemical kinetics equations is linearized, i.e., is transformed into a set of linear equations with a Jacobi matrix $A_{ij}(y_i, y_j, t) = (\partial f_i/\partial y_j)$. The locally linear system approximates the original non-linear system, if the Jacobi's matrix varies only slightly in some vicinity of the solution. In mathematical formulation, the Cauchy problem is stiff if the problem is stable (the real parts of the eigenvalues $\lambda_i(\lambda_i \in [\lambda_{\min}, \lambda_{\max}])$ of Jacobian A_{ij} are negative $(\mathrm{Re}(\lambda_i < 0))$, and the strong inequality $\mathrm{Re}(-\lambda_{\min})/\mathrm{Re}(-\lambda_{\max}) \gg 1$ is satisfied in the local domain.

The existence of fast (with the time scale $\tau_{fast} \propto 1/\mathrm{Re}(\lambda_{\max})$) and slow (with the time scale $\tau_{slow} \propto 1/\mathrm{Re}(\lambda_{\min})$) subsystems determines the obstacles encountered in numerical solution of the direct kinetic problem. In chemical kinetic problems, the magnitude of *local stiffness*, or *stiffness parameter* $\mathrm{Re}(-\lambda_{\min})/\mathrm{Re}(-\lambda_{\max})$, can reach the values of the order 10^6–10^9. Large value of stiffness parameter substantially restricts the integration time step h. For a converging and stable numerical solution of kinetic problem, it is necessary to select a small value of integration step $h \approx 1/\mathrm{Re}(-\lambda_{\max})$. Because of the stiffness of kinetic equations, the minimal number of integration steps is comparable with $|\mathrm{Re}(-\lambda_{\min})/\mathrm{Re}(-\lambda_{\max})|$, which in most cases limits the rate of numerical integration of the equations.

Widely used algorithms for numerical solution of direct kinetic problems include methods of Gear, Rosenbrock, and others (Refs. 11 and 70–78).

B. Inverse Kinetic Problem

Solution of *inverse kinetic problem* for a chemically reacting system implies creation of a model of the chemical process, which describes the experimental data. In a broad statement of the problem, creation of a model means specifying the right-hand sides (kinetic functions) of the set of differential equations for the direct kinetic problem. In the narrow statement of the problem, an inverse problem consists in evaluation of rate constants for some elementary stages of the mechanism of complex chemical reaction on the basis of comparison of simulation results and experimental data.

Inverse kinetic problem belongs to a class of *incorrectly defined problems* (Ref. 76). A problem is correctly defined if a solution exists, is unique, and is stable with respect to variation of initial data. In practice, most inverse kinetic problems have solutions, but the solutions can be non-unique and unstable, when small uncertainties of experimental data sharply affect the evaluated parameters. The basic reasons for nonuniqueness of solution of inverse kinetic problems are finite time of experiments and insufficient time resolution of the experimental techniques. The time duration of experimental study can be insufficiently long for evaluation of the rate constants of slow reactions, and the time resolution of experimental measurements can be insufficient for evaluation of rate constant of fast reactions. The sufficient condition for existence of a unique solution of inverse kinetic problem is a possibility of experimental measurement of the concentration of any component at any moment of time with arbitrarily high accuracy.

The main stages of solution of an inverse kinetic problem:

1. *Formation of the model includes*
   a) definition of a set of components participating in the reaction,
   b) selection of a type of governing kinetic law (e.g., the law of mass action, the law of surface action, non-equilibrium kinetics, etc.),
   c) selection of a hypothetical reaction mechanism or a few alternative kinetic schemes,
   d) selection of a proper functional $\Phi(K)$ (K symbolically represents the model parameters) for quantitative evaluation of discrepancy between experimental data and simulation results,
   e) search for the minimum of the functional $\Phi(K)$ in the appropriate domain of variation of the model parameters;
2. *Evaluation of model parameters* consists in fitting the calculated values of kinetic parameters to experimental data via selection of optimal values of model parameters;

3. *Validation of hypothesis* involves quantitative or qualitative estimation of the accuracy of the model, selection of the best variant among alternative models, and possibly formulation of a new hypothesis.

C. Analysis of Mechanisms of Complex Chemical Reactions

Because of the limited time allocated to research work and the limited accuracy of available experimental techniques, analyses of mechanisms of complex chemical reactions are carried out with various approximate kinetic schemes. Because the description of physico-chemical kinetics is often only a part of overall modeling of gas dynamic or thermophysical processes, reduced (compact) kinetic schemes are frequently used in practical applications.

Different approaches to analysis of mechanisms of complex reactions include at least two basic steps: *sensitivity analysis* and *rate-of-production analysis.* Sensitivity analysis investigates the influence of parameters, (such as the rates of the elementary reactions) on the output of the model (such as on the ignition delay time for combustion reactions). The goal of sensitivity analysis is identification of the rate-limiting stages. These stages are the key reactions in the main reaction pathways. The competition between different pathways and the relationship between the main reactants is studied with rate-of-production analysis. Rate-of-production analysis determines the contribution of various elementary reactions to the production of species.

The *methods of sensitivity theory* (Ref. 79) are used for quantitative estimation of importance of different stages of complex chemical reaction and for construction of reduced kinetic schemes. A hierarchy of stages of chemical reaction is based on comparison of the rates of different stages. Further reduction of the kinetic scheme is performed using stoichiometric relations. *Sensitivity theory* studies an extent of influence that variation of parameters of the model has on system behavior. Application of sensitivity theory to determination of the most important stages of chemical reaction mechanism is based on the principle that the more important the stage is the stronger is the influence of variation of its rate constant on the calculation result. This principle defines the statement of problem for *chemical kinetics sensitivity analysis*: determine how strongly a variation of each model parameter (i.e., the rate constants k_i of elementary stages) affects the concentrations y_i.

Local sensitivity analysis consists in solution of the sensitivity analysis problem for a single point in the parameter space.

Global sensitivity analysis consists in solution of the sensitivity analysis problem for a finite domain of the parameter space.

Sensitivity coefficients are the partial derivatives of the solution vector with respect to components of the vector of parameters, $\beta_{ij} = \partial y_i / \partial k_j$.

Matrix of sensitivity coefficients $\underline{B}(t) = (\beta_{ij}(t))$ is a matrix composed of the sensitivity coefficients. Analysis of sensitivity matrix shows how strongly variation of rate constants affects component concentrations, and which elementary stages determine the overall chemical kinetics of the process.

Various aspects of sensitivity theory in application to chemical kinetics are described in Refs. 80 and 81. Reviews of the basic methods of sensitivity analysis and their applications to reduction of chemical kinetic schemes are given in Refs. 82–84.

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Chapter 7

Low Temperature Plasma Kinetics (P Models)

I. Main Nomenclature

Arguments

ε	energy of relative motion of colliding particles
p	gas pressure
ρ	gas density
$\mathcal{E}$	electric field

Quantities determined in the models

T_e	electron temperature, that is, temperature of the electron gas in a plasma
T	gas temperature, temperature of translation motion of gas particles
T_X	temperature of heavy particles X
T_a	temperature of atoms
T_i	ion temperature
T_m	temperature of molecules
T_r	rotational temperature of molecules
T_v	vibrational temperature of molecules
n_a, n_e, n_m, n_i	number densities of atoms, electrons, molecules, and ions
n_A or N_A, n_X or N_X	number densities of particles A and X, respectively

Kinetic quantities

ν_e	total frequency of elastic collisions of an electron with other particles
ν_ee	electron–electron collision frequency
ν_ea	frequency of elastic electron–atom collisions
ν_em	frequency of elastic electron–molecule collisions
ν_ei	frequency of elastic electron–ions collisions
ν_eX	frequency of elastic electron–heavy particle X collisions
$\nu_{\mathrm{e}E}$	frequency of inelastic electron–heavy particle collisions with excitation (deactivation) of electronic states of atoms (molecules)
$R_{\mathrm{e}\Sigma}$	total energy exchange rate between electron and heavy particles
R_ei	energy exchange rate in elastic collisions of electrons with ions

R_{ea}	energy exchange rate in elastic collisions of electrons with atoms (molecules)
$R_{\mathrm{e}r}$	energy exchange rate in collisions of electrons with molecules with excitation (deactivation) of molecular rotations
$R_{\mathrm{e}v}$	energy exchange rate in collisions of electrons with molecules with excitation (deactivation) of molecular vibrations
$R_{\mathrm{e}E}$	energy exchange rate in collisions of electrons with molecules with excitation (deactivation) of electronic states of atoms, molecules, or ions
$R_{\mathrm{e}I}$	energy exchange rate in collisions of electrons with molecules with ionization of atoms (molecules)
$q_{\mathrm{ea,m}}(\varepsilon)$	electron–atom, electron–molecule elastic collision cross section [in models I-T.5–I-T.8, these quantities are denoted a $Q_0(\varepsilon)$]
$k_{\mathrm{e}r}$	rate constant of rotational excitation of molecules by electron impact
k_{ev}	rate constant of vibrational excitation of molecules by electron impact
$q_{1n}(\varepsilon)$	cross section for excitation of atoms from ground state $1 \to n$, by electron impact, where n is the quantum number of the excited state (see models I-E.2, I-E.3)
$q_i(\varepsilon)$	cross section of ionization of atom (molecule) by electron impact [in the models I-P.11, I-P.12, these quantities are denoted as $\sigma_i(\varepsilon)$, $\sigma_n(\varepsilon)$]
σ	electrical conductivity

Particle characteristics

m, m_{X}	mass of a particle, mass of particle X
m_{a}, m_{m}, m_{i}, m_{e}	mass of an atom, a molecule, an ion, an electron, respectively
I, IP	ionization energy
I_n	energy of ionization from nth excited level
EA	electron affinity
ω_0	fundamental vibrational frequency of diatomic molecule
θ_v	characteristic vibrational temperature of a molecule
B	rotational constant of a molecule
Q	quadrupole momentum of a molecule
E_2	excitation energy of the first excited state of atom (molecule)
a_0	Bohr radius
n_n^0	equilibrium value of number density n of particles (population) of nth excited state
Z	ion charge number
e	electron charge
Λ	Coulomb logarithm (see model I-T.13)
Λ_1	Coulomb logarithm for inelastic collisions (see model I-E.4)
Q_t	partition function of translation motion
g_m	multiplicity (degeneracy) of state with principal quantum number m

II. Definitions and Criteria

Plasma is an ionized gaseous medium which is electrically neutral in every physically small volume (quasi-neutral plasma). Partially ionized plasma includes both electrons, ions, and neutral atoms and molecules.

Criterion of plasma quasi-neutrality is:

– For plasmas containing only positive ions:

$$|n_\mathrm{i} - n_\mathrm{e}| \ll n_\mathrm{i} \tag{1}$$

– For plasmas containing both positive and negative ions

$$|n_\mathrm{i}^+ - n_\mathrm{e} - n^-| \ll n_\mathrm{i}^+ \tag{2}$$

Electron temperature, or temperature of the electron gas in plasma T_e is the module of the canonical distribution of electrons in their energy [see Eq. (6)].

Gas temperature, or temperature of translational motion of gas particles T is the module of the canonical distribution of heavy particles (atoms, molecules) in their translational energy [see Eq. (6)].

Ion temperature T_i is the module of the canonical distribution of ions in their translational energy.

Debye shielding: Because of Coulomb interaction and thermal motion, local charge separation takes place in plasmas. A test charge is surrounded by a sphere containing charges of the opposite sign. This sphere is called the Debye sphere, and its radius is called the Debye radius R_D (Refs. 1 and 2):

$$R_\mathrm{D} = \sqrt{\frac{kT_\mathrm{e}T_\mathrm{i}}{4\pi e^2 n_\mathrm{e}(T_\mathrm{i} + T_\mathrm{e})}} \tag{3}$$

Ideal plasma is a plasma in which Coulomb interaction is weak, so that the mean interaction energy among particles is small compared with their kinetic energy. Plasma temperature is the characteristic of mean kinetic energy.

Criterion of ideal plasma is:

– For interaction between charged particles

$$\frac{e^2}{R_\mathrm{D}} \ll kT \tag{4}$$

where $T = T_\mathrm{e}T_\mathrm{i}/(T_\mathrm{e} + T_\mathrm{i})$. This criterion means that a large number of charged particles should be in the Debye sphere. Example: in a hydrogen plasma with electron number density $n_\mathrm{e} = 10^{15}\,\mathrm{cm}^{-3}$ and temperature $T_\mathrm{e} = 1$ eV, there are 40 charged particles in the Debye sphere. Such plasma can be considered ideal.

– For interaction between charged and neutral particles:

$$\frac{2\pi\alpha e^2 n_\mathrm{X}}{R_0} \ll kT \tag{5}$$

where α is the polarizability of the neutral particle, and R_0 is the gas kinetic radius of collision.

Equilibrium plasma: Thermodynamically equilibrium plasma is the limiting case of the plasma state. In such plasma, there are no gradients and fluxes. All the characteristics of such plasma are constant in time. The following requirements must be satisfied in equilibrium:

1. The plasma state is completely defined by the chemical composition and two thermodynamic parameters (for example, temperature and pressure).
2. Plasma particle distribution functions in their translational energy must be Maxwellian with the temperature common to all types of the particles:

$$f(\varepsilon) = \frac{2}{\sqrt{\pi}} \frac{\sqrt{\varepsilon}}{(kT)^{3/2}} \exp\left(-\frac{\varepsilon}{kT}\right) \tag{6}$$

3. The equation of state takes into account the decrease in plasma pressure $\Delta p = e^2/3R_D$ caused by the Coulomb interaction between charged particles:

$$p = (n_a + n_m + n_i + n_e)kT - \Delta p \tag{7}$$

4. Distributions of particle among excited states (populations of excited states) are described by the Boltzmann formula

$$\frac{n_k}{n_l} = \frac{g_k}{g_l} \exp\left(-\frac{\varepsilon_k - \varepsilon_l}{kT}\right) \tag{8}$$

5. Each forward elementary process is balanced by the corresponding reverse process. Relations between particle number densities is established by the Saha equations:

$$\frac{n_e n_i}{n_{a,m}} = \frac{g_e g_i}{g_{a,m}} \left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} \exp\left(-\frac{I - \Delta I}{kT}\right) \tag{9}$$

where ΔI is the decrease in ionization energy because of the Coulomb interaction,

$$\Delta I = 2\sqrt{\pi} e^3 \sqrt{\frac{n_e}{T}} \tag{10}$$

6. The radiation field is in thermodynamic equilibrium with plasma, so that emission is compensated by absorption.

Nonequilibrium plasma is a plasma for which one or more of the six requirements previously listed are not satisfied.

If plasma is nonequilibrium in its entire volume, but one can select a small volume in which the six requirements are satisfied, the state of plasma in this volume is referred to as *local thermodynamic equilibrium* (*LTE*).

Partial local thermodynamic equilibrium state of plasma is a nonequilibrium state of plasma consisting of physically small plasma volumes, so that each of these volumes is approximately in thermodynamic equilibrium and is characterized by its own set of macroscopic parameters that may depend on time.

Unsteady nonequilibrium plasma is a nonequilibrium plasma the parameters of which (for example, temperature or particle number densities) depend on time.

Steady nonequilibrium plasma is a nonequilibrium plasma, the parameters of which do not depend on time. Plasma in the positive column of glow discharge is an example of quasi-steady nonequilibrium plasma. Electron temperature in such plasma may differ from temperature of heavy particles, $T_e \neq T$, but neither temperature depends on time. The heating of electrons by electric field is compensated by their energy loss in collisions with heavy particles. The gas temperature is sustained at constant value, because the rate at which the heavy particles receive energy from electrons is equal to the rate at which they lose energy to the surroundings. Electron and ion number densities are maintained constant because the rates of ionization and recombination reactions are equal to each other.

Criteria for existing of various plasma states and the times of their relaxation from nonequilibrium to equilibrium are described in this chapter.

Single-temperature plasma is plasma in which the temperatures of electrons, ions, and neutral particles are equal to each other: $T_e = T_i = T_X = T$.

Criterion for existence of single-temperature plasma in the presence of Joule heating, that is, under the influence of electric field, is:

- For interaction of electron with any heavy particles:

$$\frac{T_e - T}{T} = \frac{2e^2\mathrm{E}^2}{3m_e\nu_e R_{e\Sigma}(T)} \ll 1 \tag{11}$$

  Rates of energy exchange in collisions between electrons and various particles in plasmas, and the respective collision frequencies are described in model P.1. For collision frequencies, see Refs. 1, 3, and 4 and models in Vol. I, Chapters 2, 5, and 7, of this series. An estimate for $\nu_{eE}(T_e)$ transitions between electronic level of heavy particles $k \Leftrightarrow n$ in collisions with electrons is:

$$\nu_{eE}(T_e) = q_{kn}\sqrt{8kT_e/\pi m_e}\exp(-E_{kn}/kT_e) \tag{12}$$

  Here, q_{kn} is the average cross section for electronic transition $k \rightarrow n$, and E_{kn} is the energy of the transition $k \rightarrow n$ (see models I-E.2–I-E.4).
- For plasmas in monatomic gases, $R_{ea}(T) = kT\delta(\nu_{ea} + \nu_{ei})$, where $\delta = 2m_e/m_a$ is the factor of energy transfer (the average portion of electron energy transferred in a single collision), so

$$\frac{T_e - T}{T} = \frac{2e^2\mathrm{E}^2}{3kT\delta m_e\nu_e^2} \ll 1 \tag{13}$$

  where E is in V/cm, T is in K, and ν_{ea} is in s^{-1}. For values of collision frequencies $\nu_e = \nu_{ea} + \nu_{ei}$, see models I-T.7, I-T.10, and I-T.13. For example, in cold weakly ionized helium ($T = 300$ K, $\nu_{ea} \gg \nu_{ei}$), electrons become hot in relatively weak electric field $\mathrm{E}/n_a \approx 2 \times 10^{-22}\,\mathrm{V \cdot cm^2}$, where n_a is the number density of helium atoms.

- For plasmas in molecular gases, the value $(T_e - T)/T$ is calculated using Eq. (11). The rate of energy exchange taking into account rotational and vibrational excitation of molecules can be written as:

$$R(T) = kT\delta\nu + \sqrt{\frac{8kT}{\pi m_e}}\frac{8\pi Q^2 a_0^2}{15} n_m + \hbar\omega_0 k_v(T) n_m \tag{14}$$

  where $\nu = \nu_{em} + \nu_{ei}$; $\delta = 2m_e/m_m$; m_m is the mass of gas molecule; $k_v(T)$ is the rate constant for excitation of molecular vibrations by electron impact; and $\hbar\omega_0$ is the vibrational quantum of gas molecule. Values B, Q, $\hbar\omega_0$ are presented in Refs. 3 and 4. Estimation for $k_v(T)$ gives $k_v(T) = 10^{-10}$–$10^{-8}\,\mathrm{cm}^3/\mathrm{s}$, see also models I-R.6, I-R.7 and Chapter 4 in volume I of this series.

Relaxation of electron temperature is a process in which the electron temperature, T_e, approaches the gas temperature, T. This process is caused by energy exchange between electrons and heavy particles, if the plasma was initially brought into a nonequilibrium state by an external action (for example, by a pulse of electric or electromagnetic field).

Electron temperature relaxation time τ_{T_e} is:

$$\tau_{T_e} = \frac{kT_e}{R_{e\Sigma}(T_e)} \tag{15}$$

$R_{e\Sigma}(T_e)$ is the energy exchange rate (see Eq. (14) and model P.1). At high T_e, $R_{e\Sigma}$ includes electron energy losses in excitation of electronic states and ionization. For atomic plasma:

$$R(T) = kT_e\delta\nu(T_e) + E_n\nu_{eE}(T_e) \tag{16}$$

where $\nu(T_e)$ and $\nu_{eE}(T_e)$ are elastic and inelastic collision frequencies that depend on electron temperature. For methods of calculation of $\nu_{eE}(T_e)$, see I-E.2, I-E.3, and Refs. 1, 4–6. Estimation for ν_{eE} can be done as follows:

$$\nu_{eE}(T_e) = \sigma_{kn}\sqrt{8kT_e/\pi m_e}\exp(-E_2/kT_e) \tag{17}$$

where the average cross section for inelastic collision $\sigma_{kn}(\varepsilon) = 10^{-17}$–$10^{-15}\,\mathrm{cm}^2$, and E_2 is the excitation energy of the first excited state of a molecule (or atom). For values of E_2 for various atoms and molecules, see Ref. 3. The ionization frequency ν_i is calculated in a similar way.

Two temperature plasma is characterized by two Maxwellian distributions, one with temperature T_e for electrons, and another with temperature T for heavy particles.

Criterion of existence of two temperature plasma (T_e differs from T) in an external electric field is the opposite to (13):

$$\frac{T_e - T}{T} = \frac{2e^2\mathrm{E}^2}{3kT\delta m_e\nu_e^2} \geq 1 \tag{18}$$

Criteria for preservation of Maxwellian electron energy distribution because of the energy exchange between electrons in collisions are:

1. Electron–electron energy exchange rate exceeds the rate of electron heating in the external electric field:

$$kT_e\nu_{ee} \geq 3e^2\mathrm{E}^2/m_e\nu_{ee} \tag{19}$$

   This criterion can be written as a constraint on the electric field:

$$\mathrm{E} \ll \frac{1}{2}\nu_{ee}\sqrt{\frac{m_e kT_e}{3}} \tag{20}$$

   where ν_{ee} is in s^{-1}, and T_e is in K. For the values $\nu_{ee} = \nu_{ee}(T_e)$, see model I-T.13.
2. Electron–electron energy exchange rate exceeds the rate of energy exchange between electrons and atoms (or molecules):

$$\frac{kT_e\nu_{ee}}{R_{ea}(T_e)} \gg 1 \tag{21}$$

   In atomic plasmas:

$$\frac{\nu_{ee}}{\delta\nu_{ea}} \gg 1 \tag{22}$$

   Collision frequencies ν_{ee} and ν_{ea} are presented in models I-T.7, I-T.8, and I-T.13.

Unsteady two-temperature plasma can be realized under a pulse action on plasma during time

$$t \leq \tau_{T_e}$$

where τ_{T_e} is the electron temperature relaxation time, see Eq. (5). For example, behind a front of a strong shock wave, the temperature of heavy particles increases, and the electron temperature stays close to its initial value during the time shorter than τ_{T_e}. Unsteady two-temperature plasmas can also exist during a short period of time in the afterglow of glow, RF, or microwave discharges.

Plasma with nonequilibrium distribution of hot electrons is a plasma with non-Maxwellian electron energy distribution, and with high average electron energy $\bar{\varepsilon} \gg T$.

Criterion for non-Maxwellian distribution of electrons in an external electric field is the opposite to Eq. (19):

$$kT_e\nu_{ee} \ll 3e^2\mathrm{E}^2/m_e\nu_{ee} \tag{23}$$

where $T_e = (2/3)(\bar{\varepsilon}/k)$.

Generally, the particle distribution functions in plasmas are not Maxwellian. Some non-Maxwellian distribution functions, such as Davydov, Druyvestein, and Margenau distribution functions, are discussed in plasma models presented below.

Relevant material can be found in Refs. 1, 2, 5, 7, and 8.

III. Models of Low-Temperature Plasma Kinetics

The models of low-temperature plasma kinetics presented in this book comprise four groups. The first group describes thermal processes that mainly affect electron temperature. Electron gas is the plasma component most responsive to external action. Model P.1 can be used to determine the electron temperature when both elastic and inelastic collisions, as well as heating by an external electric field, are included in the balance of electron energy. Model P.2 evaluates the relaxation time for the temperature of electron gas brought out of equilibrium by an external action. Model P.3 deals with electron temperature variation in recombining plasmas, when the electron heating because of recombination can arrest the decrease in the degree of ionization with time (so that ionization freezes). Model P.4 describes atom and ion heating through collisions with electrons, which may result in an instability of a spatially homogeneous plasma.

The second group of models is focused on ionization and recombination. Model P.5 can be used to calculate a nonequilibrium degree of ionization, both time-dependent and under steady-state conditions, by taking into account ionization–recombination processes, radiation emission, and ambipolar diffusion of charged particles to the boundaries of plasma volume. Model P.6 is a special case of the preceding model, in which steady nonequilibrium regimes are analyzed in more detail. Model P.7 describes the decrease in electron concentration with time in recombining plasmas with ambipolar diffusion. Model P.8 predicts distributions of concentrations for charged particles (electrons and positive and negative ions) in substantially nonequilibrium, weakly ionized plasmas.

The third group of models deals with population densities of atomic levels. Model P.9 is based on a set of balance equations for excited states. It can be used to evaluate relaxation times of various excited states. Model P.10 describes the distribution of atomic excited states in the diffusion approximation in energy space. This model offers a qualitative analysis that is quantitatively correct at low temperatures. Model P.11 supplements the preceding model with a description of processes that occur at high temperatures. Model P.12 also describes the distribution of atomic excited states in the diffusion approximation in energy space. The model supplements models P.10 and P.11, taking into account the formation of atoms in highly excited states in recombination processes, and also deactivation of these excited states by gas atoms.

The fourth group of models is devoted to electron energy distribution functions (EEDFs). With model P.13, one can calculate the electron energy distribution function (EEDF) for a steady, weakly ionized, atomic plasma in an external electric field with elastic electron–atom collisions. The predicted EEDF differs from the Maxwellian distribution at all energies. Model P.14 deals with the EEDF for a highly ionized plasma with inelastic collisions that can substantially deplete the high-energy tail of the electron energy distribution. Model P.15 can be used to calculate the EEDF for a molecular plasma in an external field, with energy transfer between electrons and vibrational degrees of freedom, which can substantially modify the form of the EEDF. Model P.16 evaluates the EEDF relaxation time after a strong external disturbance and describes transition to a steady (equilibrium or nonequilibrium) state. Model P.17 calculates the EEDF for a weakly ionized plasma in an external electric field with inelastic collisions that are so intense that the form of the EEDF is affected at all energies.

References to models presented in Volume I of this series begin with I, which is followed by the model index, for example, I-T.7, I-T.13, and I-E.2.

A. Model of Local Electron Energy Balance (P.1)

1. *Purpose of the Model*

The model aims at the calculation of electron temperature in atomic and molecular plasmas, when the electron energy balance is controlled by processes taking place in plasma volume: elastic and inelastic collisions, and Ohmic heating.

2. *Assumptions*

a) Temperatures of electrons and heavy particles are different from each other.
b) Electron energy distribution function is Maxwellian.
c) External electric field can be applied to the plasma.
d) Plasma is neither in ionization equilibrium nor in electronic-state equilibrium.
e) The atomic plasma can contain molecules whose concentration is much lower than the atom concentration. The vibrational and rotational states of molecules are in Boltzmann equilibria characterized by distinct vibrational and rotational temperatures.
f) Both elastic and inelastic collisions of electrons with atoms and molecules, as well as Ohmic heating by external field, are taken into account in the analysis of energy transfer.

3. *Model Equations*

$$\begin{gathered} n_e R_{e\Sigma} = \sigma \mathrm{E}^2 \\ R_{e\Sigma} = R_{ei} + R_{ea} + R_{er} + R_{ev} + R_{eE} + R_{eI} \end{gathered} \tag{1}$$

$$R_{ei} = \frac{3 m_e k}{m_i}(T_e - T)\nu_{ei}(T_e) \tag{2}$$

$$\nu_{ei} = 2\sqrt{2\pi} Z^2 e^4 \Lambda n_i / \sqrt{m_e}(kT_e)^{3/2} \tag{3}$$

$$R_{ea} = \frac{3 m_e k}{m_a}(T_e - T)\nu_{ea}(T_e) \tag{4}$$

$$\nu_{ea} = \left(\frac{2^{3/2}}{\sqrt{\pi m}}\right) n_a (kT_e)^{-5/2} \int_0^\infty e^{-\varepsilon/kT_e} q_{ea}(\varepsilon)\varepsilon^2 \, d\varepsilon \tag{5}$$

$$R_{er} = \frac{8B}{T_e}(T_e - T_r) n_m k_{er} \tag{6}$$

$$\nu_{er} = q_Q n_m \sqrt{8kT_e/\pi m_e}, \qquad q_Q = \left(\frac{8}{15}\right)\pi Q a_0^2 \tag{7}$$

$$R_{ev} = \frac{\hbar\omega_0}{T_e}(T_e - T_v) n_m k_{ev} \tag{8}$$

$$R_{eE} = n_a\left(\frac{2^{3/2}}{\sqrt{\pi m}}\right)(kT_e)^{-3/2}\sum_n (I - I_n)\int_{I-I_n}^{\infty} e^{-\varepsilon/kT_e} q_{1n}(\varepsilon)\varepsilon\, d\varepsilon \tag{9}$$

$$R_{eI} = n_a\left(\frac{2^{3/2}}{\sqrt{\pi m_e}}\right)(kT_e)^{-3/2} I \int_{I}^{\infty} e^{-\varepsilon/kT_e}\sum_n q_i(\varepsilon)\varepsilon\, d\varepsilon \tag{10}$$

For collisions of electron with molecules, the subscript "ea" should be changed by index "em."

4. *Nomenclature*

a) Quantities calculated with the model:

T_e	electron temperature
T_v, T_r	vibrational and rotational temperatures
n_a, n_e, n_m, n_i	atom, electron, molecule, and ion number densities

b) Kinetic coefficients:
Quantities contained in R_Σ:

R_{ei}	rate of energy transfer in elastic collisions of electrons with ions
R_{ea}	rate of energy transfer in elastic collisions of electrons with atoms and molecules
R_{er}	rate of energy transfer in electrons collision with molecules with rotational excitation of molecules
R_{ev}	rate of energy transfer in electrons collision with molecules with vibrational excitation of molecules
R_{eE}	rate of energy transfer in electrons collision with atoms and molecules with electronic excitation of atoms and molecules
R_{eI}	rate of energy transfer in electrons collision with atoms and molecules with ionization of atoms and molecules
ν_{ei}	electron–ion elastic collision frequency (see I-T.13)

$\nu_{\mathrm{ea}}, \nu_{\mathrm{em}}$	electron–atom and electron–molecule elastic collision frequencies (see I-T.7–I-T.10)
$q_{\mathrm{ea}}(\varepsilon)$	electron–atom or electron–molecule elastic collision cross section (see I-T.7–I-T.9) ($q_{\mathrm{ea}}(\varepsilon) \equiv Q_0(\varepsilon)$ in the other chapters of this volume and in the first volume of this series)
k_{ev}	rate constant for vibrational excitation of molecules by electron impact
$q_{1n}(\varepsilon)$	cross section for atom excitation $1 \rightarrow n$ from the ground state 1 to level n by electron impact (see I-E.2, I-E.3) ($q_{1n}(\varepsilon) \equiv \sigma_{1n}(\varepsilon)$ in the other chapters of this volume and in the first volume of this series)
σ	electrical conductivity
$q_i(\varepsilon)$	cross section for atom ionization by electron impact (see I-P11, I-P.12) [$q_i(\varepsilon) \equiv \sigma_i(\varepsilon)$ in the other chapters of this volume and in the first volume of this series]

c) Other quantities:

E	electric field
θ_v	characteristic molecular vibrational temperature
$\hbar\omega_0$	magnitude of vibrational quantum of diatomic molecule
Q	quadrupole moment of a molecule
E_2	excitation energy for the lowest excited state of an atom or molecule
I	ionization energy from the ground state of atom or molecule ($I \equiv I_1, I \equiv IP$ in the other chapters of this volume and in the first volume of this series)
I_n	ionization energy from the level with principal quantum number n
ε	electron energy
a_0	Bohr radius
$m_{\mathrm{a}}, m_{\mathrm{m}}, m_{\mathrm{i}}, m_{\mathrm{e}}$	masses of atom, molecule, ion, and electron
n_n^0	equilibrium value of the population density in level n
Z	charge number of ion
e	electron charge
Λ	Coulomb logarithm (see I-T.13)
B	rotational constant of a molecule

5. *Model Description*

The governing equation is an expression for the energy conservation law.

The expressions for $R_{\mathrm{ei}}, R_{\mathrm{ea}}, R_{er}, R_{\mathrm{ev}}$ satisfy detailed balance relations, vanishing at $T_{\mathrm{e}} = T$, $T_{\mathrm{e}} = T_r$, $T_{\mathrm{e}} = T_v$, respectively.

a) In a weakly ionized atomic plasma, when the energy lost in elastic electron–ion collisions and inelastic collisions is negligible,

$$\frac{3m_e k}{m_a}(T_e - T)\nu_{ea} n_e = \sigma \mathrm{E}^2 \tag{11}$$

$$\sigma = e^2 n_e / m_e \nu_{ea} \tag{12}$$

b) In a weakly ionized atomic plasma seeded with molecules, when energy transfer is controlled by elastic electron–atom collisions and vibrational excitation,

$$\frac{3m_e}{m_a}(T_e - T)\nu_{ea} + \frac{\theta_v}{T_e}(T_e - T_v) n_m k_{ev} = 0 \tag{13}$$

c) In an atomic plasma in strong electric field, Ohmic heating is balanced by energy loss in excitation processes:

$$\sigma \mathrm{E}^2 = R_{eE} \tag{14}$$

At moderate temperatures, when $T_e \leq 0.2 \cdot I/k$, excitation cross sections can be treated approximately (Refs. 1 and 9), $\sum_n q_{1n} = C(\varepsilon - E_2)$, where C is a constant. Then,

$$R_{eE} = n_1 E_2 C T_e \left(\frac{8E_2}{\pi m_e} \frac{E_2}{kT_e} \right)^{1/2} \exp\left(\frac{-E_2}{kT_e} \right)$$

where n_1 is the number density of atoms in the ground state.

6. *General and Particular Solutions*

There is no general solution.

a) Particular solutions

1. In a high-frequency electric field $\mathrm{E}(t) = \mathrm{E}_0 \cos \omega t$, if $\omega \geq 10(m_e/m_a)\nu_{ea}$, then E^2 in Eq. (11) can be replaced by

$$E_{eff}^2 = \frac{1}{2} \mathrm{E}_0^2 \nu_{ea}^2 (\nu_{ea}^2 + \omega^2)$$

(see Ref. 1). Under these conditions, when the frequency is very high, $\omega \geq 3\nu_{ea}$, the solution to Eq. (11) is

$$T_e = T + e^2 \mathrm{E}_0^2 m_a / 6 m_e^2 \omega^2 k. \tag{15}$$

2. If an elastic collision cross section can be approximately expressed as $q_{ea}(\varepsilon) = c/\varepsilon^{3/2}$, where c is a constant, then the corresponding

collision frequency is $\nu_{\mathrm{ea}} = n_{\mathrm{a}} c (kT_{\mathrm{e}})^{-3/2} \sqrt{2kT_{\mathrm{e}}/m}$. The solution of Eq. (11) is then

$$T_{\mathrm{e}} = T + T_v \frac{n_{\mathrm{m}}}{n_{\mathrm{a}}} \frac{3m_{\mathrm{e}}}{m_{\mathrm{m}}} \frac{c\sqrt{2m_{\mathrm{e}}}}{\theta_v k_{\mathrm{e}v}} \tag{16}$$

3. When $E_2 \gg kT_{\mathrm{e}}$, an approximate solution to Eq. (14) can be obtained by using the fact that the dependence of T_{e} on plasma parameters is primarily determined by the exponential in the expression $R_{\mathrm{e}E} \sim \exp(-E_2/kT_{\mathrm{e}})$. Then

$$kT_{\mathrm{e}} = \frac{E_2}{\ln[\sigma \mathrm{E}^2/(n_1 E_2 c T_{\mathrm{e}} \sqrt{8E_2^2/\pi mkT_{\mathrm{e}}})]} \tag{17}$$

7. *Restrictions*

a) Gradients of T_{e} are sufficiently weak for heat fluxes to be neglected. Conductive heat loss is negligible compared to the energy loss through elastic electron–ion collisions if

$$\frac{3m_{\mathrm{e}}}{m_{\mathrm{i}}} \nu_{\mathrm{ei}} \geq \frac{\kappa_e}{l^2}$$

where κ_e is the electron thermal conductivity and l is the characteristic length of substantial variation of T_{e}.

b) Electric field is too week to perturb the core of electron energy distribution function:

$$kT_{\mathrm{e}} \geq e^2 \mathrm{E}^2 m_{\mathrm{a}} / m_{\mathrm{e}}^2 \nu_{\mathrm{ee}} \tag{18}$$

where the electron–electron collision frequency $\nu_{\mathrm{ee}}(\varepsilon) = 3\pi e^4 n_{\mathrm{e}} \Lambda / \sqrt{2m_{\mathrm{e}}} \varepsilon^{3/2}$ is calculated for $\varepsilon = kT_{\mathrm{e}}$ (see I-T.13).

c) The atomic excited levels are characterized by a strongly nonequilibrium distribution. Deactivation processes play a negligible role, so that the energy lost in any act of excitation equals the excitation energy. For this to be the case, the population densities n_n of excited states must be low as compared to the corresponding Boltzmann equilibrium values, n_n^0:

$$n_n \leq 0.1 \cdot n_n^0(T_{\mathrm{e}})$$

d) The electron energy distribution function has a Maxwellian tail at $\varepsilon \geq E_2$. This requires that $(2n_2/n_{\mathrm{e}})(kT_{\mathrm{e}}/E_2)\Lambda^{-1} \leq 1$.

8. *Example of Application*

Across a shock wave, the gas velocity drops and gas temperature increases while ionization lags behind. In the course of ionization, which proceeds at a quasi-steady, T_{e}, electrons lose energy through excitation and subsequent ionization and gain energy through elastic collisions with "warmer" ions at $T > T_e$. The equation $R_{ei} = R_{eE} + R_{eI}$ can be used to calculate T_e. For a shock wave propagating in air at a velocity of 14 km/s, with pressure $p_1 = 10^{-3}$ atm behind the front, the degree of ionization $n_e/(n_e + n_a)$ reaches 0.1 when the gas temperature is $T = 35 \times 10^3$ K. As a result, $T_e = 15.2 \times 10^3$ K (Ref. 1).

9. *Comments*

a) In intense electric fields, condition Eq. (18) is violated and the distribution function is far from Maxwellian, so that the form of the quantities contained in $R_{e\Sigma}$ is substantially modified (Ref. 4). Formulas of the present model can be used to evaluate the average electron energy $\bar{\varepsilon}$ (see comments to model P.2).
b) The complete formulation, which includes not only electron energy lost through excitation and ionization, but also energy gained through deactivation and recombination, is presented in Ref. 1.
c) A more general expression for R_{ev} (including resonances in scattering) can be found in Ref. 1.

Relevant material can be found in Refs. 1, 3, and 4.

B. Model of Electron Temperature Relaxation (P.2)

1. *Purpose of the Model*

The model aims at the calculation of electron temperature in atomic and molecular plasmas as a function of time when electron energy changes through electron–atom and electron–molecule elastic collisions and vibrational excitation of molecules.

2. *Assumptions*

a) Different electron, atom, ion, and vibrational temperatures.
b) Maxwellian distribution of thermal electrons.
c) Boltzmann distribution in vibrational degrees of freedom.
d) Energy transfer is controlled by elastic collisions and vibrational excitation.

3. *Model Equations*

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{3}{2}T_e n_e\right) = n_e \frac{3m_e}{m_i}(T_e - T)[\nu_{ei}(T_e) + \nu_{ea}(T_e)] + n_e \frac{\theta_v}{T_e}(T_e - T_v) n_m k_{ev} f(T_e, T_v) \qquad (1)$$

$$\nu_{ei} = \frac{2\sqrt{2\pi}e^4 \Lambda Z^2}{\sqrt{m_e}(kT_e)^{3/2}} n_i$$

$$\nu_{ea} = \left(\frac{2^{3/2}}{\sqrt{\pi m_e}}\right) n_a (kT_e)^{-5/2} \int_0^\infty e^{-\varepsilon/kT_e} q_{ea}(\varepsilon)\varepsilon^2 \, d\varepsilon$$

where $f(T_e, T_v) = 1$ at $T_e \gg T_v$ for molecules that are not involved in resonant electron scattering.

Initial and boundary conditions

Initial conditions are set at $t = 0$: $T_e(0)$, $n_e(0)$, $n_i(0)$, $n_m(0)$, $n_a(0)$.

The functions $n_e(t)$, $n_a(t)$, $n_i(t)$, $n_m(t)$ must be either prescribed in explicit form or determined by other models to be employed in conjunction with this model.

The temperatures T and T_v are either prescribed as functions $T(t)$, $T_v(t)$, or determined by other models.

4. *Nomenclature*

a) Quantities calculated with the model:

T_e	electron temperature

b) Kinetic coefficients:

ν_{ei}	electron–ion elastic collision frequency (see I-T.13)
ν_{ea}, ν_{em}	electron–atom and electron–molecule elastic collision frequencies (see I-T.7–I-T.10)
$q_{ea}(\varepsilon)$	electron–atom or electron–molecule elastic collision cross section (see I-T.7–I-T.10)
k_{ev}	rate constant for molecule excitation by electron impact
$f(T_e, T_v)$	correction factor allowing for vibrational energy transfer in resonant scattering

c) Other quantities:

m_e, m_a, m_i	electron, atomic, and ion masses
T_v, T	vibrational and translational temperatures
n_a, n_e, n_m, n_i	atom, electron, molecule, and ion number densities
Z	charge number of ion
e	electron charge
Λ	Coulomb logarithm (see I-T.13)
E_2	excitation energy for the lowest excited state of an atom or molecule
θ_v	characteristic vibrational temperature of molecule
ε	electron energy
$\hbar\omega_0$	vibrational quantum of diatomic molecule

5. *Model Description*

The model equation is an expression for the energy conservation law.

Specific model representations

a) If n_e, n_a, n_i, n_m are quasi-steady quantities, i.e., if they effectively remain constant during the electron relaxation time, then Eq. (1) becomes

$$\frac{3}{2}\frac{dT_e}{dt} = \frac{3m_e}{m_i}(T_e - T)[\nu_{ei}(T_e) + \nu_{ea}(T_e)] + \theta_v n_m k_{ev} f(T_e, T_v) \tag{2}$$

b) In a highly ionized atomic plasma, when $\nu_{ei} \gg \nu_{ea}$,

$$\frac{dT_e}{dt} = \frac{2m_e}{m_i}(T_e - T)\nu_{ei}(T_e) \tag{3}$$

c) In a weakly ionized atomic plasma, when $\nu_{ei} \ll \nu_{ea}$,

$$\frac{3}{2}\frac{dT_e}{dt} = \frac{2m_e}{m_a}(T_e - T)\nu_{ea}(T_e) \tag{4}$$

6. *General and Particular Solutions*

There is no general solution.

Particular solutions

1. Equation (2) is solved to determine the time Δt required for electron temperature to change from $T_e(0)$ to $T_e(t)$:

$$\Delta t = \int_{T_e(0)}^{T_e(t)} dT_e \left\{ \frac{2m}{m_i}(T_e - T)[\nu_{ei}(T_e) + \nu_{ea}(T_e)] + \frac{\hbar\omega_0}{kT_e}(T_e - T_v) n_m k_{ev} f(T_e, T_v) \right\}^{-1} \tag{5}$$

2. The solution to Eq. (3) is

$$\Delta t = \left[\frac{2m_e}{m_i}\nu_{ei}(T)\right]^{-1} \int_{T_e(0)/T}^{T_e(t)/T} \frac{dx \cdot x^{3/2}}{x - 1}, \quad x = \frac{T_e}{T} \tag{6}$$

When the difference between T and T_e is large, i.e., $T_e(t) \gg T$, the solution is

$$\Delta t = \left\{\frac{2m_e}{m_i}\nu_{ei}[T_e(t)]\right\}^{-1} \left\{1 - \left[\frac{T_e(0)}{T_e(t)}\right]^{3/2}\right\} \tag{7}$$

7. *Restrictions*

a) In the absence of strong electric fields, when the Ohmic heating rate $Q_J = \sigma \mathrm{E}^2$ (σ is the electrical conductivity and E is the electric field) is low as compared to energy losses in elastic collisions:

$$\frac{T_e - T}{T_e} \gg \frac{2e^2\mathrm{E}^2}{3kT\delta m_e \nu^2}, \quad \delta = \frac{2m_e}{m_a}$$

where $\nu = \nu_{ei} + \nu_{ea}$ is the total frequency of elastic electron collisions with ions and atoms (see I-T.8, I-T.11, and I-T.13).

b) Energy lost to inelastic collisions is negligible: $kT_e \leq 0.1E_2$, where E_2 is the excitation energy. The value $E_2 \approx 10\,\mathrm{eV}$ is frequently used for estimates, but E_2 is considerably lower for atoms of some metals (the minimal value is $E_2 = 1.6\,\mathrm{eV}$ in the case of cesium atoms).

c) Gradients of T_e are sufficiently small for electron thermal conductivity to be negligible: $n_e(t)\Delta t^{-1} \geq \kappa_e(\Delta l)^{-2}$, where κ_e is the electron thermal conductivity and Δl is the characteristic length of substantial variation of T_e.

d) Boltzmann distribution of vibrational states at a temperature T_v is realized.

8. *Example*

With the cross section $q_{ea} = 0.6 \times 10^{-15}\,\mathrm{cm}^2$, the gas just behind a strong shock in helium has a high temperature, $T = 3 \times 10^4\,\mathrm{K}$, while the electron temperature is close to that of cold gas ahead of the front; the atom concentration is high, $n_a = 10^{17}\,\mathrm{cm}^{-3}$, and the degree of ionization is very low. As a result of electron–atom energy transfer, T_e increases to $T_{eff} = 10^4\,\mathrm{K}$ during the time interval

$$\Delta t = \left[\left(\frac{6m_e}{m_i}\right) n_a \left(\frac{T_{eff}}{T}\right) q_{ea}\sqrt{8kT_{eff}/\pi m_e}\right]^{-1} = 10^{-7}\,\mathrm{s}$$

9. *Comment*

The formula of this model can be used as an estimate in cases of non-Maxwellian distributions. Then, the value of T_e would characterize the average electron energy, $\bar{\varepsilon} = \int_0^\infty \varepsilon^{3/2} f(\varepsilon)\,d\varepsilon$, where $f(\varepsilon)$ is the electron energy distribution function. In this case, $T_e = 2\bar{\varepsilon}/3k$.

Relevant material can be found in Refs. 1, 10, and 11.

C. Model of Electron Heating Because of Recombination (P.3)

1. *Purpose of the Model*

The model aims at the calculation of electron temperature and number density as functions of time for a decaying recombination-controlled atomic plasma.

2. *Assumptions*

a) Electron number density is higher than its equilibrium value at temperature T_e. As a consequence, recombination prevails over ionization, which leads to plasma decay.
b) Electron temperature is substantially higher than the gas temperature.
c) Heat conduction is negligible.
d) The system is spatially uniform.
e) Recombination, ionization, and elastic electron–ion collisions are taken into account.
f) Recombination is controlled by the Thomson (electron–electron–ion) collisional mechanism.
g) Radiation effects are negligible.

3. *Model Equations*

$$\frac{dn_e}{dt} = n_a n_e k_i - n_e^2 n_i k_r \tag{1}$$

$$\frac{d}{dt}\left(\frac{3}{2}kT_e n_e\right) = -R_{ei} - I\frac{dn_e}{dt} \tag{2}$$

$$R_{ei} = \frac{3m_e k}{m_i}(T_e - T)n_i k_{ei}(T_e) \tag{3}$$

$$k_{ei} = 2\sqrt{2\pi}e^4\Lambda/\sqrt{m_i}(kT_e)^{3/2} \tag{4}$$

Initial conditions are set at $t = 0$: $n_e(0)$, $T_e(0)$.

4. *Nomenclature*

a) Quantities calculated with the model:

n_e	electron number density
T_e	electron temperature

b) Kinetic coefficients:

$k_i(T_e)$, $k_r(T_e)$	ionization rate coefficient for electron–atom colli-sions and recombination rate coefficient for electron–electron–ion collisions (see models I-P.14, I-P.15)
$k_{ei}(T_e)$	electron–ion elastic collision rate constant (see model I-T.13)

c) Other quantities:

n_a, n_i	atom and ion number densities
T	gas temperature
I	ionization energy
$\delta = 2m_e/m_a$	energy transfer factor for elastic collisions
m_e, m_a, m_i	masses of electron, atom, and ion
e	electron charge
Λ	Coulomb logarithm (see model I-T.13)

5. *Model Description*

The model equations are derived from energy and species conservation laws. The expression for energy exchange because of elastic electron–ion collisions satisfies detailed balance relations, vanishing at $T_e = T$.

The expression for ionization–recombination rate vanishes in Saha equilibrium. Quasi-neutrality is obeyed: $|n_e - n_i| \ll n_e$.

Specific Model Representation

Recombination-controlled decay of a highly nonequilibrium plasma is governed by the equations

$$\frac{dn_e}{dt} = -n_e^3 k_r(T_e) \tag{5}$$

$$\frac{d}{dt}\left(\frac{3}{2}kT_e n_e\right) = -I\frac{dn_e}{dt} \tag{6}$$

$$k_r(T_e) = -A(kT_e)^{-9/2}$$

The factor A depends on the ion type and on electron number density (Ref. 2). Calculation with model I-P.15 gives $A = 5.4 \times 10^{-27}\,\mathrm{cm^6/s \cdot eV^{9/2}}$.

6. *General and Particular Solutions*

There is no general solution.

Particular solutions

When $I \gg (3/2)\,kT_e$, a particular solution of Eqs. (5) and (6) has the form

$$T_e(t) = T_e(0) + \frac{2}{3}I \ln\frac{[n_e(t)/n_e(0)]}{k} \tag{7}$$

$$\int_{n_e(0)}^{n_e} \frac{dn_e'}{(n_e')^3}\left[\ln\left(\frac{n_e(0)}{n_e'} + 1\right)^{9/2}\right] = -\frac{At}{(2I/3)^{9/2}} \tag{8}$$

The integral is calculated numerically.

7. *Restrictions*

a) The model can be applied to a decaying atomic plasma that can be treated as spatially uniform and optically thick.

b) Conductive heat loss is negligible as compared to energy loss through electron–ion collisions:

$$\frac{3m_e}{m_i}\nu_{ei} \geq \frac{\kappa_e}{l^2}$$

where κ_e is the electron thermal conductivity and l is the characteristic length of substantial variation of T_e.

c) Radiation emission can be neglected in the case of optically thin plasma when the electron number density is sufficiently high:

$$n_e \geq 9.2 \times 10^7 \sqrt{\frac{kT_e}{I_1}} \left[\frac{(I_1 - I_2)}{I_1} \right]^3 \text{ cm}^{-3}$$

where I_1 and I_2 are the ionization energies for the ground state and for the lowest excited level that can be depopulated by radiation emission, respectively.

8. *Example*

With $kT_e(0) = 2\,\text{eV}$ and $I = 15\,\text{eV}$, temperature increases by a factor of 12.5 by the moment t_1 when the electron number density drops by a factor of 10, that is, $n_e(t_1)/n_e(0) = 10$, which results in electron heating owing to recombination. The rate of recombination is proportional to $T_e^{-9/2}$; therefore, it additionally drops by a factor of $(12.5)^{9/2} \approx 8600$. The electron heating because of recombination increases the plasma lifetime by orders of magnitude without any external ionization source (so that ionization freezing occurs).

9. *Comments*

a) In equilibrium state, the electron, ion, and neutral number densities are related to the electron temperature by the Saha equation:

$$\frac{n_e^0 n_i^0}{n_a^0} = \frac{2Q_a}{Q_i} \left(\frac{2\pi m k T_e}{h^2} \right)^{3/2} \exp\left(-\frac{I}{kT_e} \right) = B \frac{Q_a}{Q_i} T_e^{3/2} \exp\left(-\frac{I}{kT_e} \right)$$

Here, equilibrium species densities are denoted by superscript 0, $B = 4.85 \times 10^{15}\,\text{cm}^{-3} \cdot \text{K}^{3/2} = 6.06 \times 10^{21}\,\text{cm}^{-3} \cdot \text{eV}^{-3/2}$; and Q_a and Q_i are the atom and ion partition functions, respectively. They are temperature-dependent quantities, but the dependence on T_e is weak over wide ranges of electron temperature. The value of T_e characteristic of plasmas is on the order of electron-volt. For alkaline metals, $Q_a \approx 2$ and $Q_i \approx 1$; for nitrogen, $Q_a \approx 4$ and $Q_i \approx 9$; for oxygen, $Q_i = 9$ and $Q_i \approx 4$; and for inert gases, $Q_a \approx 1$ and $Q_i \approx 6$. For an electrically neutral, uniformly ionized plasma, $n_e^0 = n_i^0$. When the degree of ionization is low, $n_e^0 \ll n_a^0$, then

$$n_e \approx \left(B \frac{Q_a}{Q_i} n_a \right)^{1/2} T_e^{3/4} \exp(-I/2kT_e)$$

If $I \gg kT_e$, then $n_e(T_e)$ is dominated by the exponential dependence.

b) See comment in the description of model P.7.

Relevant material can be found in Refs. 1, 2, and 9.

D. Model of Gas Heating in a Plasma (P.4)

1. *Purpose of the Model*

The model aims at the calculation of the atomic gas temperature controlled by Ohmic heating owing to atom–electron collisions and conductive heat loss in atomic plasmas.

2. *Assumptions*

a) Different temperatures of electrons and heavy particles.
b) External electric field E is applied.
c) The gas is weakly ionized. The plasma is in ionizational equilibrium.
d) Gas pressure is constant (that is, an isobaric system is considered).
e) Analysis of energy transfer processes includes elastic electron–atom collisions, Ohmic heating by an external electric field, and conductive heat flux to plasma boundaries.

3. *Model Equations*

$$\sigma \mathrm{E}^2 - n_c(R_{ci} + R_{ca}) + \frac{1}{r}\frac{\partial}{\partial r}\left(r\kappa_c \frac{\partial kT_e}{\partial r}\right) = 0 \tag{1}$$

$$n_e(R_{ei} + R_{ea}) + \frac{1}{r}\frac{\partial}{\partial r}\left(r\kappa_e \frac{\partial kT}{\partial r}\right) = 0 \tag{2}$$

$$R_{ei} = \frac{3m_e k}{m_i}(T_e - T)\nu_{ei}(T_e) \tag{3}$$

$$\nu_{ei} = 2\sqrt{2\pi}Z^2 e^4 \cdot n_i/\sqrt{km_e}(kT_e)^{3/2} \tag{4}$$

$$R_{ea} = \frac{3m_e k}{m_a}(T_e - T)\nu_{ea}(T_e) \tag{5}$$

$$\nu_{ea} = \left(\frac{2^{3/2}}{\sqrt{\pi m_e}}\right) n_a (kT_e)^{-5/2} \int_0^\infty e^{-\varepsilon/kT_e} q_{ea}(\varepsilon)\varepsilon^2 \mathrm{d}\varepsilon \tag{6}$$

$$\sigma = \frac{n_e e^2}{m_e \nu_{ea}} \tag{7}$$

Boundary conditions

$T(R) \equiv T_R$ (gas temperature at the plasma boundary)
$\frac{\partial T}{\partial r}(0) = 0$ (symmetry condition)

4. *Nomenclature*

a) Argument:

r	distance from the plasma column axis

b) Quantities calculated with the model:

$T(r)$	gas temperature
n_e	electron number density

c) Kinetic coefficients:

R_{ei}, R_{ea}	rates of energy transfer through elastic collisions with ions and atoms
$\nu_{ea}(T_e)$	electron–atom elastic collision frequency (see models I-T.7–I-T.9)
ν_{ei}, ν_{ee}	electron–electron and electron–ion collision cross sections (see I-T.13)
$q_{ea}(T_e)$	electron–atom elastic collision cross section [see models I-T.7–I-T.9, where these quantities were denoted as $Q_0(\varepsilon)$]
κ_e, κ	electron and gas thermal conductivities
σ	plasma electrical conductivity

d) Other quantities:

T_e	electron temperature
n_a	atom number density
E	electric field
p	pressure
m_a, m_e	atom/ion and electron masses
e	electron charge
Λ	Coulomb logarithm (see model I-T.13)
R	plasma length scale (the column radius)
I	ionization energy

5. *Model Description*

The model equations express energy conservation laws.

The expressions for R_{ei} and R_{ea} satisfy detailed balance relations, vanishing at $T_e = T$.

Electron number density obeys the Saha equation. Because the degree of ionization is low, then

$$n_e = n_e(T_e)e^{-I/2kT_e} \tag{8}$$

where $n_e(T_e)$ weakly depends on T_e. At low degree of ionization, the condition for isobaric state has the form

$$p = n_e kT_e + (n_i + n_a)kT \approx n_a kT \tag{9}$$

Specific model representation

In a weakly ionized plasma, when the contributions of energy losses due to electron–ion elastic collisions and heat conduction can be neglected in the electron energy balance,

$$\sigma \mathrm{E}^2 = n_e R_{ea} \tag{10}$$

$$n_e R_{ea} = -\frac{1}{r}\frac{\partial}{\partial r}\left(r\kappa \frac{\partial kT}{\partial r}\right) \tag{11}$$

6. *General and Particular Solutions*

There is no general solution.

Particular solutions

The particular solution can be found for T_e that is low as compared to I/k, but high as compared to T:

$$\frac{I}{kT_e} \gg 1, \quad T_e \gg T \tag{12}$$

Assuming that q_{ea} is independent of ε, solution to Eq. (10) is calculated as

$$(kT_e)^{-1} = \sqrt{\frac{24q_{ea}^2 m_e}{\pi e^2 m_a \mathrm{E}^2}}\, p(kT)^{-1} \tag{13}$$

When gas heating is not significant, Eq. (10) yields

$$\frac{I}{kT_e} \approx [I/kT_e(R)]\left(1 - \frac{\Delta T}{T_R}\right), \quad \Delta T = T(r) - T_R, \quad \Delta T \ll T_R \tag{14}$$

Substituting Eq. (14) into Eq. (11) and retaining only the exponential arising from Eq. (8),

$$\frac{1}{\kappa} n_e(T_e)R_{ea}\bigg|_{T_e(R)} \cdot e^{I/kT_e(R)(\Delta T/T_R)} = \frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(r\frac{\mathrm{d}\Delta T}{\mathrm{d}r}\right) \tag{15}$$

the desired dimensionless gas temperature θ is obtained as a function of the dimensionless coordinate $x = r/R$,

$$e^{\theta} = \frac{1}{x}\frac{\mathrm{d}}{\mathrm{d}x}\left(x\frac{\mathrm{d}\theta}{\mathrm{d}x}\right), \quad \theta = \frac{I}{kT_e(R)} \cdot \frac{\Delta T}{T_R} \tag{16}$$

with the following boundary conditions: $\theta(x_R) = 0$ at the plasma boundary, $\mathrm{d}\theta/\mathrm{d}x(0) = 0$ on the column axis. The solution is

$$\theta = 2\ln\frac{\sqrt{8}a}{a^2 + x^2} \tag{17}$$

where a is calculated as the root of a quadratic equation:

$$a_{1,2} = \sqrt{2} \pm \sqrt{2 - x_R^2} \tag{18}$$

where

$$x_R = R\left[\frac{\kappa}{n_e R_{ea}}\bigg|_{T_e(R)} \cdot \frac{kT_R \cdot kT_e(R)}{I}\right]^{-1/2} \tag{19}$$

and $T_e(R)$ is the electron temperature at the plasma boundary.

According to Eq. (18), if $x_R^2 < 2$, there are two solutions:

$$a_1 \approx 2\sqrt{2}, \quad a_2 = \frac{x_R^2}{2\sqrt{2}} \tag{20}$$

The first one corresponds to a plasma with temperature and degree of ionization weakly varying across its volume. The second solution corresponds to a highly nonuniform plasma with degree of ionization steeply increasing toward the center of the plasma volume (see Comments).

7. *Restrictions*

a) Gradients of T_e are sufficiently weak for heat conduction to be negligible. Conductive heat loss is negligible as compared to elastic electron–ion collisions if

$$\frac{3m_e}{m_i} n_e \nu_{ei} \geq \frac{\kappa_e}{l^2}$$

where κ_e is the electron thermal conductivity and l is the characteristic length of substantial variation of T_e.

b) Electric field is insufficiently strong to perturb the core of electron energy distribution function:

$$kT_e \geq e^2 \mathrm{E}^2 m_a / m_e^2 \nu_{ee} \tag{21}$$

where the electron–electron collision frequency $\nu_{ee}(\varepsilon) = 3\pi e^4 n_e \Lambda / \sqrt{2m_e}\varepsilon^{3/2}$ is calculated at $\varepsilon = kT_e$ (see I-T.13).

c) At ionization equilibrium, radiation emission that would cause deviations from the equilibrium can be neglected when $n_e \geq 10^{14}\,\mathrm{cm}^{-3}$ [see Eq. (10)]. Another mechanism that violates the equilibrium, electron diffusion to plasma boundaries, is negligible if $n_e k_i(T_e) \geq 3n_e/\tau_d$, where k_i is the ionization rate coefficient (see P.7), and τ_d is the time required for electrons to diffuse to plasma boundary.

8. *Example*

Consider a helium plasma column of radius R at a constant pressure of $p = 10\,\mathrm{Torr}$ across the volume. The gas temperature at the column boundaries is maintained at $T(R) = 2000\,\mathrm{K}$, and $\mathrm{E} = 3\,\mathrm{V/cm}$. The value of x_R in (19) determines the thermal regime of the plasma.

The electron temperature at the boundary is $T_e(R) \approx 11{,}600\,\mathrm{K}$ according to Eq. (13), where $q_{ea} \approx 4 \times 10^{-16}\,\mathrm{cm}^2$, and the electron number density is $n_e(R) \approx 10^{14}\,\mathrm{cm}^{-3}$ according to Eq. (7). These parameters are typical for a weakly ionized plasma. Thermal conductivity is $\kappa = 1.3 \times 10^{20}\,\mathrm{cm}^{-1}\,\mathrm{s}^{-1}$ for helium at $T = 2000\,\mathrm{K}$. If $R = 5\,\mathrm{cm}$, then $x_R = 1.3$. This regime corresponds to two solutions of Eq. (18). The stable state corresponds to the lower value of a, in which case the gas temperature is more nonuniform (Ref. 12).

If $R = 10\,\mathrm{cm}$, then $x_R = 2.6$. This value is higher than $x_R = \sqrt{2}$ that corresponds to the critical conditions for existence of a solution.

9. *Comments*

When $x_R^2 < 2$ [see Eq. (19)], one solution describes an almost uniform state of the plasma, and the other corresponds to a stable state with electron number density rapidly increasing toward the column axis.

When $x_R^2 > 2$, there are no steady solutions, and a "thermal explosion" regime is observed, with electron number density rapidly increasing with time as a result of Ohmic heating. This thermal instability brings the plasma into a highly ionized steady state that is intractable in terms of the present model.

Relevant material can be found in Refs. 1, 12, and 13.

E. Model of Nonequilibrium Ionization (P.5)

1. *Purpose of the Model*

The model aims at the calculation of electron number density, n_e, both as a function of time and under steady-state conditions for a radiating atomic plasma with ambipolar diffusion.

2. *Assumptions*

a) A non-Maxwellian high-energy tail is assumed to be superimposed on a Maxwellian energy distribution of thermal (low-energy) electrons. The non-Maxwellian high-energy tail may be caused by lack of balance between collisional excitation and deactivation of atoms by electrons.
b) Radiation can leave the plasma volume, and electrons can leave the plasma volume via ambipolar diffusion.
c) Ionization may be sustained by external sources. External ionization sources may include intense ionizing radiation or electron beams.
d) Ionization and excitation processes are determined by inelastic atom–electron collisions, and recombination is determined by three-body electron–electron–ion collisions.
e) Radiation effects on nonequilibrium ionization are determined by spectral line emission.
f) Electron temperature is prescribed.

3. *Model Equation*

$$\frac{\mathrm{d}n_e}{\mathrm{d}t} = n_a n_e k_i - n_e^2 n_i k_r + \mathrm{div}(D_a \mathrm{grad}\, n_e) + S(t) \tag{1}$$

$$k_i^{-1} = k_{i1}^{-1} + k_{i2}^{-1}\Pi_1 \chi\left(\frac{\tilde{I}}{kT_e}\right) \tag{2}$$

$$k_r^{-1} = (k_{r1}\Pi_1)^{-1} + (k_{r2})^{-1}\chi\left(\frac{\tilde{I}}{kT_e}\right) \tag{3}$$

$$\Pi_1 = \prod_{n\geq 1}\left(1+\frac{A^R_{n+1}}{n_e k_{n+1,n}}\right),\quad A^R_{n+1} = \sum_{k\geq n+1} A^*_{kn},\quad A^*_{kn} = A_{kn}\theta_{kn} \tag{4}$$

$$\tilde{I} = \min(I_2, I_R),\quad I_R = \left[\frac{n_e}{4.5\times 10^{13}}\right]^{1/4}\left(\frac{T_e}{1.16\times 10^4}\right)^{-1/8}\ \mathrm{eV}$$

where n_e is in cm^3, and T_e is in K.

Initial conditions are set at $t = 0$: $n_e(0)$.

If T_e and n_a are time-dependent functions, they must be either prescribed or determined by invoking appropriate models.

4. *Nomenclature*

a) Quantities calculated with the model:

n_e	electron number density
T_e	electron temperature
n_a	atom concentration
n_i	ion concentration

b) Kinetic coefficients:

k_i, k_r	ionization and recombination rate constants involving radiative contributions
β, β^*, β_r, β_r^*	collisional contributions to k_i and k_r due to electron impact (see models I-P.14 and I-P.15)
$k_{n+1,n}$	effective rate constant in the single-quantum approximation (see model I-E.4)
A_{kn}	Einstein coefficient for spontaneous transition $k \rightarrow n$ (see Refs. 14–16)
θ_{kn}	probability for the photon emitted in transition $k \rightarrow n$ to escape from the plasma volume
D_a	ambipolar diffusion coefficient (see Refs. 4, 10, and 17)

c) Other quantities:

S	intensity of external ionization sources
I_2	ionization energy from the lowest excited state
I_R	ionization energy for excited states coupled through radiative transitions
n	quantum number of an atomic state ($n = 1$ for the ground state and $n \geq 2$ for excited states)
$\chi(x)$	function involved in the modified diffusion approximation
Π_1	factor accounting for radiative transitions to the ground state

5. *Model Description*

a) For a steady state plasma $dn_e/dt = 0$; plasma is spatially homogeneous if $\mathrm{div}(D_a\,\mathrm{grad}\,n_e) = 0$.

b) Detailed-balance relation is:

$$n_{\mathrm{a}}^0 n_{\mathrm{e}}^0 k_i = (n_{\mathrm{e}}^0)^2 n_{\mathrm{i}}^0 k_r$$

where k_i and k_r are rate constants in the absence of radiative processes ($\Pi_1 = 1, \tilde{I} = I_2$). Here, n_{a}^0, n_{e}^0, n_{i}^0 are local equilibrium number densities related by the Saha equation for ionization equilibrium

$$n_{\mathrm{i}}^0 n_{\mathrm{e}}^0 / n_{\mathrm{a}}^0 = K(T_{\mathrm{e}})$$

where $K(T_{\mathrm{e}})$ is the ionization equilibrium constant.

c) Quasi-neutrality is obeyed: $|n_{\mathrm{e}}(t) - n_{\mathrm{i}}(t)| \ll n_{\mathrm{e}}$.

d) In an isochoric process, the total number density of heavy particles is $n_{\mathrm{i}}(t) + n_{\mathrm{a}}(t) = n_{\mathrm{i}}(0) + n_{\mathrm{a}}(0) = n(0)$.

e) The initial electron number density in the process of developing ionization is lower than the local thermodynamic equilibrium (LTE) value: $n_{\mathrm{e}}(0) < n_{\mathrm{e}}^0$.

Specific model representation

- Balance equation in the case of nonequilibrium ionization with diffusive charged particle loss described in the "diffusion time" approximation is

$$\frac{\mathrm{d}n_{\mathrm{e}}}{\mathrm{d}t} = n_{\mathrm{a}} n_{\mathrm{e}} k_i - n_{\mathrm{e}}^2 n_{\mathrm{i}} k_r - \frac{n_{\mathrm{e}}}{\tau_d} \tag{5}$$

  where τ_d is the diffusion time, $\tau_d \approx L^2/bD_a$, L is the reference length, and b is a constant. For diffusion of species to the wall of a tube of radius R, $\tau_d \approx R^2/(2.4)^2 D_a$ (see model P.7).

- Balance equation in the case of recombination-controlled plasma decay:

$$\frac{\mathrm{d}n_{\mathrm{e}}}{\mathrm{d}t} = -n_{\mathrm{e}}^2 n_{\mathrm{i}} k_r + \mathrm{div}(D_a \mathrm{grad}\, n_{\mathrm{e}}) \tag{6}$$

- Balance equation at the initial ionization stage:

$$\frac{\mathrm{d}n_{\mathrm{e}}}{\mathrm{d}t} = n_{\mathrm{a}} n_{\mathrm{e}} k_i + S \tag{7}$$

  Equations (5) and (6) are considered in models P.6 and P.7, which supplement the present model.

6. *General and Particular Solutions*

There is no general solution.

Particular solutions

- Development of an electron avalanche

When both ionization source intensity S and k_i are time-independent, the solution to Eq. (7) subject to the initial condition $n_e(0) = 0$ is

$$n_e(t) = \frac{S}{n_a k_i}[\exp(n_a k_i t) - 1] \tag{8}$$

At $t \gg (n_a k_i)^{-1}$ the electron number density grows exponentially.

- Explosive ionization development

At low initial electron number density $n_e(0)$, the high-energy tail of the electron energy distribution is non-Maxwellian (see model P.13), and the ionization rate constant $k_i = k_{i1}$ is proportional to n_e. Calculated with the electron energy distribution predicted by model P.13 for these conditions, it is expressed as

$$k_{i1} = 2\sqrt{2\pi}\left(\frac{e^2}{kT_e}\right)^2 \sqrt{\frac{kT_e}{m_e}}\Lambda\left(\frac{n_e}{n_a}\right) \tag{9}$$

where Λ is the Coulomb logarithm (see I-T.13).

In the absence of an external ionization source, the solution to (7) for $T_e =$ const is

$$n_e(t) = n_e(0)\left[1 - \left(\frac{t}{\tau}\right)\right]^{-1}, \quad \tau = \left[2\sqrt{2\pi}\left(\frac{e^2}{kT_e}\right)^2 \sqrt{\frac{kT_e}{m_e}}\Lambda n_e(0)\right]^{-1} \tag{10}$$

The electron number density grows infinitely as $t \to \tau$; i.e., ionization develops in an explosive manner.

- Ionization instability

Instability means that random fluctuations of n_e grow rather than decay with time. As a result of instability, plasma volume can develop into a new, substantially inhomogeneous (e.g., constricted) state (Ref. 10).

The instability develops when ionization rate increases with n_e faster than does recombination rate. For example, if the recombination rate is proportional to n_e^3 (i.e., $dn_e/dt|_{rec} = -n_e^3 k_r$, where k_r is independent of n_e), then the instability develops when $k_i \sim n_e^k$, where $k > 2$. This situation is characterized by a low n_e, when the value of k_i is affected not only by the non-Maxwellian distribution (as in (9)), but also by intense radiative losses.

- Thermal ionization

If ionization kinetics is controlled by collisions, then the principle of detailed balance dictates that

$$\frac{\mathrm{d}n_\mathrm{e}}{\mathrm{d}t} = n_\mathrm{a} n_\mathrm{e} k_i - n_\mathrm{e}^2 n_\mathrm{i} k_r = n_\mathrm{a} n_\mathrm{e} k_i \left[1 - \left(\frac{n_\mathrm{e}}{n_\mathrm{e}^0} \right)^2 \frac{n_\mathrm{i}}{n_\mathrm{i}^0} \cdot \frac{n_\mathrm{a}^0}{n_\mathrm{a}} \right] \tag{11}$$

In the case of a slowly developing ionization, the quantity in brackets in Eq. (11) is close to zero. This means that the ionization rate is controlled by electron heating rather than collisional kinetics:

$$\frac{\mathrm{d}n_\mathrm{e}}{\mathrm{d}t} = \frac{\mathrm{d}n_\mathrm{e}^0}{\mathrm{d}t} = \frac{\mathrm{d}n_\mathrm{e}^0}{\mathrm{d}T_\mathrm{e}} \frac{\mathrm{d}T_\mathrm{e}}{\mathrm{d}t} \approx n_\mathrm{e}^0 \frac{I}{2kT_\mathrm{e}} \cdot \frac{\mathrm{d} \ln T_\mathrm{e}}{\mathrm{d}t} \tag{12}$$

This approximate equation is valid at low temperatures, $T_\mathrm{e} \leq 0.1\, I/k$ (I is the ionization energy), and low degrees of ionization, $n_\mathrm{e} \leq 0.1 n_\mathrm{a}$ (see P.3).

7. *Restrictions*

The balance equation (1) governing the development of ionization processes is universally applicable to low-temperature, singly ionized plasmas. Certain restrictions may arise when the values of k_i, k_r, and S are specified.

8. *Example*

In the case of ionization developing behind a shock wave (Ref. 9), the electron temperature varies weakly during the final ionization stage. For example, in an argon plasma with $T_\mathrm{e} = 1.8 \times 10^4$ K and $n_\mathrm{a} = 10^{18}\,\mathrm{cm}^3$, electron number density increases through ionization by electron impact ($k_i = 0.8 \times 10^{-11}\,\mathrm{cm}^3/\mathrm{s}$) from $n_\mathrm{e}(0) = 10^{14}\,\mathrm{cm}^{-3}$ to $n_\mathrm{e} = 0.2 \times 10^{18}\,\mathrm{cm}^{-3}$ during the interval t determined by Eq. (7):

$$t = \frac{1}{n_\mathrm{a} k_i} \ln \frac{n_\mathrm{e}(t)}{n_\mathrm{e}(0)} = 4.75\ \mu\mathrm{s} \tag{13}$$

In this case, the ionization due to atom–atom collisions plays the role of a source, S.

9. *Comments*

a) Equation (1) can be derived from the balance equation for electrons streaming through a gas flow with relative velocity u:

$$\frac{\mathrm{d}(n_\mathrm{e} u)}{\mathrm{d}x} = \sum_i S_i,$$

where the right-hand side is the same as in (1), but is written as the sum of terms representing local processes and diffusion.

b) When the time dependence of T_e is related to $n_\mathrm{e}(t)$, the balance equation in the case of nonequilibrium ionization should be solved simultaneously with the balance equation for electron energy (see models P.1 and P.2).

c) In a highly nonequilibrium plasma, when the ionization coefficient behaves as a large power of n_e, the solution to the steady-state equation may be nonunique, and the time-dependent equation may have an unstable solution.

Relevant material can be found in Refs. 1, 9, and 10.

F. Model of Nonequilibrium Steady Ionization (P.6)

1. *Purpose of the Model*

The model aims at calculation of electron number density n_e in a steady-state atomic plasma when the nonequilibrium is because of radiative losses and ambipolar diffusion to the walls.

2. *Assumptions*

See items a–b in the corresponding section of model P.5.

3. *Model Equation*

$$n_a n_e k_i - n_e^2 n_i k_r + \operatorname{div}(D_a \operatorname{grad} n_e) = 0 \tag{1}$$

$$k_i^{-1} = k_{i1}^{-1} + k_{i2}^{-1}\Pi_1 \chi\left(\frac{\tilde{I}}{kT_e}\right) \tag{2}$$

$$k_r^{-1} = (k_{r1}\Pi_1)^{-1} + (k_{r2})^{-1}\chi\left(\frac{\tilde{I}}{kT_e}\right) \tag{3}$$

$$\Pi_1 = \prod_{n\geq 1}\left(\frac{1 + A_{n+1}^R}{k_{n+1,n}n_e}\right), \qquad A_{n+1}^R = \sum_{k\geq n+1} A_{kn}^*, \quad A_{kn}^* = A_{kn}\theta_{kn} \tag{4}$$

Escape probability for radiation emitted at a point on the axis of a plasma cylinder of radius R:

$$\theta_{kn} = \begin{cases} (2\sqrt{(k_0)_{kn}R})^{-1} & \text{for a collisionally broadened line } k \to n \\ \sqrt{\pi}\{4(k_0)_{kn}R\sqrt{\ln[(k_0)_{kn}R]}\}^{-1} & \text{for a Doppler-broadened line } k \to n \end{cases} \tag{5}$$

Escape probability for radiation emitted at a distance x from the boundary of a plasma slab:

$$\theta_{kn} = \begin{cases} (3\sqrt{\pi(k_0)_{kn}x})^{-1} & \text{for a collisionally broadened line } k \to n \\ \{4(k_0)_{kn}R\sqrt{\pi\ln[(k_0)_{kn}x]}\}^{-1} & \text{for a Doppler-broadened line } k \to n \end{cases} \tag{6}$$

$$\tilde{I} = \min(I_2, I_R) \tag{7}$$

$$I_R = \left[\frac{n_e}{4.5\times 10^{13}}\right]^{1/4}\left[\frac{T_e}{1.16\times 10^4}\right]^{-1/8} \tag{8}$$

where n_e is in cm^{-3}, and T_e is in K.

4. *Nomenclature*

a) Quantities calculated with the model:

n_e	electron number density
T_e	electron temperature
n_a, n_i	atom and ion number density

b) Kinetic coefficients:

k_i, k_r	ionization and recombination rate constants (coefficients) involving radiative contributions
β, β^*, β_r, β_r^*	collisional contributions to k_i and k_r because of electron impact (see models I-P.14 and I-P.15)
$k_{n+1,n}$	effective rate constant in the single-quantum approximation (see model I-E.4)
A_{kn}	Einstein coefficient for spontaneous transition $k \rightarrow n$ (see Ref. 14)
θ_{kn}	probability for a photon emitted in the line $k \rightarrow n$ to leave a given plasma volume
$(k_0)_{nk}$	absorption coefficient at the center of line $k \rightarrow n$ (Ref. 15)
D_a	ambipolar diffusion coefficient (Ref. 10)

c) Other quantities:

I_2	ionization energy from the lowest excited state (see Ref. 16)
I_R	ionization energy for excited states coupled through radiative transitions
n	quantum number of an atomic state ($n = 1$ for the ground state, and $n \geq 2$ for excited states)
$\chi(x)$	function involved in the modified diffusion approximation (see models I-P.14 and I-P.15)
Π_1	factor accounting for radiative transitions to the ground state
n_e^0	electron number density predicted by the Saha equation at electron temperature T_e (see model P.3)
$K(T_e)$	ionization equilibrium constant (see model P.3)

5. *Model Description*

a) See items 2–5 of the corresponding section of model P.5.

b) The electron concentration is lower than the equilibrium one: $n_e < n_e^0$.

6. *Specific Model Representation*

a) Balance equation with diffusive charged particle losses described in the "diffusion time" approximation:

$$n_e^2 + n_e \frac{K(T_c)}{\Pi_1} - \frac{K(T_c)}{\Pi_1}(n_a + n_i)\left[1 - \frac{1}{(n_a + n_i)\tau_d k_{i1}}\right] + \frac{K(T_c)}{\tau_d k_{i2}}\chi\left(\frac{\tilde{I}}{kT_c}\right) = 0 \tag{9}$$

where the diffusion time (Refs. 10 and 17) is

$$\tau_d = \begin{cases} \dfrac{(R/2.4)^2}{D_a} & \text{for a cylindrical plasma column of radius } R \\ \dfrac{(L/\pi)^2}{D_a} & \text{for a plasma slab of thickness } L \\ \dfrac{(R/\pi)^2}{D_a} & \text{for a ball of radius } R \end{cases} \tag{10}$$

b) When n_e is large, radiation effects can be neglected ($\Pi_1 = 1, \tilde{I} = I_2$), and Eq. (9) reduces to the equation

$$n_e^2 + K(T_e)n_e - K(T_e)(n_a + n_i)[1 - (k_i\tau_d(n_a + n_i))^{-1}] = 0 \tag{11}$$

c) In large plasma volumes, diffusion plays a negligible role (if $k_i\tau_d (n_a + n_i) \geq 10$), and the nonequilibrium state of the plasma is because of radiation emission only:

$$n_e^2 + n_e\frac{K(T_e)}{\Pi_1} - \frac{K(T_e)}{\Pi_1}(n_a + n_i) = 0 \tag{12}$$

d) When the electron number density is such that radiative transitions are essential for the lowest three states only, then:

$$\Pi_1 = \left(\frac{1 + A_2^R}{n_e k_{21}}\right)\left(\frac{1 + A_3^R}{n_e k_{32}}\right) \tag{13}$$

For example, this is the case with helium when $n_e > 10^{14}\,\text{cm}^{-3}$, and in cesium when $n_e \geq 10^{11}\,\text{cm}^{-3}$. Nonequilibrium ionization is described by the balance equation

$$n_e^2 + n_e\left(\frac{A_2^R}{k_{21}} + \frac{A_3^R}{k_{32}}\right) - n_a K(T_e) + \frac{A_2^R A_3^R}{k_{21}k_{32}} = 0 \tag{14}$$

7. *General and Particular Solutions*

There is no general solution.

Particular solutions to the balance equation in the case of steady nonequilibrium ionization are:

1. Radial electron density distribution for a glow discharge plasma column in the case when ionization rate is higher than recombination rate in the plasma volume ($n_e \leq 0.1n_e^0$). Electrons diffuse to the boundaries of the

column of radius R and disappear there. The quantities n_a, T_e, D_a are supposed to be constant. The governing equation is written as

$$n_a n_e k_{i1} + D_a \frac{1}{r}\frac{\mathrm{d}^2(rn_e)}{\mathrm{d}r^2} = 0 \tag{15}$$

Boundary conditions are: $\mathrm{d}n_e/\mathrm{d}r|_{r=0} = 0$, $n_e|_{r=R} = 0$. The solution is:

$$n_e(r) = n_e(0)J_0\left(\frac{2.4r}{R}\right) \tag{16}$$

where $J_0(x)$ is the Bessel function of the zeroth order whose first root is $x = 2.4$.

2. Electron number density on the axis of arc discharge in the case of diffusion-controlled nonequilibrium is governed by Eq. (15). It has the following solution when $k_i\tau_d(n_a + n_i) \geq 1$:

$$n_e = \left[\frac{(K(T_e))^2}{4} + K(T_e)(n_a + n_i)\left(1 - \frac{1}{k_i\tau_d(n_a + n_i)}\right)\right]^{1/2} - \frac{K(T_e)}{2} \tag{17}$$

3. Electron number density in the plasma volume in the case when diffusion plays a negligible role ($k_i\tau_d(n_a + n_i) \geq 10$), and only radiative transitions to the ground state are taken into account ($A_3^R/n_e k_{32} \leq 0.1$), is given by the following solution to Eq. (14):

$$n_e = \left[\frac{(K(T_e) + A_2^R/k_{21})^2}{4} + K(T_e)(n_a + n_i)\right]^{1/2} - \frac{K(T_e) + A_2^R/k_{21}}{2} \tag{18}$$

8. *Restrictions*

a) The model described by Eq. (1) can be applied to a steady-state, singly ionized plasma when the nonequilibrium condition is determined by radiation and diffusion.

b) Formulas (5) and (6) can be applied to an optically thick plasma, i.e., when $(k_0)_{nk}R \gg 1$ or $(k_0)_{nk}x \gg 1$. If the opposite inequalities are satisfied, i.e., the plasma is optically thin, then $\theta_{kn} \approx 1$. At an intermediate case, interpolation is recommended (Ref. 1).

9. *Examples*

a) In argon plasma in an atmospheric pressure arc-discharge column, nonequilibrium ionization is determined by diffusive loss of electrons. For $n = 2.2 \times 10^{18}\,\mathrm{cm}^{-3}$, $T_e = 9.3 \times 10^3\,\mathrm{K}$, and $R = 0.15\,\mathrm{cm}$, the solution to Eq. (13) is $n_e = 2.8 \times 10^{15}\,\mathrm{cm}^{-3}$.

b) In an optically thin helium plasma ($\theta_{kn} = 1$) at temperatures ranging from 2×10^3 to 2×10^4 K and $n_e \geq 10^{14}\,\mathrm{cm}^{-3}$, the radiation-escape factor Π_1 has the form

$$\Pi_1 = (1 + 1.6 \times 10^3 T_e^{1/18} n_e^{-1})(1 + 2.6 T_e^{-1/3} n_e^{-1})$$

where n_e is measured in $10^{15}\,\mathrm{cm}^{-3}$, and T_e in eV. For example, $\Pi_1 = 3.4 \times 10^4$, when $n_e = 10^{14}\,\mathrm{cm}^{-3}$ and $T_e = 1$ eV.

10. Comments

The model equation is a special case of the balance equation for nonequilibrium ionization (see model P.5).

Relevant material can be found in Refs. 1, 2, and 10.

G. Model of Recombination- and Diffusion-Controlled Plasma Decay (P.7)

1. Purpose of the Model

The model aims at the calculation of electron number density as a function of time in a decaying atomic plasma with ambipolar diffusion.

2. Assumptions

a) Electron number density is higher than the equilibrium value at the temperature, T_e, and, therefore, the recombination rate is higher than the ionization rate.
b) Electrons and ions can leave the plasma volume via ambipolar diffusion.
c) The effect of radiation on recombination rate is negligible.
d) See item 1 in the corresponding section of model P.5.

3. Model Equation

$$\begin{aligned} \frac{dn_e}{dt} &= n_a n_e k_i - n_e^2 n_i k_r + \mathrm{div}(D_a \,\mathrm{grad}\, n_e) \\ k_i^{-1} &= \beta^{-1} + (\beta^*)^{-1} \chi(I_2/kT_e) \qquad (1) \\ k_r^{-1} &= \beta_r^{-1} + (\beta_r^*)^{-1} \chi(I_2/kT_e) \end{aligned}$$

Initial and boundary conditions

Initial condition is set at $t = 0$: $n_e(0)$.

Boundary condition for electron number density is set equal to zero at the plasma boundary: $n_e = 0$.

If n_a and T_e depend on time, then they must be either prescribed or determined by invoking other models.

4. *Nomenclature*

a) Quantity calculated with the model:

n_e	electron number density

b) Kinetic coefficients:

$k_i(T_e)$, $k_r(T_e)$	ionization and recombination rate constant, see models I-P.14 and I-P.15
β, β^*, β_r, β_r^*	components of k_i and k_r (see models I-P.14 and I-P.15)
D_a	ambipolar diffusion coefficient (Refs. 4 and 10)

c) Other quantities:

T_e	electron temperature
n_e^0	electron number density corresponding to equilibrium ionization at T_e
n_a	atom number density
I_2	ionization energy from the lowest excited state
$K(T_e)$	ionization equilibrium constant (see Comments to models P.3 and P.5)
$\chi(x)$	function involved in the modified diffusion approximation (see model I-P.14)

5. *Model Description*

a) See items b–e of the corresponding section of model P.5.

b) The initial electron concentration in the recombination-controlled regime is higher than that in local equilibrium: $n_e(0) > n_e^0$.

Specific model representation

a) Recombination-controlled decay of a spatially inhomogeneous plasma is described by the equation

$$\frac{dn_e}{dt} = -k_r n_e[n_e^2 - K(T_e)n_e - K(T_e)(n_a - n_i)] \tag{2}$$

b) Diffusion-controlled decay is described by the equation

$$\frac{dn_e}{dt} = \mathrm{div}(D_a \mathrm{grad}\ n_e) \tag{3}$$

In the diffusion time approximation, $n_e(\vec{r}, t) = N(\vec{r})\exp(-t/\tau)$, and (3) reduces to

$$-\tau^{-1}N(\vec{r}) = \mathrm{div}[D_a \mathrm{grad}\ N(\vec{r})] \tag{4}$$

where τ is the diffusion-controlled plasma decay time.

c) Recombination and diffusion controlled decay is described by the equation

$$\frac{\mathrm{d}n_e}{\mathrm{d}t} = -k_r n_e^3 - \frac{n_e}{\tau_d} \tag{5}$$

The diffusion time is specified in Eq. (10) of model P.6.

6. *General and Particular Solutions*

There is no general solution.

Particular solutions for plasma decay:

a) Recombination-controlled plasma decay. The solution to Eq. (2) is

$$t = -\frac{1}{k_r}\int_{n_e(0)}^{n_e(t)} \frac{\mathrm{d}n_e}{n_c[n_c^2 - K(T_c)n_c - K(T_c)(n_a + n_i)]} \tag{6}$$

When T_e and $(n_a + n_i)$ are constant, it reduces to a tabulated integral. Moreover, if $n_e(0) \ll n_a$, then the solution has a simple form:

$$n_e^2 = (n_e^0)^2\left[1 - \left(1 - \frac{(n_e^0)^2}{n_e^2(0)}\right)e^{-t/\tau_r}\right]^{-1} \tag{7}$$

where $\tau_r = 2k_i K(T_e)n_a \approx 2k_r(n_e^0)^2$ is the characteristic recombination time.

b) Diffusion-controlled plasma decay in the diffusion time approximation. In the case of a constant diffusivity, Eq. (4) has the form

$$\Delta N(r) + N(r)(D_a\tau)^{-1} = 0 \tag{8}$$

where Δ is the Laplace operator (Ref. 27). The solution of Eq. (8) with zero conditions at the plasma boundaries depends on the plasma volume geometry:

1) Plasma slab of thickness L in the x direction:

$$n_e(x, t) = \sum_{k=1}^{\infty} A_k \cos\left(\frac{x}{\sqrt{D_a\tau_{rk}}}\right)\exp\left(-\frac{t}{\tau_{rk}}\right) \tag{9}$$

If $L/2\sqrt{D_a\tau_{rk}} = (2k-1)\pi/2$, then $n_e(0, 0) = \sum_{k=1}^{\infty} A_k$. Here, A_k are the series-expansion coefficients defined by boundary conditions and normalization. The asymptotic ($t \to \infty$) decay of $n_e(x, t)$ is determined by the largest time scale τ_{r0}.

2) For a sphere of radius R:

$$n_e(r, t) = \sum_{k=1}^{\infty} \frac{B_k}{R}\sin\left(\frac{R}{\sqrt{D_a\tau_{rk}}}\right)\exp\left(-\frac{t}{\tau_{rk}}\right) \tag{10}$$

where $R/\sqrt{D_a \tau_{rk}} = k\pi$. Here B_k are the series-expansion coefficients defined by boundary conditions.

Solutions for parallelepiped and cylinder can be found in Ref. 18.

c) Recombination and diffusion controlled plasma decay. Solution to Eq. (5) is

$$t = -\frac{1}{k_r}\int_{n_e(0)}^{n_e(t)} \frac{dn_e}{n_e[n_e^2 + (k_r\tau_d)^{-1}]} \tag{11}$$

When k_r and τ_d are constant, the solution is

$$n_e^2(t) = \frac{1}{k_r\tau_d}\left[\left(1 + \frac{1}{n_e^2(0)k_r\tau_d}\right)e^{t/\tau_d} - 1\right]^{-1} \tag{12}$$

7. *Restrictions*

The model described by Eq. (1) can be applied to decaying plasmas when radiation effects are negligible.

8. *Example*

Suppose that the initial electron number density in a cesium plasma at pressure $p = 10^{-2}$ Torr, gas temperature $T = 300$ K, and electron temperature $T_e = 2 \times 10^3$ K, is $n_e(0) = 10^{14}\,\text{cm}^{-3}$. The corresponding recombination coefficient is $k_r = 6.5 \times 10^{-24}\,\text{cm}^6/\text{s}$ (see model I-P.15), the ambipolar diffusion coefficient is $D_a = 1.7 \times 10^3\,\text{cm}^2/\text{s}$, and the diffusion time across a tube of radius $R = 2.4$ cm is $\tau_d = 6 \times 10^{-4}$ s. According to (1), the electron number density will drop by a factor of 13 in $t = 10^{-3}$ s as a result of recombination and diffusion controlled decay.

9. *Comments*

a) Ionization freezing (Ref. 9):

When a plasma heated to $T_e \sim 10{,}000$ K expands into vacuum, recombination may be incomplete; i.e., the degree of ionization tends to a finite value. This effect is known as ionization freezing and is explained by decrease in the density of expanding plasma, which inhibits recombination. The freezing is enhanced by electron heating through recombination (see model P.3).

b) Alternative recombination mechanisms:

When decay is determined by dissociative rather than three-body recombination, the rate of recombination is a quadratic function of charged-particle number density: $(\partial n_e/\partial t)_p = -\beta n_e n_i$, where β is the dissociative recombination coefficient (see model I-P.17). This case is described by the solutions for Eqs. (6), (7), (11) and (12).

Relevant material can be found in Refs. 4 and 18.

H. Model of Kinetics for Electrons and Positive and Negative Ions (P.8)

1. *Purpose of the Model*

The model aims at calculation of the charged-particle number density in atomic and molecular plasmas as a function of time determined by charge production and neutralization taking place in the plasma volume.

2. *Assumptions*

a) The plasma is substantially nonequilibrium. Electron number density is higher than the equilibrium value at a temperature T_e.

b) The dimensions of the plasma volume are sufficiently large for the ionization–recombination balance to be controlled by bulk processes.

c) The following bulk processes are taken into account: electrons are produced by ionization of atoms and associative detachment from negative ions, and disappear in recombination and dissociative attachment. Negative ions can also recombine in encounters with positive ions. Bulk processes dominate—their frequency is higher than the frequency associated with particle diffusion to the boundaries of the plasma volume.

d) The number densities of atoms and molecules and electron temperature do not vary. The variations of n_a and n_m can be neglected because the degree of ionization is much lower than unity.

e) When the electron temperature T_e varies, it is determined by a model of electron energy balance to be used in conjunction with the present model.

3. *Model Equations*

$$\frac{\mathrm{d}n_e}{\mathrm{d}t} = k_i n_e n_a - k_r n_e^2 n_i^+ + k_d n_a n_i^- - k_a n_e n_m \tag{1}$$

$$\frac{\mathrm{d}n_i^+}{\mathrm{d}t} = k_i n_e n_a - k_r n_e^2 n_i^+ - k_r^{ii} n_i^+ n_i^- \tag{2}$$

$$\frac{\mathrm{d}n_i^-}{\mathrm{d}t} = k_a n_e n_m - k_d n_a n_i^- - k_r^{ii} n_i^+ n_i^- \tag{3}$$

Initial and boundary conditions

Initial conditions are set at $t = 0$: $n_e(0)$, $n_i^+(0)$, $n_i^-(0)$.

4. *Nomenclature*

a) Quantities calculated with the model:

n_c, n_i^+, n_i^-	electron and positive/negative ion number densities

b) Kinetic coefficients:

$k_i(T_e)$	rate constant for ionization of atoms by electron impact (see models I-P.11 and I-P.12)

$k_r(T_e)$	rate constant for recombination in three-body ion–electron–electron encounters (see model I-P.16)
$k_a(T_e)$	rate constant for dissociative attachment in electron–molecule encounters (see Refs. 19 and 20)
$k_d(T)$	rate constant for associative detachment in ion–atom encounters (see Refs. 19 and 20)
$k_r^{ii}(T)$	rate constant for ion–ion recombination (see models I-P.9 and I-P.10)

c) Other quantities:

T_e, T	electron and gas temperatures
n_a, n_m	atom and molecule number densities

5. *Model Description*

a) In a steady nonequilibrium state, number densities of all components are time independent:

$$\frac{dn_e}{dt} = 0, \qquad \frac{dn_i^+}{dt} = 0, \qquad \frac{dn_i^-}{dt} = 0$$

b) The plasma neutrality condition is $n_c(t) + n_i^-(t) = n_i^+(t)$. Therefore, only two differential equations are independent; e.g., (1) and (3).

Specific model representation

a) Recombination-controlled regime

In view of the high rate constant for associative detachment, at times longer than $(k_d n_a)^{-1}$, the number density n_i^- can be treated as a quasi-steady quantity:

$$n_i^- = \left(\frac{k_a n_m}{k_d n_a}\right) n_e = n_e \xi \tag{4}$$

Then, Eq. (1) reduces to the following equation:

$$\frac{dn_e}{dt} = \frac{k_i}{1+\xi} n_a n_e - (k_r + \xi k_r^{ii}) n_e^2 \tag{5}$$

b) Attachment-controlled regime

When the rate of dissociative attachment is higher than the rates of associative detachment and electron–ion recombination ($k_a n_m \gg k_d n_a$, $k_r n_i n_e$), the rate of ion–ion recombination is high. Then, the negative ions can be assumed to disappear instantly in ion–ion recombination. Under these conditions, Eq. (3) has the following time-independent form:

$$k_a n_e n_m - k_r^{ii} n_i^+ n_i^- n_m = 0 \tag{6}$$

Then, Eq. (1) reduces to

$$\frac{\mathrm{d}n_\mathrm{e}}{\mathrm{d}t} = n_\mathrm{a} n_\mathrm{e}\left(k_i - k_a\frac{n_\mathrm{m}}{n_\mathrm{a}} - k_r\frac{n_\mathrm{i}^+ n_\mathrm{e}}{n_\mathrm{a}}\right) \tag{7}$$

6. *General and Particular Solutions*

There is no general solution.

Particular solutions

1. Recombination-controlled regime. The solution to Eq. (5) is

$$t = -\frac{1}{k_p + \xi k_r^{ii}}\int_{n_\mathrm{e}(0)}^{n_\mathrm{e}(t)} \frac{\mathrm{d}t}{n_\mathrm{e}(n_\mathrm{e}^\mathrm{st} - n_\mathrm{e})}, \qquad n_\mathrm{e}^\mathrm{st} = \frac{k_i n_\mathrm{a}}{(1+\xi)(k_r + \xi k_r^{ii})} \tag{8}$$

where n_e^st is the electron number density in a steady-state nonequilibrium regime. When T_e and n_a are constant, the solution has the form:

$$t = \frac{1+\xi}{k_i n_\mathrm{a}}\ln\left[\frac{n_\mathrm{e}(t)}{n_\mathrm{e}(0)}\left(\frac{n_\mathrm{e}^\mathrm{st} - n_\mathrm{e}(t)}{n_\mathrm{e}^\mathrm{st} - n_\mathrm{e}(0)}\right)^{-1}\right] \tag{9}$$

Criterion for the recombination-controlled regime:

$$k_d \geq 3\frac{(k_i - k_a n_\mathrm{m}/n_\mathrm{a})k_r^{ii}}{k_r n_\mathrm{e}} \tag{10}$$

2. Attachment-controlled regime. The solution of Eq. (7) is

$$n_\mathrm{i}^- = k_a n_\mathrm{m}/k_r^{ii}, \qquad n_\mathrm{i}^- \ll n_\mathrm{i}^+, \qquad n_\mathrm{e} \approx n_\mathrm{i}^+ \tag{11}$$

$$t = -k_r^{-1}\int_{n_\mathrm{e}(0)}^{n_\mathrm{e}(t)} \frac{\mathrm{d}t}{n_\mathrm{e}[(n_\mathrm{e}^\mathrm{st})^2 - n_\mathrm{e}^2(t)]}, \qquad (n_\mathrm{e}^\mathrm{st})^2 = n_\mathrm{a}\frac{k_i - k_a n_\mathrm{m}/n_\mathrm{a}}{k_r} \tag{12}$$

where n_e^st is previously specified.
When T_e and n_a are constant, the solution has the form

$$t = \frac{1}{k_r(n_\mathrm{e}^\mathrm{st})^2}\ln\left[\frac{n_\mathrm{e}(t)}{n_\mathrm{e}(0)}\left(\frac{(n_\mathrm{e}^\mathrm{st})^2 - n_\mathrm{e}^2(t)}{(n_\mathrm{e}^\mathrm{st})^2 - n_\mathrm{e}^2(0)}\right)^{-1}\right] \tag{13}$$

Criterion for the attachment-controlled regime:

$$k_d \geq 3\frac{(k_i - k_a n_\mathrm{m}/n_\mathrm{a})k_r^{ii}}{k_r n_\mathrm{e}} \tag{14}$$

7. *Restrictions*

The criterion for a regime controlled by processes taking place in the plasma volume is that collisional frequency is higher than the frequency associated with losses to walls. An example is $\beta n_a \gg \tau_d^{-1}$, where τ_d is the diffusion time (see model P.7). This condition limits the plasma pressure to several Torr if the gas temperature is close to normal conditions.

8. *Example*

In certain plasma chemical processes (such as dissociation of CO_2 and H_2O, and synthesis of nitrogen oxides in a N_2—O_2 mixture), associative detachment of electrons from negative ions (e.g., $O^- + CO \rightarrow CO_2 + e$, $O^- + NO \rightarrow NO_2 + e$, $O^- + H_2 \rightarrow H_2O + e$) is very fast. When the number density of molecules is $10^{17}\,\mathrm{cm}^{-3}$, the time scale of associative detachment is $10^{-7}\,\mathrm{s}$.

9. *Comments*

Models of this type are applied to describe plasma chemical processes in multicomponent gas-discharge plasmas. This model is one of the simplest models of this type, well suited for conditions when the gas temperature is close to room temperature, and $T_e \gg T$.

In this model, only one of several mechanisms of negative ion production, dissociative attachment, and only one mechanism of electron detachment from negative ions, associative detachment, are considered. Other mechanisms of negative ion production and loss are discussed in Refs. 19 and 20.

Relevant material can be found in Refs. 10, 21, and 22.

I. System of Balance Equations for Excited Atoms: Relaxation of Excited States (P.9)

1. *Purpose of the Model*

The model aims at the calculation of nonequilibrium populations of atomic excited states and their relaxation times in atomic plasmas.

2. *Assumptions*

a) Nonequilibrium populations of atomic excited states are considered.
b) The medium is optically thick. Radiation effects are negligible.
c) Inelastic collisions of excited atoms with electrons and atoms in ground states and diffusion of excited atoms are taken into account.

3. Model Equations

$$\frac{\mathrm{d}n_k}{\mathrm{d}t} = \sum_{m=1}^{\tilde{k}} (n_m n_e k_{mk} - n_k n_e k_{km}) + (n_e^2 n_i k_{rk} - n_e n_k k_{ik})$$

$$+ \sum_{m=1}^{\tilde{k}} (n_m n_1 K_{mk} - n_k n_1 K_{km}) + (n_e n_1 n_i K_{rk} - n_k n_1 K_{ik}) - \operatorname{div} \mathbf{J}_k \qquad (1)$$

$$\mathbf{J}_k = D_k \operatorname{grad} n_k$$

Initial conditions are set at $t = 0$, $n_k(0)$.

Prescribed functions include $n_e(t)$ and $n_a(t)$ (n_a is the total atom number density, which is close to the number density of atoms in the ground state, n_1). If electron temperature, T_e, and temperature, T, of the gas of heavy particles are time-dependent, then the kinetic coefficients, k_{mk} and K_{mk}, are also functions of time, and this model should be used in conjunction with model P.2.

4. Nomenclature

a) Quantities calculated with the model:

n_k	population of atomic level k
n_1, n_e, n_i	number densities of atoms in ground state, electrons, and ions

b) Kinetic coefficients:

k_{mk}	rate constant for atomic excitation to level m, if $m < k$, or deactivation rate constant, if $m > k$, by electron impact (see models I-E.2, I-E.3, I-E.4, and I-E.16)
K_{mk}	similar rate constant for collisions with atoms in the ground state
k_{rk}	rate constant for recombination to level k in electron–electron–ion encounters (see model I-P.16)
K_{rk}	similar rate constant for electron–ion–atom encounters
k_{ik}	rate constant for ionization in encounters of electrons with atoms in level k (see models I-P.11–I-P.13 and I-P.16)
K_{ik}	similar rate constant for encounters with atoms in the ground state
D_k	diffusion coefficient for atoms in level k

c) Other quantities:

k	quantum number of an atomic state
$k = 1$	ground state
$k = 2,3,\ldots,\tilde{k}$	excited states
$\tilde{k}$	quantum number of the highest excited state taken into account in the system of governing equations
$\mathbf{J}_k$	diffusive flux of atoms in level k
$Ry = 13.6\,\mathrm{eV}$	Rydberg constant

$\bar{\Lambda}_1$	mean value of the Coulomb logarithm for inelastic processes
I_k	energy of ionization from level k

5. *Model Description*

a) At steady state, $\mathrm{d}n_k/\mathrm{d}t = 0$.
b) For spatially homogeneous systems, div $\mathbf{J}_k = 0$.
c) Equations of detailed balance:

- $n_m^0 n_\mathrm{e}^0 k_{mk}^0 = n_k^0 n_\mathrm{e}^0 k_{km}^0$ and $(n_\mathrm{e}^0)^2 n_\mathrm{i}^0 k_{rk}^0 = n_\mathrm{e}^0 n_k^0 k_{ik}^0$ for equilibria determined by electron temperature T_e. In this case, n_m^0, n_e^0, and n_i^0 are locally equilibrium number densities related to T_e; k_{km}^0, k_{pk}^0, and k_{ik}^0 are the rate coefficients calculated for the Maxwellian electron energy distribution.
- $n_m^0 n_1^0 K_{mk}^0 = n_k^0 n_1^0 K_{km}^0$ and $n_1^0 n_\mathrm{e}^0 n_\mathrm{i}^0 K_{rk}^0 = n_1^0 n_k^0 K_{ik}^0$ for equilibria determined by the atom temperature T. All quantities contained in these equations are determined by this temperature in a similar manner.

d) Quasi-neutrality is obeyed: $|n_\mathrm{e}(t) - n_\mathrm{i}(t)| \ll n_\mathrm{e}(t)$.
e) In an isochoric process, $n_\mathrm{i}(t) + \sum_{k=1}^{k} n_k(t) = n(0)$ is the total number density of heavy particles.

Specific model representation

a) The time-independent system of balance equations in the case when collisions of excited atoms with atoms and diffusion are negligible:

$$\sum_{n=1}^{\tilde{k}} [(n_m n_\mathrm{e} k_{mk} - n_k n_\mathrm{e} k_{km}) + (n_\mathrm{e}^2 n_\mathrm{i} k_{rk} - n_\mathrm{e} n_k k_{ik})] = 0 \qquad (2)$$

Equation (2) is analyzed in the context of models P.10 and P.11 that supplement this model.

b) The model of a "two-level" atom, in which kinetics is determined by electrons and by transport of excited atoms in the first excited state:

$$\frac{\mathrm{d}n_2}{\mathrm{d}t} = (n_1 n_\mathrm{e} k_{12} - n_2 n_\mathrm{e} k_{21}) + (n_\mathrm{e}^2 n_\mathrm{i} k_{r2} - n_\mathrm{e} n_2 k_{i2}) - \operatorname{div} \mathbf{J}_2 \qquad (3)$$

c) A time τ_k is required for the kth excited state to evolve into a quasi-steady state through the process described by the system of Eq. (1). The time τ_k is referred to as the time of relaxation of the kth state and is determined by the expression:

$$\tau_k^{-1} = n_\mathrm{e} \sum_{k=1}^{\tilde{k}} k_{km} + n_\mathrm{e} k_{ik} + n_1 \sum_{k=1}^{\tilde{k}} K_{km} + n_1 K_{ik} \qquad (4)$$

If the kinetics is determined by collisions with electrons, then τ_k can be evaluated (Ref. 1) as:

$$\tau_2^{-1} = (k_{21} + k_{23})n_e, \qquad \tau_{k>2}^{-1} = \frac{\sqrt{2\pi}\Lambda n_e e^4}{Ry\sqrt{mkT_e}}\left(\frac{Ry}{I_k}\right)^2 \tag{5}$$

where k_{21} and k_{23} are the 2→3 and 3→2 excitation and deactivation rate coefficients, respectively (see models I-E.4 and I-E.6).

After a time interval τ_k has elapsed, there is no explicit time dependence of n_k, and only an implicit dependence remains, which manifests itself in $n_e(t)$, $T_e(t)$. These slowly varying quantities are followed by $n_k(t)$. Under these conditions, Eq. (1) reduces to Eq. (2).

d) Effective cross sections for inelastic collisions with electrons increase with decreasing ionization energy I_k, that is, with the number k of the excited state. As a result, highly excited states are in relative equilibrium with free electrons:

$$y_k = y_e^2, \qquad k \geq k* \tag{6}$$

Here:

$y_k = n_k/n_k^0(T_e)$ is the relative population in level k,
$y_e = n_e/n_e^0(T_e)$ is the relative electron number density,
$I_{k*} \approx (3/2)kT_e$, $I_{k*} \approx Ry/(k*)^2$ is the energy of ionization from level $k*$.

6. General and Particular Solutions

There is no general solution.

Particular solutions to Eq. (3)

When diffusive loss of excited atoms is taken into account in the "diffusion time" approximation, Eq. (3) has the form

$$\frac{dn_2}{dt} = n_1 n_e k_{12} - n_2 n_e k_{21} - \frac{n_2}{\tau_{2d}} \tag{7}$$

where τ_{2d} is the diffusion time, $\tau_{2d} \approx L^2/bD_2$, L is the reference length, b is a constant, and D_2 is the diffusivity of excited atoms. The loss of atoms through diffusion to the wall of a tube of radius R is characterized by $\tau_{2d} \approx R^2/5.76D_2$, (see model P.7). The solution is:

$$n_2(t) = n_2(0)e^{-F(t)} + e^{F(t)} \int_0^t n_1 n_e k_{12} e^{-F(t')} dt' \tag{8}$$

where $F(t) = \int_0^t (n_e k_{21} + \tau_{2d}^{-1})\, dt$.

The "two-level" approximation is applicable when the coupling of the second level with higher levels (through collisions with electrons) is weakened, for example, as a result of a more intense loss of excited atoms to the walls.

7. *Restrictions*

Equations (1) can be applied to a low-temperature, optically thick, singly ionized plasma.

8. *Example*

The times of relaxation to quasi-steady excited states in a hydrogen plasma at $T_e = 16 \times 10^3$ K and $n_e = 10^{18}$ cm^{-3}, calculated by Eq. (5) are:

$$\tau_2 = 0.7 \times 10^{-12}\,\text{s}, \qquad \tau_3 = 4.5 \times 10^{-13}\,\text{s}, \qquad \tau_5 = 7.2 \times 10^{-16}\,\text{s}$$

The relaxation times, τ_k, rapidly decrease with increasing k.

9. *Comments*

a) In a wide range of low-temperature plasma conditions, an important role is played by radiation. When n_e is low, the values of n_k tend to decrease because of radiative deactivation. Electron number densities for which radiative deactivation is negligible in an optically thin plasma are higher than a certain value:

$$n_e \geq 9.2 \times 10^{17} \sqrt{\frac{kT_e}{I_1}} \left[\frac{I_1 - I_2}{I_1} \right]^3 \text{cm}^{-3}$$

where I_1 and I_2 are, respectively, the ionization energies for the ground state and the first excited state from which a radiative transition is possible. Kinetics determined by radiation effects are discussed in Refs. 1–3, and 24.

b) In the presence of sources of excited atoms (such as external radiation sources), the source intensity $S_k(t)$ is added to the right-hand side of the corresponding balance equation.

c) In the literature, balance equation for number densities of neutral, charged, and excited particles are also called rate equations or master equations.

Relevant material can be found in Refs. 1, 2, 6, and 23.

J. Atomic Excited State Populations in Steady or Quasi-steady Plasmas: Single-Quantum Approximation (P.10)

1. *Purpose of the Model*

The model aims at the calculation of nonequilibrium populations of atomic excited states in a steady or quasi-steady spatially homogeneous atomic plasma.

2. *Assumptions*

a) Nonequilibrium populations of atomic excited states in the absence of ionization equilibrium are considered.

b) The plasma is optically thick.

c) The plasma is spatially homogeneous.
d) Free electron kinetics is substantially affected by electron–electron collisions.
e) Inelastic collisions of atoms with electrons are taken into account.

3. *Model Equations*

The model is described by balance equations for the populations of excited atoms, which can be derived from those of model P.9 as a special case. The balance equation for the population of level k has the form:

$$\sum_m (n_m w_{mk} - n_k w_{km}) + (n_\mathrm{e} w_{ek} - n_k w_{ke}) = 0 \tag{1}$$

The sum extends over all levels m with which the current level k is coupled through transitions induced by collisions with free electrons, characterized by probabilities $w_{mk} = n_\mathrm{e} k_{mk}$, where k_{mk} is the rate constant for excitation $m \to k$, if $m < k$, or deactivation, if $m > k$. The ionization and recombination probabilities are

$$w_{ke} = n_\mathrm{e} k_{ik}, \qquad w_{ek} = n_\mathrm{e}^2 k_{rk} \tag{2}$$

Initial conditions

To solve the governing equations, the probabilities w_{mk} and atom number densities n_a must be prescribed.

4. *Nomenclature*

a) Quantities calculated with the model:

n_k	population in atomic level k

b) Kinetic coefficients:

w_{km}	probabilities of excitation of atoms to level m, if $k < m$, or deactivation, if $k > m$.
w_{ke}	probabilities of ionization from level k.
w_{ek}	probabilities of recombination to level k.
k_{ik}	rate constant for ionization from level k
k_{rk}	rate constant for recombination to level k

5. *Model Description*

a) Detailed balance relations are:

$$n_m^0 w_{mk}(T_\mathrm{e}) = n_k^0 w_{km}(T_\mathrm{e}), \qquad (n_\mathrm{e}^0)^3 k_{rk}(T_\mathrm{e}) = n_k^0 n_\mathrm{e}^0 k_{ik}(T_\mathrm{e}) \tag{3}$$

where

n_m^0, n_k^0, n_e^0	are equilibrium number densities related through the Boltzmann distribution and Saha equation at T_e (see model P.3),

$w_{mk}(T_e)$ are transition probabilities in the case of Maxwellian electron energy distribution at T_e.

b) Quasi-neutrality is obeyed: $|n_e - n_i| \ll n_e$.

c) In an isochoric process, $n_a + n_i = \text{const}$, where $n_a = \sum_{k=1}^{\tilde{k}} n_k$ is the total number density of atoms, and $\tilde{k}$ is the highest excited level. Most often, the approximation $n_a \approx n_1$ can be used, and the number density of excited atoms is much lower than the number density of nonexcited atoms.

6. *Specific Model Representation*

a) When the distribution of electrons over energy is a Maxwellian one, Eq. (1) becomes

$$\sum_m n_k^0 w_{km}(y_k - y_m) + n_e^0 w_{ke}(y_k - y_e^2) = 0 \tag{4}$$

with kinetic coefficients $k_{km}(T_e)$ and $k_{ik}(T_e)$ treated as functions of electron temperature only, and relative number densities of atoms and electrons defined as

$$y_k = \frac{n_k}{n_k^0}, \qquad y_e = \frac{n_e}{n_e^0} \tag{5}$$

b) In the single-quantum approximation, only transitions between adjacent levels ($k \Leftrightarrow k+1$) are taken into account, because they are characterized by the highest probabilities. Then Eq. (4) reduces to

$$n_k^0 w_{k,k+1}(y_k - y_{k+1}) + n_k^0 w_{k,k-1}(y_k - y_{k-1}) = 0 \tag{6}$$

7. *General and Particular Solutions*

There is no general solution to Eq. (1).

The general solution to Eq. (4) has the form

$$y_k = y_1 r_{1k} + y_e^2 r_{0k} \tag{7}$$

where r_{1k} and r_{0k} are functions of temperature. Because $y_k \to y_e^2$ as k increases (see the preceding model), the coefficient r_{0k} tends to unity with increasing k, whereas r_{1k} decreases to a negligible value. Conversely, as $k \to 1$, the coefficient r_{0k} decreases to a negligible value, whereas r_{1k} increases. General expressions for r_{0k} and r_{1k} can be found in Ref. 1.

The solution to Eq. (6) has a simple form in the single-quantum approximation (see model I-E.4):

$$y_k = \frac{y_1 R_{ke} + y_e^2 R_{1k}}{R_{1e}} \tag{8}$$

where

$$R_{nm} = \sum_{k=n}^{m-1} R_{k,k+1}, \qquad R_{k,k+1} = (n_k^0 w_{k,k+1})^{-1} \tag{9}$$

Highly excited states are close to equilibrium with electrons. This is particularly true for the highest level, $y_{\tilde{k}} = y_e^2$. The probabilities $w_{k,k+1}$ are proportional to the corresponding excitation rate coefficients, $w_{k,k+1} = n_e k_{k,k+1}(T_e)$, defined by the formulas of model I-E.4.

The solution to Eq. (1) can be obtained numerically. An approximate analytical solution that goes beyond the single-quantum approximation is obtained in the modified diffusion approximation (see Ref. 1).

8. *Restrictions*

The model can be applied to a steady, singly ionized plasma controlled by electron collisions.

9. *Example*

Formulas for $k_{k+1}(T_e)$ (see model I-E.4) can be used to determine the point of minimum for $n_k^0 w_{k,k+1}$ as a function of k. The resulting value k^* corresponds to a binding energy $E_{k^*} \approx (3/2)kT_e$ that divides the set of excited levels into two groups. Highly excited states (with $k > k^*$) are near equilibrium with electrons ($y_k \approx y_e^2$). The lower levels $k < k^*$ are almost in equilibrium with the ground state ($y_k \approx y_1$). This scheme works better for lower temperatures ($T_e \ll I_1/k$). In Refs. 1 and 6, the single-quantum approximation is developed with allowance for radiative transitions.

10. *Comment*

The solution to Eq. (8) remains valid when the electron energy distribution has a non-Maxwellian tail in the range of high energies comparable to the first-level excitation energy $\varepsilon = I_1 - I_2$, where I_1 and I_2 are the ionization energies for the ground state and the first excited state, respectively. Under these conditions, the value of k_{12} is determined by using the fact that 1→2 inelastic collisions deplete the high-energy tail of the electron energy distribution $f(\varepsilon)$. In the first approximation, $k_{12} = k_{12}^0(1 + 2n_1 kT_e\Lambda_1/n_e I_2\Lambda)^{-1}$, where Λ is the Coulomb logarithm (see model I-T.13) and Λ_1 is the Coulomb logarithm for inelastic collisions (see models I-E.3 and I-E.4).

Relevant material can be found in Refs. 1, 2, and 6.

K. Atomic Excited-State Distribution in Steady or Quasi-steady Plasmas: Diffusion Approximation (P.11)

1. Purpose of the Model

The model aims at the calculation of a nonequilibrium atomic excited-state distribution in a steady or quasi-steady spatially homogeneous atomic plasma.

2. Assumptions

a) See items 1–5 in the corresponding section of model P.10.

b) The model is based on analogy between transitions of a bound electron induced by free-electron impact and the diffusive random walk of a Brownian particle. The set of discrete excited atomic states is modeled by a continuous distribution of level populations in the energy space. The model equation describes diffusion with $\operatorname{div} j = 0$, where j is the ionization- or recombination-induced electron flux in the level energy space.

3. Model Equation

$$\frac{\partial}{\partial E}\left[B(E)n(E) + D(E)\frac{\partial n(E)}{\partial E}\right] = 0 \tag{1}$$

$$D(E) = 2\sqrt{2\pi}e^4 n_e E\Lambda_1(E)[3\sqrt{m_e kT_e}]^{-1} \tag{2}$$

Boundary conditions

$$y|_{E=I_1} = y_1, \qquad y|_{E=0} = y_e^2 \tag{3}$$

where

$$y(E) = \frac{n(E)}{n^0(E)} \tag{4}$$

$$n^0(E) = (n_e^0)^2 \frac{2^{1/2} Ry^{3/2} \exp(E/kT_e)}{E^{5/2}(2\pi m_e kT_e)^{3/2}} \tag{5}$$

4. Nomenclature

a) Argument:

E	electron binding energy (i.e., the minimum energy that has to be given to electron to bring it from a given bound state into a free state)

b) Quantity calculated with the model:

$n(E) = y(E)n^0(E)$	energy distribution for bound electrons

c) Kinetic coefficients:

$D(E)$	coefficient of diffusion (diffusivity) in the energy space
$B(E)$	dynamic friction coefficient in the energy space

$\Lambda_1(E)$	Coulomb logarithm for inelastic processes (see model I-E.4)

d) Other quantities:

$y(E)$	normalized energy distribution for bound electrons
T_e	electron temperature
n_e^0	electron number density in a Saha equilibrium (see model P.3)
I_1	ionization energy from the ground state
y_1, y_e	relative values of the ground-state populations and electron number density determined by known values of n_1, n_e, and T_e
$Ry = 13.6\,\mathrm{eV}$	Rydberg constant

5. *Model Description*

a) Detailed balance relation:

$$B(E) = -D(E)\frac{1}{n^0(E)} \cdot \frac{\mathrm{d}n^0(E)}{\mathrm{d}E} \tag{6}$$

b) If $y_e^2 < y_1$, then $y(E)$ decreases as a function of E from y_1 to y_e^2. If $y_e^2 > y_1$, then $y(E)$ increases from y_1 to y_e^2.

6. *General and Particular Solutions*

An approximate solution can be written by using the fact that $\Lambda_1(E)$ is a slowly varying function in the energy domain where $y(E)$ varies substantially:

$$y(E) = \frac{y_1\chi(E/kT_e) + y_e^2[\chi(I_1/kT_e) - \chi(E/kT_e)]}{\chi(I_1/kT_e)} \tag{7}$$

where

$$\chi(x) = \frac{4}{3\sqrt{\pi}}\int_0^x \mathrm{d}t\, e^{-t}t^{3/2}, \quad x = \frac{E}{kT_e} \tag{8}$$

At $x \gg 1$,

$$\chi(x) = 1 - \frac{4e^{-x}x^{3/2}}{3\sqrt{\pi}}$$

At $x \ll 1$,

$$\chi(x) = \left(\frac{8}{15\sqrt{\pi}}\right)x^{5/2}$$

If $I_1 \gg kT_e$, then

$$y(E) = y_1 \chi\left(\frac{E}{kT_e}\right) + y_e^2\left[1 - \chi\left(\frac{E}{kT_e}\right)\right] \tag{9}$$

If $E \ll kT_e$, then (9) yields:

$$y(E) = y_e^2\left[1 - \frac{8}{15\sqrt{\pi}}\left(\frac{E}{kT_e}\right)^{5/2}\right] + y_1 \frac{8}{15\sqrt{\pi}}\left(\frac{E}{kT_e}\right)^{5/2} \tag{10}$$

If $E \gg kT_e$, then (9) yields:

$$y(E) = y_1 + y_e^2 \frac{4}{3\sqrt{\pi}} e^{-E/kT_e}\left(\frac{E}{kT_e}\right)^{3/2} \tag{11}$$

The qualitative behavior of $y(E)$ is similar to that predicted by model P.10. The most substantial variation of this function is localized around $E^* \approx (3/2)kT_e$.

7. *Restrictions*

a) The model can be applied to a steady-state, singly ionized plasma determined by electron collisions.
b) The model can be applied to hydrogen and hydrogen-like atoms.

8. *Example*

Consider an optically thick cesium plasma at $T_e = 3000$ K, where the number densities of electrons and atoms are assumed to be equal: $n_e = 5 \times 10^{12}\,\mathrm{cm}^{-3}$, $n_a = 5 \times 10^{14}\,\mathrm{cm}^{-3}$. Under these conditions, the deviations of number densities of excited atoms from their equilibrium values at T_e can be analyzed.

The relative populations in the ground state and at the bound-continuum boundary are calculated with the Saha equation. Using Eqs. (3)–(5), one obtains: $y_1 \approx 1$ and $y_e^2 = 1.0 \times 10^{-4}$. Therefore, this regime should be interpreted as a regime of subequilibrium ionization: $y(E)$ is a decreasing function.

Suppose that $I_1/kT_e = 15 \gg 1$. The first excited state of a Cs atom is characterized by the binding energy $E_2 = 2.47$ eV. Since $E_2/kT_e \gg 1$, and Eq. (11) is valid, the population at this level is close to its equilibrium value: $y_2(E_2) \approx 1$. A deviation from equilibrium should be expected to occur when $E \le kT_e$. The binding energy $E \approx 0.46$ eV is characteristic of excited levels with the principal quantum number $n = 6$. Since $E/kT = 1.78$, Eq. (8) yields $\chi(E/kT) = 0.36$, and Eq. (9) can be used to show that this state is well underpopulated: $y(E) = 0.36$. With a further decrease in E, $y(E)$ decreases to y_e^2. Values of $y(E)$, close to y_e^2, are characteristic of excited states very close to continuum.

9. *Comments*

a) See Comments to model P.1.
b) The modified diffusion approximation has also been developed to allow for discrete excited states (particularly at the lowest excited levels) and radiative transitions, see Ref. 1.

c) The electron binding energy is $E = Ry/k^2$, here k is the principal quantum number.

Relevant material can be found in Refs. 1 and 6.

L. Model of Recombination and Relaxation of Highly Excited Atoms Induced by Collisions with Electrons and by Resonant Deactivation by Neutral Particles (P.12)

1. Purpose of the Model

The model aims at determination of nonequilibrium distribution function for highly excited atomic states and of the flux of three-body recombination of electrons with atomic ions A^+ in a quasi-steady plasma of binary rare gas mixture $A + B$.

2. Assumptions

a) Electron number density in a recombining plasma of the rare gas mixture A + B (e.g. Xe + He, Xe + Ar, Xe + Kr) is much greater than its equilibrium value at temperature T_e. Thus, a decrease of electron number density is determined by the recombination process, while the ionization of atoms can be neglected.
b) The number density of the buffer rare gas atoms B is much greater than that of heavy rare gas atoms A. The number density of homonuclear ions A_2^+ is very small, and their dissociative recombination is not significant.
c) The ionization degree is $\alpha_i \geq 10^{-8}$, so that the diffusion flux over the energy levels with high principal quantum numbers is primarily determined by collisions with free electrons.
d) The mean electron energy in a low-temperature plasma is much lower than the ionization energy I of an atom A.
e) In the range $E \sim kT_e$, which is the most critical energy range for recombination induced by electron impact, inelastic collisions with the buffer gas atoms B lead mainly to deactivation of the Rydberg atom A(k). This is certainly justified when $T_e \gg T$.

3. Model Equations

In the case of a quasi-steady regime of recombination, the basic equation has the form

$$-\left[D(E)\frac{\partial n(E)}{\partial E} + B(E)n(e)\right] + W_B(E)n(E) = \Gamma \tag{1}$$

$$D(E) = 2\sqrt{2\pi}e^4 E\Lambda_1 n_e (3\sqrt{m_e kT_e})^{-1}$$

$$B(E) = -D(E)\left(\frac{1}{kT_e} - \frac{5}{2E}\right), \qquad W_B(E) = W^B_{k(E)}\frac{dE}{dk} \tag{2}$$

$$W^B_{k(E)} = n_B\sqrt{\frac{8kT}{\pi\mu_{AB}}}, \qquad \mu = \frac{m_A m_B}{m_A + m_B}$$

Equivalent equation for the normalized distribution function is

$$-D(E)\frac{\mathrm{d}y(E)}{\mathrm{d}E}+W_{\mathrm{B}}(E)y(E)=\frac{\Gamma}{n^{0}(E)},\qquad y(E)=\frac{n(E)}{n^{(0)}(E)} \tag{3}$$

$$n^{(0)}(E)=\frac{\pi^{3/2}e^{6}\exp(E/kT_{\mathrm{e}})}{2(kT_{\mathrm{e}})^{3/2}E^{5/2}}n_{\mathrm{e}}n_{\mathrm{i}} \tag{4}$$

Boundary conditions

a) The Rydberg electrons with binding energy $E \ll kT_{\mathrm{e}}$ are in equilibrium with electrons in the continuum, i.e., $n(E)=n^{(0)}(E)$ near the ionization limit ($E=0$) of the atom A. This yields $y(0)=1$.

b) At large binding energies, the distribution function $n(E)$ is not perturbed by free electrons and is independent of them. It is determined by the equilibrium value of number density $n_{\mathrm{e}}^{(0)}$. Since $n_{\mathrm{e}}^{(0)} \ll n_{\mathrm{e}}$, one can set $y(E)=0$, $E \sim I_{\mathrm{A}}$.

4. *Nomenclature*

a) Argument:

E	electron binding energy (i.e., the minimum energy that has to be given to electron to bring it from a given bound state into a free state)

b) Quantity calculated with the model:

$n(E)$	energy distribution for bound electrons

c) Kinetic coefficients:

β_r	coefficient of three-body recombination
α_r	effective binary recombination coefficient
$D(E)$	coefficient of diffusion (diffusivity) in the energy space [see Eq. (2) of model P.11]
$B(E)$	dynamic friction coefficient in the energy space [see Eq. (6) of model P.11]
$\Lambda_{\mathrm{I}}(E)$	Coulomb logarithm for inelastic processes (see model I-E.4)

d) Other quantities:

Γ	recombination flux
$A(k)$, $A(n)$	atoms in excited states with principal quantum number k, n
E_{B}	energy at which deactivation mechanism is changed
$y(E)$	normalized electron distribution for bound electrons
T_{e}	electron temperature
n_{e}^{0}	electron number density in Saha equilibrium (see model P.3)
I_{A}	ionization energy from ground state of atom A, $I_{\mathrm{A}}=E_1$
α_i	ionization degree (fraction)

$W_B(E)$	total probability of deactivation of Rydberg electron in the quasi-continuous spectrum
W_k^B	total rate of resonant deactivation of Rydberg atom A(k) by the ground state atom B of the buffer gas
m_e, m_A, m_B	electron, atom A and B masses
μ_{AB}	reduced mass of particles A and B
K	coefficient in the exponent dependence for energy splitting
r	distance between atoms B^+ and A
ν	exponent in the expression for energy splitting
$Ry = 13.6\,\text{eV}$	Rydberg constant

5. *Model Description*

a) In the model (Refs. 25 and 26), the capture of electron by an atomic ion A^+ and its relaxation over the highly excited levels of atom $A(n)$ initially occurs as diffusion over energy states, prompted by collisions with electrons. However, starting from certain levels $E_n \geq E_B$, the relaxation of electron energy is primarily determined by an efficient deactivation mechanism, associated with scattering of the buffer gas atom B on the parent core A^+ of the Rydberg A(n) atom.

b) Simple expression for the probability $W_B(E)$ of resonant deactivation of Rydberg electron can be obtained for a power law approximation of the energy splitting $\Delta U_{fi}(r) = K(a_0/r)^\nu$ of the lower terms U_i and U_f of the heteronuclear rare gas ion $B^+ - A$ temporarily formed during collision of the $B - A^+$ particles (Ref. 25):

$$W_B(E) = C_\nu(T)\left(\frac{E}{2Ry}\right)^{8\nu-9/2\nu} n_B \tag{7}$$

$$C_\nu(T) = \frac{e^2\hbar\pi^2}{m_e}\frac{\gamma 2^{8-9/2\nu}}{25\nu}\zeta\left(\frac{1+3}{\nu}\right)A(T)\left(\frac{K}{2Ry}\right)^{3/\nu} \tag{8}$$

Here, $\zeta(z)$ is the Riemann function (see Ref. 27; the coupling constant γ and the factor $A(T)$ are described in Ref. 28).

6. *General and Particular Solutions*

a) The general solution to (3), taking into account condition Eq. (11) (see below), is

$$y(E) = P(E)\left[1 - |\Gamma| \int_0^E \frac{\mathrm{d}E'}{n^{(0)}(E')D(E')P(E')}\right] \tag{9}$$

where $P(E)$ is the solution on the homogeneous equation (3):

$$P(E) = \exp\left\{\int_0^E \mathrm{d}E' \frac{W_B(E')}{D(E')}\right\} \tag{10}$$

b) For the specific form Eq. (7) of the probability $W_B(E)$, the $P(E)$ function can be written as

$$P(E) = \exp\left\{0.2\left(\frac{E}{E_B}\right)^{\eta}\right\}, \qquad \eta = \frac{8\nu - 9}{2\nu} \tag{11}$$

$$E_B = Ry\left[\frac{5(8\nu-9)\alpha_i\Lambda}{6(2\pi)^{3/2}\gamma A(T)\varsigma(1+3/\nu)}\left(\frac{2Ry}{K}\right)^{3/\nu}\sqrt{\frac{2Ry}{kT_e}}\right]^{2\nu/8\nu-9},$$

$$\alpha_i = \frac{n_e}{n_B} \tag{12}$$

The value of E_B is a function of T_e, T, and α_i of the plasma.

Specific model representation

a) At $E < E_B$, one can set $P(E) \approx 1$, so that the solution (9) for $y(E)$ corresponds to the result (Refs. 29 and 30):

$$y(E) = 1 - \frac{|\Gamma|}{\beta_r^{(e)} n_e^2 n_i} \frac{\gamma(5/2, |E|/kT_e)}{\Gamma(5/2)} \tag{13}$$

$$\beta_r^{(e)} = \frac{4\pi(2\pi)^{1/2} e^{10}\Lambda}{9\sqrt{m_e}(kT_e)^{9/2}} \tag{14}$$

Here, $\gamma(5/2, x)$ is the incomplete gamma function of the argument $x = E/kT_e$. Thus, in the range of $E < E_B$ the resonant quenching by neutral atoms B is negligible.

b) At $E > E_B$, we have from the Eq. (10): $P(E) \gg 1$, that is, collisions with free electrons can be neglected.

c) Because the transition from the diffusion region $E < E_B$ to the predominant "sink" region $E > E_B$ occurs in a narrow vicinity of the point E_B, one can set $P(E) \approx 1$ for all energy levels with $E < E_B$. Then, imposing a second boundary condition $y(E_B) = 0$, one can determine Eqs. (9), (11) and (12), and also the recombination flux Γ and the recombination coefficient $\beta_r^{(e,B)} = \Gamma/n_e^2 n_i$ involving collisions with electrons and neutral particles B.

Approximate solution for the recombination flux

The resulting formula for Γ can be written in terms of the standard three-body recombination coefficient $\beta_r^{(e)}$ Eq. (14) associated with electron-ion-electron collisions and some quantity $\chi(E_B/kT_e)$, which is a function of T_e and the ionization degree $\alpha_I = n_e/n_B$:

$$\Gamma = -\beta_r^{(e,B)}(T_e, \alpha_i) n_e^2 n_i, \qquad \beta_r^{(e,B)} = \beta_r^{(e)}(T_e)\chi^{-1}\left(\frac{E_B}{kT_e}\right) \tag{15}$$

$$\chi(x) = \frac{4}{3\pi^{1/2}}\gamma(5/2, x), \qquad (0 \le \chi \le 1) \tag{16}$$

The factor $\chi^{-1}(E_B/kT_e)$ describes the increase of recombination coefficient $\beta_r^{(e,B)}$ because of the resonant deactivation of Rydberg levels of A(n) atoms by the buffer rare gas B atoms.

7. *Restrictions*

a) As is apparent from Eqs. (15) and (16), at $kT_e \sim E_B$ the recombination regime switches from a steep decrease $|\Gamma| \propto T_e^{-9/2}$ with T_e at $kT_e \ll E_B$ to a much slower decrease with temperature and anomalously large values of $\beta_r^{(e,B)} \gg \beta_r^{(e)}$ at $kT_e \gg E_B$.

b) The model can be applied to hydrogen and hydrogen-like atoms.

8. *Example*

Experimental studies (Refs. 25 and 26) of this type of recombination were performed for afterglow plasma of a pulsed discharge in Xe + He mixture ($n_{He} = 2.6 \times 10^{17}$–$4.4 \times 10^{18}\,cm^{-3}$, $n_{Xe} = 10^{14}$–$10^{16}\,cm^{-3}$, and $T =$ 300–600 K). The dependence of the recombination coefficients $\beta_r^{e,He}(T_e, n_e)$ of electrons with Xe^+ ions, and of the emission intensities $J_\lambda(T_e, n_e)$ for a number of Xe atom spectral lines on T_e and n_e were obtained in the ranges of $T_e =$ 400–2500 K and $n_e = 2 \times 10^{10}$–$3 \times 10^{12}\,cm^{-3}$. A characteristic feature of the obtained functions is a steep decrease (close to $\propto T_e^{-9/2}$) in the region $T_e \leq 800$ K, and anomalously high recombination rates at $T_e \geq 800$ K. It was also established that the recombination flux $\Gamma = \beta_r^{(e,He)} n_e^3$ depends considerably on the ionization degree and on the He density.

This behavior is quantitatively explained by the present model. Calculations (Refs. 25 and 26) lead to the following scaling of the recombination flux:

$$\begin{aligned} |\Gamma| &\propto n_e^3 \cdot T_e^{-9/2} && kT_e \ll E_{He} \\ |\Gamma| &\propto n_e^{2.3} n_{He}^{0.7} \cdot T_e^{-1/6} && kT_e \gg E_{He} \end{aligned} \tag{17}$$

Because of the efficient resonant deactivation of the Rydberg Xe(n) levels by He atoms, the recombination coefficient $\beta_r^{(e,He)}$ is higher than the value $\beta_r^{(e)}$ obtained within the framework of the "diffusion" recombination with free electrons. In particular, for $T_e \approx 0.2$ eV and $\alpha_i = n_e/n_{He} = 10^{-5}, 10^{-6}, 10^{-7}$, and 10^{-8}, an increase in recombination rate $\beta_r^{(e,He)}/\beta_r^{(e)}$ turns out to be equal to 4, 10, 57, and 325 times, respectively.

9. *Comment*

References 25 and 26 indicate the efficiency of the resonant deactivation mechanism of Rydberg atomic levels by neutral particles in electron–ion recombination of low-temperature plasma of rare gas mixtures at degrees of ionization up to $\sim 10^{-5}$–10^{-4}.

Relevant material can be found in Refs. 25, 26, and 28–30.

M. Model for Electron Energy Distribution Function (EEDF) in Weakly Ionized Atomic Plasmas (P.13)

1. *Purpose of the Model*

The model aims at calculation of EEDFs for steady plasmas in external electric field, taking into account elastic collisions of electrons with atoms.

2. *Assumptions*

a) The distribution of atoms over energy is an equilibrium one at gas temperature, T.
b) The plasma is weakly ionized, so that collisions between charged particles play a negligible role.
c) Electric field E is applied.
d) Energy exchange in collisions of electrons with atoms and electron heating by the external field are taken into account in calculating the EEDF.

3. *Model Equation*

$$-\frac{2e^2\mathrm{E}^2}{3m_\mathrm{e}}\left[\frac{\varepsilon^2 k}{\nu_\mathrm{ea}(\varepsilon)}\frac{\partial f}{\partial\varepsilon}\right] = \varepsilon^{3/2}\delta\nu_\mathrm{ea}(\varepsilon)\left(f + kT\frac{\partial f}{\partial\varepsilon}\right) \tag{1}$$

Boundary conditions

Boundary condition: $f(\varepsilon) \to 0$ at $\varepsilon \to \infty$.
Normalization: $\int_0^\infty f(\varepsilon)\sqrt{\varepsilon}\,\mathrm{d}\varepsilon = 1$.
The number densities of electrons (n_e) and atoms (n_a) must be prescribed.

4. *Nomenclature*

a) Argument:

ε	electron energy

b) Quantity calculated with the model:

$f(\varepsilon)$	electron energy distribution function (EEDF)

c) Kinetic coefficients:

$\nu_\mathrm{ea}(\varepsilon) = n_\mathrm{a}\sqrt{2\varepsilon/m_\mathrm{e}}\,q_\mathrm{ea}(\varepsilon)$	collision frequency of electron with energy ε with atoms
$q_\mathrm{ea}(\varepsilon)$	elastic collision cross section (in models I-T.1, I-T.7, and I-T.8, this quantity is denoted as $Q_0(\varepsilon)$)

d) Other quantities:

T	atom temperature
e, m_e	electron charge and mass
m_a	atomic mass
E	electric field
$\delta = 2m_\mathrm{e}/m_\mathrm{a}$	energy transfer factor
ω	frequency of alternating electric field

5. *Model Description*

The model equation describes the balance of electrons with energy ε.

6. *General and Particular Solutions*

The *general solution* is given by Davydov's formula (Ref. 31):

$$f(\varepsilon) = C\exp\left\{-\int d\varepsilon'\left[kT + 2e^2\mathrm{E}^2/3m_e\delta\nu_{\mathrm{ea}}^2(\varepsilon')\right]^{-1}\right\} \tag{2}$$

where C is a normalization constant.

Particular solutions

a) The Druyvesteyn distribution is obtained when $q_{\mathrm{ea}}(\varepsilon)$ is independent of ε, and in the limit of strong heating by the field, when the mean electron energy $\bar{\varepsilon} \gg kT$ (see Comment to model P.2). This requires

$$kT \leq 2e^2\mathrm{E}^2/3m_e\nu_{\mathrm{ea}}^2\delta$$

$$\text{i.e.,} \quad \frac{\mathrm{E}}{n_{\mathrm{a}}} \geq 4.6 \times 10^{-22} T q_{\mathrm{ea}} m_{\mathrm{a}}^{-1/2}, \quad \mathrm{V}\cdot\mathrm{cm}^2$$

where T is in K, q_{ea} in Å^2, and m_a in amu.
The Druyvesteyn distribution is:

$$f(\varepsilon) = C\exp\left(-\frac{3\delta n_{\mathrm{a}}^2 q_{\mathrm{ea}}^2}{2e^2\mathrm{E}^2}\varepsilon^2\right), \qquad C = 2\left[\Gamma\left(\frac{3}{4}\right)\right]^{-1}\left(\frac{3\delta n_{\mathrm{a}}^2 q_{\mathrm{ea}}^2}{2e^2\mathrm{E}^2}\right)^{3/4} \tag{3}$$

where $\Gamma(3/4 \cong 1.23$ is the value of gamma function.

b) If the collision frequency ν_{ea} is independent of ε, then $f(\varepsilon)$ is a Maxwellian function, $f^0(\varepsilon) = (2/\sqrt{\pi})(kT_e)^{-3/2}\exp(-\varepsilon/kT_e)$, where

$$T_e = T + \left(e^2\mathrm{E}^2/3m_e k\nu_{\mathrm{ea}}^2\delta\right) \tag{4}$$

c) When the electric $\mathrm{E} = \mathrm{E}_0\cos\omega t$ field has a very high frequency, $\omega \gg \delta\nu_{\mathrm{ea}}(\varepsilon)$, it can be replaced with a constant effective field $E_{eff}^2 = \frac{1}{2}\mathrm{E}_0^2\nu_{\mathrm{ea}}^2/\omega^2$. Then, the Margenau distribution is obtained as a Maxwellian $f^0(\varepsilon)$ one with the temperature

$$T_e = T + \left(e^2\mathrm{E}_0^2/3m_e k\omega^2\delta\right) \tag{5}$$

7. *Restriction*

The ionization fraction should be sufficiently low, so that electron–electron collision could be neglected: $\nu_{\mathrm{ee}} \ll \delta\nu_{\mathrm{ea}}$.

8. *Example*

In a helium plasma, $q_{\mathrm{ea}} \approx 6$ Å^2 = const; at $T = 10^3$ K, the distribution is close to the Druyvesteyn form if $\mathrm{E}/n_{\mathrm{a}} \geq 1.4 \times 10^{-18}\,\mathrm{V}\cdot\mathrm{cm}^2$. If $\mathrm{E}/n_{\mathrm{a}} = 1.4 \times 10^{-18}\,\mathrm{V}\cdot\mathrm{cm}^2$, then the mean electron energy is $\bar{\varepsilon}/k = \sqrt{2}e\mathrm{E}/\sqrt{8\delta}n_{\mathrm{a}}q_{\mathrm{ea}} = 10^4$ K. Then, electron–electron collisions can be neglected if the degree of ionization $n_e/n_{\mathrm{a}} < 10^{-6}$.

9. Comments

a) The model is based on the Boltzmann kinetic equation for EEDF, with electron–atom elastic collision integral written in the Fokker–Planck form.

b) The Maxwellian EEDF is symmetric. In an external electric field, the EEDF is asymmetric in the field direction. In weak fields, the asymmetric EEDF component is small as compared to the symmetric one. The symmetric component of the EEDF determines the energy characteristics of a plasma, including $\bar{\varepsilon}$.

Relevant material can be found in Refs. 8, 31, and 32.

N. Model for Electron Energy Distribution Function (EEDF) in a Highly Ionized Atomic Plasma (P.14)

1. Purpose of the Model

The model aims at the calculation of EEDFs for steady atomic plasmas, taking into account inelastic collisions.

2. Assumptions

a) The plasma is highly ionized, so that collisions between thermal charged particles are important in its kinetics.

b) Excitation and ionization of atoms lead to energy losses of free electrons.

c) Electron–electron collisions and excitation and ionization of atoms or molecules by electron impact are taken into account in calculating the EEDF.

3. Model Equation:

$$\frac{1}{\sqrt{\varepsilon}}\frac{\partial}{\partial\varepsilon}\left\{2\varepsilon^{3/2}\nu_{ee}(\varepsilon)\left[f(\varepsilon)+kT_e\frac{\partial f}{\partial\varepsilon}\right]\right\}=f(\varepsilon)\nu_{1\Sigma}(\varepsilon),$$

$$\nu_{1\Sigma}(\varepsilon)=\sum_{k\geq 2}\nu_{1k}(\varepsilon)+\nu_i(\varepsilon),\qquad \nu_{ee}(\varepsilon)=\pi e^4 n_e\Lambda\sqrt{2m_e}/\varepsilon^{3/2} \tag{1}$$

Initial and boundary conditions

Boundary condition: $f(\varepsilon)$ as $\varepsilon\to\infty$.
Normalization: $\int_0^\infty f(\varepsilon)\sqrt{\varepsilon}\,d\varepsilon=1$.
The number densities of electrons, n_e, atoms, n_a, must be prescribed.

4. Nomenclature

a) Argument:

ε	electron energy

b) Quantity calculated with the model:

$f(\varepsilon)$	electron energy distribution function (EEDF)

c) Kinetic coefficients:

$\nu_{\mathrm{ee}}(\varepsilon)$	electron–electron collision frequency at energy ε
$\nu_{1\Sigma} = \sum_k \nu_{1k}(\varepsilon)$	total frequency of $1 \to k$ excitation of atoms from the ground state by electron impact, where k is the number of an excited state
$\nu_{1k}(\varepsilon) = n_{\mathrm{a}}\sqrt{2\varepsilon/m_{\mathrm{e}}}\,q_{1k}(\varepsilon)$	
$q_{1k}(\varepsilon)$	cross section for excitation to atomic level k by electron impact (in models I-E.2–I-E.4, this quantity is denoted as σ_{1k})
$\nu_i(\varepsilon) = n_{\mathrm{a}}\sqrt{2\varepsilon/m_{\mathrm{e}}}\,q_i(\varepsilon)$	frequency of ionizing collisions of an electron (with energy ε) with atoms
$q_i(\varepsilon)$	cross section for ionization of atoms by electron impact (see models I-P.11 and I-P.12, values σ_i)

d) Other quantities:

T_{e}	electron temperature
Λ	Coulomb logarithm (see model I-T.13)
e	electron charge
$m_{\mathrm{e}}, m_{\mathrm{a}}$	electron and atomic masses

5. *Model Description*

The governing equation describes the balance of the number of electrons of energy ε.

6. *General and Particular Solutions*

There is no general solution. Integrating Eq. (1) once, one obtains:

$$2\varepsilon^{3/2}\nu_{\mathrm{ee}}(\varepsilon)\left[f(\varepsilon) + kT_{\mathrm{e}}\frac{\partial f}{\partial \varepsilon}\right] = \int_{\varepsilon}^{\infty} f(\varepsilon')\sqrt{\varepsilon'}\,\nu_{1\Sigma}(\varepsilon')\mathrm{d}\varepsilon' \tag{2}$$

which is solved by numerical iteration. A particular solution is obtained for $\nu_{1\Sigma}(\varepsilon)$ modeled as $\nu_{1\Sigma}(\varepsilon) \sim 1/\sqrt{\varepsilon}$:

$$\frac{f(\varepsilon)}{f^0(\varepsilon)} = \frac{2}{a+1}\exp\left[-\frac{a-1}{2}\frac{\varepsilon - E_2}{kT_{\mathrm{e}}}\right], \qquad \varepsilon \geq E_2 \tag{3}$$

$$\frac{f(\varepsilon)}{f^0(\varepsilon)} = 1 - \frac{a-1}{a+1}\exp\left(\frac{\varepsilon - E_2}{kT_{\mathrm{e}}}\right), \qquad \varepsilon < E_2 \tag{4}$$

where $f^0(\varepsilon) = (2/\sqrt{\pi})(kT_{\mathrm{e}})^{3/2}\exp(-\varepsilon/kT_{\mathrm{e}})$ is the Maxwellian EEDF, E_2 is the excitation energy for the first excited level with $k = 2$, and

$$a(T_{\mathrm{e}}) = \sqrt{1 + 2\nu_{1\Sigma}(T_{\mathrm{e}})/2\nu_{\mathrm{ee}}(T_{\mathrm{e}})} \tag{5}$$

If $a(T_e) \gg 1$, then inelastic collisions substantially deplete the high-energy tail of the EEDF:

$$f(\varepsilon) \cong f^0(\varepsilon)\frac{2}{a}\exp\left(-\frac{a}{2}\frac{\varepsilon - E_2}{kT_e}\right), \qquad \varepsilon \geq E_2 \tag{6}$$

If $a(T_e) \ll 1$, the EEDF is close to Maxwellian form: $f(\varepsilon) \cong f^0(\varepsilon)$.

7. *Restriction*

a) The plasma can be treated as highly ionized if the electron–electron collision frequency is higher than the electron–atom collision frequency, ν_{ea}, multiplied by the energy exchange factor $\delta = 2m_e/m_a$:

$$\frac{\nu_{ee}(T_e)}{\delta\nu_{ea}(T_e)} \gg 1 \tag{7}$$

Here, $\nu_{ea}(\varepsilon) = n_a\sqrt{2\varepsilon/m_e}q_{ea}(\varepsilon)$, and $q_{ea}(\varepsilon)$ is the electron–atom collision cross section (see models I-T.5 and I-T.6). The left-hand side of criterion Eq. (7) can be expressed as

$$\frac{\nu_{ee}(T_e)}{\delta\nu_{ea}} = 6 \times 10^7 \frac{n_e}{n_a(kT_e)^2 q_{ea}\delta} \tag{8}$$

where kT_e is in eV, q_{ea} in Å^2, and δ in 10^{-4}.

b) The atomic excited state distribution is substantially nonequilibrium:

$$n_k \ll n_k^0$$

where n_k^0 is the number density of excited atoms corresponding to the Boltzmann distribution at the temperature, T_e.

8. *Example*

According to the model of excitation and ionization kinetics (see model I-P.15),

$$a(T_e) = \sqrt{\frac{8n_a}{n_e}\frac{kT_e\Lambda_1}{E_2\Lambda} + 1}, \quad \text{where } \Lambda_1 \cong 0.02\text{–}0.05$$

Hence, when $T_e \cong 0.1E_2/k$, the distribution has the Maxwellian form if $n_e/n_a > 10^{-4}$. At lower degrees of ionization, the tail of the EEDF corresponding to $\varepsilon \geq E_2$ is substantially depleted.

9. *Comment*

The EEDF tail is always depleted during the initial stage of ionization by electron impact. At degrees of ionization lower than 10^{-5}, this leads to a sharp decrease in ionization rate, that is, to a deceleration of the process. The corresponding EEDF can be treated as time-independent, and the present model can be applied. The EEDF relaxation time is estimated by invoking model P.16.

Relevant material can be found in Refs. 1, 8, 31, and 32.

O. Model for Electron Energy Distribution Function (EEDF) in an Atomic and Molecular Plasma (P.15)

1. Purpose of the Model

The model aims at the calculation of EEDFs for steady atomic and molecular plasmas in external electric fields allowing for vibrationally excited molecular states.

2. Assumptions

a) Electric field E is applied.
b) The plasma is weakly ionized, so that collisions between charged particles play a negligible role.
c) Excitation and deactivation of molecular vibrational states play an essential role in the balance of electron energy.
d) The atomic and molecular gas is cold: $T \ll T_{eff}$.
e) Energy exchange in collisions of electrons with molecules and heating by the external field of intensity E are taken into account.

3. Model Equation

$$-\frac{\partial}{\partial\varepsilon}\left[\frac{2e^2\mathrm{E}^2}{3m_\mathrm{e}}\frac{\varepsilon^{3/2}}{\nu_\mathrm{ea}(\varepsilon)}\frac{\partial f}{\partial\varepsilon}+\delta\nu_\mathrm{ea}(\varepsilon)\varepsilon^{3/2}f(\varepsilon)\right]+I_v(\varepsilon)=0 \tag{1}$$

$$\begin{aligned}I_v(\varepsilon) = -\sum_{v'<v''}&[\nu_{v'v''}(\varepsilon)f(\varepsilon)\sqrt{\varepsilon}-\nu_{v'v''}(\varepsilon+E_{v''}-E_{v'})\sqrt{\varepsilon+E_{v''}-E_{v'}}\\&\times f(\varepsilon+E_{v''}-E_{v'})-\nu_{v''v'}(\varepsilon)f(\varepsilon)\sqrt{\varepsilon}\\&+\nu_{v''v'}(\varepsilon-E_{v''}+E_{v'})\sqrt{\varepsilon-E_{v''}+E_{v'}}f(\varepsilon-E_{v''}+E_{v'})]\end{aligned} \tag{2}$$

Boundary conditions

Boundary condition: $f(\varepsilon)$ as $\varepsilon \to \infty$.
Normalization: $\int_0^\infty f(\varepsilon)\sqrt{\varepsilon}\,\mathrm{d}\varepsilon = 1$.
The number densities of electrons n_e, atoms n_a, and molecules n_m must be prescribed.

4. Nomenclature

a) Argument:

ε	electron energy

b) Quantity calculated with the model:

$f(\varepsilon)$	electron energy distribution function (EEDF)

c) Kinetic coefficients:

$\nu_{\rm ea}(\varepsilon) = n_{\rm a}\sqrt{2\varepsilon/m_{\rm e}}q_{\rm ea}(\varepsilon)$	collisional frequency of electron (at energy ε) with atoms
$q_{\rm ea}(\varepsilon)$	elastic collision cross section (in models I-T.7 and I-T.8, this quantity is denoted as $Q_0(\varepsilon)$)

The values $q_{\rm ea}$ and $\nu_{\rm ea}$ are replaced by $q_{\rm em}$ and $\nu_{\rm em}$ for collisions of electrons with molecules.

d) Other quantities:

e, $m_{\rm e}$	electron charge and mass
$m_{\rm a}$, $m_{\rm m}$	atomic and molecular masses
$\delta = 2m_{\rm e}/m_{\rm a}$	energy transfer factor
E	electric field
$I_v(\varepsilon)$	collision integral for inelastic collisions of electrons with molecules
v', v''	vibrational quantum numbers of the ground electronic state of a molecule, $v' < v''$
$E_{v'}$, $E_{v''}$	vibrational energy of molecules at levels v', v''
$n_{v'}$	number density of molecules at level v'
$\nu_{v'v''}(\varepsilon)$	frequency of electron–molecule inelastic collisions leading to transition $v' \rightarrow v''$
k_{ev}	rate coefficient for vibrational excitation by electron impact
T_{eff}	effective electron temperature
T_v	vibrational temperature
$\hbar\omega_0$	vibrational energy quantum

5. *Model Description*

The governing equation describes the balance of electrons of energy ε.

6. *General and Particular Solutions*

There is no general solution.

Particular solutions

a) When a molecule is completely de-excited vibrationally by collision with an atom, only the transition 0 → 1 is taken into account in the integral $I_v(\varepsilon)$:

$$I_v = -\nu_{01}(\varepsilon)f(\varepsilon)\sqrt{\varepsilon} + \nu_{01}(\varepsilon + \hbar\,\omega_0)\sqrt{\varepsilon + \hbar\omega_0}f(\varepsilon + \hbar\omega_0) \qquad (3)$$

At high energies, when $\varepsilon \gg \hbar\omega_0$,

$$I_v \approx \hbar\omega_0 \frac{d}{d\varepsilon}[\sqrt{\varepsilon}\nu_{01}(\varepsilon)f(\varepsilon)] \tag{4}$$

the solution has the form

$$f(\varepsilon) = C\exp\left[-\int_0^{\varepsilon} \frac{3\delta m_e \nu_{ea}^2(\varepsilon')}{2e^2\mathrm{E}^2} d\varepsilon' \left(1 + \frac{\hbar\omega_0}{\delta\varepsilon'} \frac{\nu_{01}(\varepsilon')}{\nu_{ea}(\varepsilon')}\right)\right] \tag{5}$$

The effective electron temperature is calculated as

$$T_{eff} = \left[\frac{2e^2\mathrm{E}^2}{3k\delta m_e \nu_{ea}^2}\right]\left[1 + \hbar\omega_0\nu_{01}/\delta\varepsilon\nu\right]^{-1} \tag{6}$$

where C is a normalization constant.

b) If the role of electron–atom collisions in the energy exchange is neglected, the solution has the form

$$f(\varepsilon) = C_0 + \frac{3\sqrt{m_e}}{\sqrt{2}e^2\mathrm{E}^2}\int_0^{\varepsilon} \frac{q_{em}(\varepsilon')}{\varepsilon'} d\varepsilon' \int_0^{\varepsilon'} I_v(\varepsilon'')\, d\varepsilon'' \tag{7}$$

where C_0 is a normalization constant.

The resulting EEDF can be obtained by numerical iteration.

If the analysis is restricted to transitions 0 → 1 and 1 → 0, and the Boltzmann population at the vibrational temperature T_v is assumed to hold for the level with $v'' = 1$, then the inelastic collision integral at high energies, $\varepsilon \gg \hbar\omega_0$, is

$$I_v = \frac{d}{d\varepsilon}\left[\frac{\hbar\omega_0}{\varepsilon}\varepsilon^{3/2}\left(f + kT_v\frac{\partial f}{\partial \varepsilon}\right)\right] \tag{8}$$

The corresponding solution has the form

$$f(\varepsilon) = C\exp\left\{-\int_0^{\varepsilon} \frac{d\varepsilon'}{kT_v + [2e^2\mathrm{E}^2\varepsilon/3\hbar\omega_0\nu_{em}(\varepsilon)\nu_{01}(\varepsilon)]}\right\} \tag{9}$$

In weak fields, electrons are in equilibrium with molecular vibrations, and $T_{eff} \to T_v$.

7. *Restrictions*

a) The plasma can be treated as weakly ionized if the ratio of energy transfer rates in encounters with ions and atoms is small:

$$\frac{\nu_{ei}(T_{eff})}{\delta\nu_{ea}(T_{eff})} \ll 1$$

b) Energy transfer is controlled by vibrational excitation if energy transfer in elastic encounters is relatively slow:

$$\frac{\delta \nu_{\mathrm{em}}(T_{eff})}{\delta_1 k_{ev} n_{\mathrm{m}}} \ll 1$$

where $\delta_1 = \hbar\omega_0/kT_{\mathrm{e}}$ ($\hbar\omega_0$ is the vibrational quantum) and $k_{\mathrm{e}v} = 10^{-10}$–$10^{-8}\,\mathrm{cm}^3/\mathrm{s}$.

c) The electron momentum distribution is controlled by electron–atom collisions if the frequency ν_{ea} is much higher than the frequency of inelastic collisions with molecules:

$$\frac{\nu_{\mathrm{ea}}(T_{eff})}{k_{\mathrm{e}v} n_{\mathrm{m}}} \gg 1$$

d) Inelastic atom–molecule collisions quench vibrational excitation if

$$\frac{n_{\mathrm{m}} k_{10}}{n_{\mathrm{e}} k_{\mathrm{e}v}} \gg 1$$

where k_{10} and $k_{\mathrm{e}v}$ are the rate constants for the transition $1 \rightarrow 0$ in encounters with atoms and electrons, respectively (see Chapter 4 in the first volume of this series).

8. Example

In a weakly ionized nitrogen plasma with $E/n_{\mathrm{m}} = 6 \times 10^{-16}\,\mathrm{V}\cdot\mathrm{cm}^2$ and $n_{\mathrm{m}} = 10^{16}\,\mathrm{cm}^{-3}$, electron energy is primarily lost in vibrational excitations of N_2 characterized by the rate constant $k_{\mathrm{e}v} = 4 \times 10^{-9}\,\mathrm{cm}^3/\mathrm{s}$. The energy is then irreversibly transferred to the translational and rotational degrees of freedom of the gas, so that the EEDF is substantially decreasing at $\varepsilon \geq 1.7\,\mathrm{eV}$. Electrons are heated by the electric field, and their mean energy is

$$\bar{\varepsilon} = \frac{3}{2} kT_{eff} = \frac{1}{2} \frac{e^2 \mathrm{E}^2}{\hbar\omega_0 n_{\mathrm{m}}^2} \cdot \frac{1}{q_{01} q_{\mathrm{ea}}} \approx 1.3\ \mathrm{eV} \qquad (10)$$

9. Comment

Energy transfer between free electrons and vibrationally excited molecules determines the EEDF and the mean electron energy in gas-discharge plasmas employed as active media in molecular lasers.

Relevant material can be found in Refs. 1, 7, 8, and 31.

P. Model of Relaxation of Electron Energy Distribution Function (EEDF) (P.16)

1. Purpose of the Model

The model aims at calculation of the EEDF relaxation time in atomic and molecular plasmas.

2. *Assumptions*

a) At the initial moment $t = 0$, the plasma starts to evolve from a state characterized by an EEDF $f(\varepsilon, t)$ that does not correspond to any steady, equilibrium or nonequilibrium, distribution to such a distribution.
b) Electric field of finite or zero intensity E is applied.
c) The EEDF relaxation time is calculated by taking into account elastic and inelastic collisions and heating of electrons in electric field of intensity E.

3. *Model Equation*

$$\frac{\partial f(\varepsilon, t)}{\partial t} = -\frac{1}{\tau(\varepsilon)}[f(\varepsilon, t) - f(\varepsilon)] \tag{1}$$

where $\tau(\varepsilon)$ is the EEDF relaxation time calculated in terms of the frequencies of electron–electron and elastic and inelastic electron–atom and electron–molecule collisions.

Initial conditions

Initial condition $f(\varepsilon, 0)$ is prescribed.
The EEDF $f(\varepsilon)$ in the state approached by $f(\varepsilon, t)$ as $t \to \infty$ is also known.

4. *Nomenclature*

a) Argument:

ε	electron energy

b) Quantity calculated with the model:

$\tau(\varepsilon)$	relaxation time of the electron energy distribution function (EEDF) in the vicinity of ε

c) Kinetic coefficients:

$\nu_{ee}(\varepsilon)$	electron–electron collision frequency (see model I-T.13)
$\nu_{ea}(\varepsilon)$	collision frequency of electron (at energy ε) with atoms (see model P.13) for molecular plasmas, ν_{ea} is replaced by ν_{em}
$\nu_{1\Sigma} = \sum_k \nu_{1k}(\varepsilon)$	total frequency of excitations of atoms from the ground state to level k by electron impact

d) Other quantities:

l	electron mean free path
L_e	length scale of electron number density spatial nonuniformity
L_T	length scale of the nonuniformity of mean electron energy
ε/eE	length over which an electron accelerated by an electric field of intensity E gains an amount of energy comparable to its mean energy $\bar{\varepsilon}$
Λ	Coulomb logarithm (see model I-T.13)

5. *Model Description*

The model equation describes the balance of electrons with energy, ε

6. *General and Particular Solutions*

General solution

$$f(\varepsilon, t) = f(\varepsilon, 0)e^{-t/\tau} + f(\varepsilon)(1 - e^{-t/\tau}) \tag{2}$$

Particular solutions

a) For a highly ionized plasma (model P.14), the time of relaxation to $f(\varepsilon)$ predicted by the model is

$$\tau(\varepsilon) = [\nu_{ee}(\varepsilon)]^{-1}, \quad \text{if } \varepsilon \leq E_2$$
$$\tau(\varepsilon) = [\nu_{ee}(\varepsilon) + \nu_{1\Sigma}(\varepsilon)]^{-1}, \quad \text{if } \varepsilon > E_2$$

where E_2 is the energy of the first excited level.

b) For a weakly ionized plasma (model P.13), the time of relaxation to $f^0(\varepsilon)$ at a temperature T after the field E is switched off is

$$\tau(\varepsilon) = [\delta\nu_{ea}(\varepsilon)]^{-1} \tag{3}$$

The time of relaxation to Davydov's distribution function $f(\varepsilon)$ after the field is switched on is

$$\tau(\varepsilon) = \left[\frac{e^2\mathrm{E}^2}{m_e\varepsilon\nu(\varepsilon)}\right]^{-1} \tag{4}$$

To calculate $\tau(\varepsilon)$ for a molecular plasma, collisional frequency ν_{ea} is replaced by the frequency of collisions with molecules $\nu_{em}(\varepsilon)$.

7. *Restrictions*

The criteria for plasma homogeneity are given by the inequalities

$$l \ll L_e, \qquad l \ll L_T, \qquad l \ll \varepsilon/e\mathrm{E} \tag{5}$$

where the electron mean free path is calculated as

$$l = \sqrt{\frac{2\varepsilon}{m_e}}\left(\sum_k \nu_k\right)^{-1} \tag{6}$$

The value of l must be small as compared to the lengths L_e and L_T of substantial variation of the electron number density and energy and to the length $\varepsilon/e\mathrm{E}$ over which an electron accelerated by the electric field E gains an amount of energy comparable to ε.

8. *Example*

Suppose that a fully ionized argon plasma characterized by $n_e = 10^{12}\ \mathrm{cm}^{-3}$ and mean electron energy $\bar{\varepsilon} = 2\,\mathrm{eV}$ is injected into neutral argon of number density

$n_a = 10^{12}\,\mathrm{cm}^{-3}$ heated to the temperature $T = 1.5 \times 10^4$ K. The Maxwellian EEDF core develops in the time interval

$$\tau(\varepsilon) = [\nu_{ee}(\varepsilon)]^{-1} = \left[\frac{\pi e^4 n_e \Lambda \sqrt{2m_e}}{\varepsilon^{3/2}}\right]^{-1} \tag{7}$$

calculated at $\bar{\varepsilon} = 2\,\mathrm{eV}$. Numerically, $\tau(\varepsilon) = 1.5 \times 10^{-7}$ s. The distribution tail develops during the interval

$$\tau(\varepsilon) = [\nu_{1\Sigma}(\varepsilon = E_2 + \bar{\varepsilon})]^{-1} = 1.0 \times 10^{-9}\,\mathrm{s} \tag{8}$$

Therefore, the initial EEDF tail is depleted much faster than the EEDF core develops.

9. *Comment*

The linear approximation is applicable when the deviation of the distribution function from equilibrium is small. However, correct values of relaxation times are predicted even for large deviations.

Relevant material can be found in Refs. 8, 31, and 32.

Q. Model for Electron Energy Distribution Function (EEDF) in Weakly Ionized Plasmas with Inelastic Collisions (P.17)

1. *Purpose of the Model*

The model aims at calculation of the EEDF for a steady atomic and molecular plasma in external electric field, taking into account intense inelastic collisions.

2. *Assumptions*

a) The plasma is weakly ionized, so that collisions between charged particles can be neglected.
b) The atomic and molecular energy distribution corresponds to equilibrium at gas temperature T.
c) Electric field of intensity E is applied.
d) Excitation and ionization of atoms lead to losses of energy of fast electrons.
e) The processes taken into account include energy transfer in electron–atom and electron–molecule encounters, heating by the external field, and excitation and ionization of atoms and molecules by electron impact.

3. *Model Equation*

$$\frac{1}{\sqrt{\varepsilon}}\frac{\partial}{\partial\varepsilon}\left\{\varepsilon^{3/2}\delta\nu(\varepsilon)\left[f + \left(kT + \frac{2e^2\mathrm{E}^2}{3m_e\delta\nu_{ea}^2(\varepsilon)}\right)\frac{\partial f}{\partial\varepsilon}\right]\right\} = f\nu_{1\Sigma}(\varepsilon) \tag{1}$$

$$\nu_{1\Sigma}(\varepsilon) = \sum_{k\geq 2}\nu_{1k}(\varepsilon) + \nu_i(\varepsilon) \tag{2}$$

4. *Boundary Conditions*

Boundary condition: $f(\varepsilon) \to 0$ as $\varepsilon \to \infty$.
Normalization: $\int_0^\varepsilon f(\varepsilon)\sqrt{\varepsilon}\,\mathrm{d}\varepsilon = 1$.
The number densities of electrons n_e, atoms n_a, and molecules n_m must be prescribed.

5. *Nomenclature*

a) Argument:

ε	electron energy

b) Quantity calculated with the model:

$f(\varepsilon)$	electron energy distribution function (EEDF)

c) Kinetic coefficients:

$\nu_\mathrm{ea}(\varepsilon) = n_\mathrm{a}\sqrt{2\varepsilon/m_\mathrm{e}}q_\mathrm{ea}(\varepsilon)$	collision frequency of electron (at energy ε) with atoms
$q_\mathrm{ea}(\varepsilon)$	electron–atom elastic collision cross section (in models I-T.6 and I-T.7, this quantity is denoted as $Q_0(\varepsilon)$) for molecular plasmas, ν_ea and q_ea are replaced by ν_em and q_em
$\nu_i(\varepsilon)$	frequency of ionizing electron–atom collisions at electron energy ε
$\sum_k \nu_{1k}(\varepsilon)$	total frequency of $1 \to k$ excitations of atoms from the ground state by electron impact, where k is the number of an excited state
$q_{1k}(\varepsilon)$	excitation cross section (in models I-E.2–I-E.4, this quantity is denoted as σ_{1k})
$q_i(\varepsilon)$	ionization cross section (see models I-P.11 and I-P.12)

d) Other quantities:

T	gas temperature
e, m_e	electron charge and mass
E	electric field
$\delta = 2m_\mathrm{e}/m_\mathrm{a}$, $\delta = 2m_\mathrm{e}/m_\mathrm{m}$	energy exchange factor
m_a, m_m	mass of atom and molecule
n_a, n_m	number densities of atoms and molecules
E_2	energy threshold for inelastic collisions, specifically, the excitation energy of the first excited level

6. *Model description*

The model equation describes the balance of electrons with energy ε.

7. *General and Particular Solutions*

There is no general solution. The integrated equation should be solved by numerical iteration:

$$\varepsilon^{3/2}\delta\nu(\varepsilon)\left[f+\left(kT+\frac{2e^2\mathrm{E}^2}{3m_\mathrm{e}\delta\nu_\mathrm{ea}^2(\varepsilon)}\right)\frac{\partial f}{\partial\varepsilon}\right]=\int_\varepsilon^\infty f(\varepsilon')\sqrt{\varepsilon'}\nu_{\mathrm{I}\Sigma}(\varepsilon')\,\mathrm{d}\varepsilon' \qquad (3)$$

Particular solutions for $f(\varepsilon)$ with a high-energy tail ($\varepsilon \geq E_2$) substantially depleted by inelastic collisions are:

a) The method of infinitely intense sink can be used to predict $f(\varepsilon)$ at $\varepsilon \leq E_2$ in the limiting case when the value of $f(\varepsilon)$ at $\varepsilon \geq E_2$ is negligible:

$$f(\varepsilon)=C\left\{\exp\left[-\int_0^\varepsilon\frac{\mathrm{d}\varepsilon'}{kT+(2e^2\mathrm{E}^2/3m_\mathrm{e}\delta\nu_\mathrm{ea}^2(\varepsilon))}\right]\right.$$
$$\left.-\exp\left[-\int_0^{E_2}\frac{\mathrm{d}\varepsilon'}{kT+(2e^2\mathrm{E}^2/3m_\mathrm{e}\delta\nu_\mathrm{ea}^2(\varepsilon'))}\right]\right\} \qquad (4)$$

where C is a normalization constant.
If $\nu_\mathrm{ea}(\varepsilon)$ is independent of energy, then (4) becomes

$$f(\varepsilon)=\frac{2}{\sqrt{\pi}}(kT_\mathrm{e})^{-3/2}\left[\exp\left(-\frac{\varepsilon}{kT_\mathrm{e}}\right)-\exp\left(-\frac{E_2}{kT_\mathrm{e}}\right)\right] \qquad (5)$$

where the electron temperature is calculated as

$$T_\mathrm{e}=T+\frac{2e^2\mathrm{E}^2/3m_\mathrm{e}\delta\nu_\mathrm{ea}^2(\varepsilon')}{k} \qquad (6)$$

The mean electron energy is $\bar{\varepsilon} \approx (3/2)kT_\mathrm{e}$.
Under these conditions, the total frequency of inelastic collisions is

$$\nu_{\mathrm{I}\Sigma}=\int_{E_2}^\infty\nu_{\mathrm{I}\Sigma}(\varepsilon)f(\varepsilon)\sqrt{\varepsilon}\,\mathrm{d}\varepsilon=\delta\nu_\mathrm{ea}(E_2)E_2^{3/2}\tilde{f}(E_2) \qquad (7)$$

where $\tilde{f}(E_2)$ is the EEDF value at $\varepsilon = E_2$, calculated without the contribution of inelastic collisions (see P.12).

b) The "quasi-classical" method can be used to determine $f(\varepsilon)$ at $\varepsilon \geq E_2$, as complementary to solution (4) for $\varepsilon \leq E_2$:

$$f(\varepsilon)=f(E_2)\exp[S(\varepsilon)],\qquad S(\varepsilon)=-\int_{E_2}^\varepsilon\frac{\mathrm{d}\varepsilon'}{\sqrt{\varepsilon'}}\sqrt{\frac{3m_\mathrm{e}\nu_\mathrm{ea}(\varepsilon')\nu_{\mathrm{I}\Sigma}(\varepsilon')}{2e^2\mathrm{E}^2}} \qquad (8)$$

where $\varepsilon \geq E_2$, and $f(E_2)$ is the value of EEDF obtained as a result of matching $\tilde{f}(E_2)$ and EEDF at $\varepsilon \geq E_2$, so that the resulting EEDF satisfies Eq. (1), and based on inelastic collisions only.

If ν_{ea} is independent of ε, and $\nu_{1\Sigma}(\varepsilon)$ is proportional to ε, then Eq. (8) reduces to

$$f(\varepsilon) = \frac{2}{\sqrt{\pi}}\bar{\varepsilon}^{-3/2}\frac{1}{\sqrt{K}}\exp\left[\frac{\varepsilon - E_2}{\bar{\varepsilon}}\sqrt{K} - \frac{E_2}{\bar{\varepsilon}}\right], \tag{9}$$

see values of K below.

The following approximate relation holds irrespective of the assumption that ν_{ea} is constant:

$$f(E_2) = \frac{\tilde{f}(E_2)}{\sqrt{K}} \tag{10}$$

where $\tilde{f}(E_2)$ is the EEDF calculated without the contribution of inelastic collisions.

8. *Restrictions*

a) The plasma can be treated as weakly ionized if $\nu_{ee} \ll \nu_{ea}$, which is opposite to the condition adopted in model P.14.

b) The mean electron energy is much lower than the inelastic collision threshold:

$$\bar{\varepsilon} \ll E_2 \tag{11}$$

c) The parameter K, equal to the ratio of the rate of energy loss in inelastic collisions to the rate of energy transfer in elastic collisions, is large:

$$K = \frac{\nu_{1\Sigma}(E_2)\bar{\varepsilon}}{\delta\nu_{ea}(E_2)E_2} \gg 1 \tag{12}$$

9. *Example*

Consider a neon plasma in the positive column of a glow discharge characterized by the ratio of electric field to atom number density $E/n_a = 1.4 \times 10^{-17}\,\mathrm{V \cdot cm^2}$. The cross section for elastic scattering of electrons by neon atoms is approximated as $q_{ea}(\varepsilon) = a\varepsilon^{1/6}$, where $a = 1.6 \times 10^{-16}\,\mathrm{cm^2\,(eV)^{-1/6}}$. The threshold energy for inelastic processes here is $E_2 = 16.6\,\mathrm{eV}$.

The EEDF is calculated with Eq. (4), where the term kT in the denominator can be neglected at the gas temperature $T = 300\,\mathrm{K}$: $f(E_2) = 4 \times 10^{-4}\,\mathrm{eV^{-3/2}}$. The inelastic collision frequency determined by Eq. (7) is $\nu_{1\Sigma} = 2.2 \times 10^{-13} n_a\,\mathrm{s^{-1}}$, where n_a is measured in cm^3.

10. Comment

In very intense electric fields, the mean electron energy may be higher than the threshold energy. The EEDF corresponding to the conditions when the inequality opposite to Eq. (11) is true is discussed in Ref. 1.

Relevant material can be found in Refs. 8 and 31.

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Chapter 8

Thermodynamics of Gases and Plasmas

I. Nomenclature

T	temperature
V	volume
p	pressure
Q	heat
W	work done on a system
U	internal energy
H	enthalpy
F	free energy
Φ	Gibbs thermodynamic potential
Ω	thermodynamic potential of an open system
S	entropy
M	mass of a system
N_i	number of particles of the *i*th component
n_i	number of moles of the *i*th component
μ_i	chemical potential of the *i*th component
$N = \sum N_i$	total number of particles
$n = \sum n_i$	total number of moles
m	mass of particles

Other symbols are explained in the text.

II. Basic Concepts

A. Definitions

Thermodynamics deals with general properties of macroscopic systems in equilibrium and also with general behavior of the systems in attaining the equilibrium.

Thermodynamic system (statistical system is an equivalent term) is a totality of macroscopic bodies that can interact with each other and with other bodies (with surroundings) and can exchange energy and matter with those bodies.

The mandatory features of thermodynamic systems are the following:

1. Presence of a large number of particles interacting with each other and with external fields; the corresponding scale is defined by the Avogadro number $N_A = 6.02 \times 10^{23}$, which is equal to the number of particles (atoms, molecules, or ions) per mole of a substance.

2. The existence of thermodynamic-equilibrium state to which a system tends spontaneously in the course of time when the system is isolated from the surrounding medium.

Thermodynamic equilibrium (an equivalent term is statistical equilibrium) is a state of thermodynamic system in which the system's macroscopic parameters (that is, the parameters measured with macroscopic instruments) are constant with time, and there are no fluxes of any type in the system.

Thermodynamic state is the state of thermodynamic equilibrium. In a more general sense, a thermodynamic state is a state in which various components of the system are in their equilibrium states, whereas the system as a whole can be in a state different from thermodynamic equilibrium.

Nonequilibrium state of a system is a state of a system disturbed from the thermodynamic (statistical) equilibrium.

Local thermodynamic equilibrium is a nonequilibrium state of a system for which a thermodynamic equilibrium approximately exists in each physically infinitesimal volume, although the system macroscopic parameters depend on spatial coordinates and time.

Partial (incomplete) thermodynamic equilibrium is a nonequilibrium state of a system composed of spatially coexisting subsystems, each of which is in approximate thermodynamic equilibrium and is described by specific set of time-dependent macroscopic parameters.

Homogeneous medium is a medium in which the gradients of macroscopic quantities are equal to zero.

Inhomogeneous medium is a medium in which the gradients of macroscopic quantities are nonzero.

B. Processes

Thermodynamic process is a sequence of changes in the state of a thermodynamic system.

Thermodynamic processes are classified according to the following features:

1. The degree of deviation of a system from the equilibrium state

According to this criterion, we identify the reversible and irreversible processes.

Reversible process is a process that can occur in reverse direction in such a way that the system passes through the same states as in the direct process, but in the reverse order.

Irreversible process is a process that cannot be reversed so that the system would pass through the same sequence of states as in the direct process without changes in the surroundings.

Quasi-static process is an infinitely slow process consisting of a sequence of equilibrium states. A quasi-static process is invariably reversible.

Thermodynamics in the narrow sense is confined to consideration of reversible processes. The special case of irreversible processes in the vicinity of state of thermodynamic equilibrium is considered in the context of nonequilibrium thermodynamics (see Thermodynamics of Irreversible Processes in this chapter).

Examples

The quasi-static compression of gas is a reversible process. Compression of gas by a shock wave is an irreversible process. All transport processes related to equalization of differences in temperatures, pressures, and concentrations are irreversible. Such processes cannot be conducted in the reverse direction without inducing changes in the states of surrounding bodies.

2. Specific physical conditions

Under which the certain process occurs; thus, we distinguish isothermal, isochoric, isobaric, isentropic, adiabatic, and polytropic processes.

Isothermal process is a thermodynamic process that takes place at constant temperature (T = const).

Isochoric process is a thermodynamic process occurring under the conditions of constant volume (V = const).

Isobaric process is a thermodynamic process that takes place under constant pressure (p = const).

Isentropic process is a thermodynamic process occurring under the conditions of constant entropy (S = const).

Adiabatic process is a thermodynamic process that occurs without heat exchange with surroundings.

Polytropic process is a thermodynamic process that takes place under the conditions of constant heat capacity.

3. According to the final state

We distinguish cyclic processes (cycles) among all possible processes.

Cyclic process (thermodynamic cycle) is a thermodynamic process in which a system passes a number of successive states and returns to the initial state. The Carnot cycle is an example of reversible cyclic process (Refs. 4).

C. Quantities

The thermodynamic *principle of additivity* is valid for thermodynamic systems: all the quantities describing the thermodynamic properties can belong to either of two classes of additivity. If the value of a thermodynamic quantity for a partitioned system is equal to the sum of its values for separate parts of the system, that is, $\varphi = \sum \varphi_i$, such a quantity is referred to as *additive* or *extensive.* If the value of thermodynamic quantity is preserved for each part of the partitioned system,

$$\varphi = \varphi_1 = \varphi_2 = \cdots = \varphi_n,$$

such a quantity is referred to as *nonadditive* or *intensive.*

The examples of extensive quantities include total number of particles in a system, volume, mass, internal energy, and entropy. Temperature and pressure are intensive quantities. The class of intensive quantities also includes specific and molar quantities (the extensive quantities per unit mass or a mole).

D. Systems

Thermodynamic systems are differentiated according to the following criteria:

1. The degree of isolation from the surrounding medium

Thus, *Isolated thermodynamic system* is a system that is not involved in an exchange of either matter or energy with the surroundings.

Closed thermodynamic system is a system that is not involved in exchange of matter, but may exchange energy with the surroundings.

Open thermodynamic system is a system that can exchange both matter and energy with the surroundings.

2. Composition

Thus, we distinguish single-component, two-component (binary), and multicomponent systems.

3. Homogeneity

We distinguish homogeneous and heterogeneous systems.

Homogeneous systems are thermodynamic systems in which the macroscopic parameters vary continuously in space (the spatially nonuniform homogeneous systems) or are constant (spatially uniform homogeneous systems).

Heterogeneous systems are thermodynamic systems composed of parts (phases) which differ in physical or chemical properties and are separated from each other by interfaces.

4. Phase composition

Here, we distinguish single-phase, two-phase, and multiphase systems. Phase in thermodynamics is a thermodynamically equilibrium state of matter; this state differs in physical properties from other possible equilibrium states (other phases) of the same substance.

Each homogeneous system is a single-phase system; that is, there are no internal interfaces in such a system. A heterogeneous system contains at least two phases.

E. Functions of State

A physical quantity whose value is independent of the system history and is completely defined by the state of the system at a given point in time is referred to as a *function of state.*

Temperature, entropy, internal energy, and other such quantities are the examples of functions of state.

III. Laws of Thermodynamics

The zeroth, first, second, and third laws of thermodynamics are valid for thermodynamic systems.

A. Zeroth Law of Thermodynamics

Temperature is a state function. Equality of temperatures in all points represents the condition for thermal equilibrium between two systems or between two parts of the same system (the Sommerfeld statement, see Ref. 5).

In such a formulation, the zeroth law thermodynamics is equivalent to the law of *thermodynamic transitivity*: if a thermodynamic system A is separately in equilibrium with thermodynamic systems B and C, then B and C are also in thermodynamic equilibrium with each other. The fact that there exists a temperature as a characteristic of the above equilibrium state follows from the law of transitivity.

B. First Law of Thermodynamics

Each thermodynamic system possesses a characteristic function of state: internal energy U. This state function is increased by the amount of heat δQ transferred to the system and is decreased by the amount equivalent to the work δW performed by the system. For a closed system, the law of conservation of energy is valid (the Sommerfeld formulation, see Ref. 5).

The first law of thermodynamics is essentially equivalent to the law of conservation and conversion of energy. For a system with varying mass M, we have

$$\mathrm{d}U = \delta Q - \delta W + \tilde{\mu}\mathrm{d}M \tag{1}$$

where $\tilde{\mu}$ is the chemical potential per unit mass; this potential is defined as a quantity corresponding to a change in the internal energy of the system if the unit mass is added to the system in such a way that the system does not perform work ($\delta W = 0$) and does not acquire heat ($\delta Q = 0$).

Eq. (1) may be also rewritten as

$$\mathrm{d}U = \delta Q - \delta W + \mu\mathrm{d}n \tag{2}$$

$$\mathrm{d}U = \delta Q - \delta W + \bar{\mu}\mathrm{d}N \tag{3}$$

where N is the number of particles comprising the mass M, $n = N/N_{\mathrm{A}}$ is the number of moles in the mass M, N_{A} is the Avogadro number, $\mu = \tilde{\mu} \cdot m$, $\bar{\mu} = \mu/N_{\mathrm{A}}$, and m is the particle mass expressed in the same units as M.

The work δW performed by a system and the amount of heat δQ transferred to the system are the characteristics of the process of heat transfer from one body to another. These quantities depend on the path of transition of a system from one state to another; therefore, in general, the quantities δW and δQ are not exact differentials (in contrast to $\mathrm{d}U$).

Examples

1. If a gas is expanded in a cylinder with piston, we have $\delta W = p\mathrm{d}V$, where p is pressure and V is the gas volume.
2. If a gas is heated at constant volume, $V = \mathrm{const}$, we have $\delta Q = c_v\mathrm{d}T$, where c_v is the heat capacity of gas at constant volume. If a gas is heated under the conditions of $p = \mathrm{const}$, then $\delta Q = c_p\mathrm{d}T$, where c_p is the heat capacity at constant pressure. Note that $c_p \neq c_v$.

C. Second Law of Thermodynamics

Entropy S is a function of state of thermodynamic system and is calculated in the following way. The system is transferred from an arbitrarily chosen initial state to the final state for which S needs to be found through a sequence of equilibrium states; all the portions of heat δQ supplied to the system are first determined; each portion δQ is then divided by the corresponding absolute temperature T; finally, all the obtained values are summed (the first part of the Second Law). The thermodynamic process described in the previous sentence must be internally reversible (that is, only irreversibilities in the surroundings are allowed). For irreversible processes, the entropy of an isolated system increases (the second part of the Second Law in the Sommerfeld formulation, see Ref. 5).

There are other, equivalent formulations of the Second Law; namely,

1. Heat cannot pass on its own (that is, without changes in the surroundings) from a lower-temperature body to a higher-temperature body (the Clausius statement).
2. It is impossible to devise a *perpetuum mobile* (eternal engine) of the second kind, i.e., a continuously cycling engine, which would perform work while only taking heat from a heat reservoir (the Thomson statement, see Ref. 1).

In the context of this terminology, the first law of thermodynamics prohibits the existence of a *perpetuum mobile* of the first kind as an engine whose operation is inconsistent with the law of conservation of energy (Refs. 1–4).

D. Third Law of Thermodynamics

At absolute zero of temperature, the entropy of system attains the value of $S_0 = 0$ (the Planck statement, see Ref. 1).

The Third Law (in contrast to the Zeroth, First, and Second Laws) does not introduce a new state function; rather, it defines the absolute reference point of state functions.

IV. Thermodynamic Potentials

Thermodynamic potentials (or *characteristic functions*) are state functions whose partial derivatives define completely the properties of a thermodynamic system.

Thermodynamic potentials can be derived from the Gibbs equation that is equivalent to a generalized representation of the first and second laws of thermodynamics. The Maxwell reciprocity relations are a consequence of the equality of mixed second derivatives of potentials with respect to the variables on which the potential depends.

Each thermodynamic potential depends on a specific set of independent variables, a_i. These variables are referred to as *natural*. The full differential of thermodynamic potential with respect to natural variables is the sum of terms written as $X_i \mathrm{d}a_i$, for example, $p\mathrm{d}V$, $T\mathrm{d}S$, and so on. The quantities X and a are referred to as conjugated quantities (parameters). In a pair of conjugated quantities X_i and a_i, one of the parameters is extensive (for example, V), whereas the other is intensive (for example, p). If a thermodynamic potential is defined as a function of its natural variables, thermodynamic properties of the system are specified completely. However, if the potential is specified as a function of another set of variables, this is found to be insufficient for determining all the thermodynamic properties (see an example in the section Internal Energy). Derivatives of thermodynamic potential with respect to natural variables are conjugated parameters.

Explicit expressions for thermodynamic potentials are not introduced in classical thermodynamics. These expressions are either derived from analysis of experimental data or are calculated by the methods of statistical physics.

A. Internal Energy U

Natural variables (parameters) here are S, V, and n.
Conjugated parameters are T, p, and μ.

1. Formula

According to the first and the second laws of thermodynamics,

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}n \qquad \textit{(the Gibbs equation)}$$

This equation defines the function $U = U(S, V, n)$. For a multicomponent system, $\sum_{i=1}^{l} \mu_i \mathrm{d}n_i$ should be introduced instead of $\mu\mathrm{d}n$; therefore,

$$U = U(S, V, n_1, n_2, \dots, n_l) \equiv U(S, V, n)$$

Henceforth, n designates the total set of numbers of moles of all components comprising a system; that is, $n = \{n_1, n_2, \dots, n_l\}$.

2. Comments

a) Internal energy is a physical system energy dependent on its internal state. This energy includes the energy of thermal motion of all microscopic particles (molecules, atoms, ions, and so on) in the system and the energy of their interaction with each other and with external fields. The kinetic and potential energy of a system as a whole is not included in the internal energy.

b) In general, an expression for work performed by the system is written as $\delta W = p\mathrm{d}V + \sum A_i \mathrm{d}a_i$, where the terms $A_i\mathrm{d}a_i$ describe the work of electric fields, magnetic fields, and so on.

c) The internal energy U is defined to within an arbitrary constant U_0. In thermodynamics, the choice of a specific value of U_0 is of no importance.

d) Internal energy expressed in natural variables (S, V, and n) is sufficient for a complete description of a system in these variables.

e) For an ideal gas (see Chapter 9, Equations of State) that obeys classical statistics, we have $U = c_v nT$, where c_v is the specific heat per mole at constant volume. The energy of ideal gas is independent of volume only if the mean de Broglie wavelength of particles (atoms and molecules) is much shorter than the average interparticle distance,

$$T \gg \frac{\hbar^2}{km}\left(\frac{N}{V}\right)^{2/3}$$

where N is the number of particles in the volume V.

3. Thermodynamic relations

- If the function $U = U(S, V, n)$ is specified explicitly, the first derivatives of U determine the values of conjugated parameters, i.e.,

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,n}, \quad T = \left(\frac{\partial U}{\partial S}\right)_{V,n}, \quad \mu = \left(\frac{\partial U}{\partial n}\right)_{S,V}$$

the second derivatives define the specific heat and compressibility

$$\frac{T}{c_v} = \left(\frac{\partial^2 U}{\partial S^2}\right)_{V,n}, \quad -\left(\frac{\partial p}{\partial V}\right)_{S,n} = \left(\frac{\partial^2 U}{\partial V^2}\right)_{S,n}$$

The coefficient of adiabatic compressibility is given by

$$\beta_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{S,n}$$

The Maxwell reciprocity relation is written as

$$-\left(\frac{\partial p}{\partial S}\right)_{V,n} = \left(\frac{\partial T}{\partial V}\right)_{S,n}$$

All quantities are defined as the functions of S, V, and n. Transformation to other variables can be performed using the above formulas. In order to express pressure in terms of T, V, and n, one should use the expression for temperature

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n} = T(S, V, n)$$

Using this expression, one can determine $S(T, V, n)$ and $p = p[S(T, V, n), V, n] = p(T, V, n)$.

- If internal energy is specified as a function of a set of independent variables different from the set of natural variables (S, V, n), not all thermodynamic characteristics can be defined; it is necessary to have an explicit expression for another characteristic function. Thus, for a function $U(T, V)$, we have

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V = T\left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left[T\left(\frac{\partial S}{\partial V}\right)_T - p\right]\mathrm{d}V$$

To describe the thermodynamic properties, characterized, for example, in terms of T and p, it is insufficient to know the derivatives $(\partial U/\partial T)_V$ and $(\partial U/\partial V)_T$; it is necessary to also know the function $S = S(T, V)$. If internal energy is specified as a function of T, p, and n, the specific heat at constant volume is equal to $c_v = (\partial U/\partial T)_{V,n}$.

B. Enthalpy H

Natural variables (parameters) are S, p, and n ($n = \{n_1, n_2, \ldots, n_l\}$).
Conjugated parameters are T, V, and μ.

1. Formulas

$$H = U + pV$$

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p + \sum_{i=1}^{l} \mu_i \mathrm{d}n_i$$

2. Comments

a) Enthalpy corresponds to the energy of an extended system, and includes the potential energy pV in addition to the internal energy U.

b) For slow adiabatic flow, the specific enthalpy H/M (where M is the mass of fluid) is constant along the entire streamline.

c) A change in the enthalpy ΔH is equal to the amount of heat that is supplied to or removed from a system at constant pressure (and for unchanged numbers of moles n); therefore, the values of ΔH specify thermal effects of phase transitions (melting, boiling, and so on), chemical reactions, and other processes that take place at constant pressure.

3. Thermodynamic relations

- If enthalpy H is specified as a function of the natural variables S, P, and n, then

$$T = \left(\frac{\partial H}{\partial S}\right)_{p,n}, \quad V = \left(\frac{\partial H}{\partial p}\right)_{V,n}, \quad \mu = \left(\frac{\partial H}{\partial n}\right)_{S,p} \quad \frac{T}{c_p} = \left(\frac{\partial T}{\partial S}\right)_{p,n}$$

$$\left(\frac{\partial V}{\partial S}\right)_{p,n} = \left(\frac{\partial T}{\partial p}\right)_{S,n} \qquad \text{(the Maxwell reciprocity relation).}$$

All quantities are expressed here as functions of S, p, and n. Transformation to other variables can be performed according to the scheme outlined in the section "Internal Energy".

- If enthalpy is specified as a function of T, p, and n, then the heat capacity at constant pressure is given by

$$c_p = \left(\frac{\partial H}{\partial T}\right)_{p,n}$$

C. Free Energy (Helmholtz Free Energy) F

Natural variables (parameters) are T, V, and n ($n = \{n_1, n_2, \ldots, n_l\}$).
Conjugated parameters are S, p, and μ.

1. Formulas

$$F = U - TS$$

$$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V + \sum_{i=1}^{l} \mu_i \mathrm{d}n_i$$

2. Comments

a) In statistical physics, free energy is expressed as $F = -kT \ln \bar{Q}$, where $\bar{Q} = Q_c$ is the statistical integral in classical systems, and $\bar{Q} = Q_q$ is the partition function for quantum states in quantum-mechanical systems.

b) The work performed by a system in the course of a reversible isothermal process is equal to the decrement of free energy. The difference in free energies ΔF represents the part of a decrease in the internal energy ΔU that can be converted to work. The quantity TS that, added to the free energy F, gives the internal energy of a system ($U = F + TS$) is not converted to work in the course of a reversible process, and is sometimes referred to as the bound energy.

c) In endothermic processes at $T =$ const, a decrease in ΔF may exceed ΔU; in this case, the work is performed by a system partially at the expense of a heat reservoir that supplies, rather than removes, heat.

3. Thermodynamic relations

- The free energy, F, is related to the internal energy U and enthalpy H by the formulas

$$U = F - T\left(\frac{\partial F}{\partial T}\right)_{V,n}, \qquad H = F - T\left(\frac{\partial F}{\partial T}\right)_{V,n} - V\left(\frac{\partial F}{\partial V}\right)_{T,n}$$

referred to as the Gibbs–Helmholtz equations. In this case, the potentials U and H are functions of T, V, and n.

- If the free energy, F, is defined as a function of its natural variables T, V, and n, we have

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,n}, \qquad p = -\left(\frac{\partial F}{\partial V}\right)_{T,n}, \qquad \mu = \left(\frac{\partial F}{\partial n}\right)_{T,V}$$

The second derivatives of F with respect to T and V define the following quantities: heat capacity at constant volume c_v,

$$\frac{c_v}{T} = \left(\frac{\partial^2 F}{\partial T^2}\right)_{V,n}$$

isothermal pressure coefficient,

$$\gamma_T = -\frac{1}{p}\left(\frac{\partial p}{\partial V}\right)_{T,n} = \frac{1}{p}\left(\frac{\partial^2 F}{\partial V^2}\right)_{T,n}$$

isothermal compressibility coefficient β_T,

$$\frac{1}{\beta_T} = -V\left(\frac{\partial p}{\partial V}\right)_{T,n} = V\left(\frac{\partial^2 F}{\partial V^2}\right)_{T,n}$$

thermal (isochoric) pressure coefficient,

$$\gamma_V = -\frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_{V,n} = \frac{1}{p}\left[\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_{T,n}\right]_{V,n}$$

$$\left(\frac{\partial p}{\partial T}\right)_{V,n} = \left(\frac{\partial S}{\partial V}\right)_{T,n} \qquad \text{(the Maxwell reciprocity relation)}$$

$$c_p - c_v = -T\left(\frac{\partial V}{\partial T}\right)_{p,n}^2 \Big/ \left(\frac{\partial V}{\partial p}\right)_{T,n}, \qquad \left(\frac{\partial V}{\partial p}\right)_{S,n} = \frac{c_p}{c_v}\left(\frac{\partial V}{\partial p}\right)_{T,n}$$

D. Gibbs Thermodynamic Potential Φ

Natural variables (parameters) are T, p, and n ($n = \{n_1, n_2, \ldots, n_l\}$). Conjugated parameters are S, V, and μ.

1. Formulas

$$\Phi = U + pV - TS$$

$$d\Phi = -SdT + Vdp + \sum_{i=1}^{l} \mu_i dn_i \qquad \Phi = \sum_{i=1}^{l} \mu_i n_i$$

2. Comments

a) Chemical potentials μ_i are related by the Gibbs–Duhem equation

$$-SdT + Vdp = \sum_{i=1}^{l} n_i d\mu_i$$

b) The Gibbs thermodynamic potential expressed in terms of the natural variables T, p, and n is most convenient for description of an equilibrium heterogeneous system (because, in this case, the pressure p and temperature T are identical in all phases of the system), and also for description of chemical equilibrium at constant p and T.

3. Thermodynamic relations

- Gibbs thermodynamic potential Φ is related to enthalpy H and free energy F by the Gibbs–Helmholtz equations

$$H = \Phi - T\left(\frac{\partial \Phi}{\partial T}\right)_{p,n}, \qquad \Phi = F - V\left(\frac{\partial F}{\partial V}\right)_{T,n}$$

- If the Gibbs thermodynamic potential Φ is specified as a function of its natural variables T, p, and n, we have

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{p,n}, \qquad V = \left(\frac{\partial \Phi}{\partial p}\right)_{T,n}, \qquad \mu = \left(\frac{\partial \Phi}{\partial n}\right)_{T,p}$$

The second derivatives of the potential Φ with respect to T and p determine the heat capacity at constant pressure c_p and the coefficient of isothermal compressibility β_T; that is,

$$-\frac{c_p}{T} = \left(\frac{\partial^2 \Phi}{\partial T^2}\right)_{p,n}, \qquad \beta_T = \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,n}, \qquad \left(\frac{\partial V}{\partial p}\right)_{T,n} = \left(\frac{\partial^2 \Phi}{\partial p^2}\right)_{T,n}$$

The thermal expansion coefficient $\alpha_p = (1/V)(\partial V/\partial T)_{p,n}$, the coefficients of isothermal β_T and adiabatic β_S compressibility, and thermal coefficient of pressure γ_V (see above) are related by the formulas:

$$\frac{1}{p} \cdot \frac{\alpha_p}{\beta_T \gamma_V} = 1, \qquad c_p - c_v = \frac{VT\alpha_p^2}{\beta_T}, \qquad \frac{c_p}{c_v} = \frac{\beta_T}{\beta_S}$$

We also have

$$\left(\frac{\partial V}{\partial T}\right)_{p,n} = -\left(\frac{\partial S}{\partial p}\right)_{T,n} \qquad \text{(the Maxwell reciprocity relation)}$$

E. Thermodynamic Potential Ω of an Open System

Natural variables (parameters) are T, V, and μ ($\mu = \{\mu_1, \mu_2, \ldots, \mu_l\}$). Conjugated parameters are S, p, and n ($n = \{n_1, n_2, \ldots, n_l\}$).

1. Formulas

$$\Omega = F - \Phi = -pV$$

$$\mathrm{d}\Omega = -S\mathrm{d}T - p\mathrm{d}V + \sum_{i=1}^{l} \mu_i \mathrm{d}n_i$$

2. Thermodynamic relations

- If the potential is specified in terms of its natural variables T, V, and μ, we have

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu}, \qquad p = -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu}, \qquad n = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{V,T}$$

We also have *the Maxwell reciprocity relation*

$$\left(\frac{\partial S}{\partial V}\right)_{T,\mu} = \left(\frac{\partial p}{\partial T}\right)_{V,\mu}$$

- Replacement of natural variables T, V, and μ by the variables T, V, and n, which are more convenient for applications, is performed according to the procedure outlined in the section Internal Energy. The expression for the number of moles

$$n(T, V, \mu) = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{V,T}$$

is solved for the chemical potential $\mu = \mu(T, V, n)$ which is then substituted into the relevant formula. For example,

$$p = -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu} = p(T, V, \mu) = p[T, V, \mu(T, V, n)]$$

F. Entropy S

Natural variables (parameters) are U, V, and n or H, p, and n ($n = \{n_1, n_2, \ldots, n_l\}$).

Conjugated parameters are $1/T, p/T, -\mu/T$, and $1/T, -V/T, -\mu/T$.

1. Formulas

Differentially, the entropy is defined as

$$\mathrm{d}S = \frac{\delta Q_{rev}}{T} = \frac{1}{T}\mathrm{d}U + \frac{p}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}n$$

where δQ_{rev} is the amount of heat supplied to a system when its state is changed infinitesimally and quasi-statically, and T is the absolute temperature at which heat is absorbed by the system.

Integrally, entropy is defined as the difference of entropies of a system in arbitrary equilibrium states A and B; namely,

$$S_A - S_B = \int_A^B \frac{\delta Q_{rev}}{T}$$

where the integral is taken along any reversible path connecting the above states.

2. Comments

a) In quasi-static adiabatic processes ($\delta Q_{rev} = 0$), the entropy of a system remains unchanged (those are *isentropic processes*, with $S = \text{const}$).

b) In statistical physics, entropy is defined in terms of logarithm of statistical weight Γ for a given equilibrium state

$$S = k \ln \Gamma$$

where $\Gamma(U, n)$ is the number of quantum-mechanical energy levels in a narrow range ΔU in the vicinity of the energy U of a particle system composed of n moles. In classical statistical physics, Γ is understood as a volume in the phase space of a system for the specified V and n.

c) Entropy of an isolated system increases in irreversible processes. However, the entropy of individual bodies (or subsystems) incorporated in the whole system should not necessarily increase; only the total entropy increases.

3. Thermodynamic relations

- If the entropy, S, is specified as a function of the corresponding natural variables U, V, and n, we have

$$\frac{1}{T}=\left(\frac{\partial S}{\partial U}\right)_{V,n}, \qquad \frac{p}{T}=\left(\frac{\partial S}{\partial V}\right)_{U,n}, \qquad \frac{\mu}{T}=-\left(\frac{\partial S}{\partial n}\right)_{U,V}$$

- For the natural variables H, p, and n, we obtain

$$\frac{1}{T}=\left(\frac{\partial S}{\partial H}\right)_{p,n}, \qquad \frac{V}{T}=-\left(\frac{\partial S}{\partial p}\right)_{H,n}, \qquad \frac{\mu}{T}=-\left(\frac{\partial S}{\partial n}\right)_{H,p}$$

In addition, we have the *Maxwell reciprocity relation* as

$$\left.\frac{\partial(1/T)}{\partial V}\right|_U=\left.\frac{\partial(p/T)}{\partial U}\right|_V$$

If the independent parameters V and T are used, we have

$$\left(\frac{\partial S}{\partial V}\right)_T=\left(\frac{\partial p}{\partial T}\right)_V, \qquad \left(\frac{\partial S}{\partial V}\right)_T=\frac{1}{T}\left[p+\left(\frac{\partial U}{\partial V}\right)_T\right]$$

$$\left(\frac{\partial H}{\partial V}\right)_T=T\left(\frac{\partial p}{\partial T}\right)_V+V\left(\frac{\partial p}{\partial V}\right)_T, \qquad \left(\frac{\partial H}{\partial T}\right)_V=c_v+V\left(\frac{\partial p}{\partial T}\right)_V$$

$$\left(\frac{\partial c_v}{\partial V}\right)_T=T\left(\frac{\partial^2 p}{\partial T^2}\right)_V$$

If the independent parameters p and T are used, we have

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_V, \quad \left(\frac{\partial U}{\partial p}\right)_T = -T\left[\left(\frac{\partial V}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial p}\right)_T\right]$$

$$\left(\frac{\partial U}{\partial T}\right)_p = c_p - p\left(\frac{\partial V}{\partial T}\right)_p, \quad \left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p$$

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p$$

$$c_p - c_v = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p = -T\left(\frac{\partial V}{\partial T}\right)_p^2 \Big/ \left(\frac{\partial V}{\partial p}\right)_T$$

$$\frac{c_p}{c_v} \equiv \gamma = \left(\frac{\partial p}{\partial V}\right)_s \Big/ \left(\frac{\partial p}{\partial V}\right)_T \qquad \text{(adiabatic exponent).}$$

4. Comment

The previously described relations are widely used to determine thermal characteristics of substances. For example, using the relation $(\partial c_p/\partial p)_T = -T(\partial^2 V/\partial T^2)_p$ and the results of measurements of the quantity c_p, one can derive the dependence of V on T and vice versa.

V. Conditions for Thermodynamic Equilibrium and for Thermodynamic Stability of Systems (Refs. 1, 2 and 6)

In a state of thermodynamic equilibrium, we have

- at constant internal energy and volume, the entropy of a closed system has the *largest* value, $(\delta S)_{V,U} \leq 0$;
- internal energy of a closed system whose entropy and volume remain unchanged has the *smallest* value, $(\delta U)_{S,V} \geq 0$;
- enthalpy of a closed system, in which the entropy and pressure remain unchanged, has the *smallest* value, $(\delta H)_{S,p} \geq 0$;
- the free energy of closed system whose volume and temperature remain unchanged has the *smallest* value, $(\delta F)_{V,T} \geq 0$;
- the Gibbs thermodynamic potential of a closed system in which pressure and temperature remain unchanged has the *smallest* value, $(\delta\Phi)_{p,T,n} \geq 0$.

In all the previously mentioned cases, the total number of particles (or the number of moles) in a system was considered constant (n = const). The symbol δ corresponds to the variations in state such that the varying system parameters are those that can take nonequilibrium values for the specified fixed conditions. Such quantities, for example, are n/V and T in separate parts of the system, the amount of matter in different phases, and so on.

The following thermodynamic inequalities arise as a consequence of the condition for stability of equilibrium:

$$\left(\frac{\partial T}{\partial S}\right)_{V,n} = \frac{T}{c_v} \geq 0 \ (c_v \geq 0), \qquad \left(\frac{\partial T}{\partial S}\right)_{p,n} = \frac{T}{c_p} \geq 0 \ (c_p \geq 0)$$

$$\left(\frac{\partial p}{\partial V}\right)_{S,n} \leq 0, \quad \left(\frac{\partial p}{\partial V}\right)_{T,n} \leq 0$$

$$\left(\frac{\partial \mu_i}{\partial n_i}\right)_{S,V,n_j \neq n_i} \geq 0, \quad \left(\frac{\partial \mu_i}{\partial n_i}\right)_{T,p,n_j \neq n_i} \geq 0$$

$$\left(\frac{\partial T}{\partial S}\right)_{p,n} < \left(\frac{\partial T}{\partial S}\right)_{V,n}, \quad \text{i.e.} \quad c_p > c_v$$

$$\left(\frac{\partial p}{\partial V}\right)_T > \left(\frac{\partial p}{\partial V}\right)_S, \quad \left|\left(\frac{\partial p}{\partial V}\right)_S\right| > \left|\left(\frac{\partial p}{\partial V}\right)_T\right|$$

Mechanical, Thermal, and Chemical Equilibrium

If systems A and B are in contact, the conditions for equilibrium are written as

$$\begin{aligned} p_A &= p_B \quad \text{(mechanical equilibrium)}, \\ T_A &= T_B \quad \text{(thermal equilibrium)}, \\ \mu_i^A &= \mu_i^B \quad \text{(chemical equilibrium)}. \end{aligned}$$

If the boundary between the systems is not planar, and if there is a nonzero surface tension, the pressures in systems A and B are not identical.

The mass action law in chemical thermodynamics is a law that establishes a relation between equilibrium concentrations of the products and reactants in chemical reactions.

For a chemically reacting system, the equation of reaction is written as

$$\sum \nu_i \mathrm{X}_i = 0,$$

where X_i are the symbols of substances and ν_i are the stoichiometric coefficients ($\nu_i < 0$ for reactants and $\nu_i > 0$ for products of reaction, see Chapter 6, Chemical Kinetics, in this volume). For reacting ideal gases in equilibrium, the mass action law is given by

- $\prod_i p_i^{\nu_i} = K_p(T)$ for partial pressures p_i of reaction components
- $\prod_i \xi_i^{\nu_i} = K_p(T)/p^{\nu}$ for molar concentrations (molar fractions) ξ_i of reaction components $\xi_i = n_i/n$ $\nu = \sum \nu_i$, K_p is the chemical equilibrium constant.

The chemical equilibrium constant cannot be determined in the context of thermodynamics; it has to be found by the methods of statistical physics. The explicit expressions of constant K_p are presented in Refs. 1, 4, and 7; calculation methods and table data are presented in Refs. 8–10.

Example

For the reaction $2H_2 + O_2 — 2H_2O = 0$, we have $\nu_1 = 2$, $\nu_2 = 1$, $\nu_3 = -2$, and $\sum \nu_i = 1$; therefore,

$$\frac{\xi_1^2 \xi_2}{\xi_3^2} = \frac{K_p(T)}{p}$$

The extension of mass action law for two-temperature gases can be found in Refs. 11 and 12 and the literature cited there.

Comments

In chemical kinetics, the mass action law establishes the relation between the rate of chemical reaction and the concentrations of products and reactants (the kinetic mass action law, see Chapter 6, Chemical Kinetics, model C.1, in this volume).

VI. Gibbs Distributions and Their Relations to Thermodynamic Quantities

A quantum-mechanical statistical system in thermodynamic equilibrium is characterized by the distribution function for microstates ω_l; this function governs the probability of observing the microscopic state with an energy E_l in the quantum-mechanical system. The distribution function for ω_l satisfies the following condition: the mean values calculated using this function correspond to the observed experimental quantities that appear in thermodynamic relations.

A classical statistical system in thermodynamic equilibrium is characterized by the distribution function $\omega(p, q)$ that specifies the probability of observing the microscopic state of the system in an infinitesimal $6N$-dimensional volume of the phase space $\mathrm{d}p\mathrm{d}q = \mathrm{d}\vec{r}_1, \ldots, \mathrm{d}\vec{r}_N \mathrm{d}\vec{p}_1, \ldots, \mathrm{d}\vec{p}_N$ in the vicinity of the point (p, q).

The specific form of the distribution functions ω_l and $\omega(p, q)$ depends on the system under consideration and is defined by one of the Gibbs distributions (Ref. 13).

Gibbs distributions are the equilibrium distributions of probabilities of states in a statistical system under various conditions (see the following sections concerning the domain of applicability).

1. The microcanonical distribution

A quantum-mechanical system:

$$\omega_l(U, V, N) = \frac{\Delta[U - E_l(V, N)]}{\Gamma}$$

where

$$\Delta(\xi) = \left\{ \begin{matrix} 1, & \text{if } |\xi| < \delta U \\ 0, & \text{if } |\xi| > \delta U \end{matrix} \right\} \xi = [U - E_l(V, N)]$$

$\Gamma(U, V, N) = \sum_l \Delta[U - E_l(V, N)]$ is the statistical weight, that is, the total number of microscopic states through which the specified macroscopic state with the preassigned values of U, V, and N can be realized; and $E_l(V, N)$ is the energy of a system composed of N particles in the volume V and found in the lth state.

The microcanonical distribution is related to thermodynamic functions through the entropy defined as

$$S(U, V, N) = k \ln \Gamma$$

A classical system:

$$\omega(p, q)\mathrm{d}p\mathrm{d}q = \frac{\int_{U-\mathrm{d}U}^{U} \delta\{H(p, q) - U\}\mathrm{d}U\mathrm{d}P\,\mathrm{d}q}{(2\pi\hbar)^{3N}\Gamma(U, V, N)N!}$$

where $\delta\{x\}$ is the Dirac function, $H(p, q)$ is the Hamiltonian function in the phase space of coordinates q and momenta p of all particles involved in the system, and

$$\Gamma(U, V, N) = \frac{1}{N!} \int \frac{\mathrm{d}q\,\mathrm{d}p}{(2\pi\hbar)^{3N}} \int_{U-\delta U}^{U} \delta\{H(p, q) - U\}\,\mathrm{d}U$$

The statistical weight $\Gamma(U, V, N)$ is equal to the volume of a layer in a $6N$-dimensional phase space (p, q); this layer is confined by the energy surfaces $H(p, q) = U - \delta U$ and $H(p, q) = U$; the volume is divided by $N!$ and $(2\pi\hbar)^{3N}$.

The domain of applicability

The Gibbs microcanonical distribution is applicable to systems with a given total energy at constant volume and with a constant number of particles; the system must be isolated from a surrounding medium (an isolated system).

2. Canonical distribution

A quantum-mechanical system:

$$\omega_l(T, V, N) = \frac{1}{Q_q} \exp\left[-\frac{E_l(V, N)}{kT}\right]$$

where $Q_q(T, V, N) = \sum \exp[-E_l(V, N)/kT]$ is the partition function (see below).

The canonical distribution and thermodynamic functions are related through free energy defined as

$$F(T, V, N) = -kT \ln Q_q$$

A classical system:

$$\omega(p, q) = \frac{1}{Q_c} \exp\left[-\frac{H(p, q)}{kT}\right]$$

where $Q_c = 1/N! \int \exp[-H(p, q)/kT] \mathrm{d}q \, \mathrm{d}p/(2\pi\hbar)^{3N}$ is a statistical integral (see below).

The domain of applicability

The Gibbs canonical distribution is applicable to systems with a given number of particles and constant volume; these systems must be in thermodynamic equilibrium with the surrounding medium and can exchange energy with that medium (that is, to systems in a thermostat, or a thermal reservoir).

3. The Gibbs grand canonical distribution

A quantum-mechanical system:

$$\omega_{l,N}(T, V, \mu) = \frac{1}{\xi_q} \exp\left[-\frac{E_l(V, N) - \mu N}{kT}\right]$$

where $\xi_q(T, V, N) = \sum_{N,l} \exp[-(E_l(V, N) - \mu N)/kT]$ is the grand partition function.

The grand canonical distribution is related to thermodynamic functions via the grand potential Ω defined as

$$\Omega(T, V, \mu) = -kT \ln \xi_q$$

A classical system; we have

$$\omega_N(p, q) = \frac{1}{\xi_c} \exp\left[-\frac{H_N(p, q) - \mu N}{kT}\right]$$

where $\xi_c = \sum_N \exp(\mu N/kT)/N! \int \exp[-H_N(p, q)/kT] \, \mathrm{d}q \, \mathrm{d}p/(2\pi\hbar)^{3N}$.

The domain of applicability

The Gibbs grand canonical distribution is applicable to systems with constant volume, which are in thermodynamic equilibrium with surrounding medium and can exchange energy and particles with that medium (that is, to equilibrium open systems with variable number of particles).

4. Gibbs isobaric distribution

Systems that are in thermal and mechanical contact with surrounding medium (that is, systems with varying energy and volume but with constant pressure equal to the pressure of the surrounding medium) and are in thermodynamic equilibrium can be described by the following Gibbs isobaric distribution:

$$\omega(T, p, N) = \frac{1}{Q_\Phi} \exp\left[-\frac{E_l(V, N) + pV}{kT}\right]$$

$$Q_\Phi(T, p, N) = \sum_{V,l} \exp\left[-\frac{E_l(V, N) + pV}{kT}\right]$$

where Q_Φ is the Gibbs partition function (Ref. 1).

The isobaric distribution is related to thermodynamic functions via the Gibbs potential Φ:

$$\Phi(T, p, n) = -kT \ln Q_{\Phi}$$

Comments

To calculate thermodynamic potentials, one can use any Gibbs distribution. In classical theory, the Gibbs canonical distribution $\omega(p, q)$ and the statistical integral $Q_c(T, V, N)$ are primarily used. The grand canonical distribution $\omega_{l,N}$ and the grand partition function $\xi(T, V, \mu)$ are usually used in quantum mechanics. Generally, transformation to more convenient variables (T, V, N) is performed.

VII. Partition Functions and Statistical Integrals

1. Ideal gas consisting of N structureless particles of mass m in the volume V: The statistical integral is written as

$$Q_c = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N$$

where $\lambda = h/(2\pi mkT)^{1/2}$ is the de Broglie wavelength, $N! = (N/e)^N$ for $N \gg 1$ (the Stirling formula), and $e = 2.71828\ldots$ is henceforth the Napierian base of natural logarithms. The expression for Q_c is valid if $N/V \ll (2\pi mkT)^{3/2}/h^3$ and if the interaction of particles may be ignored. For a single particle, we then have

$$Q_c \equiv Q_t(T) = \frac{eV}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

2. Ideal gas consisting of N particles with internal degrees of freedom (also see section V in Chapter 1 of the first volume of this series). The partition function is given by

$$Q_q = Q_c(Q_j)^N$$

Here, Q_c is the statistical integral per particle for an ideal gas consisting of N structureless particles, and Q_j is the partition function corresponding to the jth internal degree of freedom of a particle

$$Q_j = \sum_i g_i \exp\left(\frac{-E_i}{kT}\right)$$

where E_i is the particle energy in the ith quantum state (with translational motion of the particles disregarded), and g_i is the degeneracy (the statistical weight) of the state i.

- Rotational partition functions for a gas consisting of rigid rotators (with vibrations of molecules and the centrifugal stretching disregarded):
$\Rightarrow$ *for linear molecules at high temperatures* ($T \gg \hbar/2I_B k$),

$$Q_r = \frac{2I_B kT}{\delta_s \hbar^2} = \frac{kT}{\delta_s B}$$

- for H_2 and D_2 molecules in the quantum-mechanical (low temperature) limit, for $T \ll \hbar^2/2I_Bk$, the partition functions Q_r can be broken into two terms that correspond to summation over even and odd values of the orbital quantum number with the statistical weights dependent on the spin of nuclei.

$\Rightarrow$ *for nonlinear molecules at high temperatures*, $T \gg \hbar/2I_Ak$ (and the same inequality for I_B and I_C),

$$Q_r = \frac{\sqrt{\pi}}{\delta_s}\left(\frac{2I_AkT}{\hbar^2}\right)^{1/2} \cdot \left(\frac{2I_BkT}{\hbar^2}\right)^{1/2} \cdot \left(\frac{2I_CkT}{\hbar^2}\right)^{1/2} \equiv \frac{1}{\delta_s}\sqrt{\frac{\pi}{ABC}(kT)^3}$$

where I_A, I_B, and I_C are the principal moments of inertia of the molecule (expressed in units g·cm), i.e.,

$$I_A = \frac{\hbar^2}{2A}, \qquad I_B = \frac{\hbar^2}{2B}, \qquad I_C = \frac{\hbar^2}{2C}$$

A, B, and C are the rotational constants of a molecule (in ergs); in other units,

$$A = \frac{\hbar}{4\pi I_A}, \quad B = \frac{\hbar}{3\pi I_B}, \quad C = \frac{\hbar}{4\pi I_C} \quad (\text{in s}^{-1})$$

$$A = \frac{\hbar}{4\pi I_A c}, \quad B = \frac{\hbar}{4\pi I_B c}, \quad C = \frac{\hbar}{4\pi I_C c} \quad (\text{in cm}^{-1});$$

δ_s is the symmetry number equal to the number of identical configurations arising in molecular rotations (examples: $\delta_s = 1$ for diatomic heteronuclear molecules, $\delta_s = 2$ for homonuclear diatomic molecules, and $\delta_s = 3$ for NH_3).

- Vibrational partition functions for a gas consisting of harmonic oscillators with circular vibrational frequency ω:

$\Rightarrow$ *for diatomic molecules*:

- taking into account the zero-point vibrational energy $E_z = \hbar\omega/2$,

$$Q_v(T) = \frac{\exp(-\hbar\omega/2kT)}{1 - \exp(-\hbar\omega/kT)}$$

- when the vibrational energy is measured from the zero level, then

$$Q_v(T) = \left[1 - \exp\left(\frac{-\hbar\omega}{kT}\right)\right]^{-1}$$

- for truncated harmonic oscillators,

$$Q_v(T) = \frac{1 - \exp(-D_0/kT)}{1 - \exp(-\hbar\omega/kT)}$$

where D_0 is the dissociation energy.

$\Rightarrow$ *for polyatomic molecules with t-fold degenerate modes,*

$$Q_v(T) = \prod_{i=1}^{m}\left[1 - \exp\left(\frac{-\hbar\,\omega_i}{kT}\right)\right]^{-g_i}$$

where

$$m = 3N^a - 5 - \sum_{i=1}^{t}(g_i - 1) \qquad \text{for linear molecules}$$

$$m = 3N^a - 6 - \sum_{i=1}^{t}(g_i - 1) \qquad \text{for nonlinear molecules.}$$

Here, N^a is the number of atoms in a molecule.

- Electronic partition functions:

$$Q_e(T) = \sum_n g_n \exp\left(\frac{-E_n}{kT}\right)$$

where n numbers individual electron states of atoms, molecules, and ions, and g_n is the statistical weight of the state, n.

Description of specific electronic states of atoms, molecules, and ions can be found in some handbooks (see, for example Ref. 8).

  - For the majority of diatomic molecules, the ground electron state is nondegenerate, and the energy spacing ΔE_1 between the ground state and the first excited state far exceeds kT, so that $g_{n=0} = 1$ and $q_e = 1$. The exception is provided by certain molecules, for example,

$$O_2\left(Q_e = 3 + 2\exp\left(-\frac{\Delta E_1}{kT}\right), \qquad \Delta E_1 = 0.974\ \text{eV}\right)$$

$$NO\left(Q_e = 2 + 2\exp\left(-\frac{\Delta E_1}{kT}\right), \qquad \Delta E_1 = 0.0153\ \text{eV}\right)$$

- The total partition function is written as

$$Q(T) = \begin{cases} Q_t \cdot Q_e & \text{for atoms and atomic ions} \\ Q_t \cdot Q_r \cdot Q_v \cdot Q_e & \text{(for molecules and molecular ions.} \end{cases}$$

The assumptions used in derivation of the above formulas are mentioned in section VIII.C in Volume I of this series. When calculating the partition functions, one should take into account the degeneracy caused by the nuclear spin (Ref. 2).

Formulas for the partition functions that were derived with allowance for realistic interaction potentials and other characteristics of particles can be found in Ref. 8.

VIII. Summary of Basic Thermodynamic Quantities

1. Ideal gas consisting of N structureless particles with mass m in volume V.
   - Internal energy U

$$U = \frac{3}{2}NkT \equiv U_t$$

- Enthalpy H

$$H = \frac{5}{2}NkT$$

- Free energy F

$$F = -NkT\ln\left[\frac{(2\pi mkT)^{3/2}}{h^3}\cdot\frac{V}{N}\right] - NkT$$

- Gibbs thermodynamic potential Φ

$$\Phi = NkT\ln\left[\frac{h^3}{(2\pi mkT)^{3/2}}\cdot\frac{p}{kT}\right]$$

- Entropy S

$$S = Nk\ln\left[\frac{(2\pi mkT)^{3/2}}{h^3}\cdot\frac{V}{N}\right] + \frac{5}{2}Nk$$

- Specific heat ratio, $\gamma = c_p/c_v$

$$\gamma = \frac{5}{3} = 1.667$$

2. Ideal gas consisting of N molecules that behave as rigid rotators (disregarding vibrations of molecules and the effect of centrifugal stretching) in the high-temperature approximation ($T \gg \hbar/2I_A k$, and similarly for I_B, and I_C, where I_A, I_B, and I_C are the principal moments of inertia for molecules; see the previous section Partition Functions and Statistical Integrals):

$$U = \frac{5}{2}NkT, \quad H = \frac{7}{2}NkT, \quad \gamma = \frac{7}{5} = 1.4 \quad \text{for linear molecules;}$$

$$U = 3NkT, \quad H = 4NkT, \quad \gamma = \frac{4}{3} = 1.333 \quad \text{for nonlinear molecules.}$$

Other quantities have to be determined from thermodynamic relations given in the section Thermodynamic Potentials, using the expressions for U and H.

3. Ideal gas consisting of N nonrotating harmonic oscillators (ω is the circular frequency of oscillations); for vibrational degrees of freedom, we have

$$U_v = N\hbar\omega\left[\exp\left(\frac{\hbar\omega}{kT}\right) - 1\right]^{-1}$$

- in the high-temperature approximation ($T \gg \hbar\omega/k$),

$$U_v = NkT$$

Ideal gas consisting of N nonrotating vibrating molecules considered as an ensemble of harmonic oscillators (ω_i is the circular frequency of ith vibrational mode); for vibrational degrees of freedom, we have

$$U_v = N\sum_{i=1}^{m}\left\{\hbar\omega_i\left[\exp\left(\frac{\hbar\omega_i}{kT}\right) - 1\right]\right\},$$

where

$$m = 3N^a - 5 - \sum_{i=1}^{t}(g_i - 1) \qquad \text{for linear molecules}$$

$$m = 3N^a - 6 - \sum_{i=1}^{t}(g_i - 1) \qquad \text{for nonlinear molecules}$$

g_i is the degeneracy of ith vibrational mode; t is the number of degenerate modes; and N^a is the number of atoms in a molecule.

Other quantities are determined from thermodynamic relations given in the section "Thermodynamic Potentials," using the above expressions for the partition functions and statistical integrals.

4. Ideal gas consisting of N particles with electronic degrees of freedom; we have

$$U_e = kT^2\left(\frac{\partial \ln Q_e}{\partial T}\right).$$

Summary of quantities:

$U = U_t + U_e$ for atoms and atomic ions and for structureless particles;

$$\left.\begin{aligned} U &= U_t + U_r + U_v + U_e \\ H &= U_t + U_r + U_v + U_e + pV \end{aligned}\right\} \quad \text{for molecules and molecular ions;}$$

$$\gamma = \left(\frac{\partial H}{\partial T}\right)_p \Big/ \left(\frac{\partial U}{\partial T}\right)_V$$

IX. Calculation of Thermodynamic Parameters in Chemically Reacting Media*

Purpose of the Section

This section describes calculations of thermodynamic characteristics of individual substances and their mixtures, including condensed phase, and calculation of equilibrium chemical composition.

Assumptions

1. The gas phase of the system obeys the ideal gas equation of state. Chemical composition and particle energy distribution correspond to equilibrium states, but change with temperature.

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*This section was written by M. A. Deminsky.

2. Equilibrium analysis is carried out for multiphase mixtures that consist of a gas phase and condensed phase.
3. It is assumed that the boundary between gas and condensed phases is a flat surface. Surface tension forces are not taken into consideration. Different phases are regarded as immiscible. Condensed phase is an ideal solution, that is, the volume and internal energy of the condensed phase is assumed to be additive (namely, the sum of volumes and internal energies of the constituents); this implies no interaction between the components.
4. The pressure in a system is determined by its gas-phase components, and the volume of condensed phase is neglected.
5. The system as a whole is electrically neutral, although it can consist of neutral and charged components.
6. Complex substances (compounds) are considered as made of atoms and molecules whose enthalpy of formation at standard conditions is zero. Ions are considered as made of the corresponding neutral molecules and electrons.
7. Thermodynamic equilibrium of the system corresponds to the minimum of Gibbs thermodynamic potential.
8. For "chemically frozen" specific heat, chemical composition is considered not to change in infinitesimally small variation of thermodynamic parameters (p, T), so that $(\mathrm{d}n/\mathrm{d}p)_T = (\mathrm{d}n/\mathrm{d}T)_p = 0$, while particle distributions in their internal degrees of freedom can change with temperature.
9. The calculations of thermodynamic characteristics are based on the Chemical Workbench code (Ref. 14).

Applied Data

Critical review of thermodynamic databases is presented in Refs. 8, 10, 15, and 16. Chemical Workbench database used in this volume contains the following information on substances:

- Molecular weight of substances
- Enthalpies of formation of substances in reference state minus the differences between substance enthalpies in reference state and at 0 K:

$$\Delta H_f^0(298.15) - [H(298.15) - H(0)].$$

- Seven coefficients (φ_i) of polynomial approximation of reduced Gibbs thermodynamic potential $\hat{\phi}(T) = \varphi_1 + \varphi_2 \ln x + \varphi_3 x^{-2} + \varphi_4 x^{-1} + \varphi_5 x + \varphi_6 x^2 + \varphi_7 x^3$, where $x = T/10^4$ (Ref. 11).
- Temperature range of approximation.

Nomenclature

p	pressure, atm
T	temperature, K
U	internal energy, J/mole
H	enthalpy, J/mole
ΔH	formation enthalpy, J/mole

F	free energy, J/mole
Φ	Gibbs thermodynamic potential, J/mole
ϕ	specific Gibbs thermodynamic potential, J/g
$\hat{\phi}$	reduced Gibbs thermodynamic potential, J/(mole K)
S	entropy, J/(mole·K)
Q_i	partition function of *i*th gas-phase component
μ_{gi}	molar mass (molecular weight) of *i*th gas-phase component, g/mole
μ_{ci}	molar mass (molecular weight) of *i*th condensed-phase component, g/mole
c_p	molar specific heat at constant pressure, J/(mole·K)
c'_p	specific heat at constant pressure, J/(g·K)
c^*_p	"chemically frozen" molar specific heat at constant pressure, J/(mole·K)
c_v	molar specific heat at constant volume, J/(mole·K)
c'_v	specific heat at constant volume, J/(g·K)
c^*_v	"chemically frozen" molar specific heat at constant volume, J/(mole·K)
γ	specific heat ratio for a system
γ^*	"chemically frozen" specific heat ratio for a system
a	speed of sound, m/s
a^*	"chemically frozen" speed of sound, m/s
R	universal gas constant 8.3145 J/mole·K

Subscripts

g	gas-phase component
c	condensed-phase component
298.15	room temperature state
0	0 K temperature state
T	state at temperature T
i	number of component (substance) in the list of substances

Superscripts

0	value at standard temperature and pressure: $T = 298.15$, $p =$ 1 atm

Thermodynamic Characteristics of Individual Substances

1. H.1. Gibbs thermodynamic potential of substance *i* relative to that at 0 K, in J/(mole·K)

$$\Phi_{Ti} = H_{0i} - \hat{\phi}_{Ti} T$$

2. H.2. Gibbs thermodynamic potential of substance *i* relative to that at 298.15 K, in J/(mole·K)

$$\Phi_{Ti} = H_{298.15i} - \hat{\phi}_{Ti} T$$

3. H.3. Enthalpy of substance *i* relative to that at 0 K, in J/mole

$$H_{Ti} - H_{0i} = T^2 \cdot \frac{\partial}{\partial T}\hat{\phi}_T$$

4. H.4. Enthalpy of substance *i* relative to that at 298.15 K, in J/mole

$$H_{Ti} - H_{298.15i} = T^2 \cdot \frac{\partial}{\partial T}\hat{\phi}_T - (H_{298.15} - H_0)$$

5. H.5. Entropy of substance *i*, J/(mole·K)

$$S_{Ti} = \frac{\partial}{\partial T}(\hat{\phi}_T \cdot T)$$

6. H.6. Molar specific heat of substance *i* at constant pressure, in J/(mole·K)

$$C_{pTi} = \frac{\partial}{\partial T}\left[T^2 \frac{\partial}{\partial T}\hat{\phi}_{Ti}\right]$$

7. H.7. Partition function of gas-phase substance *i*

$$Q_i = \exp\left(\frac{-F^0_{Ti}}{RT+1}\right)$$

8. H.8. Formation enthalpy of substance *i*, J/mole (see Ref. 11)

$$\Delta H^0_{Ti} = H^0_{Ti}\,(\text{individual substance}) - \sum_j H^0_{Tj}$$

Example

Calculated molar specific heat of water vapor as a function of temperature:

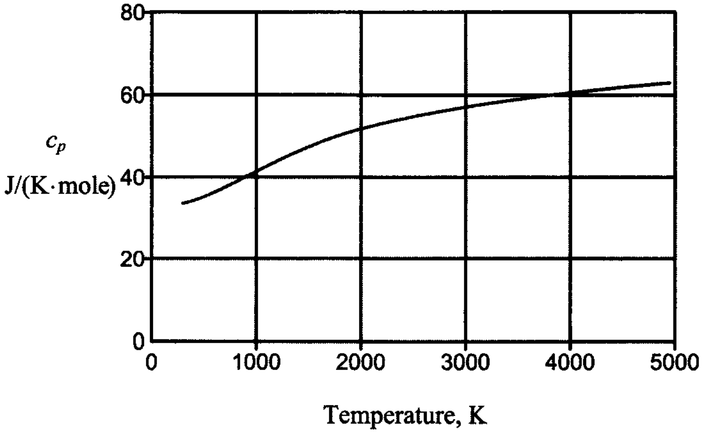

Fig. 8.1

Thermodynamic Characteristic of Mixtures

Calculation of thermodynamic characteristics of mixtures is carried out based on thermodynamic functions of substances and following combinations of molar mass and number of moles:

$n_g = \sum_i n_{gi}$	number of moles of gas-phase components
$n_c = \sum_i n_{ci}$	number of moles of condensed components
$n = n_g + n_c$	total number of moles
$x_{gi} = n_{gi}/n_g$	relative molar fraction of substance in gas phase
$x_{ci} = n_{ci}/n_c$	relative molar fraction of substance in condensed phase
$\mu_g = \sum_i x_{gi}\mu_{gi}$	molar mass (molecular weight) of gas phase
$\mu_c = \sum_i x_{ci}\mu_{ci}$	molar mass (molecular weight) of condensed phase
$\mu = \mu_g x_g + \mu_c x_c$	average molar mass (molecular weight)

Gibbs Thermodynamic Potential (H.9)

1. Specific Gibbs thermodynamic potential of gas phase, J/g

$$\phi_g = \frac{\sum_i \Phi^0_{Ti} x_{gi} + RT \sum_i x_{gi} \ln x_{gi}}{\mu_g}$$

2. Specific Gibbs thermodynamic potential of condensed phase, J/g

$$\phi_c = \frac{\sum_i \Phi^0_{Ti} x_{ci} + RT \sum_i x_{ci} \ln x_{ci}}{\mu_c}$$

3. Specific Gibbs thermodynamic potential of heterogeneous mixture, J/g

$$\phi = \frac{\mu_g n_g \Phi_g + \mu_c n_c \Phi_c}{\mu n}$$

Enthalpy (H.10)

1. Specific enthalpy of gas phase, J/g

$$h_g = \frac{\sum_i H^0_{Ti} x_{gi}}{\mu_g}$$

2. Specific enthalpy of condensed phase, J/g

$$h_c = \frac{\sum_i H^0_{Ti} x_{ci}}{\mu_c}$$

3. Specific enthalpy of heterogeneous mixture, J/g

$$h = \frac{\mu_g n_g h_g + \mu_c n_c h_c}{\mu n}$$

Internal Energy (H.11)

1. Specific internal energy of gas phase, J/g

$$u_g = \frac{\sum_i H^0_{Ti} x_{gi} - RT}{\mu_g}$$

2. Specific internal energy of condensed phase, J/g

$$u_c = \frac{\sum_i H^0_{Ti} x_{ci}}{\mu_c}$$

Example

Calculated specific internal energy and specific enthalpy of air (at fixed chemical composition) versus temperature:

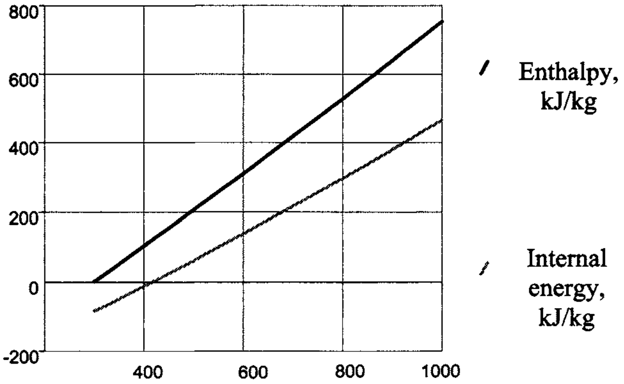

Fig. 8.2

Entropy (H.12)

- Specific entropy of gas phase, J/(g·K)

$$s_g = \frac{\sum_i S^0_{Ti} x_{gi} + R \ln (p/p_0) - R \sum_i x_{gi} \ln x_{gi}}{\mu_g}$$

- Specific entropy of condensed phase, J/(g·K)

$$s_c = \frac{\sum_i S^0_{Ti} x_{ci} - R \sum_i x_{ci} \ln x_{ci}}{\mu_c}$$

- Specific entropy of heterogeneous mixture, J/(g·K)

$$s = \frac{\mu_g n_g s_g + \mu_c n_c s_c}{\mu n}$$

Example

Calculated specific entropy of air vs temperature (at fixed chemical composition):

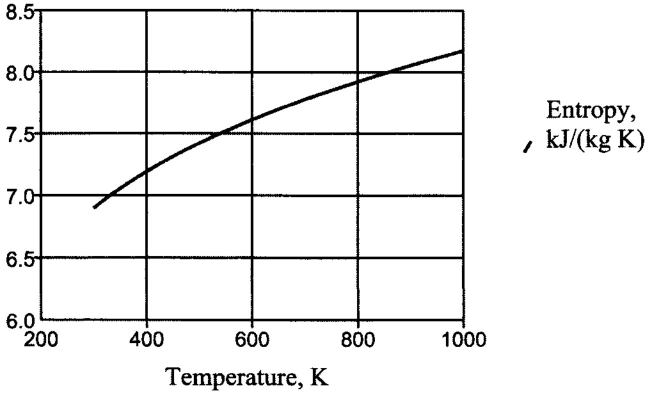

Fig. 8.3

Specific Heat at Constant Pressure (H.13)

1. Specific heat of gas phase at constant pressure, J/(g·K)

$$c'_{pg} = \frac{\mathrm{d}h_g}{\mathrm{d}T}$$

2. Specific heat of condensed phase at constant pressure, J/(g·K)

$$c'_{pc} = \frac{\mathrm{d}h_c}{\mathrm{d}T}$$

3. "Chemically frozen" specific heat of mixture at constant pressure, J/(g·K)

$$c_p^* = \sum_i c_{pi} x_i$$

4. Specific heat of heterogeneous mixture at constant pressure, J/(g·K)

$$c'_p = \mu_g x_g c'_{pg} + \mu_c x_c c'_{pc}$$

Example

Calculated specific heat of air at constant pressure $p = 1\,\text{atm}$ (at fixed chemical composition) vs temperature:

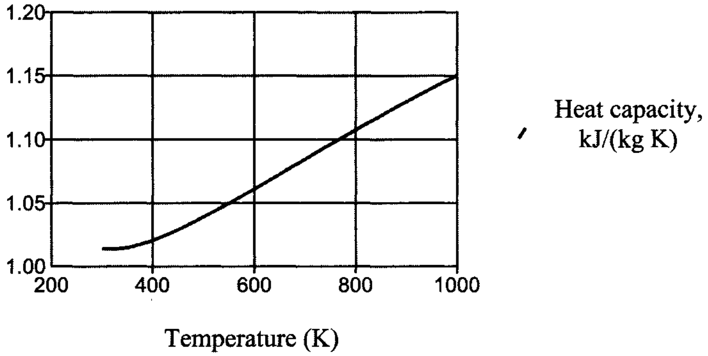

Fig. 8.4

Specific Heat at Constant Volume (H.14)

1. Specific heat of gas phase at constant volume, J/g·K

$$c'_{vg} = c'_{pg} - \left(\frac{R}{\mu_g}\right)\frac{[1-(\partial \ln \mu_g/\partial \ln T)_p]^2}{[(\partial \ln \mu_g/\partial \ln T)_T + 1]}$$

2. Specific heat of condensed phase at constant volume, J/g·K

$$c'_{vc} = c'_{pc} - \left(\frac{R}{\mu_c}\right)\frac{[1-(\partial \ln \mu_c/\partial \ln T)_p]^2}{[(\partial \ln \mu_c/\partial \ln T)_T + 1]}$$

3. Specific heat of heterogeneous mixture at constant volume, J/g·K

$$c'_v = \mu_g n_g c'_{vg} + \mu_c n_c c'_{vc}$$

4. "Chemically frozen" specific heat of mixture at constant volume, J/g·K

$$c_v^* = c_{pc}^* - \frac{R}{\mu}$$

Specific Heat Ratio (H.15)

- Specific heat ratio

$$\gamma = \frac{c_p}{c_v}$$

- "Chemically frozen" specific heat ratio

$$\gamma = \frac{c_p^*}{c_v^*}$$

Example

Calculated specific heat ratio for air vs temperature:

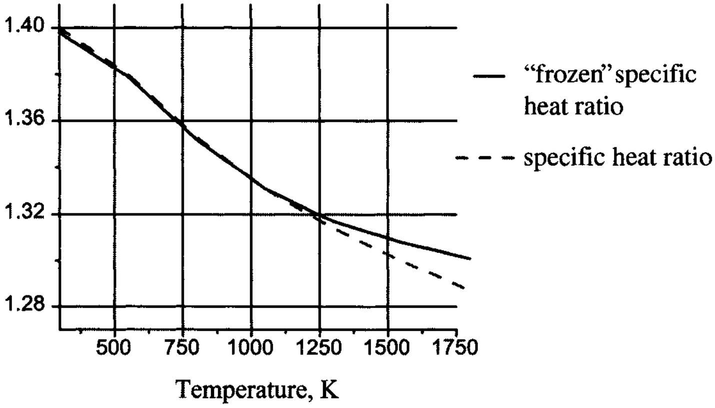

Fig. 8.5

Density (H.16)

1. Gas phase density, g/cm^3 or kg/m^3

$$\rho = \frac{p\mu_g}{RT}$$

Example

Calculated density of air (fixed composition) vs temperature:

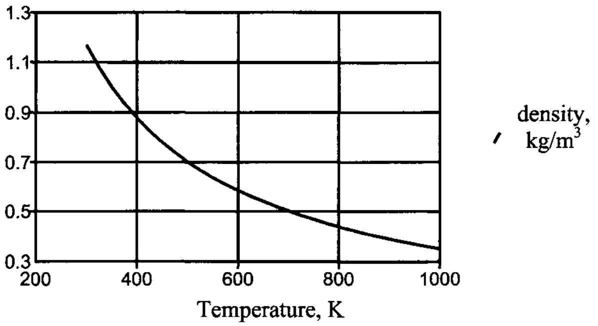

Fig. 8.6

Speed of Sound in Chemically Reacting Gas (H.17)

1. Speed of sound in gas phase, m/s

$$a = \sqrt{\frac{(\gamma R/\mu_g)}{[1 - (\partial \ln n_g/\partial \ln p)_T]}}$$

2. "Frozen" speed of sound in gas phase, m/s

$$a^* = \left(\frac{\gamma^* RT}{\mu_g}\right)^{1/2}$$

Example

Calculated speed of sound in air vs temperature:

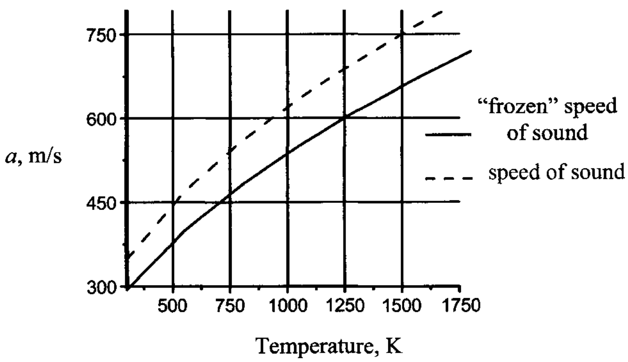

Fig. 8.7

Equilibrium Composition of Multicomponent Mixture

To calculate equilibrium composition, the following set of parameters should be given:

1. initial elemental or substantive composition, i.e., initial values of relative volume or mass fraction for atoms or substances in the mixture
2. list of substances in equilibrium
3. values of two thermodynamic parameters from the list of thermodynamic variables: p, V, U, S, H, T.

The following quantities are calculated:

Molar Fraction of Substance (H.18)

$$x_i = \frac{n_i}{\sum_i n_i}$$

Mass Fraction of Substance (H.19)

$$x_{mi} = \frac{n_i \mu_i}{\sum_i n_i \mu_i}$$

Example

Calculated equilibrium molar fractions of nitrogen oxides at atmospheric pressure in air versus temperature:

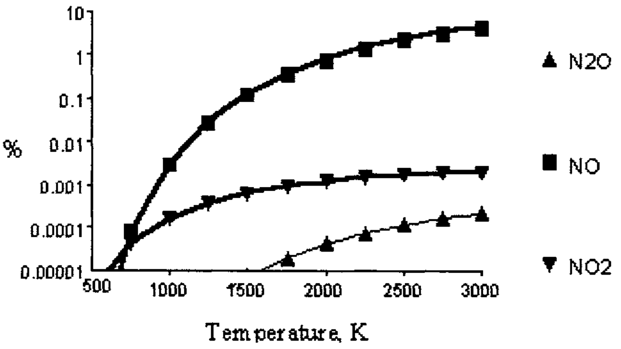

Fig. 8.8

Chemical Equilibrium Constant of Reaction (H.20)

1. $K_p = \exp[(T\Delta S^0 - \Delta H^0)/RT]$ ΔS^0, ΔH^0 are the entropy and enthalpy of reaction.

Example

Calculated equilibrium constant of reaction $NO_2 = NO + 1/2(O_2)$ versus temperature:

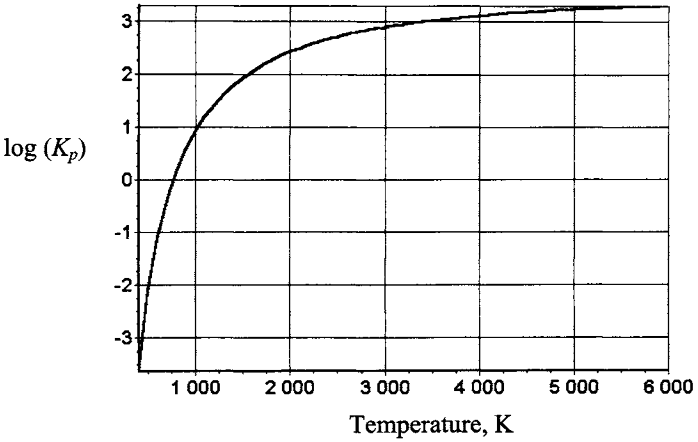

Fig. 8.9

X. Thermodynamics of Irreversible Processes

A. Definition

Thermodynamics of irreversible processes, also called nonequilibrium thermodynamics, is a phenomenological theory that provides macroscopic description of nonequilibrium processes.

The main task of thermodynamics of irreversible processes consists in providing a quantitative description of nonequilibrium processes in systems in which each local region is characterized by certain values of thermodynamic parameters (Refs. 13, 17–23).

Thermodynamics of irreversible processes originated from a combination of methods of the theory of transport phenomena with classical thermodynamics, and it is intended primarily for description of transport phenomena (see the third volume in this series).

B. Postulates of Thermodynamics of Irreversible Processes

1. Principle of local equilibrium

Thermodynamics of irreversible processes treats statistical systems that can be described with the local values of thermodynamic parameters (the state of local equilibrium).

Local equilibrium exists in those macroscopically nonequilibrium systems where the rates of change in the macroscopic state are much lower than the rates of processes that restore the equilibrium.

A quantitative criterion for the existence of local thermodynamic equilibrium is determined from the condition for the validity of the Gibbs equation $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \sum \mu_i \mathrm{d}n_i$ in each specific nonequilibrium system (see Thermodynamic Potentials).

Practical significance of the local-equilibrium principle is that it makes it possible to use the laws of thermodynamics to describe nonequilibrium processes.

2. Comments

a. Gas flow is in a state of local equilibrium if the variation of velocity or temperature across the mean free path is small compared to the local values of these quantities; namely

$$l|\mathrm{grad}\mathbf{v}| \ll |\mathbf{v}| \text{ or } l|\mathrm{grad}T| \ll T$$

where l is the mean free path.

b. Gas in the field of sonic wave is in a local-equilibrium state if $\omega\tau \ll 1$, where ω is the acoustic frequency, and τ is the relaxation time for the energy of internal degrees of freedom.

c. Gas at the front of strong shock wave is not locally equilibrium because the temperature jump across the front whose width is on the order of the mean free path is larger or much larger than the temperature ahead of the front. In weak shock waves, where the thickness of the front is much larger than the mean free path, local equilibrium takes place.

3. The postulate of linear relation among fluxes and thermodynamic forces

Fluxes of macroscopic quantities J_i and *thermodynamic forces* X_i giving rise to these fluxes are linked by linear relations

$$J_i = \sum_{j=1}^{n} L_{ij} X_j, \quad i = 1, 2, \ldots, n$$

where L_{ij} are the kinetic coefficients. Examples illustrating this postulate are given later in the subsection Fluxes and Thermodynamic Forces.

In contrast to mechanics, where forces are vectors, thermodynamic forces may be scalars, vectors, or tensors.

The matrix of kinetic coefficients L_{ij} is independent of J_i and X_i, but may depend on temperature and other parameters of the system.

The fluxes and thermodynamic forces are chosen from the condition

$$\sigma = \sum J_i X_i$$

where σ is the *entropy production* that represents the entropy generation rate because of internal dissipative processes. Specific choice of J_i and X_i is not unique and depends on the problem to be solved; any choice of J_i and X_i must satisfy the equality $\sigma = \sum J_i X_i = \sum J_i' X_i'$, where J_i' and X_i' represent a set of fluxes and thermodynamic forces linearly related to J_i and X_i (Ref. 17).

In thermodynamics of irreversible processes, the *Curie principle* states that the linear relation $J_i = \sum_{j=1}^{n} L_{ij} X_j$ is invariant with respect to orthogonal transformations of spatial coordinates allowed by the system; in isotropic media, inversion and rotation are such transformations. In view of symmetry properties of the system under consideration, the flux components can depend only on some of the thermodynamic force components. According to the Curie principle, in an isotropic system, the fluxes and thermodynamic forces having different tensor dimension cannot be related to each other. Thus, in an isotropic system, heat flux (a vector quantity) cannot depend on chemical affinity (a scalar quantity), namely, on the chemical reaction rate.

The assumption about linear relation between fluxes and thermodynamic forces is a hypothesis, which is beyond the scope of equilibrium thermodynamics. This assumption is well justified in the theory of transport phenomena, where the Fourier ($\mathbf{J_q} = -\lambda \mathrm{grad} T$), Fick's ($\mathbf{J_M} = -D \mathrm{grad} C$, where C is the local particle number density), and other empirical laws are known and are valid in a fairly wide range of temperature and concentration gradients (see the third volume in this series). In chemically reacting systems, the domain of applicability of linear relations between the chemical reaction rates and chemical affinity is restricted to the states that are close to chemical equilibrium and exist in the final stage of the reaction.

4. Example

In chemical kinetics, the rate of the reaction $N_2 + O_2 \rightleftarrows 2NO$ is written as

$$\mathbf{J_w} = k_+ n_{N_2} n_{O_2} - k_- n_{NO}^2 = w\left[1 - \exp\left(-\frac{A}{kT}\right)\right]$$

where $A = \mu_{N_2} + \mu_{O_2} - 2\mu_{NO}$ is the chemical affinity, and $w = k_+ n_{N_2} n_{O_2}$.

In thermodynamics of irreversible processes, a linear relation between the fluxes and thermodynamic forces $J_w = LA$ is postulated; this relationship holds (according to the above formula) only for $|A/kT| \ll 1$ (Ref. 18).

5. Principle of symmetry of kinetic coefficients (the Onsager symmetry relations)

The matrix of kinetic coefficients L_{ij} is symmetric under the condition that $\sigma = \sum J_i X_i$; that is, $L_{ij} = L_{ji}$.

Practically, the significance of the Onsager relations consists in the establishment of a link between seemingly different phenomena that correspond to the direct and reverse effects. Thus, for example, the relationship of symmetry in a binary system results in equality between the kinetic coefficients corresponding to thermal diffusion (mass flux caused by grad$T$) and to the Dufour diffusion thermoeffect (energy flux caused by concentration gradient).

6. Generalized symmetry relations (the Onsager–Casimir relations)

$$L_{ij} = \varepsilon_i \varepsilon_j L_{ji}$$

where

$$\varepsilon_k(k = i, j) = \begin{cases} 1 & \text{if the thermodynamic forces } X_k \text{ are even functions} \\ -1 & \text{if these forces are odd functions} \end{cases}$$

with respect to the time reversal. For example, temperature gradient is an even function of time, whereas velocity gradient is an odd function of time.

The Onsager symmetry relations combined with the Curie principle restrict the number of independent kinetic coefficients L_{ij}, since $L_{ij} = L_{ji}$ according to the Onsager relation, whereas $L_{ij} = 0$ according to the Curie principle if the indices i and j refer to the fluxes J_i and thermodynamic forces X_j (or their components) that have different vector dimensions (Ref. 17).

7. The Prigogine theorem

In the state of thermodynamic equilibrium, the entropy of a system attains a minimum, whereas the entropy production is $\sigma = 0$. An analogue of this statement for nonequilibrium systems described in terms of linear nonequilibrium thermodynamics is the statement that the production of entropy is minimal in stationary states. This statement is a corollary of the Prigogine theorem:

> If there are n thermodynamic forces in a system, of which the first p forces are fixed ($X_j = \text{const}, j \leq p$), then the fluxes corresponding to forces that are not constant vanish ($J_j = 0, j > p$) in a state with the minimal production of entropy ($\sigma = \min$). The states with minimal production of entropy are stationary and stable.

Applicability of the Prigogine theorem is restricted by the following conditions:

a) Linear relations between the fluxes and thermodynamic forces are valid;
b) The Onsager–Casimir relations are valid;
c) Kinetic coefficients are assumed to be constant;
d) Variations in nonequilibrium parameters $\alpha_j(J_j = \mathrm{d}\alpha_j/\mathrm{d}t, j > p)$ are equal to zero owing to interaction with surroundings.

In a planar gas layer bounded by walls with different temperatures, the state with minimal production of entropy corresponds to the steady state.

The Prigogine theorem specifies the direction of system evolution. If a system cannot reach the equilibrium state (in view of conditions $X_j = \text{const}, j \leq p$), then this system will tend to the stationary state with the lowest dissipation ($\sigma = \min$). This tendency manifests itself monotonically, namely, $\mathrm{d}\sigma/\mathrm{d}t \leq 0$; therefore, there is no oscillatory mode in the changes in the parameters during approach to equilibrium in linear thermodynamics. To describe possible oscillatory modes, methods of nonlinear thermodynamics are required.

C. Nonlinear Thermodynamics of Irreversible Processes

Nonlinear thermodynamics of irreversible processes, like the linear one, deals with systems in states of local thermodynamic equilibrium; that is, it is assumed that the Gibbs equation $dU = TdS - pdV + \sum \mu_i dn_i$ is valid.

The fluxes J_i and thermodynamic forces X_i are chosen (as in the linear thermodynamics of irreversible processes) from the condition

$$\sigma = \sum J_i X_i$$

However, in contrast to linear thermodynamics, the fluxes here are not linear functions of thermodynamic forces.

Example

The rate of reaction $N_2 + O_2 \rightleftarrows 2NO$ is written as (see the previous example):

$$J_w = w\left[1 - \exp\left(-\frac{A}{kT}\right)\right]$$

In the vicinity of equilibrium, if $|A/kT| \ll 1$, we have

$$J_w = \frac{w_\infty A}{kT}$$

which is consistent with the laws of linear nonequilibrium thermodynamics (w_∞ is the equilibrium value of w).

In the opposite limiting case of $|A/kT| \gg 1$, which corresponds to the initial stage of the reaction in a closed system, we have

$$J_w = w_0$$

(w_0 is the value of w at the initial point in time).

In this saturation limit, the flux is independent of thermodynamic force (affinity), and the entropy production becomes a linear function of affinity (Ref. 18).

In general, the steady state in nonlinear thermodynamics of irreversible processes does not correspond to a minimum in the entropy production and can be unstable. The process of reaching the steady state obeys the Glansdorff–Prigogine evolution criterion, according to which a change in the entropy production with time at fixed fluxes is a negative quantity; namely

$$\left.\frac{d\sigma}{dt}\right|_{J_i=\mathrm{const}} = \sum J_i \frac{dX_i}{dt} \le 0$$

Example

For a single-component isotropic system in a finite volume whose walls are maintained at different constant temperatures, we have

$$\sigma_L = \mathbf{J}_q \operatorname{grad} \frac{1}{T}$$

The total entropy production is equal to $\sigma = \int \sigma_L \mathrm{d}V$, and the rate of entropy production at a constant heat flux $\mathbf{J_q}$ is given by

$$\left.\frac{\mathrm{d}\sigma}{\mathrm{d}t}\right|_{J_q} = \int J_q \frac{\partial}{\partial t} \mathrm{grad} \frac{1}{T} \,\mathrm{d}V \equiv -\int \frac{\rho c_v}{T^2} \left|\frac{\partial T}{\partial t}\right|^2 \mathrm{d}V \leq 0$$

where ρ is the density, and c_v is the specific heat at constant volume.

The Glansdorff–Prigogine criterion demonstrates that a change in the thermodynamic forces, X_i, in the course of evolution reduces the entropy production. This criterion does not provide information about the sign and magnitude of $\mathrm{d}\sigma/\mathrm{d}t|_{X_i=\mathrm{const}} = \sum X_i(\mathrm{d}J_i/\mathrm{d}t)$; in general, the sign of the full derivative

$$\frac{\mathrm{d}\sigma}{\mathrm{d}t} = \sum J_i \frac{\mathrm{d}X_i}{\mathrm{d}t} + \sum X_i \frac{\mathrm{d}J_i}{\mathrm{d}t}$$

is undetermined in nonlinear thermodynamics of irreversible processes.

In linear thermodynamics of irreversible processes, we have $\sum J_i \frac{\mathrm{d}X_i}{\mathrm{d}t} = \sum X_i \frac{\mathrm{d}J_i}{\mathrm{d}t}$; therefore, the Glansdorff–Prigogine criterion is reduced to $\frac{\mathrm{d}\sigma}{\mathrm{d}t} \leq 0$ (Ref. 18).

D. Dissipative Structures

In open systems, where matter and energy can be exchanged with the surroundings, ordered structures stabilized by external fluxes can be spontaneously formed.

Examples (see Ref. 23)

1. Formation of Benard hexagonal cells in a horizontal plane liquid layer, when the bottom surface is heated.
2. Laminar-turbulent transition.
3. The onset of laser generation when pumping rate exceeds a certain threshold value.
4. Oscillatory chemical reaction of the Belousov–Zhabotinskii type (see Chapter 6 in this volume).

Special features of formation of dissipative structures

Formation of dissipative structures is a threshold process. Thus, the Benard cells are formed during convective motion in a liquid only if the difference in temperatures between the bottom and top surfaces in the horizontal layer exceeds a critical value.

Dissipative structures may form only in open systems; the ordered state is sustained owing to transfer of entropy produced in the system to the surrounding medium.

Dissipative structures arise only in macroscopic systems whose behavior is described by nonlinear equations.

Three types of dissipative structures are observed: temporal, spatial, and spatial–temporal. Description of each type of structure is based on nonlinear macroscopic equations that characterize the specific phenomenon; for example, the formation and structure of Benard cells are described in terms of hydrodynamics of viscous and heat-conducting liquid (Refs. 13 and 23).

E. Fluxes and Thermodynamic Forces in Thermodynamics of Irreversible Processes

1. Case 1

An individual chemical reaction $\sum_{i=1}^{n} \nu_i X_i = 0$.

a. Fluxes

The rate of chemical reaction is given by $J_w = (\rho/\nu_i m_i N_\mathrm{A})(\partial c_i/\partial t)$, or $J_w = \rho(\partial \xi/\partial t)$, where $\partial \xi/\partial t = (1/\nu_i m_i N_\mathrm{A})(\partial c_i/\partial t)$.

b. Thermodynamic forces

$-A/T$, where $A = \sum_{i=1} \nu_i \mu_i$ is the chemical affinity.

c. Linear relations

$$J_w = -\frac{L}{T}A$$

d. Entropy production

$$\sigma = -J\frac{A}{T} = L\frac{A^2}{T}$$

e. Nomenclature

X_i	symbols of substances involved in the reaction
ν_i	stoichiometric coefficients ($\nu_i < 0$ for reactants, $\nu_i > 0$ for reaction products)
ρ	gas density
ρ_i	density of the *i*th gas component
$c_i = \rho_i/\rho$	mass concentration of the *i*th component
A	chemical affinity
μ_i	chemical potential per mole of the *i*th component
ξ	degree of development (or completeness) of chemical reaction
L	kinetic coefficient
m_i	mass of a particle of the *i*th component
N_A	Avogadro's number

f. Comment

Sometimes, chemical affinity is defined as $A = -\sum_{i=1}^{n} \nu_i \mu_i$ instead of $A = \sum_{i=1}^{n} \nu_i \mu_i$ used above. The sign reversal of A results in the sign reversal of the corresponding thermodynamic force; A/T should be then used instead of $-A/T$.

2. Case 2

Several chemical reactions proceeding simultaneously; *n* substances, of which *i* ($i = 1, 2, \ldots, n$) are involved in *j* ($j = 1, 2, \ldots, r$) chemical reactions, are considered. Thus, we have

$$\sum_{i=1}^{n} \nu_{ij} X_i = 0, \qquad (j = 1, 2, \ldots, r)$$

a. Fluxes

The rate of the jth chemical reaction is given by

$$J_{wj} = \rho \frac{\partial \xi_i}{\partial t} \text{ (see Case 1), so that } \rho \frac{\partial c_i}{\partial t} = \sum_{j=1}^{r} \nu_{ij} m_i N_A J_{wj}$$

b. Thermodynamic forces

$-A_j/T$, where $A_j = \sum_{i=1}^{n} \nu_{ij} \mu_i$ is the chemical affinity of jth reaction.

c. Linear relations

$$J_{wi} = -\sum_{j=1}^{r} L_{ij} \frac{A_j}{T}$$

d. The entropy production

$$\sigma = -\sum_{j=1}^{r} J_{wj} \frac{A_j}{T}$$

e. Nomenclature

See Case 1.

f. Comment

1. In chemical reactions, the fluxes and thermodynamic forces are scalar quantities.
2. It is assumed that $r \leq n - 1$, and that all r reactions are independent.
3. For r chemical reactions, the values of ξ_i are determined from the equations

$$\frac{\partial c_i}{\partial t} = \sum_{j=1}^{r} \nu_{ij} m_i N_A \frac{\partial \xi_j}{\partial t}, \qquad i = 1, 2, \ldots, n$$

Integration of these equations yields

$$c_i(t) - c_i(0) = \sum_{j=1}^{r} \nu_{ij} m_i N_A \xi_j(t)$$

3. Case 3

Energy transfer in a two-temperature system with constant volume.

a. Fluxes

The energy transfer rate:

$$\frac{dU_1}{dt} \left(= -\frac{dU_2}{dt} \right) = \frac{c_{v1} dT_1}{dt}$$

b. Thermodynamic forces

The difference in reciprocal temperatures between the subsystems:

$$\frac{1}{T_1} - \frac{1}{T_2}$$

c. Linear relations

$$\frac{\mathrm{d}U_1}{\mathrm{d}t} = L\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \text{or} \quad \frac{\mathrm{d}T_1}{\mathrm{d}t} = \frac{L}{c_{v1}} \frac{T_2 - T_1}{T_1 T_2}$$

d. The entropy production

$$\sigma = \frac{\mathrm{d}U_1}{\mathrm{d}t}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \equiv L\left(\frac{1}{T_1} - \frac{1}{T_2}\right)^2$$

e. Nomenclature

U_i	energy per unit mass of the *i*th component
c_{v1}	specific heat of the first subsystem at constant volume
L	kinetic coefficient

f. Comment

For $T_1 \cong T_2 \cong T$, we have

$$\frac{\mathrm{d}T_1}{\mathrm{d}t} = \frac{L}{c_{v1}} \frac{T_2 - T_1}{T^2}$$

The phenomena of transport of mass (diffusion), energy (heat conduction), and momentum (viscosity), as described by thermodynamics of irreversible processes, are considered in the third volume of this series.

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Chapter 9

Equations of State

I. Nomenclature

See nomenclature in the beginning of Chapter 8.

II. Thermal and Caloric Equations of State

Thermal equation of state is an equation that relates the pressure p, volume V, and temperature T of a homogeneous system in a state of thermodynamic equilibrium: $f(p, V, T) = 0$ or $p = p(V, T)$.

Caloric equation of state is an equation that determines the internal energy U of a system in a state of thermodynamic equilibrium as a function of any two of the three parameters p, V, or T. The dependence of specific heat at constant volume on temperature and volume $c_V = c_V(T, V)$ is also referred to as caloric equation of state.

The existence of thermal equation of state follows from the zeroth law of thermodynamics, in particular, from the transitivity property. The existence of caloric equation of state follows from the first law of thermodynamics. The formula

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

relating thermal and caloric equations of state follows from the second law of thermodynamics.

Equations of state cannot be derived solely from the laws of thermodynamics; they are determined experimentally or are derived by the methods of statistical physics. To derive the equation of state, it is sufficient to know any one of thermodynamic potentials as a function of the relevant natural variables. For example, if the free energy $F(V, T)$ is known, then

$$p = -\left(\frac{\partial F}{\partial V}\right)_T, \qquad U = -T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right)_V$$

An explicit form of equation of state makes it possible to describe the properties of a thermodynamic system using thermodynamic equalities (see Thermodynamic Potentials in Chapter 8).

Henceforth, we consider a gas that obeys classical statistics, so that $T \gg (\hbar/mk)\bar{N}^{2/3}$, where $\bar{N}$ is the number of particles in unit volume.

III. Equation of State for an Ideal Gas

An ideal gas is a gas in which the mean kinetic energy of particles (atoms, molecules, ions, and electrons) is much larger than the mean potential energy of particle–particle interactions; the interactions occur only during short-duration collisions (Refs. 1–3).

The criterion for a gas consisting of neutral particles to be ideal: $|B(T)/v| \ll 1$, where v is the molar volume of the gas, and $B(T)$ is the second virial coefficient (see Real Gases, Refs. 4 and 5).

The criterion for a plasma to be ideal:

1. In the case of interaction between charged particles: $e^2/R_{\mathrm{D}} \ll kT$, where e is the elementary charge, and R_{D} is the Debye shielding radius (see Chapter G in the first volume of this series, and Chapter 7 of this volume; Ref. 6).
2. In the case of interaction between charged and neutral particles: $2\pi\alpha e^2 N/R_0 \ll kT$, where α is the polarizability of neutral particles, and R_0 is the gas-kinetic radius (see the description of model I-T.1; Ref. 6).

A perfect gas is a term often used (see Refs. 3, 12 and 13) for an ideal gas whose specific heats are constant and independent of temperature, even though the gas may contain particles with internal degrees of freedom. Also, in many scientific publications and textbooks devoted to gas dynamics (see Refs. 7–10), a perfect gas is the term used for a gas that is called an ideal gas in this volume. In those publications (see also Ref. 11), a gas where viscosity and heat conduction are absent is called an ideal gas.

Thermal equation of state of an ideal gas (Clapeyron equation)

– for a single-component system:

$$p = \bar{N}kT$$

$$p = \frac{\rho RT}{M} \qquad \rho = m\bar{N} \qquad M = mN_{\mathrm{A}}$$

$$pV = nRT$$

– for a gas mixture composed of l components of the ith type:

$$p = \left(\sum_{i=1}^{l} \bar{N}_i\right)kT \qquad \rho = \sum_{i=1}^{l} \rho_i$$

$$p = \frac{\rho RT}{\bar{M}} \qquad \bar{M} = \frac{\sum_{i=1}^{l} \bar{N}_i M_i}{\sum_{i=1}^{l} \bar{N}_i}$$

$$p = \left(\frac{\sum_{i=1}^{l} \rho_i}{M_i}\right) RT \quad \rho_i = m_i \tilde{N}_i, \qquad M_i = m_i N_{\mathrm{A}}$$

$$pV = \left(\sum_{i=1}^{l} n_i\right) RT$$

The following laws are valid for an ideal gas:

1. Gay–Lussac law

   $$\frac{V}{T} = \text{const, or } V_T = V_0[1 + \alpha_p(T - T_0)], \quad \text{for } p = \text{const and } M = \text{const}$$

   where V_0 and V_T are the gas volumes at a reference temperature T_0 and at the temperature T, and α_p is the coefficient of thermal expansion at constant pressure of the gas equal to $(1/273.16)\ \mathrm{K}^{-1}$.
2. Boyle–Mariotte law

   $$pV = \text{const for } T = \text{const and } M = \text{const}$$

3. Charles's law

   $$\frac{p}{T} = \text{const, or } p_T = p_0[1 + \gamma_V(T - T_0)], \text{ for } V = \text{const and } M = \text{const}$$

   where p_0 and p_T are the pressures at a reference temperature T_0 and at the temperature T, γ_V is the thermal-pressure coefficient equal to $(1/273.16)\ \mathrm{K}^{-1}$, and M is the gas mass.

Caloric equation of state for an ideal gas

The internal energy U of an ideal gas depends only on temperature, $U = U(T)$ (Joule law), whereas the internal energy of nonreacting gas mixture is the sum of contributions of each component $U_i(T)$ and their heats of formation U_{fi}^0, so that we have the following expression for the energy per mole:

$$U = \sum_i \xi_i [U_i(T) + U_{fi}^0]$$

Here, ξ_i is the mole fraction of ith component, and U_{fi}^0 is the heat of formation of ith component from chemical elements in the standard reference state ($T = 298.15$ K and $p = 1$ atm) (see Refs. 14 and 15). The relations and formulas for caloric equation of state are given in Chapter 8, Thermodynamics of Gases and Plasmas.

Energy and enthalpy of reacting mixtures of ideal gases depend not only on temperature, but also on pressure; the latter, in addition to temperature, governs the chemical composition of a mixture (for example, see Ref. 16).

IV. Real Gases

A. Virial Equation of State for a Nonideal Gas

A single-component system

Expansion in power series of $1/v$:

$$\frac{pv}{RT} = 1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \cdots$$

Expansion in power series of p:

$$\frac{pv}{RT} = 1 + B'p + C'p^2 + \cdots$$

Relation to the virial coefficients:

$$B = RTB',\ C = (RT)^2(C' + B'^2)$$

Virial coefficients determine the deviation of a gas from the ideal gas model due to intermolecular forces [4].

1. Nomenclature

$v = V/n$	molar volume
$B(T)$, $C(T)$	second and third virial coefficients; their values are determined by binary and ternary collisions

2. Parameters

For the model of hard spheres with diameter σ [see the model I-T.1 and (Ref. 4)], we have

$$B = \frac{2}{3}\pi N_A \sigma^3 \equiv b_0, \qquad C = \frac{5}{8}b_0^2$$

Recommended values of virial coefficients for various models of intermolecular interaction can be found in Refs. 4, 5, 15 and 17–19.

3. Domain of applicability

The domain of applicability of the virial equation is limited by the convergence of series. The series diverges for densities that correspond to the liquid state. Accuracy of a virial equation depends on the number of retained terms.

4. Example

For nitrogen at 0°C, the virial expansion is written as

$$\frac{pv}{RT} = 1 - 0.00023 + 0.0000025 + \cdots \text{ at 1 atm}$$

$$\frac{pv}{RT} = 1 - 0.0023 + 0.00025 + \cdots \text{ at } 10\,\text{atm}$$

$$\frac{pv}{RT} = 1 - 0.023 + 0.025 + \cdots \text{ at } 100\,\text{atm}$$

An example of thermodynamic analysis of combustion products at high temperature and pressure, using virial equation of state for a nonideal gas, can be found in Ref. 20.

5. Comments

If the terms on the order of v^{-1} (for $|B(T)/v| \ll 1$) are ignored, the virial equation of state is transformed into the Clapeyron equation of state for an ideal gas.

The virial equation of state is considered in detail in Refs. 5 and 16–18).

A multicomponent system

$$\frac{pv}{RT} = 1 + \frac{B_{mix}(T)}{v} + \frac{C_{mix}(T)}{v^2} + \cdots$$

$$B_{mix}(T) = \sum_{\alpha=1}^{l}\sum_{\beta=1}^{l} B_{\alpha\beta}(T)\xi_\alpha\xi_\beta$$

$$C_{mix}(T) = \sum_{\alpha=1}^{l}\sum_{\beta=1}^{l}\sum_{\gamma=1}^{l} C_{\alpha\beta\gamma}(T)\xi_\alpha\xi_\beta\xi_\gamma$$

1. Nomenclature

l	number of components in the mixture
v	molar volume
ξ_α	molar fraction of the αth component in the mixture
B_{mix}, C_{mix}	second and third virial coefficients in mixtures
$B_{\alpha\alpha}(T)$	second virial coefficient for component α in a single-component gas
$B_{\alpha\beta}(T)$	second virial coefficient calculated for intermolecular potential that describes the interaction between molecules of the components α and β
$C_{\alpha\beta\gamma}(T)$	third virial coefficient determined by pairwise interactions in a system composed of three particles that belong to the components α, β, and γ (Refs. 4 and 5)

2. Parameters and the domain of applicability

Collections of data and recommended values of second virial coefficients for neutral gases and their mixtures can be found in Refs. 15, 18, and 19.

B. Empirical Equations of State

The van der Waals equation for a single-component system consisting of n moles is

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT.$$

Nomenclature

a, b are constants that depend on the gas and account for the effect of attractive forces between molecules and for finite volume occupied by the molecules, respectively.

The reduced van der Waals equation of state is written as

$$\pi = \frac{8\tau}{3\omega - 1} - \frac{3}{\omega^2},$$

where

$$\pi = \frac{p}{p_c}, \quad \omega = \frac{v}{v_c}, \quad \tau = \frac{T}{T_c}.$$

Parameters

$p_c = (1/27)(a/b^2)$, $v_c = 3b$, and $T_c = (8/27)(a/bR)$ are the values of pressure, specific volume, and temperature at the critical point (critical parameters) that are determined from the van der Waals equation at the conditions $(\partial p/\partial v)_T = 0$ and $(\partial^2 p/\partial v^2)_T = 0$ (see Ref. 4). If the critical parameters are known, then

$$a = \frac{27}{64}\frac{(RT_c)^2}{p_c}, \qquad b = \frac{1}{8}\frac{RT_c}{p_c v_c}$$

The values of parameters a and b are given in Ref. 19.

Domain of applicability

For $p \gg a/v^2$ and $v \gg b$, van der Waals equation transforms into the equation of state for an ideal gas. Van der Waals equation works at relatively high temperatures and low pressures. Qualitatively, it also describes the behavior of gases at high pressures, condensation of gases, and the critical state.

A binary mixture; in this case, van der Waals equation is

$$\left(\frac{p + a}{v^2}\right)(v - b) = RT$$

$$a = a_{11}\xi_1^2 + 2a_{12}\xi_1 x_2 + a_{22}\xi_2^2, \qquad b = b_{11}\xi_1^2 + 2b_{12}\xi_1 x_2 + b_{22}\xi_2^2$$

Nomenclature

$\xi_{1,2}$ are the mole fractions of components ($\xi_i = n_i/\sum n_i$).

a_{11}, a_{22}, b_{11}, b_{22} are the van der Waals constants of individual components.

Parameters

The quantities a_{12} and b_{12} characterize the interaction of dissimilar molecules. If experimental data on the quantities a_{12} and b_{12} are lacking, they can be estimated with empirical relations

$$\sqrt[3]{b_{12}} = \frac{1}{2}(\sqrt[3]{b_{11}} + \sqrt[3]{b_{22}}), \qquad a_{12} = \sqrt{a_{11}a_{12}}$$

The Berthelot equation (Ref. 4) is written as

$$\left(p + \frac{a}{Tv^2}\right)(v - b) = RT$$

Parameters

The constants a and b are determined from the critical parameters p_c, v_c, and T_c; specifically, $a = (9/8)RT_c^2 v_c$ or $a = (24/R)p_c^2 v_c^2$, and $b = v_c/3$.

The values of critical parameters are given in Ref. 19.

The Dieterici equation (Ref. 4):

$$\left[p \exp\left(\frac{a}{vRT}\right)\right](v - b) = RT$$

where

$$a = 2RT_c v_c \quad \text{or} \quad a = 7.39 p_c v_c^2, \text{ and } b = \frac{v_c}{2}.$$

The critical parameters are given in Ref. 17.

Domain of applicability

Berthelot and Dieterici equations are applicable to binary mixtures (see the van der Waals equation) in addition to single-component systems.

The domain of applicability of empirical equations of state is determined by the approximation accuracy, is different for each gas, and depends on the range of variation of variables. The Dieterici equation describes adequately the (p, v, T) behavior of a gas in the vicinity of the critical point, giving $p_c v_c / RT_c = 0.2706$, which is consistent with the mean value of this quantity for nonpolar gases (0.272). Van der Waals and Berthelot equations of state predict $p_c v_c / RT_c = 0.375$.

Redlich–Qwong equation (Ref. 4):

$$p = \frac{RT}{v - b} - \frac{a}{\sqrt{T}v(v + b)}$$

Parameters

$$a = \frac{0.4278 R^2 T_c^{5/2}}{p_c}; \qquad b = 0.26 v_c$$

Beattie–Bridgeman equation (Ref. 4):

$$pv^2 = RT\left(1 - \frac{c}{vT^3}\right)\left(v + B_0 - \frac{bB_0}{v}\right) - A_0\left(1 - \frac{a}{v}\right)$$

The values of parameters A_0, B_0, a, b, and c are given in Ref. 4.

Domain of applicability

The Beattie–Bridgeman equation contains five parameters; therefore, it yields, in a number of cases, more accurate results than the two-parameter van der

Waals, Dieterici, and other such equations do; for example, in calculations of the internal energy of CO_2.

The Beattie–Bridgeman equation is one of the most accurate empirical representations of the relation between p, v, and T for gases at pressures up to 250 atm.

At higher pressures (1000 atm and above), Haldorff–Kistyakovskii–Wilson equation of state and the gunpowder-combustion gas equation of state can be used (see Ref. 4). A summary of 150 principal equations of state can be found in Ref. 5.

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