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Kinetics of Chemical Reactions Initiated by Hot Atoms

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A general account is given of modern ideas on the kinetics of hot-atom reactions and the fundamental postulates of the phenomenological theories, namely the Wolfgang-Estrup "kinetic theory" of hot-atom reactions and Porter's theory of the "integral reaction probability" are described. The physicochemical models of elastic and non-elastic collisions used for the solution of the Boltzmann integrodifferential equations and of the stochastic equations in Porter's theory are examined. The fundamental formulae describing the probabilities or yields of chemical reactions initiated by hot atoms in relation to the energy distribution functions of hot species are presented and a brief account is given of the methods and the results of the application of the phenomenological theories in the interpretation of the results of experiments involving hot atoms in nuclear reactions, photochemical studies, etc.
The bibliography includes 96 references.

CONTENTS

I. Kinetic equations in the chemistry of hot atoms 189
II. The application of kinetic equations in the chemistry of recoil atoms 195

I. KINETIC EQUATIONS IN THE CHEMISTRY OF HOT ATOMS

Chemical processes involving high-energy atoms or ions under the conditions of a non-uniform distribution of these species in time and space and a non-Maxwellian energy distribution of "hot" atoms or ions are widely investigated at the present time. The chemical reactions of hot atoms are of interest in connection with the high efficiency of the collisions, the dominant role of high-energy processes, and the possibility of carrying out new types of reactions. Hot atoms or ions are obtained as a result of radiation-chemical, plasma-chemical, or nuclear transformations in chemical accelerators, in photochemical reactions, in shock waves, and in cold flames. Extensive experimental data have accumulated on the yield of products in processes involving hot atoms [1-3]. During the last decade, there has been intense development of theoretical ideas about the kinetics of reactions of hot species, mainly in two directions, the first of which is associated with the study of the dynamics of the collisions of hot atoms leading to their cooling and chemical capture [4]. The second led to the establishment of phenomenological theories describing the yield of products as a function of the cross-sections of various elastic and non-elastic collisions and also the energy distribution functions of hot atoms [5,6]. Among these, the most productive have been the "kinetic theory" of hot-atom reactions proposed by Wolfgang and Estrup [7,8] and the theory of the "integral reaction probability" developed by Porter [9]. In the present review, attention has been concentrated on the fundamental postulates of the above phenomenological theories and on the results of their application in the analysis of numerous experimental data on the chemistry of recoil atoms.

1. Transport Equations in the Kinetics of Hot-atom Reactions

The nature of the chemical reaction of a species (atom or ion) with the target material depends on the parameters for the species at the instant of reaction and on the properties of the medium at the point of interaction, which depend in their turn on the previous history of both the given hot species and the entire set of species bombarding the target as well as the previous history of the target material. In systems where high-energy species are introduced, relaxation processes and chemical reactions are indissolubly linked. In a rigorous study of kinetic relations, it is therefore necessary to take into account the set of processes involving high-energy species:

(1) elastic and non-elastic scattering of the species and the penetration, caused by these processes, of the species into the bulk of the target with establishment of a definite spatial distribution and retardation of the species accompanied by the establishment of a definite energy distribution (taking into account both the kinetic energy and the energies of vibrational, rotational, electronic, etc. excitation);

(2) the escape of species from the boundaries of the target and their absorption by the material of the target owing to chemical reactions or retention in various types of traps;

(3) the recombination reactions of the bombarding species.

The relaxation processes of hot species are accompanied by the transfer of their excess energy to the target material with subsequent microscopic and macroscopic transformations. Such transformations include the change in the internal state of the target molecules and in their chemical energy, ionisation, dissociation, and other chemical reactions, as well as the atomisation of the surface layers, heating, and other primary radiation effects. The primary radiation processes also include the displacement and dislodgement of atoms from the crystal lattice; the dislodgement of secondary high-energy species in a system where the target contains atoms equivalent to those used in the bombardment may be regarded as the development of a cascade process. Together with the primary radiation-induced transformations, there is a possibility of secondary transformations, in particular chemical reactions of the bombarding species with the product of the radiation-induced decomposition and reactions of unstable primary products with one another or with the molecules of the target material.

The distribution of the bombarding species in space, time, and with respect to energy and their absorption are determined by the large number of random collisions leading to the above processes. The macroscopic effects, for example the release of the products of the capture of hot species or their retention in the bombarded target, are treated in hot-atom chemistry on the basis of the study of single collisions and their properties. The main task in theoretical hot-atom chemistry involves the determination of the probabilities of reactions involving hot atoms and of the reaction rates or rate constants with the aid of one of the equivalent kinetic equations, for example:

$$P = \int p_r(E) \cdot n(E)\,\mathrm{d}E\,,$$
$$k = \int \sigma_r(E) n(E) v\,\mathrm{d}E \Big/ \int n(E)\,\mathrm{d}E\,, \qquad (I.1)$$
$$R = \int \Sigma_r(E) \cdot \varphi(E)\,\mathrm{d}E,$$

where P, k, and R are the probability, rate constant, and the rate of the chemical reaction respectively, $p_r(E)$ the probability of reaction on collision of an atom having the energy E with the target, $n(E)\mathrm{d}E$ the number of collisions of hot atoms in the range $E-E+\mathrm{d}E$, $\Sigma_r(E)$ the reaction cross-section of the species for the energy E or velocity $v(E)$, $\sigma_r(E)$ the reaction microsection, and $\varphi(E)$ the flux of species with the energy E.

In contrast to traditional kinetics, in hot-atom chemistry the above problems have to be solved for species having a non-equilibrium non-Maxwellian distribution, determined by their initial energy, their mass, the retarding capacity of the medium, its reactivity, etc. One of the fundamental problems in the theory of chemical reactions initiated by hot atoms is therefore associated with the search for the distribution functions of the reacting species with respect to energies or velocities and internal states, or their distribution functions within the bulk of the target. In theoretical models describing the chemical effects of hot atoms, particular attention has been concentrated at the present time on the energy distribution of the retarding species in spatially homogeneous cases[5-9], and in addition on the spatial distribution of species under spatially inhomogeneous conditions.

Models used to describe the chemical effects of recoil atoms are described in the first place in the present review, since this field has now been developed fairly extensively. A characteristic feature of the models is their spatial restriction by independent factors with a homogeneous distribution of the sources of hot species in an infinite medium, account being taken only of the energy distribution of the recoil atoms or, more precisely, of their distribution with respect to kinetic energy.

The kinetics of non-equilibrium chemical hot-atom processes may be based on the Boltzmann, Pauli, or Liouville equations[11,12]. It has been pointed out that[11] the difficulty of the solution of the Liouville equations, the inapplicability of the Boltzmann equations to three-particle processes, and the obscure nature of the problem of the uniqueness of the solutions of these equations in the general case necessitate the hypothesis that the Pauli equation is the most promising for the description of the kinetics of non-equilibrium processes; this equation is particularly convenient in numerical methods of calculation.

However, mainly the Boltzmann integrodifferential equations have been used hitherto in hot-atom chemistry. A rigorous treatment taking into account the various effects accompanying the bombardment of targets by high-energy species requires the solution of integrodifferential transport equations with many independent variables (three spatial coordinates, two variables defining the direction of motion, and the energy and time variables). The problem is complicated by the fact that, if it is necessary to take into account secondary effects, the equations become non-linear.

The neglect of secondary processes is quite valid for low flux intensities of the bombarding species and small integral fluxes. If, in addition, one disregards the internal degrees of freedom, i.e. the colliding species are assumed to be material points, or the collision cross-sections and other quantities are averaged with respect to internal states (taking into account the statistical weights), then the behaviour of the entire set of species in a scattering and absorbing medium can be described on the basis of the laws of conservation of matter and energy by linear equations with independent variables: the radius-vector $\boldsymbol{r}$, the time t, the solid angle Ω, the energy E, or the velocity v.

The set of bombarding species may be characterised by the differential density or the differential vector flux; these quantities are linked by the equation $\rho(r, \Omega, E)v = \varphi(r, \Omega, E)$. The change in differential density or flux must depend on the ratio of the supply and loss of species in the region of phase space characterised by the quantities r, Ω, E. The supply is determined by independent sources, atom migration chain processes, and the scattering of species from neighbouring regions. The loss may occur as a result of slipping of the species from the external boundaries of the target, scattering, and capture by chemical or physical traps.

In many instances, one can disregard atom migration chain processes, whereupon the change in the differential density of species or the differential vector flux in the volume element dV with the energy of the species in the range dE and the direction of motion in the solid angle $d\Omega$ is defined by the following factors:

(1) the density of the sources $S(r, \Omega, E)$;

(2) the loss of species from the given volume element $\Omega \cdot \mathrm{grad}\varphi(r, \Omega, E)dV d\Omega dE$;

(3) the losses on scattering and absorption $\Sigma_t \cdot \varphi(r, \Omega, E)dV d\Omega dE$ ($\Sigma_t = \Sigma_S + \Sigma_r$, where Σ_r is the absorption cross-section and Σ_S the scattering cross-section);

(4) the increment in the number of species as a result of displacement or scattering from neighbouring regions of phase space with the coordinates (r, Ω', E'):

$$\int_{4\pi}\int_{0}^{\infty} \Sigma_s(\Omega', \Omega; E', E) \cdot \varphi(r, \Omega', E')\, d\Omega\, dE\, dV\, d\Omega'\, dE',$$

where $\Sigma_S(\Omega', \Omega; E', E)d\Omega\, dE$ is the scattering cross-section of the species with the energy E' and the direction of motion Ω', the direction of motion becoming Ω (in the range $\Omega - \Omega + d\Omega$) and the energy becoming E (in the range $E - E + dE$) after the collision. Hence the change in the differential density or the differential flux of the species must obey the equation

$$\frac{\partial \rho(r, \Omega, E)}{\partial t} = \frac{1}{v}\frac{\partial \varphi(r, \Omega, E)}{\partial t} = S(r, \Omega, E) - \Omega \cdot \mathrm{grad}\,\varphi(r, \Omega, E) + \int_{4\pi}\int_{0}^{\infty} \Sigma_s(\Omega', \Omega, E', E) \times \varphi(r, \Omega', E')\, d\Omega'\, dE' - \Sigma_t(E) \cdot \varphi(r, \Omega, E). \quad (I.2)$$

The rate of formation of recoil atoms may be assumed to be constant, except over long periods, where the loss of parent nuclei as a result of the reactions involving the formation of recoil atoms becomes significant. The constancy of the strength of the source of hot species makes it possible to treat the problem of the determination of $\rho(r, \Omega, E)$ or $\varphi(r, \Omega, E)$ as stationary, if one excludes from consideration also the region of very short times during which nearly stationary energy or spatial distributions of the species are established. This makes it possible to formulate the transport equation for hot species in the following way:

$$\Omega \cdot \mathrm{grad}\,\varphi(r, \Omega, E) + \Sigma_t(E) \cdot \varphi(r, \Omega, E) = S(r, \Omega, E) + \int_{4\pi}\int_{0}^{\infty} \Sigma_s(\Omega', \Omega; E', E)\varphi(r, \Omega', E')\, d\Omega'\, dE'. \quad (I.3)$$

If the target is isotropic and is so large compared with the paths traversed by the hot species before retardation in the region of chemical interaction and compared with the diffusion paths that it can be regarded as infinite and the boundary effects may be neglected, in particular the loss of species as a result of recoil or diffusion, one may eliminate from Eqn. (I.3) all spatial variables and average with respect to directions of motions quantities such as, for example, the scattering cross-sections. Under these conditions, the transport equation (I.3) may be reduced to the form:

$$\Sigma_t(E) \cdot \varphi(E) = S(E) + \int_{0}^{\infty} \Sigma_s(E', E) \cdot \varphi(E')\, dE', \quad (I.4)$$

where $\varphi(E)$ is the flux of species with the energy E and $\Sigma_S(E', E)$ the scattering cross-section with a change of energy from E' to a value in the range $E - E + dE$. Eqn. (I.4) is the initial equation for many specific forms of kinetic expressions in the chemistry of recoil atoms uniformly distributed within the space of infinite isotropic targets. In the case of recoil atoms, one usually operates with the density of the collisions of hot atoms with the atoms or molecules of the target and not with the fluxes of hot species. The collision density $\psi(E)$, i.e. the number of species colliding per unit volume per unit time, is related to the flux by the expression $\psi(E) = \varphi(E) \cdot \Sigma_t(E)$.

Evidently Eqn. (I.4) for the density of collisions can be written in the form:

$$\psi(E) = S(E) + \int_{0}^{\infty} \frac{\Sigma_s(E', E)}{\Sigma_s(E') + \Sigma_r(E')} \psi(E')\, dE'. \quad (I.5)$$

The applicability of Eqn. (I.5) is based not only on the stationary nature of the sources and $\psi(E)$, but also on the absence of non-uniformity in the spatial distribution of hot species due to the homogeneity of the distribution of the sources, the isotropic nature of the medium, and the large size of the target.

In order to obtain analytical solutions of equations of type (I.5), additional conditions are introduced in the chemistry of recoil atoms which vary as a function of the characteristics of the models proposed by a particular investigator. It is usually assumed that elastic collisions with the free atoms of the target at rest are of fundamental importance. For fairly high energies of hot atoms (recoil atoms usually have identical initial energies greatly exceeding the upper limit of the energy range of the chemical reactions), neglect of the thermal motions of the target atoms and the effects due to their chemical bonds cannot give rise to significant errors, but neglect of inelastic scattering can entail appreciable errors. However, in the range of energies not exceeding $E = (m/8m_e)I^*$ (where I^* is the ionisation potential and m_e and m are the masses of the electron and the hot atom), the energy losses in inelastic collisions, particularly in electronic excitation and ionisation, are small. The above hypotheses make it possible to simplify the expression relating $\Sigma_S(E')$ and $\Sigma_S(E', E)$.

Suppose that $g(E', E)dE$ is the probability that the species with the energy E' acquires after collision an energy in the range $E - E + dE$. Evidently $\Sigma_S(E', E) = \Sigma_S(E') \cdot g(E', E)$. Substitution of $\Sigma_S(E', E)$ in Eqn. (I.5) leads to the expression

$$\psi(E) = S(E) + \int_{E}^{E/\alpha} \frac{\Sigma_s(E')}{\Sigma_s(E') + \Sigma_r(E')} \psi(E')\, g(E', E)\, dE'. \quad (I.6)$$

The integration limits are determined by the quantities $\alpha = [(m - m_1)/(m + m_1)]^2$ which depend on the masses of the hot atom (m) and the target atoms (m_1). If $\alpha = 0$ or $\alpha \neq 0$ but $\alpha E_0 < E$, then the upper integration limit may be assumed equal to E_0; in other instances, the upper limit is E/α. Eqn. (I.6) makes it possible to take into account the change in collision density as a result of the "erosion" of the species from the energy spectrum in chemical processes, since it includes the reaction cross-sections $\Sigma_r(E)$. If the ratio $\Sigma_S(E')/[\Sigma_S(E') + \Sigma_r(E')]$ is expressed in the form $1 - \Sigma_r(E')/[\Sigma_S(E') + \Sigma_r(E')] = 1 - p_r(E')$,

where $p_r(E)$ is the probability of chemical reaction on collision of the recoil atom having the energy E, then it follows from Eqn.(I.6) that

$$\psi(E)=S(E)+\int_{E}^{E/\alpha}[1-p_r(E')]\cdot\psi(E')\cdot g(E', E)\,dE'. \quad (I.7)$$

For identical initial energies of all the recoil atoms, the source function of the hot species $S(E)$ can be written in the form $S(E)=S_0\delta(E_0, E)$, where $\delta(E_0, E)$ is the delta-function. Thus, for all $E\neq E_0$, the function $S(E)$ is zero. When $\Sigma_r(E)=0$, we have $p_r(E)=0$ and Eqn.(I.7) becomes

$$\psi(E)=S(E)+\int_{E}^{E/\alpha}\psi(E')\cdot g(E', E)\,dE'. \quad (I.8)$$

The quantities $g(E', E)$ may be estimated on the basis of the laws of mechanics[13-15]. The quantities $G(E', E)=\int_{\alpha E'}^{E} g(E', E'')dE''$, characterising the probability that the species having the energy E' before collision have an energy in the range $E-0$ after collision, are estimated similarly. If the scattering is isotropic, then we have for $E'>E>\alpha E'$

$$g(E', E)=\frac{1}{E'(1-\alpha)} \quad (I.9)$$

$$G(E', E)=\frac{E-\alpha E'}{E'(1-\alpha)}. \quad (I.10)$$

Using the value of $g(E', E)$ obtained, Eqns.(I.7) and (I.8) for elastic isotropic collisions may be transformed into

$$\psi(E)=S(E)+\frac{1}{1-\alpha}\int_{E}^{E/\alpha}\psi(E')\frac{dE'}{E'} \quad (I.11)$$

$$\psi(E)=S(E)+\frac{1}{1-\alpha}\int_{E}^{E/\alpha}[1-p_r(E')]\psi(E')\frac{dE'}{E'}. \quad (I.12)$$

Eqn.(I.11) has a simple asymptotic solution. The collision densities for energies less then E_0 are defined by the approximate expression

$$\psi_0(E)=S_0/\xi E, \quad (I.13)$$

where ξ is the average logarithmic energy loss in the collision. $\psi_0(E)$ can be regarded as the asymptotic solution of Eqn.(I.11) not only for billiard collisions but also for any elastic collisions, provided that account it taken of the dependence of $g(E', E)$, $G(E', E)$, and ξ on the form of the interaction potential. The asymptotic solution shows that, for any elastic collisions characterised by a spherically symmetrical potential, the collision density function decreases with increase of E; the nature of $\psi_0(E)$ depends on the form of the interaction potential through the function $\xi(E, \alpha)$.[16-21] In the general case, the average logarithmic energy loss in the collision can be represented by the formula

$$\xi=\overline{\ln\frac{E'}{E}}=\int_{\alpha E'}^{E'}\ln\frac{E'}{E}\cdot g(E', E)\,dE. \quad (I.14)$$

For the hard-core interaction potential, we have

$$\xi_{hs}=1+\frac{\alpha}{1-\alpha}\ln\alpha. \quad (I.15)$$

In a mixture of moderators, $\bar{\xi}=\sum_i f_i\xi_i$, where $f_i=\sigma_{si}N_i/\sum_j\sigma_{sj}N_j$ (N_j is the mole fraction of the component j) is the fraction of the collisions of the hot atoms with the component i and ξ_i is determined by the potential of the interaction of the hot atoms with the atoms i.

In non-absorbing systems, the asymptotic solution of equations of type (I.8) for sources with an arbitrary distribution spectrum (for example in β-decomposition) in terms of collision density is

$$\psi_0(E)=S(E)+\frac{1}{\xi E}\int_{E_{min}}^{E_{max}}S(E')\,dE', \quad (I.16)$$

where E_{max} is the maximum energy of the recoil atoms in the spectrum. For energies less than the minimum value, we have in the spectrum

$$\psi_0(E)=S_0/\zeta E, \quad (I.17)$$

where $S_0=\int_{E_{min}}^{E_{max}}S(E')dE'$. If the non-absorbing medium contains a mixture of moderating atoms, then Eqn.(I.11) can be written as follows:

$$\psi(E)=S(E)+\sum_i\int_{E}^{E/\alpha_i}f_i\psi(E')\frac{dE'}{E'(1-\alpha_i)}. \quad (I.18)$$

If the ratio $\sigma_{si}/\sum_j\sigma_{sj}$ is independent of the energy, the asymptotic solution of Eqn.(I.18) for a monochromatic source is

$$\psi_0(E)=S_0/\bar{\xi}E. \quad (I.19)$$

In the general case, considerable mathematical difficulties arise in the solution of Eqn.(I.7) for absorbing systems. An exact and fairly simple analytical solution is available only for $\alpha=0$, when there are no oscillations in the collision density near the sources and the upper integration limit, involving in the general case the variable E, is replaced by E_0. For a monochromatic source and $E\ll E_0$, the asymptotic solution is

$$\psi_0(E)=\frac{S_0}{E}[1-p_r(E_0)]\exp\left[-\int_{E}^{E_0}\frac{p_r(E')}{E'}dE'\right]. \quad (I.20)$$

In the β-decomposition, where the recoil atoms have a definite distribution with respect to E_0, it is particularly important to obtain a solution of Eqn.(I.7) for an arbitrary source $S(E)$. The solution is

$$\psi_0(E)=S(E)+\frac{1}{E}\int_{E}^{E_{max}}[1-p_r(E')]S(E')\cdot\exp\left[-\int_{E}^{E'}p_r(E'')\frac{dE''}{E''}\right]dE. \quad (I.21)$$

Solutions (I.20) and (I.21) show that, owing to "erosion" during absorption, the flux of hot species increases more slowly with decrease of the energy than would be expected from the $1/E$ law. In particular, if the ratio $\Sigma_s(E)/\Sigma_r(E)$ is independent of the energy and close to C, the flux for low energies is proportional to $E^{-C/(1+C)}$; the corresponding collision density is

$$\psi(E)\propto\frac{S_0}{\xi E^{\frac{C}{1+C}}}. \quad (I.22)$$

In those cases where $\alpha\neq 0$, fairly complex relations were obtained in the solution of equations (I.7) and (I.12).[22] Instead of complex solutions, one can employ in many instances simple Wigner and Fermi approximations[23].

Their use is possible, firstly, when the initial energy of the species is fairly high and the absorption region with the boundaries E_1 and E_2 lies considerably lower and, secondly, when absorption leads to a weak perturbation of the spectrum of hot species. This corresponds to a very weak absorption when $\Sigma_r < \Sigma_s$ or to absorption due to strong but well resolved resonances; the width of the resonances should then be small compared with the values of $\ln(1/\alpha)$ and the distances between the individual resonances should greatly exceed $\ln(1/\alpha)$. When the above conditions are fulfilled, one can neglect non-asymptotic oscillations near the sources of hot species and also near the absorption zone, which may be regarded as a negative source with possible non-asymptotic oscillations, and an approximate solution may be used. The solution is of the form

$$\psi_0(E) = q(E)/\xi E, \tag{I.23}$$

where $q(E)$ is the retardation density, i.e. the number of species retarded per cm^3 per second down to energies below E. In the general case, the following expression is valid for $q(E)$:

$$q(E) = \int_E^{E/\alpha} [1 - p_r(E')] \cdot \psi(E') \cdot G(E', E)\, dE'. \tag{I.24}$$

In non-absorbing media, $q(E) = S_0$ for a monochromatic source and $q(E) = \int_E^{E_{max}} S(E')dE'$ for an arbitrary source. In absorbing media with $\alpha = 0$, we have

$$q(E) = S_0[1 - p_r(E_0)] \exp\left[-\int_E^{E_0} \frac{p_r(E')}{E'} dE'\right] = S_0 p(E) \tag{I.25}$$

for a monochromatic source and

$$q(E) = \int_E^{E_0} S(E')[1 - p_r(E')] \exp\left[-\int_E^{E'} \frac{p_r(E'')}{E''} dE''\right] dE' \tag{I.26}$$

for an arbitrary source. Here $p(E)$ is the probability of avoiding capture in the retardation process until the attainment of the specified energy. In terms of the Wigner–Fermi approximation, we obtain the following expression for absorbing systems with $\alpha \neq 0$ and a monochromatic source when $p_r(E_0) \simeq 0$:

$$q(E) = S_0 p(E) = S_0 \exp\left[-\int_E^{E_0} \frac{p_r(E')}{\xi E'} dE'\right]. \tag{I.27}$$

The chemical effects of the recoil atoms can be described also in terms of other approximations obtained in neutron physics. In particular, for a flux subjected to only a slight perturbation under conditions where the cross-section Σ_r varies only slightly with the energy, one can probably employ the Goertzel–Greuling approximation[24], according to which the following expression is valid for $p(E)$:

$$p(E) = \exp\left[-\int_E^{E_0} \frac{\Sigma_r}{\xi\Sigma_s + \gamma\Sigma_r} \frac{dE'}{E'}\right], \tag{I.28}$$

where $\gamma = 1 - \alpha \ln^2(1/\alpha)/2(1-\alpha)\xi$; for example, when $\Sigma_r(E) \sim E^{1/2}$, $\Sigma_s(E) = \text{const.}$, and $E_0 \to \infty$, we have

$$p(E) = \left[1 + \frac{\gamma}{\xi} \frac{\Sigma_r(E)}{\Sigma_s}\right]^{-2/\gamma}.$$

For an absorbing medium containing the components j, each of which may be involved in chemical reactions, the solutions of equations of type (I.7) for $\psi(E)$ are formulated as follows in terms of the Wigner–Fermi approximation:

$$\psi_0(E) = \frac{S_0}{\xi E} \exp\left[-\sum_j \int_E^{E_0} \frac{f_j p_{rj}(E')}{\xi E'} dE'\right]. \tag{I.29}$$

Many investigators of hot-atom chemistry also use the quantities $n(E)$ as functions characterising the distribution of species with respect to energy, together with the collision density $\psi(E)$ and the flux of the species $\varphi(E) = [1/\Sigma_t(E)]\psi(E)$; $n(E)dE$ is the number of collisions of the hot atom in the range from E to $E + dE$. If the source of recoil atoms is monochromatic, then $n(E) = \psi(E)/S_0$. Transport equations and their solutions of the same types as those quoted previously for $\psi(E)$ and $\varphi(E)$ are valid for $n(E)$. One may also note that the velocity v or the lethargy $\ln(E_0/E)$ may be used as variables instead of E.

2. Porter's Equations for the Integral Probability of Hot-atom Reactions

Equations analogous to Eqns. (I.7) or (I.8) can be obtained by the direct determination of the probability of the transfer of a specified energy in the elementary collision step[9,25]. The method led to the creation of Porter's phenomenological theory of the "integral reaction probability"[9,26], which is particularly interesting because it makes it possible to take into account the thermal motion of the molecules or atoms of the bombarded targets, at least in numerical computer calculations. Evidently the probability that a hot atom with the energy E' retains the energy E after the first collision can be represented as the ratio of the differential cross-section $\Sigma_s(E', E)$ to the sum of the average cross-sections $\Sigma_s(E')$ and $\Sigma_r(E')$; the cross-sections are averaged taking into account the distribution functions for the relative velocities of the colliding species v_{rel}; they can also be averaged taking into account the energy (for example Maxwellian) distribution of the target species. Then, for a particular angle γ between the vectors of the velocities v_1 and v, we have

$$g_1(E', E) = \frac{\int \Sigma_s(E', E, v_1, \gamma) \cdot v_{rel} \cdot \Omega(E', v_{rel})\, dv_{rel}}{\int [\Sigma_s(v_{rel}) + \Sigma_r(v_{rel})] v_{rel} \cdot \Omega(E', v_{rel})\, dv_{rel}}, \tag{I.30}$$

where $\Omega(E', v_{rel})$ can be determined in terms of Eqn. (II.35) (see below) when the target has a Maxwellian spectrum. For arbitrary cross-sections, $g_1(E', E)$ may be calculated numerically; in the case of an elastic isotropic collision with species at rest and in many other specific instances, an analytical determination of $g_1(E', E)$ is possible (see subsection 1 of this Section)

It is also evident that the following expressions are valid for the analogous probabilities for two, three, and n collisions:

$$g_n(E', E) = \int_0^{\infty} g_{n-1}(E', E') \cdot g_1(E'', E)\, dE''. \tag{I.30a}$$

For a monoenergetic source, we have

$$g_0(E', E) = \delta(E', E). \tag{I.30b}$$

The average number of collisions of the species in the energy range $E-E+dE$, when the first collision occurs for the energy E', can be determined in terms of $g_n(E', E)$ as follows:

$$n(E', E)dE = \sum_n g_n(E', E)dE. \tag{I.31}$$

Substitution of Eqns. (I.30a) and (I.30b) in (I.31) yields

$$n(E', E)=\delta(E', E)+\int_0^\infty n(E', E'')g_1(E'', E)\,dE''. \quad (I.32)$$

If it is assumed that $p_r(E) = \Sigma_r(E)/\Sigma_t(E)$ and $g(E', E) = \Sigma_s(E', E)/\Sigma_s(E')$, it follows from Eqn. (I.30) that

$$g_1(E', E)=[1-p_r(E')]\cdot g(E', E). \quad (I.33)$$

Then

$$n(E', E)=\delta(E', E)+\int_0^\infty [1-p_r(E'')]\cdot g(E'', E)\cdot n(E', E')\,dE''. \quad (I.34)$$

Thus an expression analogous to Eqn. (I.7) is obtained for the function $n(E', E)$.

The solution of transport equations for the flux of the species, the collision density, the retardation density, or another equivalent distribution function of hot species opens a pathway for solving the problem of the determination for the rates and probabilities of the reactions or their yields and also to the analysis of parametric relations governing the above quantities. However, the estimation of the distribution function of hot species with respect to energy is not obligatory for the determination of the probability of the chemical reaction [9,27-30].

If the probability of the chemical interaction in the nth collision of the hot atom $P_n(E')$ is introduced, then evidently the probability of chemical stabilisation is defined as follows when account is taken of all the collisions for E':

$$P(E')=\sum_n P_n(E'). \quad (I.35)$$

However, it is also evident that

$$P_n(E')=\int_{E_1}^{E_2} g_{n-1}(E', E)\,p_r(E)\,dE. \quad (I.36)$$

Substitution of Eqn. (I.36) in Eqn. (I.35) and transformations of $P_n(E)$ analogous to those performed for $g_n(E', E)$ (see above) lead to the expression

$$P(E')=p_r(E')+[1-p_r(E')]\int_{E_1}^{E'} g(E', E)P(E)\,dE. \quad (I.37)$$

For isotropic scattering and $\alpha = 0$, Eqn. (I.37) becomes

$$P(E')=\bar{p}_r(E)+\frac{1-p_r(E')}{E'}\int_{E_1}^{E'} P(E)\,dE. \quad (I.38)$$

The solution of Eqn. (I.38) yields

$$P(E')=1-[1-p_r(E')]\exp\left[-\int_{E_1}^{E'} p_r(E)\frac{dE}{E}\right]. \quad (I.39)$$

For anisotropic scattering, mainly at small angles, or for isotropic scattering and α close to unity, one obtains

$$P(E')=1-\exp\left\{-\int_{E_1}^{E'}\frac{p_r(E')\,dE'}{E'[1-p_r(E')]\int_0^{E'} g(E', E)(1-E/E')\,dE}\right\}. \quad (I.40)$$

The solution (I.39) is the same as the value obtained under analogous conditions in the determination of P in terms of the distribution functions with respect to energy. In the general case, Eqn. (I.37) can be solved for P by numerical, in particular iterative, methods, and $p_r(E)$ constitutes the first approximation [9,26,31].

For systems containing several components (i, z) involved in several types of reactions (j, x), $P(E)$ is defined by the equation

$$P_{ix}(E')=f_i(E')p_{rix}(E')+\int_0^\infty H(E', E)\cdot P_{ix}(E)\,dE, \quad (I.41)$$

where

$$H(E', E)=\sum_{z=1}^{N_r} f_z(E')\left[1-\sum_{j=1}^{\rho_z} p_{rzj}(E')\right]g_z(E', E)+\sum_{z=1}^{N_m} f_z(E')g_z(E', E),$$

N_m is the number of moderators, N_r the number of reactants, ρ_z the number of reaction channels for the component z, and p_{rix} the probability of a reaction of type x with the component i. The method for the numerical solution of Eqns. (I.37) and (I.41) has been examined [31] with a quantum-mechanical description of elastic scattering.

Thus, without resorting to a preliminary determination of the distribution functions for the energy in terms of Boltzmann equations, one can obtain from the equations for the integral reaction probability in terms of analogous approximations (at least the simplest approximations) expressions relating the probability of chemical reactions to functions and parameters such as $p_r(E)$, $g(E', E)$, and E_0. However, this does not imply that the energy distribution functions of different species are no longer of any interest in hot-atom chemistry. Their determination is important, since, firstly, fairly well developed methods are now available for the solution of the Boltzmann equations, i.e. for the determination of the corresponding distribution functions and, secondly, the parametric relations found from the distribution functions, in particular the variation of $n(E)$ and $\psi(E)$ with the initial recoil energy and with the concentration of moderators, may reflect the corresponding parametric relations for the probability of chemical reactions.

The application of the stochastic method to the solution of non-stationary problems made it possible to obtain a number of kinetic equations describing the behaviour in time of the energy distribution function of the hot atoms [32]. For a stochastic description of time variations, it is important that the lifetime of the hot atom (t) is proportional to the number of its collisions (n) and the average time interval between them (τ): $t = n\tau$; $dt \simeq (n+1)\tau - n\tau = \tau$. In the general case, Keizer [33] describes the variation of the density of hot atoms involved in the reactions by kinetic equations with a quasi-rate constant $k(t)$. If only a small proportion of the collisions lead to chemical absorption and $k(t) < \tau^{-1}$, the distribution is stationary. Under stationary conditions, the change in the number of hot atoms (n) and the yield of products (R_i) are described by the simple equation $R_i = k_i n/\sum_i k_i$ and $dn/dt = \sum_i k_i n$, where k_i is inversely proportional to τ. Thus, in the case of stationary distributions, the absorption of hot species is described by pseudofirst-order equations and the reaction rate constants have been shown [33] to correspond to an effective temperature T^* determined by the parameters of the energy distributions of the hot species. The following expression has been obtained for light atoms ($m \ll m_i$) and the average energy of chemical reactions $\langle\epsilon\rangle_r$:

$$k=C(T^*)^{-3/2}\exp\left[\frac{\langle\epsilon\rangle_r}{k_B T^*}\right], \quad (I.42)$$

where the constant C may depend on the temperature of the surrounding medium. It is significant that, depending on the reactivity of the system, the effective temperature T^* may be close to the temperature of the target or higher.

II. THE APPLICATION OF KINETIC EQUATIONS IN THE CHEMISTRY OF RECOIL ATOMS

1. Kinetic Relations for Elastic Isotropic Scattering

The kinetics of recoil atoms were first described by Libby [34] and Miller and Dodson [35,36]. Apart from the hypotheses about the isotropic nature of the medium, the elastic billiard collisions with atoms at rest, etc., the hypothesis of a definite role of the energy of the reaction cell or the liquid cage (ϵ) in chemical stabilisation has been used to estimate the probability of the retention of hot atoms. The model postulates additional conditions for the formation of a stable chemical bond in reactions involving substitution by recoil atoms: the energy transmitted to the atom displaced from the molecule must exceed the energy of its chemical bond (ν); the recoil atom must then have an energy $E < \epsilon$. Under these conditions, the probability of retention is defined as follows:

$$P = \frac{\int_{\nu}^{E_0} f_i \psi(E) \frac{\varepsilon}{E} \mathrm{d}E}{\sum_i \int_{\nu/\alpha_i}^{E_0} f_i \psi(E) \frac{\nu - \alpha_i E}{E(1-\alpha_i)} \mathrm{d}E} . \qquad \text{(II.1)}$$

In order to determine $\psi(E)$, one can employ methods examined previously. The form of the solution (II.1) depends on ν, α, and E_0. Analysis of the solutions obtained led to the conclusion that the probability of the chemical stabilisation of hot atoms is independent of their initial energy in all cases except those where account must be taken of collisions for $\alpha \neq 0$ when $\alpha E_0 < \nu$. The expressions obtained by Miller and Dodson also define the form of the dependence of the retention of hot atoms on the composition of two-component systems. It is significant that $P(E) \propto R$ increases in the presence of a second component having atoms with masses different from m (Fig.1).

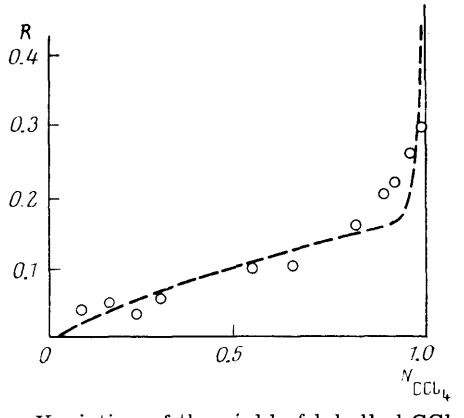


Figure 1. Variation of the yield of labelled CCl_4 with its mole fraction in a mixture with benzene; dashed curve—calculation; circles—experiment.

The characteristic features of the Miller–Dodson model are its applicability for relatively low recoil energies; their are no limitations on E_0 of the kind which occur in other models.

Postulates analogous to those put forward by Miller and coworkers [35,36] have been used by Capron and Oshima [37]. Analysis of the probability of retention for different ratios of E_0, ϵ, and ν led them to the conclusion that the dependence of R on E_0 may be manifested only for low initial energies and $\alpha \neq 0$ (Fig. 2). A similar method for the estimation of R was subsequently developed by Nesmeyanov and Borisov [38].

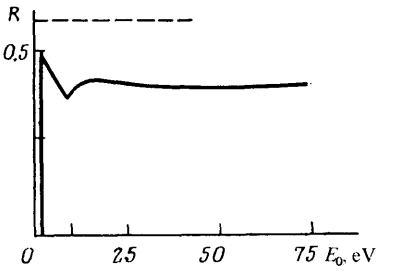


Figure 2. Variation of the yields of substitution products with the initial energy of hot atoms; continuous curve—$\alpha = 0.5$; dashed line—$\alpha = 0$.

Considerable progress in the theoretical interpretation of experimental results in the chemistry of recoil atoms has been achieved as a result of studies by Wolfgang and Estrup [7,8]. The "kinetic theory" of hot-atom reactions developed by these investigators is based mainly on the hypotheses used previously [35,36], but only instances with fairly high initial energies (exceeding the upper threshold for chemical reactions) were considered for a weak perturbation of the particle flux by chemical "erosion" [23]. It was assumed that, without reacting chemically, the recoil atoms undergo repeated elastic scattering and are retarded to energies below $\alpha^3 E_0$ or E_2. When the above conditions are fulfilled for weakly absorbing media, one can adopt the Wigner–Fermi approximation, according to which the solution of the transport equation for the values of $n(E)$ used by Wolfgang and Estrup can be formulated as follows:

$$n(E) = \frac{1}{\xi E} \exp\left[-\sum_I \int_E^{E_2} f_I \frac{p_{rI}(E')}{\xi E'} \mathrm{d}E' \right] . \qquad \text{(II.2)}$$

Substitution of the values of $n(E)$ obtained in equations of type (I.1) yields

$$P = \sum_I \int_{E_1}^{E_2} f_I \frac{p_{rI}(E)}{\xi E} \cdot \exp\left[-\sum_I \int_E^{E_2} \frac{f_I p_{rI}(E')}{\xi E'} \mathrm{d}E' \right] \mathrm{d}E . \qquad \text{(II.3)}$$

The Wolfgang–Estrup approximation, corresponding to small perturbations of the flux of hot atoms as a result of chemical absorption or the presence of sources, holds more exactly the lower the value of E compared with E_0 and the greater the difference between E and the resonance absorption energies. The accuracy of the determination of P increases with decreased reactivity of the medium, characterised by the quantity $\int f p_r(E) n(E) \mathrm{d}E$. In the derivation of Eqn. (II.3), it was assumed that f and ξ are independent of energy; this condition is fulfilled fairly reliably for f. Although σ_{sj} is a function of energy, the

variation of the ratio $\sigma_{sj}N_j/\sum_j \sigma_{sj}N_j = f_j$ with the energy may be neglected. The hypothesis of the constancy of ξ is fulfilled only in specific instances, for example for isotropic scattering or when $g(E', E) \propto (1/E').\Phi(E/E')$. This limits the region of applicability of the kinetic theory and can lead to significant errors in the determination of the probability of chemical reactions when the methods of kinetic analysis based on this model are used.

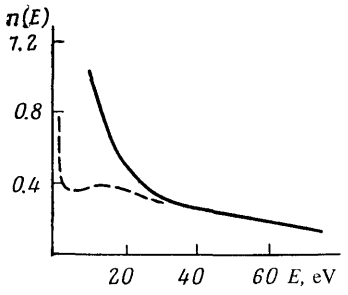


Figure 3. Variation of the number of collisions $n(E)$ in inert systems (continuous curve) and in chemical absorption of hot atoms (dashed curve).

It follows from Eqn. (II.2) that, in the range of energies $E_2 \geqslant E$, the collision density corresponding to the specified energy E decreases owing to the chemical reactions and the curves describing the collision density may have extrema, which are particularly distinct in the absence of moderators (Fig. 3).[39] In the Wolfgang–Estrup approximation for systems where the values of $p_r(E)$ or f are significant for only one component (for example, in mixtures with an inert moderator or in the presence of small amounts of added scavengers), the probability of the retention of hot atoms is described by the equation

$$P = 1 - \exp\left[-\frac{f/}{\xi}\right] = \frac{f}{\xi} I - \frac{f^2}{\xi^2} K + \frac{f^3}{\xi^3} L - \ldots \qquad \text{(II.4)}$$

Similar equations can be obtained for the probabilities of the formation of the individual products P_i. The terms of the series (II.4) have the coefficients

$$A_{nl} = \frac{1}{n!} \int_{E_1}^{E_2} \frac{p_{rj}(E)}{E} \left[\int_{E}^{E_2} \frac{\sum_j p_{rj}(E')}{E'} \, dE' \right]^n dE, \qquad \text{(II.5)}$$

where $A_{0i} = I_i$, $A_{1i} = K_i$, $A_{2i} = L_i$, etc.[40] Since the series converges rapidly, primarily because of the smallness of $(f/\xi)^{n+1}$, there is no necessity to take into account more than two–three terms of the expansion.

The quantity I_j characterises the integral probability of the formation of the product j in the range of energies $E_2 - E_1$ and reflects the form of the excitation function $p_{rj}(E)$. In the simplest case with a weak energy dependence of $p_r(E)$ we have $\bar{p}_r = I/\ln(E_2/E_1)$ over the entire $E_2 - E_1$ range. The yield of the chemical reaction is not only a function of the probability of the reaction on collision with the species having the energy E, but is also determined by the probability that the hot atom is not absorbed in the process involving retardation until the attainment of the energy E. The terms of the series (II.5) containing K, L, etc. take into account the weakening of the flux of hot atoms owing to their absorption in the range $E_2 - E$. The role of such correction terms is particularly marked in the estimation of the yield of products formed in the lower range of the energy spectrum. The quantities K or L yield information about the energy ranges where the values of $p_r(E)$ are non-zero (see below).

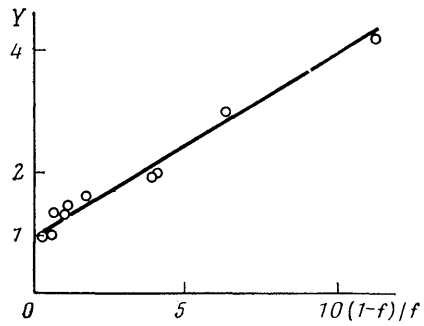


Figure 4. Variation of $y = [-1/\ln(1 - P)]$ in the $He-C_3H_8$ system with $(1 - f)/f$.

Equations of type (II.1)–(II.5) constitute the basis of the kinetic analysis (of the first and second kind) of the experimental data whereby a systematic treatment of a wide range of results can be achieved using several simple parameters (I, K, and ξ_r), measured in units of ξ_m (the subscripts r and m refer to the reactant and the moderator). For mixtures containing an inert moderator in addition to the reacting component, where $\xi = f_r\xi_r + (1 - f_r).\xi_m$, it follows from Eqn. (II.4) that

$$-\frac{1}{\ln(1-P)} = \frac{\xi_r}{I} + \frac{\xi_m}{I}\frac{1-f_r}{f_r}. \qquad \text{(II.6)}$$

When the relation between $-[1/\ln(1 - P)]$ and $(1 - f_r)/f_r$ (Fig. 4), involving the experimental yields of hot-atom reactions, is linear, Eqn. (II.6) can be used to estimate I and ξ_r, as well as ξ_{m_1}/ξ_{m_2}.[8,41,42] According to the kinetic theory, in mixtures with different moderators the following expression is valid for the ratio of the yields of products i and j:

$$\frac{I_i/\xi_{m_1}}{I_j/\xi_{m_1}} = \frac{I_i/\xi_{m_2}}{I_j/\xi_{m_2}} \qquad \text{(II.7)}$$

although the quantities I_i, expressed in units of ξ_{m_1} or ξ_{m_2}, are different. The equation

$$\frac{\xi P_i}{f_r} = I_i - \frac{f_r}{\xi} K_i, \qquad \text{(II.8)}$$

which is a corollary of Eqn. (II.4), makes it possible to determine I_i and K_i from the corresponding experimental linear relations (Fig. 5). Estimates of the K_i in individual cases[40,43,44] permit conclusions concerning the energy ranges within which various products are formed. According to Baker et al.[43], $F_i = 1 + (\frac{1}{2}I_i^2 - K_i)/[I_i(I - I_i)]$ is a criterion for the estimation of the energy ranges. If reactions (A) have a non-zero value of $p_r(E)$ in the energy range wholly above the corresponding range for reactions (B), then $K_{A,min} = \frac{1}{2}I_A^2$ and $F_A = 1$. When the energy

ranges are the same, $K_A = \frac{1}{2}I_A(I_A + I_B)$ and $F_A = 0.5$. If the energy range for reactions (A) is below that for reactions (B), then $K_{A,max} = I_A I_B + \frac{1}{2}I_A^2$ and $F_A = 0$. Methods for the comparison of the energy ranges for competing processes have been developed by Urch and coworkers[40, 44,45]. The quantities $F^* = (K - I^2/2)/(K_{max} - I^2/2)$, where $F_i^* = (K_i - I_i^2/2)/(K_{i,max} - I_i^2/2)$, varying in the range from 0 to 1, may be used as the principal criterion; all the intermediate values should correspond to overlapping energy ranges; when $F_A^* = 0$, the energy range for reactions (A) is higher than for reactions (B); when $F_A^* = 1$, the energies for which $p_{rA}(E) > 0$ lie below the corresponding energies for reactions (B).

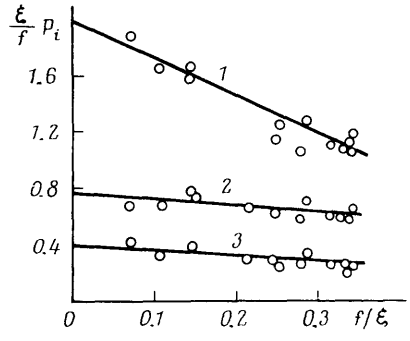


Figure 5. Variation of the probability functions for the formation of labelled products (ξ/fP_i) with the composition of the $He-C_3H_8$ mixture (f/ξ): 1) HT; 2) C_3H_7T; 3) remaining products.

The development of methods for kinetic analysis has led to a number of important conclusions for the interpretation of the results of experiments on the stabilisation of recoil atoms in binary and more complex systems. The prospects for the application of the first approximations of the kinetic theory in the analysis of experimental data for binary mixtures of weak or strong absorbers with $p_{rz}(E) = Cp_{ry}(E)$ and $P_y/P_z = f_y/C.f_z$ were examined by Wolfgang[8], who demonstrated the possibility of estimating ξ_y/I_y, ξ_z/I_z, and ξ_y/ξ_z. Differentiation of the equations obtained by Wolfgang with respect to N (N is the mole fraction of component y), assuming that $\bar{p}_r = I/\ln(E_2/E_1)$, showed that the second derivatives $\partial^2 P_z/\partial N^2$ and $\partial^2 P_y/\partial N^2$ may be non-zero.[46-49] Thus the possibility of the deviation of the yields in binary systems from additivity when $\xi_z \neq \xi_y$ or $p_{ry} \neq p_{rz}$ has been established by the analysis of the second derivatives. The causes of the deviations from additivity are evident; for example, the introduction of component z with $\xi_z < \xi_y$ causes an increase of the number of collisions in the range E_2-E_1, which leads to an increase of P_y.

Since systems containing an inert moderator and a radical acceptor in addition to the reactant are most frequently investigated experimentally in hot-atom chemistry, kinetic analysis of three-component systems is of greatest interest. Methods have now been developed for correcting the results of kinetic analysis to allow for the characteristics of the third component (R).[50-54] For mixtures where this component also fulfills effectively the functions of a moderator, the kinetic analysis can be performed using equations of the type

$$-\frac{1}{\ln(1-P)} = \frac{\xi_r}{I} + \frac{\xi_m}{I}\,\frac{f_m + \frac{\xi_R}{\xi_m}f_R}{f_r}. \qquad (II.9)$$

The presence of a scavenger may also affect the results of the kinetic analysis if the scavenger interacts chemically with the recoil atoms in the hot region[51-54]. Under these conditions, the role of the scavenger is determined by the derivatives $dP/df_R = -f_r K'/\xi^2$, $dP_i/df_R = -f_r K_i'/\xi^2$, or $Y_i = (1/\xi)(df_R/dN_R)(K_i'/I_i)$. Y_i characterises the overlapping of the excitation functions for reactions with the scavenger and the reactant, leading to the formation of the product i. The role of the competing scavenger is particularly marked when it is present in large amounts or in the presence of large amounts of a relatively ineffective moderator, where the number of collisions in the hot region is large[51,53]. It follows from Malcolme-Lawes' results[53] that in such cases one can write for $f_r \ll 1$

$$P = 1 - \exp\left(-\frac{f_r}{\xi}I - \frac{f_r f_R K'}{\xi^2}\right),$$
$$P_i = \frac{f_r}{\xi}I_i - \left(\frac{f_r}{\xi}K_i' + \frac{f_R}{f_r}K_i'\right), \qquad (II.10)$$

where

$$K' = \int_{E_1}^{E_2} \frac{p_r(E)}{\xi}\left(\int_{E'}^{E_2}\frac{p_{rR}(E'')}{E''}dE''\right)dE'\,dE;$$
$$K_i' = \int_{E_1}^{E_2} \frac{p_r(E)}{E}\left(\int_{E'}^{E_2}\frac{p_{rR}(E'')}{E''}dE''\right)dE'\,dE.$$

The equations obtained may be used to correct the results of a kinetic analysis which does not allow for the influence of radical acceptors on the yields of hot-atom reactions:

$$I_i = I_{i0} + f_R K_i',$$
$$K_i = K_{i0} + (\xi_r - 1)f_R K_i', \qquad (II.11)$$
$$\frac{\xi_r}{I} = \frac{\xi_{r0}}{I_0}$$

(the subscript zero refers to the results before correction).

Analysis of experimental data based on the kinetic theory led to a deeper understanding of the specific features of hot-atom reactions, their parameters, mechanisms, and kinetics. Without considering in detail the results thus obtained, which have been discussed in a number of reviews[1,2,5,55], we may note that kinetic analysis has yielded proof of the dependence of the quantities ξ_r and ξ_r/ξ_m on the energies of hot species and molecular structure[56]; evidence has also been obtained for a complex mechanism of the action of inert gas moderators, which are involved not only in the relaxation processes of hot atoms, but also in the deactivation of the excited products and their dissociation in collisions[57-60]. Interpretation of the experimental data on the basis of the kinetic theory yielded information about the nature of the excitation functions, about the relation between the energy ranges where the excitation functions for various reactions are significant[44,45], and about the relative widths of the energy ranges for reactions in the presence of various moderators[51]. The problem of the involvement of radical acceptors in hot-atom reactions[53,54] and a number of problems concerning the mechanisms of such reactions and the reactivity of various compounds[45] have been solved using the methods of kinetic analysis.

Thus the possibility of employing the approximate Wolfgang–Estrup model and the fruitfulness of methods of kinetic analysis in the interpretation of experimental results, obtained in the first place for gaseous systems, have thus been confirmed. At the same time, the limits of the applicability of the kinetic theory and its disadvantages were discovered in the course of developing methods for kinetic analysis and their employment. Thus it has been shown that the linear relations between $1/\ln(1-P)$ and $(1-f_r)/f_r$ or between $\xi P_i/f_r$ and f_r/ξ do not constitute a reliable criterion of the correspondence of the model to real systems. According to Malcolme-Lawes and Urch[61], the above relations hold even if the fundamental conditions for the applicability of the Wolfgang–Estrup theory are not fulfilled. Not all the *a priori* conclusions of the theory have been confirmed experimentally. In particular, in contrast to the expected Eqn. (II.7), the following experimental relation has been found for the reactions involving the abstraction and substitution of hydrogen by hot tritium atoms[62–64]:

$$\frac{I_{HT}/\xi_{He}}{I_{RT}/\xi_{He}} > \frac{I_{HT}/\xi_{Ne}}{I_{RT}/\xi_{Ne}}.$$

The majority of the above contradictions arise because the Wolfgang–Estrup model does not take into account the anisotropic scattering and the corresponding $\xi(E)$ relation or the complexity and the many-sided nature of the action of moderators and scavengers and the influence of secondary processes.

Model calculations using the Monte Carlo method and computers have been very important in determining the limits of the applicability of the kinetic theory and of the physical significance of the kinetic parameters obtained in kinetic analysis (I, K, ξ_r).[54,61,65,66]. The simulation of the behaviour of recoil atoms is based on the hypothesis put forward by Wolfgang and Estrup concerning elastic scattering, which makes it possible to assume an equal-probability distribution of energy losses in the range from zero to $E_0[1-\exp(-2\xi)]$. Thus, by selecting the random numbers u_i, it is possible to determine the energy of the hot atom after the ith elastic collision: $E_i = E_{i-1} \cdot \exp(-2\xi u_i)$. On the other hand, simulation by the Monte Carlo method makes it possible to introduce into computational schemes new postulates concerning the nature of not only the $p_r(E)$ relation but also $\xi_m(E)$ or $\xi_r(E)$; in particular, a Gaussian function has been used: $p_{ri}(E) = h_i \exp[-(E-a_i)^2/c_i^2]$. Methods of kinetic analysis, whereby the quantities P, I, and K can be estimated for the specified parameters $p_r(E)$, $\xi_r(E)$, $\xi_m(E)$, etc. were subsequently applied to the results of the numerical calculation of the probability of chemical reactions in terms of the fraction of absorbed species[61]. The calculations showed that, for low and even considerable reactivities of the components but with values of ξ which are constant in the energy range investigated, the kinetic analysis based on the Wolfgang system is justified. The parameters ξ_r, I, and K obtained by this procedure reflect (the first two less satisfactorily) the physical properties of the test objects, in particular the excitation functions. If ξ_r and ξ_m vary but their ratio remains constant in the experimental energy range, the results of the kinetic analysis require a complex interpretation. If ξ_m/ξ_r varies in the energy zone of hot-atom reactions, the employment of the Wolfgang methods leads to erroneous results. The reliability of the estimates of the kinetic parameters depends also on the degree of overlapping of the energy ranges of different chemical reactions. The overlapping of the function $p_{ri}(E)$ has a particularly strong effect on the values of K_i; the distortion of the K_i data becomes more pronounced with increase of ξ_r. The simulation data showed that one of the fundamental conditions for the improvement of the kinetic theory is allowance for the variation of ξ with the energy E.

Summarising the discussion of the application of methods of kinetic analysis, one must consider several of the most significant factors which are bound to determine the further development of theoretical studies in hot-atom chemistry.

1. The Wolfgang–Estrup model does not take into account the thermal motion of the species of the medium and is valid only for atoms with a high initial energy ($E_0 > E_2$); the extension of the application of kinetic analysis to the description of photochemical, radiation-chemical, etc. phenomena requires the removal of the above limitations.

2. The improvement of the kinetic theory and of kinetic analysis should lead to the description of the relaxation processes of the excited products of hot-atom reactions, which were not considered in the Wolfgang–Estrup theory.

3. The results of kinetic analysis depend greatly on the values of ξ. The postulate of isotropic scattering, characterised by the quantity ξ_{is}, which is independent of the energy of the hot species, does not satisfy the conditions in real systems. The Wolfgang–Estrup model does not take into account two factors, namely the occurrence of non-elastic relaxing collisions and elastic but anisotropic collisions with small energy losses per collision. The role of the non-elastic scattering component is particularly marked for polyatomic molecules, since to a first approximation the contribution of non-elastic collisions is determined by the ratio $M/(M+m)$ (M is the mass of the molecule). However at the present time there is no adequately developed theory whereby one could take into account non-elastic collisions in analytical solutions of transport equations for hot atoms; the yield of the products of hot-atom reactions has not been analysed taking into account the non-elastic scattering component. The attempts to estimate the values of ξ for complex polyatomic molecules have not been successful either. When two polar postulates are adopted, namely that the molecules can be regarded as collections of individual atoms or that the molecules are involved in collisions as simple particles with mass M, the calculated values of ξ do not agree with experimental data. For *a priori* estimates of the energy loss in non-elastic collisions of hot atoms, one of the most promising procedures is the method of statistical tests[61,66] and the analytical approach via estimates of the stopping power of the medium has also proved useful[67]. Considerable difficulties still arise also when an attempt is made to take into account the scattering anisotropy; they are associated both with the determination of the form of the functions $\xi(E)$ and with the solution of transport equations for arbitrary $\xi(E)$.

2. Kinetic Relations in the Anisotropic Scattering of Hot Atoms

It is known from the physics of atomic collisions[18] that the degree of asymmetry of scattering depends on the energy of the colliding species. Thus in the region of high energies, atomic collisions are of the strongly anisotropic Rutherford type but, as the energy falls below $E_A = (13.6)^2[(m+m_1)/m]Z_1 Z\sqrt{Z_1^{2/3}+Z^{2/3}}$, they can be described approximately in terms of the hard-core potential and ξ_{is}. In the region of low energies of the chemical interaction, the elastic component of scattering is

again characterised by an appreciable anisotropy and "soft" potentials. The change in interaction potential should lead to the corresponding changes in $g(E', E)$ and $\xi(E)$. The softer the potential, the lower the value of ξ. As a consequence of this, an increase in anisotropy increases the number of collisions of the atom in the specified energy range and a change in the energy spectrum of the species and in the yield of the hot-atom reactions. Thus the necessity to take into account the anisotropy of scattering in hot-atom chemistry is evident.

The main tasks in hot-atom chemistry are as follows: 1. The search for the form of the functions $\xi(E)$. Since there are reliable methods for estimating ξ_{is}, it is important for hot-atom chemistry to find relations between ξ and ξ_{is}. 2. Determination of the nature of the variation of the ratio $\xi_i(E)/\xi_j(E)$ with the energy, since simulation by the method of statistical tests has shown that, when ξ_m/ξ_r varies with the energy, kinetic analysis leads to considerable errors in the determination of the kinetic parameters[68,69]. 3. Solution of the transport equations and the equations for the probability of chemical reactions for specified $\xi(E)$ or $g(E', E)$. 4. Determination of the nature of the variation with the energy of $\varphi(E)$, $n(E)$, or $\Lambda(E) = E.n(E)$ for specified $\xi(E)$. In particular, the test of the possibility of using for non-absorbing or weakly absorbing media asymptotic values of distribution functions of the species energy and the functions $\Lambda(E)$, which are characterised by the strongest dependence on $\xi(E)$, since $\Lambda_0 \propto 1/\xi$.[70,71]

The nature of the variation of ξ with the energy is determined by the form of the interaction potential between the colliding species. For example, the level of anisotropy for the potential $U(r) = ar^{-s}$ depends on the value of s:[68]

$$\xi(E) = C(1-\alpha)\left[E\frac{m_1}{m_1+m}\right]^{\frac{2-s}{s(s-1)}},$$

where

$$C \propto A^{2/s}\int_0^{\infty}\sin^2\frac{1}{2}\,[\sigma(\rho)]\,\rho\,d\rho$$

(ρ is the target parameter and σ the scattering micro-cross-section). When $s \to \infty$, the scattering is isotropic; the case where $s = 1$ corresponds to Coulombic scattering with maximum anisotropy; for many types of interaction with not unduly large or not unduly small energies, the values of s are in the range 9–12; when $s \gg 2$, the ξ depend relatively little on the energy. It is significant that the ratios ξ_{m_1}/ξ_{m_2} depend little on the energy and are determined mainly by the ratio of the masses of the colliding species. Thus, for $U(r) = Ar^{-s}$ and the combined potential $U(r) = A_1r^{-s_1} + A_2r^{-s_2}$ under the conditions of preferential forward scattering, i.e. for low values of s, we have $\xi_{m_1}/\xi_{m_2} \simeq (1-\alpha_1)/(1-\alpha_2)$; when $s \to \infty$, i.e. for the hard-core-potential, we have

$$\xi_{m_1}/\xi_{m_2} = (1-\alpha_2)(1-\alpha_1+\alpha_1\ln\alpha_1)/(1-\alpha_1)(1-\alpha_2+\alpha_2\ln\alpha_2).$$

Estrup[72] was one of the first to draw attention to the necessity to consider the anisotropy of scattering in kinetic analysis. He found[72] that, when $(1-\alpha)/(1+\alpha) < 1$, then $\xi \simeq \xi_{is}.\pi r_0^2/\sigma_S(E)$, where r_0 is the distance of closest approach of the species in head-on collisions and σ_S is the scattering cross-section; for α close to zero, the best approximation is $\xi \simeq [\pi r_0^2/\sigma_S(E)][\xi_{is} - \kappa(\alpha)\gamma^{-1} + c(\gamma)]$. Special methods were developed for estimating γ, κ, c, and σ_S. Calculations and analysis of the dependence of the quantities determining ξ on the energy led Estrup to the conclusion that the energy variation of ξ becomes weaker with increase of the kinetic energy of hot atoms (Fig. 6). Numerical calculations showed that, for collisions of T atoms with He, D_2, and CH_4, the ratios ξ/ξ_{is} are respectively 0.09, 0.12, and 0.33. In the T + He + CH_4 system, the values of I proved to be an order of magnitude smaller than those of I_{is}.

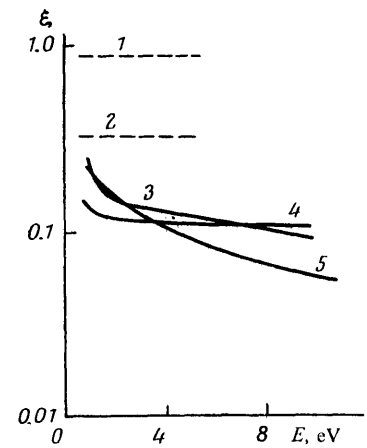


Figure 6. Variation of $\xi = \ln(E/E_0)$ with the kinetic energy of the recoil tritium atoms for isotropic (ξ_{is}) and anisotropic (ξ) elastic scattering: 1) ξ_{is} in the He–D_2 system; 2) ξ_{is} in CH_4; 3) ξ in D_2; 4) ξ in CH_4; 5) ξ in He.

Gordus and coworkers[70,71] also examined elastic anisotropic scattering under the conditions of spherically symmetrical soft potentials, for which one can assume that $\xi = \xi_{is} - b([1-\alpha^2)/2 + \alpha\ln\alpha]$. If the coefficients b are independent of the energy, i.e. $b = 1/(1-\alpha)^2$, then in all cases with $g(E', E) \propto (1/E')\Phi(E/E')$ the values of ξ remain unchanged as E is varied and are determined only by the values of α and b. If $b = 1/E(1-\alpha)^2$, the anisotropy is appreciable only for low values of E, and ξ increases with increase of the kinetic energy of hot atoms, approaching ξ_{is}.

Numerical calculations have been made of $n(E)$ and $\Lambda(E)$ under the conditions of weak absorption. They showed that the greatest differences between the calculated values of $\Lambda(E)$ and the asymptotic values of $\Lambda_0(E) = 1/\xi$ for a constant b correspond to the region where $E/E_0 > \alpha$. With decrease of α, the difference between the asymptotic values and the results of the numerical solution of transport equations taking into account the scattering anisotropy becomes smoothed out; when $\alpha = 0$, the values of $\Lambda(E)$ are close to the asymptotic values for any E. According to Gordus and coworkers[70,71], the use of the asymptotic values of $n(E)$ or $\psi(E)$ in calculations of the probability of chemical reactions should not lead to appreciable errors; for tritium atoms, the errors should not exceed 50% (Fig. 7).

Analytical solutions have been obtained[73-79] to transport equations for soft potentials of the type $U(r) = Ar^{-s}$ and the following values of $g(E', E)$:

$$g(E', E) = \frac{1}{E'} b\left(E', \frac{E}{E'}\right) \text{ when } E' \geqslant E \geqslant \gamma E';$$

$$g(E', E) = [a(E')/E'] \Phi\left(\frac{E}{E'}\right) \text{ when } \gamma E' \geqslant E \geqslant \alpha E';$$

$g(E', E) = 0$ in the remainder of the energy range; here $\gamma = (1 + \mu^2 + 2\mu \cos\theta_c)/(1 + \mu)^2$, $\mu = m_1/m$, and θ_c is the critical scattering angle.

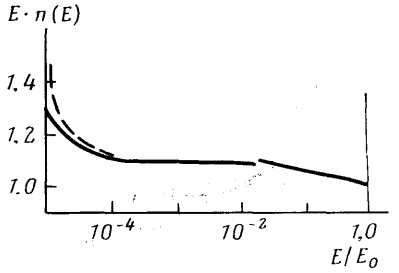


Figure 7. Variation of $E.n(E)$ with E/E_0 for $E_0 = 2.5 \times 10^5$ eV; $\alpha = 0.02$; $b = 1/E.(1 - \alpha)^2$; continuous curve—$E.n(E) = \Lambda(E)$; dashed curve—$E.n(E) = 1/\xi = \Lambda_0$.

In non-absorbing systems where $\gamma = 1$ and $a(E) = 1$ and the differential cross-sections are independent of E for any scattering angle, Eqn.(I.8) has the solution $\psi(E') = S_0/E'\zeta$; when $\gamma \neq 1$, the solution is $\psi(E') = S_0/E'\zeta a(E')$, where

$$\zeta = \int_{\gamma}^{1} \ln\frac{E}{E'} \cdot \frac{b(E, E'/E)}{a(E)} d\left(\frac{E'}{E}\right) + \int_{\alpha}^{\gamma} \ln\frac{E}{E'} \Phi\left(\frac{E'}{E}\right) d\left(\frac{E'}{E}\right).$$

Comparison of the solution obtained with the asymptotic solution showed that $\xi \simeq \zeta a(E')$. Taking into account the nature of the variation of $a(E)$ with the energy for $\Sigma_s(E) = CE^{-1}(s^{-1})$, Felder and Kostin[73] found that $\psi(E) = S_0/\zeta E^{\beta}$, where $\beta = 1 - 2/s + 1/(s - 1)$.

For reactive systems, where $\Sigma_s(E) > \Sigma_r(E) > 0$ and $\Sigma_r(E)/\Sigma_s(E) = B$, Felder and Kostin[73] examined a solution of a transport equation of type (I.7) with $g(E', E) = (1/E').\Phi(E/E')$. In this case, they used as the solution the expression $\psi(E') = C(E')^{\beta}$, the values of β being found from the equation

$$B = \int_0^1 \Phi\left(\frac{E'}{E}\right)[(E'/E)^{\beta-1} - 1] d\left(\frac{E'}{E}\right). \qquad \text{(II.12)}$$

For an arbitrary form of $\Phi(E'/E)$, the values of β are found numerically; when $\Phi(E'/E) = (n + 1)(E'/E)^n$, the analytical solution $\beta = [B + 1/(n - 1)]^{-1} - n$ was obtained. For isotropic scattering, n should be zero, an increase of n corresponding to an increase of the scattering anisotropy.

According to Felder and Kostin[73], $\psi(E) = C/E^{1/(B+1)}$ is obtained for isotropic scattering in absorbing media when $\Sigma_r(E)/\Sigma_s(E) = B > 0$. Consequently in absorbing media $\psi(E)$ varies with energy less markedly than in the absence of chemical capture. The energy spectrum is smoothed out as a result of the "erosion" of low-energy species in chemical reactions. In the most general case, where $n \neq 0$ and $B \neq 0$, an increase of n, corresponding to an increase of anisotropy, leads to a decrease of β compared with its values in isotropic scattering; this promotes the smoothing of the species distribution functions with respect to energy. This conclusion has a simple physical interpretation. When energy transfer in small portions predominates, the hot atom undergoes a greater number of collisions in the specified energy range, which leads to an increased probability of its absorption in this range before it is retarded with attainment of lower energies.

Asymptotic solutions for $\psi(E)$ have been obtained[74-76,79] in the most general cases of multicomponent absorbing systems, taking into account the influence of secondary high-energy species on the yield of hot-atom reactions. When account is taken of secondary displaced atoms in isotropic scattering in chemically inert systems, we have $\psi(E) \propto 1/E^2$ [instead of $\psi(E) \propto 1/E$].[75]

When absorbing systems were considered and a number of additional conditions were introduced {the potential is not unduly soft, $s > 6$, $\Sigma_r(E)/\Sigma_s(E) = B(E)$, $B(E)/a(E) = D$, $p_r(E) = B(E)/[1 + B(E)]$ and $E < E_2 < E_0$}, Felder[77] obtained the following solutions:

$$P_0 = D^2\left[1 - \left(\frac{E_1}{E_2}\right)^{1-\beta}\right] / \zeta\zeta_\beta(1 - \beta)^2; \qquad \text{(II.13)}$$

$$P_1 = 1 - \left(\frac{E_1}{E_2}\right)^{D/\zeta} \text{ when } \mu \gg 1 \text{ or } \mu \ll 1; \qquad \text{(II.14)}$$

$$P_2 = 1 - \left(\frac{E_1}{E_2}\right)^{D/\zeta} \cdot \left(\frac{1 + CDE_2^n}{1 + CDE_1^n}\right)^{D/n\zeta} \text{ when } a(E) = CE^n;\ n = \frac{1}{s-1} - \frac{2}{s}; \qquad \text{(II.15)}$$

$$P_3 = 1 - \left(\frac{E_1}{E_2}\right)^{D/\zeta(1+CD)} \text{ when } a(E) = C, \qquad \text{(II.16)}$$

where the quantities β, ζ, and ζ_β are defined as follows:

$$\zeta = \int_0^1 \lg\frac{E}{E'} \cdot \Phi\left(\frac{E'}{E}\right) d\left(\frac{E'}{E}\right); \quad \zeta_\beta = -\int_0^1 \left(\frac{E'}{E}\right)^{\beta-1} \lg\frac{E'}{E} \cdot \Phi\left(\frac{E'}{E}\right) d\left(\frac{E'}{E}\right); \qquad \text{(II.17)}$$

$$\int_0^1 \left(\frac{E'}{F}\right)^{\beta-1} \cdot \Phi\left(\frac{E'}{E}\right) d\left(\frac{E'}{E}\right) = 1 + D.$$

Together with calculations based on Eqns.(II.13)–(II.16), numerical solutions were also obtained to transport equations for Felder's model taking into account the scattering anisotropy. Comparison of the results of the numerical calculation (P) with the calculations by Eqns.(II.13)–(II.16) did not reveal significant differences between P and P_0. Thus, for $\mu = 1$, $E_2 = 100$, $E_1 = 25$ eV, $s = 12$, and $D = 0.2$, the values of P and P_0 differed by 2.8%; for $\mu = 0.01$, they were indistinguishable. The maximum differences between P and P_1 were of the order of 0.5% for $\mu = 0.01$ and approximately 10–15% for $\mu = 0.2$. Comparison of the values of P with P_2 and P_3 revealed a satisfactory agreement, particularly for P and P_3. The differences did not exceed 3–4% for $\mu = 0.01$, 10–15% for $\mu = 0.2$, and 20–25% for $\mu = 1$.

The results of the calculations were also compared with those obtained in terms of the Wolfgang–Estrup approximation. The comparison showed that the accuracy of the simple kinetic approximation increases with increase in the difference between the masses of hot and thermal atoms and with increase in the "hardness" of the potential for low values of $p_r(E)$ or for narrow well resolved resonances in absorption.

Interesting results, characterising the influence of the scattering asymmetry on ψ and P, were obtained by Porter

and Kunt [80]. Numerical calculations using stochastic equations yielded the values of P for three different elastic particle scattering models. Model A corresponds to isotropic collisions and model B presupposes anisotropic scattering with $g(E', E) = 2(\zeta - \alpha)/E'(1 - \alpha)^2$. Model C corresponds to anisotropic scattering with $g(E', E) = a/E'(1 - \alpha)$ for $bE' > E > \alpha E'$ or $g(E', E) = [a/E'(1-\alpha)] + 2(1 - a).(\zeta - b)/E'(1 - b)^2$ for $bE' < E < E'$, where $\zeta = E/E'$. The coefficients a and b were fitted by quantum-mechanical calculations. For all the models $g(E', E) \propto \Phi(E/E')/E'$, where ξ is independent of the energy of hot atoms, and $\xi(C) < \xi(B) < \xi(A)$.

Numerical calculations have shown that model C gives the optimum values of P, in good agreement with the experimental yields of the stabilisation products of tritium recoil atoms in hydrogen or deuterium. For all the models investigated, an increase is observed in the probability of reactions as a result of an increase in $\Sigma_r(E)$ in the range 0–20 eV; in the range 20–100 eV, the values of P varied only slightly, broad maxima being observed in the vicinity of 20 eV. Porter and Kunt [80] showed that calculation by Eqn. (I.41) and by the Wolfgang–Estrup formulae yields different results; $P_C < P_{W-E}$ for model C and $P_{A,B} > P_{W-E}$ for models A and B. In calculations for mixtures, the deviations were proportional to the content of the reactive component. The errors for H_2 are greater then for D_2, which is consistent with Σ_r; it is known that $p_r(H_2) > p_r(D_2)$. However, one must note that the discrepancies between the results are small and comparable to the experimental errors in the determination of the yields of reactions initiated by hot atoms; they do not exceed several per cent.

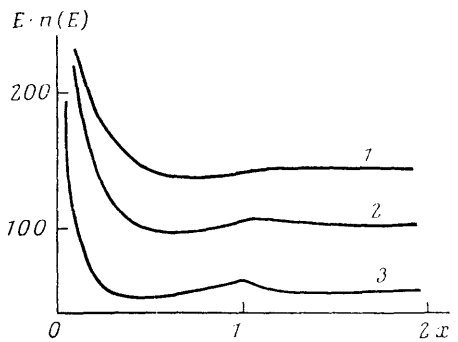


Figure 8. Variation of $E.n(E)$ with $x = \ln(E/E_0)/\ln\alpha$ for $E_0 = 10^5$ eV, $\alpha = 0.8882$, and different interaction potentials: 1) $U(r) = 10^2/r^6$; 2) $U(r) = 10^2/r^{12} \pm 10^2/r^6$; 3) $U(r) = 10^2/r^{12}$.

The series of studies designed to improve the kinetic models in hot-atom chemistry was continued by Baer and Amiel [16,17,27,28,41,69]. In the main, they used the postulates discussed previously, but, in the description of elastic scattering processes, they used the combined Lennard–Jones potential $U(r) = A_1/r^{S_1} + A_2/r^{S_2}$ (where $s_1 > s_2$) in addition to the hard-core potential and $U(r) = Ar^{-S}$. The combined potential makes it possible to describe both the short-range forces of the Coulombic repulsion of the nuclei of the colliding species and the long-range polarisation forces giving rise to repulsion or attraction. The Lennard–Jones potential also ensures flexibility in the description of the elastic scattering of species over a wide range of energies. However, methods have not yet been found whereby one can obtain an analytical solution for $g(E', E)$ or equivalent functions for a two-term potential. Numerical computer calculations were therefore made [16,17] of the quantities $g(E', E)$, $n(E)$, and $\Lambda(E)$.

The numerical calculations for $n(E)$ and $\Lambda(x)$, where $x = \ln(E/E_0)/\ln\alpha$ for one-term and two-term potentials, showed that $n(E)$ increases with decrease of the energy; the asymptotic values of $\Lambda_0(E)$ and $n_0(E)$ are attained rapidly, particularly for small α and s. For high energies ($E_0 > 1$ KeV), different values of $\Lambda(x)$ were obtained for one- and two-term potentials, the values of $\Lambda(x)$ for the two-term potential depending only slightly on the sign of A_2, i.e. on whether the second long-range term characterises repulsion or attraction. For low initial energies, the long-range terms with $A_2 > 0$ completely swamps the short-range term; when $A_2 < 0$, the values of $\Lambda(x)$ are lower than for the one-term potential or the potential with $A_2 > 0$ (Fig. 8).

The results of Amiel and Baer's calculations [16,17] indicate also a series of regularities in the variation of $\Lambda(x)$. It was shown that the variation of $\Lambda(x)$ with the coefficients A and E_0 is characterised by the equation

$$\frac{\Lambda^{(2)}(x)}{\Lambda^{(1)}(x)} = \left[\frac{A^{(2)}}{A^{(1)}}\right]^{\frac{2}{s(s-1)}} \left[\frac{E_0^{(2)}}{E_0^{(1)}}\right]^{\frac{s-2}{s(s-1)}}. \qquad \text{(II.18)}$$

Thus the variation of $\Lambda(x)$ with A and E_0 becomes weaker as s increases. The greater the difference between the masses of the colliding species the greater the value of α and the greater the sensitivity of $\Lambda(x)$ to changes in any scattering parameters.

The problem of the analytical description of $\Lambda(E)$ was solved by Baer [17] for a modified two-term potential $U + \Delta U$, where $U(r) = A'/r^S$ for $R < r < \infty$ and $U(r) \to \infty$ for $0 < r < R$. These conditions reflect the swamping of the short-range term by the long-range term for low energies, i.e. make it possible to retain the principal advantages of the combined potentials but at the same time significantly simplify the analytical solutions for $G(E', E)$, $\Lambda(E)$, or $\psi(E)$. Without considering their derivation in detail, we shall merely quote Baer's expressions:

$$\psi(E) = \frac{C}{E}\left(\frac{E_{1,2}}{E}\right)^{\frac{1}{s-1}} \left\{1 + \frac{E_1}{E}\sum_{l=0}^{\infty}\frac{4(s-1)}{(2l+3)\cdot[(2l+s)^2-1]} - \right.$$

$$\left. - \frac{2(s+1)}{s(s-1)}\cdot\left(\frac{\gamma_s^2\pi}{2}\right)^{\frac{1}{s}}\cdot\frac{(1-\alpha)\cdot(E_1/E)^{\frac{s+1}{s}}}{1 - s(1-\alpha^{\frac{2s+1}{s}})/[(2s+1)\cdot(1-\alpha)]}\cdot\left(\frac{E_1}{E}\right)^{\frac{s+1}{s}}\right\}, \qquad \text{(II.19)}$$

where R is the sum of the radii of the colliding species and $C = S_0/\xi$ is;

$$E_1 = AR^{-s};\quad E_{1,2} = \frac{m\pi}{2\hbar^2}\lambda_s^{s-1}\left(\frac{A'}{R^{s-1}}\right)^2;$$

$$A' = A\frac{m_1}{m_1 + m};\quad \gamma_s = \frac{\Gamma(s/2 + 1/2)}{\Gamma(s/2)};$$

$$\lambda_s = \sin\left(\frac{\pi}{2}\frac{s-3}{s-1}\right)\cdot\Gamma\left(\frac{s-3}{s-1}\right)\cdot\left[\frac{\Gamma(s/2-1/2)}{\Gamma(s/2)}\right]^{\frac{2}{s-1}};\quad \Gamma\left(\frac{s}{2}\right)\ldots\text{— gamma functions.}$$

It is noteworthy that the above expression is an asymptotic solution valid to within E_1/E.

Baer's treatment corresponds to the subdivision of the entire energy range into three sections: $0 < E < E_1$, where the interaction is described by the soft potential $U(r) = A/r^S$, $E_1 < E < E_{1,2}$, where a soft two-term potential also operates, and $E < E_{1,2}$, where the interaction is described by a hard-core potential.

3. Kinetic Equations Taking into Account Non-elastic Scattering and the Stopping Power of the Medium

Apart from those already discussed, Thomsen's model [67] is applicable in the case of a marked scattering anisotropy with small angles predominating. In this model, as in those already examined, no account is taken of thermal motion and the chemical bonds formed by the atoms in the target, the model being restricted to stationary conditions. Limitations are also imposed on the reactivity of the target, but, in contrast to other workers, Thomsen postulates a model whereby one can take into account, together with elastic anisotropic scattering by the nuclei, also electronic retardation, which is particularly significant for high energies. The relaxation processes are characterised in Thomsen's model by the stopping powers $-dE/dl$ and not the quantities $g(E', E)$ or $G(E', E)$. This is fairly correct if the moderation process can be regarded as continuous, if the energy losses in the collision ΔE are small compared with the energies of the hot species, if small scattering angles predominate, and if the masses of the colliding species differ markedly. The introduction of the stopping power as the main characteristic of the moderation processes has many other advantages. Firstly, satisfactory approximations are now available for estimates of $-dE/dl$ corresponding to different scattering mechanisms. Secondly, the introduction of the stopping power makes it possible to include the loss of bombarding species from targets with limited volumes, which extends the scope of the model.

Thomsen defines the probability of hot-atom reactions over the entire energy range by the formula

$$P = 1 - \exp\int_0^{E_0} \frac{\Sigma_r(E)\,dE}{dE/dl}, \qquad (II.20)$$

which permits the determination of Σ_r from the known yield of the chemical reaction and the stopping power of the medium. For low absorption cross-sections, when $P(E_0) \ll 1$, it follows from Eqn. (II.20) that

$$P \simeq -\int_0^{E_0} \frac{\Sigma_r(E)\,dE}{dE/dl}. \qquad (II.21)$$

Thomsen expresses the energy distribution function $\rho(E)dE$, the number of species per unit volume with the energy E in the range dE, by the product of the function of the source $S(E_0)$, the residence time of the species in the given energy range dE, and the probability of the attainment of this range without absorption. Then

$$\rho(E_0, E)\,dE = S_0(E_0)\exp\left[\int_0^{E_0} \frac{\Sigma_r(E')\,dE'}{dE'/dl}\right]dt, \qquad (II.22)$$

where dE and dt are related by the equation

$$-dE = \left(\frac{dE}{dl}\right)\sqrt{\frac{2E}{m}}\,dt.$$

It also follows from Eqn. (II.22) that, for a monochromatic source in weakly absorbing media, we have

$$\rho(E_0, E) = -\frac{S_0}{dE/dl}\sqrt{\frac{m}{2E}}\exp\left[\int_E^{E_0} \frac{\Sigma_r(E')\,dE'}{dE'/dl}\right]. \qquad (II.23)$$

The functions $\rho(E)$ are related in the following way to the density of chemically active collisions:

$$\psi_r(E) = S_0\,\frac{\Sigma_r(E)}{-dE/dl} = \rho(E)\,\Sigma_r(E)\sqrt{\frac{2E}{m}}. \qquad (II.24)$$

It is significant that the stopping powers are additive quantities and $-dE/dl = \sum_i N_i\Sigma_{st,i}(E)$, Σ_{st} being the stopping cross-section equal to the sum of the stopping cross-sections in collisions with electrons ($\Sigma_{s,e}$) and with atomic nuclei ($\Sigma_{s,n}$). Thus the introduction of $-dE/dl$ facilitates allowance for non-elastic collisions in estimating the quantities $\psi_r(E)$. Thomsen also examined the cases where moderation cannot be described as a continuous process and account must be taken of the discrete nature of the energy transfer, but $\Delta E \ll E$.

Comparison of the expressions obtained for the energy distribution functions and the probabilities of chemical reactions with the solutions of the transport equations for hard-core collisions and anisotropic scattering with $U(r) = Ar^{-s}$, which were discussed previously, led Thomsen to the conclusion that the formulae which he recommended give a fairly correct description of the characteristics of the distribution of hot species with respect to energy in weakly absorbing systems, but the values of $\psi(E)$ obtained from Thomsen's approximate formulae differ from the earlier asympotic solutions of the transport equations. For isotropic collisions, Eqn. (II.24) leads to $\psi_0(E) = 2S_0/(1-\alpha)E$, in contrast to $\psi_0(E) = S_0/\xi E$. The ratio of Thomsen's solution (ν) to the asymptotic solution for a hard-core potential is $2\xi/(1-\alpha)$; for $U(r) = Ar^{-s}$, the following expression is valid for ν:

$$\nu(s, \alpha) = s + [(s-1)/(1-\alpha)]\lg\alpha + (s-1)\cdot(1-\alpha)^{1/s-1}\cdot\int_0^{(1-\alpha)} x^{1-1/s}\,\frac{d\chi}{1-\chi},$$

where $\chi = N_1\Sigma_{st,1}(N_1\Sigma_{st,1} + N_2\Sigma_{st,2})^{-1}$ for a mixture of two components.

Evidently the values of ν depend on the ratio of the masses of the colliding species and on the parameters of the potential (s) (Fig. 9).

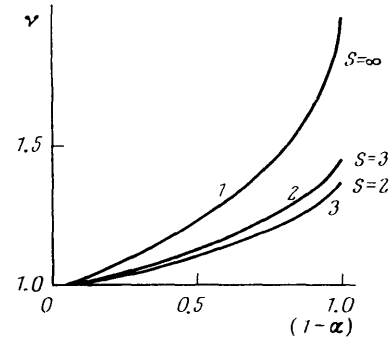


Figure 9. Variation with α of the ratio of the approximate and asymptotic solutions (ν) for the interaction potential $U(r) \propto r^{-s}$: 1) for isotropic scattering; 2) for $s = 3$; 3) for $s = 2$.

In describing relaxation processes, Malerich and Spicer [81] took into account the energy losses in non-elastic collisions accompanied by the dissociation of the molecules of the medium. As a result of such collisions, hot atoms can lose a considerable fraction of their energy in the region of relatively low energies close to the range $E_2 - E_1$.

If the collisions with hot atoms lead to a transition of the molecules of component z from the internal state i to the state f with $\Delta E_{zi \to f}$, then

$$g_z(E', E) = \frac{2\int_0^{2\pi} \sigma_{zi\to f}(V, \zeta, \eta)\, d\eta}{(1-\alpha_z)E'\left[1-\left(\frac{m+m_z}{m_z E'}\right)\Delta E_{zi\to f}\right]^{1/2}\Sigma_{sz}(E')} + \frac{4\pi\sigma_{zi=f}(V, \zeta)}{(1-\alpha_z)E'\Sigma_{sz}(E')}, \quad \text{(II.25)}$$

where V is the relative velocity, η and ζ are scattering angles, and

$$E = E' - \frac{1-\alpha_z}{2}E'\left[1-\left(1-\frac{m+m_z}{m_z E'}\Delta E_{zi\to f}\right)^{1/2}\cos\zeta\right] - \frac{m_z}{m+m_z}\Delta E_{zi\to f}. \quad \text{(II.26)}$$

For the non-elastic scattering component, $g_{zi \to f} = 0$ over the entire energy range, except

$$\frac{1}{2\alpha}(t - \sqrt{t^2 - 4\alpha s^2}) \leqslant E' \leqslant \frac{1}{2\alpha}(t + \sqrt{t^2 - 4\alpha s^2}),$$

where

$$s = E + \frac{m_z}{m_z+m}\Delta E_{dis}; \quad t = (1+\alpha_z)s - \frac{(1-\alpha_z)^2}{4}\cdot\frac{m_z+m}{m_z}\cdot\Delta E_{dis}.$$

For the non-elastic scattering component in the energy range of non-zero values, $g_{zi \to f}$, is described by the formula

$$g_{zi\to f}(E', E) = \frac{\Sigma_{z\,dis}(E')}{\Sigma_{sz}(E')(1-\alpha_z)E'\left[1-\frac{m_z+m}{m_z E'}\Delta E_{dis}\right]^{1/2}}. \quad \text{(II.27)}$$

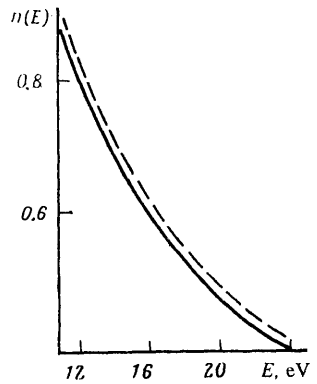


Figure 10. Variation of the asymptotic value of $n_0(E)$ with the energy; dashed curve—with allowance for dissociation; continuous curve—without allowance for dissociation (for isotropic scattering of tritium atoms by deuterium).

The limits of the energy range of non-zero values $g_{zi \to f}$ are determined by the solution of Eqn. (II.26) for the limiting scattering angles $\zeta = 0$ and $\zeta = \pi$. The minimum energy transferred in a non-elastic collision is determined by the value of ΔE_{dis} which has been set equal [81] to E_b; the quantity $\Delta E_{z,dis}$ was calculated by the method of trajectories. For the elastic scattering component, it was assumed [81] that $g_{zi=f}(E', E)$ in the range $E \leqslant E' \leqslant E/\alpha$ is given by the expression $g_{zi=f} = \Sigma_{s,is}/[(1-\alpha_z)\cdot\Sigma_{sz}(E')\cdot E']$. Numerical calculations of $\psi(E)$ and P using the above equations for $g_{zi=f}$ and $g_{zi \to f}$ showed that, for non-elastic energy losses in dissociation, the density of collisions in the region of chemical interaction is lower than for elastic isotropic scattering (Fig. 10). In the region of low energies close to the dissociation threshold, the energy losses in the non-elastic collisions considered have a smaller effect.

4. Kinetic Relations Taking Account of the Relaxation of Hot Products

In the solution of transport equations, the relaxation of the hot molecules formed on chemical capture of hot atoms and having an excess kinetic or internal energy (E_t or E_i), which makes possible dissociation and other reactions of the primary products, may be taken into account if the probability of the formation of the stable product $p_r(E)$ is represented as follows [68]:

$$p_r(E) = p_c(E) - f' q_r(E) - (1-f')q_m(E), \quad \text{(II.28)}$$

where $p_c(E)$ is the probability of the formation of the product with different sets of E_t and E_i, $q_m(E)$ and $q_r(E)$ are the probabilities of the decomposition of the hot molecules in collisions with the moderator or the reactant respectively, and f' is the fraction of the collisions of hot product molecules with reactant molecules. Then, in solutions of type (II.4), we have

$$I(E) = I_0(E) - f' I_r(E) - (1-f')I_m(E); \quad \text{(II.29)}$$

$$\text{when } I_0(E') = \int_0^{E'} p_c(E)\frac{dE}{E} \text{ we have } I_r(E') = \int_0^{E'} q_r(E)\frac{dE}{E};$$

$$I_m(E') = \int_0^{E'} q_m(E)\frac{dE}{E}.$$

Hence

$$P(E) = 1 - \exp\left\{-\frac{f}{\xi}[I_0 - f' I_r - (1-f')I_m]\right\}$$

$$[-\ln(1-P)]^{-1} = \left(\xi_r + \xi_m\frac{1-f}{f}\right)/[I_0 - f' I_r + (1-f')I_m]. \quad \text{(II.30)}$$

The results obtained are important for the interpretation of the experimental data on the non-additivity of the yields in mixtures when the deviations from additivity may be caused by processes involving energy transfer from the primary excited products to the surrounding medium. In particular, it has been shown that, when the probability of the decomposition of the primary products depends on the medium, the variation of $[-\ln(1-P)]^{-1}$ with $(1-f)/f$ when $I_r \neq I_m$ may be non-linear (Fig. 11). However, for low values of $P(E)$, f, and f', it follows from Eqn. (II.30) that

$$P^{-1} = I_0^{-1}\frac{\xi_r + \xi_m[(1-f)/f]}{1 - I_m/I_0}. \quad \text{(II.31)}$$

Eqns. (II.31) permit the estimation of the lifetimes of the hot products, since the ratios $(\xi_{m_1}/\xi_{m_2})(I_0 - I_{m_2})/(I_0 - I_{m_1})$ or $(I_0 - I_{m_2})/(I_0 - I_{m_1})$ may be determined from the experimental data for different energy acceptors.

The application of the Monte Carlo method in combination with a novel approach to the problem of describing the relaxation of hot products by binary collisions in the presence of a fraction of stabilised molecules varied by the pressure in the gas system enabled Smith et al. [82] to propose a new method for estimating the parameters of the energy distribution functions of species.

5. Kinetic Equations and Their Solutions taking into Account the Thermal Motion of the Molecules of the Target

In the studies examined previously, it was postulated that the thermal motion of the species of the target may be neglected, which is valid only for $E \gg k_B T$. In a series of studies by Kostin and coworkers [83-86] an attempt was made to take into account thermal motion under conditions where the initial energy of the epithermal species is low. Such conditions are encountered in plasma-chemical, radiation-chemical, and photo-chemical studies and in the investigation of chemical reactions in chemical accelerators, in flames, and with recoil atoms in many nuclear decomposition schemes. When account is taken of thermal effects in systems with non-Maxwellised atoms, the conservation equation should contain terms describing elastic collisions involving both a decrease and an increase of the energy of the atom. Under stationary conditions in the source of epithermal species $S(E)$, the conservation equation can be written similarly to Eqn. (I.5). Evidently, when $\Sigma_r \gg \Sigma_s$, the atoms react until there is a significant change in the energy and density of the hot species $\rho(E) \propto S(E)/p_r(E)$. If the medium is chemically inert and the power of the source is low, the species entering from outside attain equilibrium with the surrounding medium, acquiring a Maxwellian distribution corresponding to the target temperature; then

$$n(E) \propto M(E) = \frac{E^{1/2}}{(k_B T)^{3/2}} \exp\left(-\frac{E}{k_B T}\right).$$

When $p_r(E) \neq 0$, the distribution of the bombarding atoms with respect to energy is non-Maxwellian: $\rho(E) \propto M(E) \cdot L(E)$, where $L(E)$ is a correction factor.

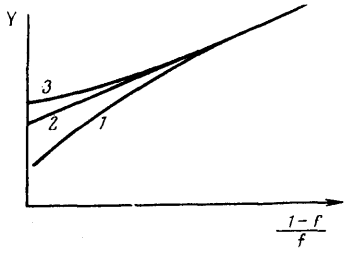


Figure 11. Variation of $Y = -[\ln(1-P)]^{-1}$ with $(1-f)/f$: 1) $I_m > I_r$; 2) $I_m = I_r$; 3) $I_m < I_r$.

The following equation was obtained for this factor on the basis of the principle of detailed balance:

$$[p_s^*(E') + p_r^*(E')] \cdot L(E') = \int_0^\infty g^*(E', E) \cdot L(E)\,dE + S(E')/M(E'), \quad \text{(II.32)}$$

where $p_s^*(E')$, $g^*(E', E)$, and $p_r^*(E')$ are the corresponding probabilities that the atom with the energy E' will be scattered in unit time, will have energy in the range $E-(E+dE)$, and will react chemically.

In a few instances it is possible to convert the integral equation (II.32) into a differential form, which has a solution, by expanding $L(E)$ in Taylor's series. Thus, for small energy changes during scattering, when the scattering anisotropy is marked and there is a large difference between the masses of the colliding species, Eqn. (II.32) gave

$$\frac{1}{2} R_2(E') \frac{d^2 L}{(dE')^2} + R_1(E') \frac{dL}{dE'} + \frac{S(E')}{M(E')} = p_r^*(E') \cdot L(E'), \quad \text{(II.33)}$$

where

$$R_1(E') = \int_0^\infty (E-E') \cdot g^*(E', E)\,dE \text{ and } R_2(E') = \int_0^\infty (E-E')^2 \cdot g^*(E', E)\,dE$$

characterise the average and mean square energies transferred. For reactions with low activation energies, where Σ_r, Σ_r/Σ_s, and the mean cosine of the scattering angle depend little on the energy, the solution of Eqn. (II.33) assumes the following form for $\epsilon_T^{-1}(m/m_1) < 1$:

$$L(\varepsilon_T) = \text{const}\left[1 + \frac{1}{2} a\varepsilon_T + \ldots + \frac{(a)_n \varepsilon_T^n}{(2)_n \cdot n!}\right], \quad \text{(II.34)}$$

where

$$\varepsilon_T = E/k_B T; \quad a = \Sigma_r \Big/ \left[2\frac{m}{m_1}\Sigma_s(1-\langle\cos\theta\rangle)\right] \text{ and } (a)_n = a(a+1) \times (a+2)\ldots(a+n-1).$$

The solution is valid for $\epsilon_0 > 1$. If, $\epsilon_0 > \epsilon_T > 1$, then

$$L(\varepsilon_T) \propto e^{\varepsilon_T} \varepsilon_T^{a-2}; \quad \psi(\varepsilon_T) = \varepsilon_T e^{-\varepsilon_T} L(\varepsilon_T) \sim \varepsilon_T^{a-1}$$

Thus the greater the value of a for a higher reactivity of the material of the target, the slower the decrease of the collision density with increase of E. In non-absorbing systems with $a = 0$, we obtain $\psi(E) \propto 1/\epsilon_T$. Analysis of the solutions leads to the conclusion that, in specimens containing a moderator and a radical acceptor in addition to the reactant and when the reactions have different activation energies, the ratio of the yields of the products of different chemical processes can vary with target temperature (Fig. 12), but only slightly—in the region of very low or very high temperatures.

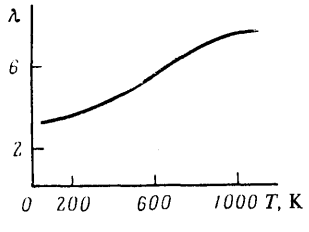


Figure 12. Variation of the ratio of the yields of the primary hot reactions to the yields of the reactions with radical acceptors (λ) as a function of target temperature ($E_0 = 2.5$ eV; $E_{thresh} = 0.3$ eV; $m_r/m_1 = 1$).

When account is taken of thermal effects, difficulties arise in many instances also in the numerical solution of Eqn. (II.32). In order to facilitate the solution, the function $g^*(E', E)$ is written in the form of a sum of g_a and g_b, where $g_a(E', E) > g_b(E', E)$ for small energy transfers and $g_a(E', E) < g_b(E', E)$ for large transfers. This procedure makes it possible to employ instead of Eqn. (II.32) approximate equations which can be solved numerically [86].

The non-stationary problem with allowance for thermal effects has also been solved numerically [87]. For this

purpose, use was made of the transport equation with the correction factors $L(E, t)$ or $L(\epsilon, \tau)$, where $\tau = v_p t/l_s$, $\epsilon = \sqrt{E/k_B T}$, $v_p = \sqrt{2k_B T/m}$, and l_s is the length of the free path of hot atoms before collision with the moderator. Calculation showed that the values of $L(\epsilon, \tau)$ are almost constant over a wide range of thermal velocities already for $\tau > 2$ (Fig. 13).

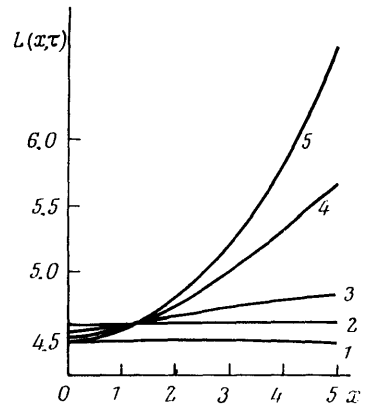


Figure 13. Variation of the correction factor $L(x, \tau)$ with the dimensionless velocity of thermalised species $x = (E/k_B T)^{1/2}$: 1) $\tau \to \infty$; 2) $\tau = 6.0$; 3) $\tau = 2.0$; 4) $\tau = 0.5$; 6) $\tau = 0$.

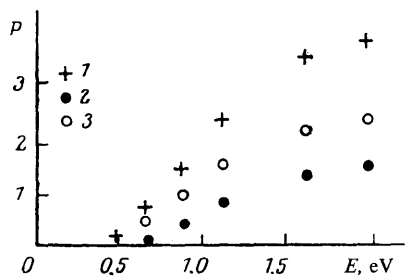


Figure 14. Variation with the energy of the integral probability P of reactions involving the abstraction of deuterium atoms by photolytic H atoms: 1) C_4D_{10}; 2) $C_4D_6H_4$; 3) $C_4D_{10}-C_4D_6H_4$).

The kinetic theory of hot-atom reactions has been used successfully to interpret experimental data in photochemistry [88-95]. Thus the variation of the integral probabilities with energy, the threshold energies, and reaction cross-sections have been determined [92] for processes involving the abstraction of deuterium atoms from primary and secondary C–D bonds in deuterobutanes by hot photolytic hydrogen atoms (Figs. 14 and 15). Similar data were obtained from the analysis of the yields of H_2 in the interaction of photolytic H atoms with HBr. [93] The kinetic analysis of the photochemical data was performed taking into account the thermal motion of the target molecules; for this purpose, a function (Fig. 16) [92] characterising the kinetic energy distribution (E_{rel}) of colliding target species, having a Maxwellian distribution with respect to velocity at the temperature T, and of hot atoms with the energy E [90] was introduced into the equations for the estimation of the integral reaction probabilities and the density or number of collisions:

$$\Omega(E_{rel}, E)\,dE_{rel} = \frac{1}{2\mu}\sqrt{\frac{mm_1}{\pi k_B TE}}\cdot\left\{\exp\left[-\frac{m_1}{2k_BT}\left(\sqrt{\frac{2E}{m}}-\sqrt{\frac{2E}{\mu}}\right)^2\right]-\right.$$
$$\left.-\exp\left[-\frac{m_1}{2k_BT}\left(\sqrt{\frac{2E}{m}}+\sqrt{\frac{2E}{\mu}}\right)^2\right]\right\}, \qquad (II.35)$$

where μ is the reduced mass.

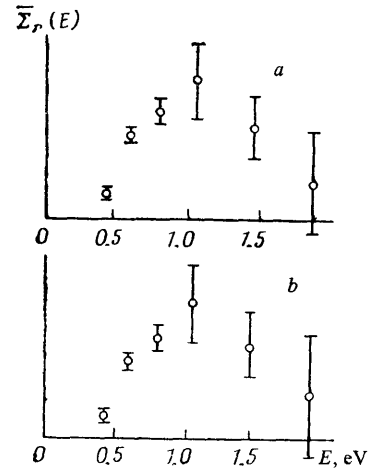


Figure 15. The cross-section of the reaction involving the abstraction of deuterium atoms by photolytic H atoms from a secondary C–D bond in C_4D_{10}: *a*) $U(r)_{H-Xe} \propto r^{-7}$; *b*) $U(r)_{H-Xe} \propto r^{-4}$.

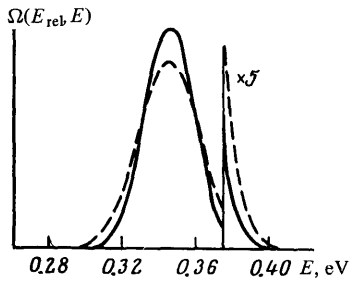


Figure 16. Variation with the energy of the function $\Omega(E_{rel}, E)$ for photolytic H atoms with $E_0 = 0.35$ eV in C_4D_{10}; continuous curve—at 229 K; dashed curve—at 323 K.

In systems where allowance for the thermal motion of molecules is necessary, i.e. for small initial energies of the hot atoms, close to non-zero values of $p_r(E)$ and $T > 0$ K, the following equations are valid:

$$n(E_{rel})\,dE_{rel} = \left[\int_0^\infty n(E)\cdot\Omega(E, E_{rel})\,dE\right]dE_{rel}, \qquad (II.36)$$

$$\Sigma_t(E) = \int_0^\infty \Sigma_t(E_{rel})\cdot\Omega(E_{rel}, E)\,dE_{rel}.$$

In this case, equations of type (I.1) for the probabilities of chemical reactions in mixtures containing considerable amounts of the moderator can be written in the form

$$P = \int_{E_1}^{E_2} \frac{\Sigma_r(E_{rel})}{\Sigma_{t,r}(E_{rel})} \int_0^\infty n_m(E) \frac{\Sigma_{t,r}(E)}{\Sigma_{t,m}(E)} \Omega(E, E_{rel})\, dE \cdot dE_{rel} \quad (II.37)$$

In estimating $n(E)$, Gann and coworkers [90-94] used different versions of the asymptotic solutions ($E \ll E_0$) where the average fractions of the transferred energy, in particular $\epsilon_{is} = \langle E' - E \rangle / E' = 2\mu/(m + m_1)$, were substituted for ξ when $m_1 \gg m$. When account is taken of the thermal motion of the target molecules during isotropic scattering, we have

$$\bar{\varepsilon}_{is} = \frac{2\mu}{m + m_1}\left(1 - \frac{3}{2}\frac{k_B T}{E}\right);$$

then

$$n_0(E) \simeq \frac{1}{\bar{\varepsilon}_{is} E} = \frac{m + m_1}{2\mu E}\left(1 - \frac{3}{2}\frac{k_B T}{E}\right)^{-1}. \quad (II.38)$$

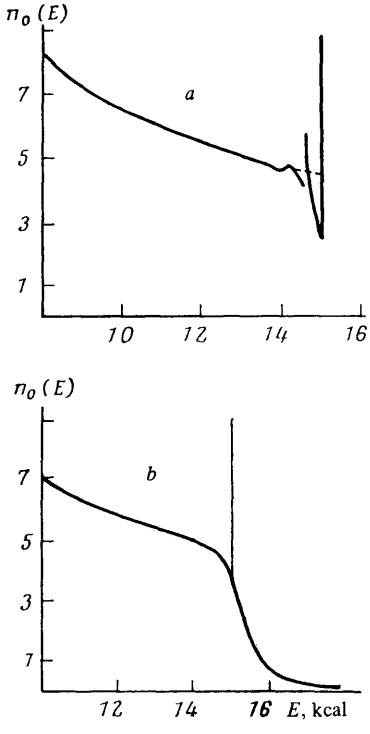


Figure 17. Variation with the energy of the asymptotic value of $n_0(E)$ for the hard-core potential of the scattering of photolytic H atoms (E_0 = 15 kcal) in xenon: *a*) at 0 K; *b*) at 273 K.

For an interaction described by potentials other than the hard-core potential, for example $U(r) = Ar^{-s}$ or the Lennard–Jones potential in the range where $E < 0.93E_0$, we have

$$\bar{\varepsilon}(E) = \frac{2\mu}{m_1 + m}\left(1 - \frac{3}{2}\frac{k_B T}{E}\right)\frac{Q(E)}{\Sigma_t(E)},$$

where $Q(E) = \int_0^\infty Q(E_{rel})\Omega(E_{rel}, E)dE_{rel}$. In the general case, $Q(E_{rel})$, the moment of the transport cross-section, is found by graphical integration [96]. The expression

$$n_0(E) \simeq \text{const} \cdot E^{-\left(1 - \frac{s}{2} + \frac{1}{s-1}\right)}\left(1 - \frac{3}{2}\frac{k_B T}{E}\right)^{-1} \quad (II.39)$$

was obtained for $U(r) = Ar^{-s}$.

Calculation of $n_0(E)$ by the above methods led to the following conclusions: (1) when $T \gg 0$ K, there are collisions in the region where $E > E_0$ (Fig. 17), the oscillations in $n(E)$ in the vicinity of E_0 being smoothed out under these conditions. 2. The form of the function $n_0(E)$ depends only slightly on the form of the interaction potential. 3. For the Lennard–Jones potential, the decrease of the collision density near E_0 is manifested less markedly than for the hard-core potential. The width at the half height level of the tail portion of the function $n_0(E)$ increases appreciably with increase of the target temperature (Figs. 18 and 19). The width of the distribution with respect to relative energy can be large even for $E_0 > k_B T$, since the relative energies are in the range $E_{max} - E_{min}$; $\Delta E \propto \mu\sqrt{k_B T E/mm_1}$.

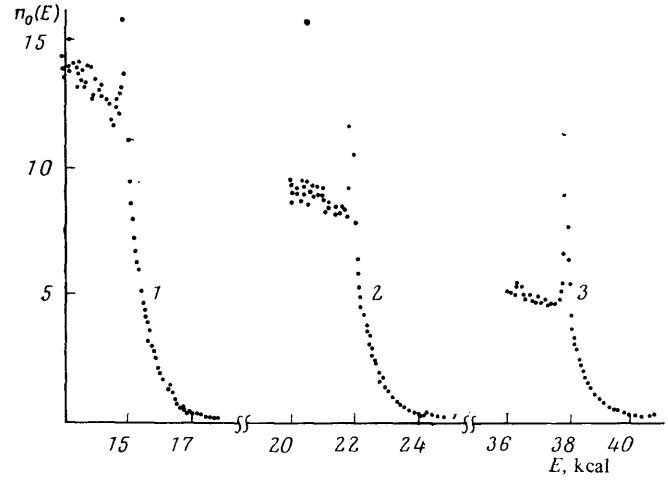


Figure 18. Variation of the asymptotic value of $n_0(E)$ for the Lennard–Jones potential in the H–Xe system (E = 273 K) as a function of the energy of the photolytic H atoms (kcal): 1) 15; 2) 22; 3) 38.

Numerical solutions of the Boltzmann equation for the collision density were also obtained by Kupperman et al. [88] with the analogous function $\Omega(E, E_{rel})$ and $g(E', E)$ expressed in terms of the normalised Gaussian function. It was assumed that the flux of hot species is fairly small and does not affect the thermal distribution of the target molecules.

In conclusion of the review of data on the analytical and numerical solutions of kinetic equations in relation to the distribution functions of hot species with respect to energy or the probabilities of the chemical reactions initiated by them, we shall specify the most important of the results obtained. For energies below the initial values, the particle distribution functions with respect to energy $\psi(E)$, $n(E)$, and $\varphi(E)$, etc. attain asymptotic values. The asymptotic values increase with decrease of the energy E.

In the vicinity of sources, more precisely for $E = \alpha E_0$, the distribution functions undergo a discontinuity and in the vicinity of $\alpha^3 E_0 < E < E_0$ they exhibit oscillations.

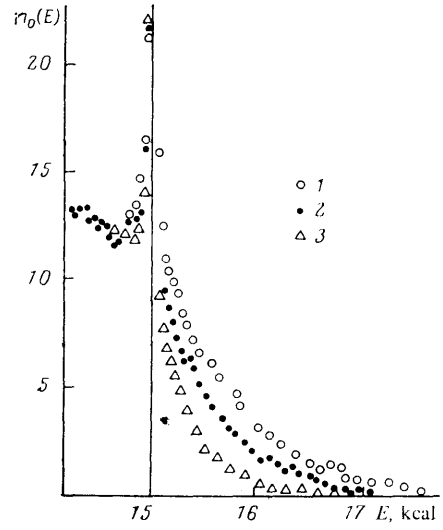


Figure 19. Variation of the asymptotic value of $n_0(E)$ for the Lennard–Jones potential of the scattering of photolytic H atoms ($E_0 = 15$ kcal) in xenon as a function of temperature (K): 1) 373; 2) 273; 3) 173.

In non-absorbing media, the asymptotic value of the collision density is inversely proportional to the energy $\psi_0(E) = S_0/E\xi(E)$. For initial energies of the species E_0 comparable to the energy of the thermal motion of target atoms and molecules, the asymptotic value of the collision density is inversely proportional to the energy normalised with respect to $k_B T$, i.e. $\psi_0(\epsilon_T) \propto 1/\epsilon_T$, where $\epsilon_T = E/k_B T$. The rate of attainment of asymptotic values is determined mainly by the ratio of the masses of the hot atom and target species and also by the parameters of the interaction potentials. For elastic isotropic collisions, the asymptotic value of $\psi_0(E)$ can be used in the region where $E < \xi_{is} E_0$. For elastic anisotropic scattering, for example for potentials of the type $U(r) = Ar^{-s}$ or $U(r) = A_1 r^{-s_1} + A_2 r^{-s_2}$, the rate of attainment of the asymptotic value is particularly large for small values of s and α, i.e. for similar masses of the colliding species. Analytical criteria of the applicability of $\psi_0(E)$ for arbitrary potentials are unknown. For individual types of potentials, the results of numerical calculations are available, showing that, for example, for $U(r) = Ar^{-s}$ with $s < 10$ and $\alpha < 0.8$, the asymptotic value of the collision density is attained already when $\ln(E/E_0)/\ln\alpha \geq 1$.

When hot species are retarded as a result of elastic collisions, the distribution functions show a general tendency to increase with decrease of the energy. However, the detailed variation of the change in $\psi_0(E)$ or $\psi(E)$ is determined by the average logarithmic energy losses and their variation with E. The values of ξ_{is} are constant over the entire range of energies of the elastic isotropic collisions. For anisotropic scattering, the values of ξ may remain constant as E varies, for example when $g(E', E) \propto 1/E'\Phi(E, E')$, but they can also vary with the energy. Since small scattering angles predominate in elastic and anisotropic collisions, it follows that $\xi_{is} > \xi$ and $\psi_{0,is}(E) < \psi_0(E)$. The decrease of $\xi(E)$ with decrease of E leads to a weakening of the dependence of the asymptotic values of the distribution functions on the energy. For example, for $U(r) = Ar^{-s}$, the collision density is inversely proportional to E^β, where $\beta = 1 - 2/s + (s-1)^{-1} \leq 1$ ($\beta = 1$ when $s = 2$, $\beta = 0.83$ when $s = 4$, etc.).

The asymptotic values of the collision densities and the equivalent distribution functions depend only slightly on the initial energy of the hot species if $E_0 \gg E$. The nature of this dependence is likewise determined by the parameters of the interaction potentials. Thus, for $U(r) = Ar^{-s}$, the ratio of the asymptotic values of $\psi_0(E, E_0^{(2)})/\psi_0(E, E_0^{(1)})$ is proportional to $[E_0^{(2)}/E_0^{(1)}]^{s-2/s(s-1)}$; consequently, for fairly large values of s and in the case of the hard-core potential, $\psi_0(E)$ is almost independent of E_0 for $E \ll E_0$.

In absorbing media, the distribution functions for hot particles with respect to energy have the same qualitative features as in inert moderators. They too can have discontinuities at $E = \alpha E_0$ and can exhibit oscillations in the vicinity of sources of hot species and intense chemical absorption zones, which may be regarded as negative sources. The distribution functions in the reactive systems likewise have asymptotic solutions in the regions of energies remote from the sources or the intense chemical reaction zones. The values of $\psi_0(E_0)$ in absorbing media also decrease with increase of E. However, those of $\psi_0(E)$ in reactive media take into account the "erosion" of the hot species from the spectrum by chemical reactions. The "erosion" has a particularly marked influence on the region of low energies. For a weak perturbation of the particle flux (see above), the asymptotic solutions of the transport equations taking into account the "erosion" have a form formally identical with that of solutions for inert moderators: $\psi_0(E) = q(E)/E\xi(E)$.

The use of asymptotic distribution functions in the calculation of the probability of chemical reactions does not lead to major errors. The results are in this case more accurate the further away is E_0 from the energy range of the reactions. The accuracy of the determination of P in terms of asymptotic distribution functions increases with decrease of α and also with decrease of the reactivity of the components, i.e. with decrease of $\int f p_r(E).n(E)dE$.

In weakly absorbing systems, $q = S_0 p(E)$, i.e. it contains the correction factor $p(E)$, characterising the probability of avoiding capture during the moderation process until the attainment of the specified energy E. Evidently, the appearance of the correction factor dependent on E may alter the variation of the distribution functions with energy in a chemically reactive medium compared with an inert medium. Interpretation of the resonance integral $p(E)$ shows that the overall tendency should be towards the smoothing out of the dependence of $\psi_0(E)$ on the energy.

Owing to "erosion" as a result of the chemical absorption of hot species, the flux or density of collisions increases more slowly with decrease of the energy than predicted by the $1/E$ law even for $\xi = \text{const}$. This is shown most clearly by the exact solutions of the transport equations for $\alpha = 0$ and for the ratio $\Sigma_s(E)/\Sigma_r(E) = c$ independent of the energy. Under these conditions, $\psi(E) \propto E^{-c/(1+c)}$; thus, with increase of the reactivity of the system owing to the decrease of c, the collision density changes with the energy less markedly. This general tendency persists for approximate solutions under the

conditions of appreciably different masses of the colliding species, when $\alpha \neq 0$, regardless of the potential used to describe the scattering processes and whether or not the scattering is isotropic or anisotropic. The smoothing out of the variation of the distribution functions with energy is characteristic also of the energy range where account must be taken of the thermal motion of the target species. In certain specific instances, the asymptotic value of $\psi_0(\epsilon_T)$ is inversely proportional to $\epsilon_T^{\gamma(1-a)}$. The values of a are proportional to the ratio $\Sigma_r(E)/\Sigma_s(E)$ and characterise the reactivity of the medium. The higher the reactivity of the material of the target, the larger the value of a and the correspondingly less marked the dependence of $\psi_0(\epsilon_T)$ on the energy.

The anisotropy of scattering for values of ξ_{anis} dependent on the energy promotes, as in non-absorbing systems, a further smoothing out of the energy spectrum and a slower variation with the energy of the asymptotic values of the distribution functions. Whereas $\psi(E) \propto E^{-c/(1+c)}$ for retardation as a result of elastic isotropic scattering, we have $\psi_0(E) \propto E^{-\beta}$ for anisotropic scattering and $|\beta| < |c/(1+c)|$. The softer the potential of the elastic interaction, the smaller the value of ξ_{anis} and the greater the number of collisions per unit energy. This leads to an increase of the overall probability of chemical capture owing to the large number of collisions for the same probability of a single collision.

The asymptotic values of the distribution functions in absorbing systems depend only slightly on the initial energy of the hot species if $E \ll E_0$. This is evident, since the values of $\psi_0(E)$ undistorted by chemical absorption (in non-absorbing systems) depend only slightly on E_0 and the probability of avoiding capture following retardation to E is almost independent of E_0 when $E_2 < E_0$. Accordingly, the probability of chemical reactions for $E_2 < E_0$ may be expected to depend only slightly on E_0. This conclusion follows from the stochastic definition of the probability of chemical reactions of hot atoms in terms of Porter's formulae.

For mixtures of inert moderators, $\psi_0(E) \propto 1/\bar{\xi}E$, where $\bar{\xi} = \sum_i f_i\xi_i = \sum_i (N_i\sigma_{si}/\sum_j N_j\sigma_{sj})\xi_i$. The dependence of $\bar{\xi}$ on the mole fraction of the components determines to a large extent the nature of the corresponding variation of the collision densities and probabilities and yields of hot reactions in binary and more complex systems. The simplest linear relations, for example between $-1/\ln(1-P)$ and $(1-f_r)/f_r$, describe the yields of chemical reactions in mixtures of the reactive components with inert moderators. Similar simple relations have been obtained also for mixtures containing, apart from the moderator, two reactants with low chemical reaction cross-sections, for mixtures of the moderator and two strong absorbers with $p_{rz}(E) = \text{const.}p_{ry}(E)$, and for mixtures of two reactants. Comparison of the above relations with the experimental data for kinetic analysis made it possible to obtain much information about the nature of the processes involving hot atoms.

In conclusions, one should note that the characteristics of the parametric relations involving distribution functions with respect to energy and the probabilities of chemical reactions, obtained by solving Boltzmann equations, agree with the results of calculations based on stochastic schemes.

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