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Present-day State of the Theory of Bimolecular Reactions

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Various simple models of bimolecular reactions are discussed which provide a qualitative interpretation of the principal aspects of the elementary act in the redistribution of atoms. The limitations imposed by the law of the conservation of total angular momentum have been elucidated for processes involving the intermediate formation of long-lived complexes. The limiting cases of the mechanisms of dislodgment and stripping have been examined for direct processes. The latter mechanism is interpreted in terms of an optical model. A list of 38 references is included.

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1. INTRODUCTION

The Review discusses the most recent development of the theory of bimolecular reactions, i.e. processes of the type

$$X + Y \rightarrow Z + U \qquad (1.1)$$

occurring in the gas phase. Since elucidation of the mechanism of this process is based in general on solving a many-body (in the simplest case the three-body) problem, the modern theory of bimolecular reactions is largely governed by progress in computational technique. Analysis of the trajectories of the representative point has yielded important results on the energy dependence of reaction cross-sections, on the energy distribution function of the reaction products, and on the angular distribution of elastically and inelastically scattered particles. Another line of research is based in large measure on models of the mechanism of the redistribution of particles and on certain hypotheses concerning the interaction of reactant molecules. This approach enables the final results to be obtained without complicated intermediate calculations, and thus permits several redistribution processes to be interpreted (if this is possible) in terms of relatively simple models. The most widely used are discussed below.

These models are most conveniently classified according to the extent to which the energy of the unstable molecular system formed on collision is able to undergo redistribution among the various degrees of freedom before the reaction can be regarded as complete. On the basis of these considerations the following classification is useful.

1. Reactions involving an intermediate complex. In these processes the mechanism of the redistribution of energy approaches a statistical process.
2. Direct reactions. According to the way in which the particles are redistributed, these are subdivided into three subgroups—(*a*) rebound mechanism, (*b*) mechanism of direct dislodgement, and (*c*) stripping or pick-up mechanism.

Several processes occurring by the above mechanisms will be examined in the present Review. We shall not in general be concerned with the rebound mechanism, since the chief advances in this field have been achieved by taking into account the simultaneous interaction of several atoms, this requiring the use of computers. Reactions having a rebound mechanism are usually considered in terms of the transition stage theory, and several problems for thermal reactions have been clarified in a previous review[1].

2. STATISTICAL THEORY OF REACTIONS. EXCHANGE OF ATOMS WITH FORMATION OF AN INTERMEDIATE COMPLEX

Discussion of General Formulation

The chief assumption in the statistical theory of bimolecular reactions is that the elementary act (1.1) takes place in two independent stages. The first stage involves formation of a complex or composite system XY*. In the second stage the complex XY* breaks down along all possible channels, the probability P of breakdown being calculated from the statistical theory of unimolecular reactions. It is clear that, for the assumed independence of the two stages to be valid, the lifetime τ of the composite system XY* should exceed substantially the characteristic times of the intramolecular motions. An estimate of τ can be obtained from the statistical theory of unimolecular reactions, which has now been quite well developed[2-4] and enables the mean lifetime of an active molecule before spontaneous breakdown to be calculated with satisfactory accuracy.

Let us suppose that the initial states of the molecules X and Y are characterised by a set of quantum numbers i. On formation of the complex the numbers i are supposed to lose their significance, the activated molecule being characterised by a new set of quantum numbers ϵ. Further, let the final products Z and U be characterised by the quantum numbers f. The cross-section of the elementary act is then written

$$\sigma_{if}(v_i) = \sum_{\varepsilon} \delta\sigma_{i\varepsilon}(v_i) P_{\varepsilon f}, \qquad (2.1)$$

where $\delta\sigma_{i\epsilon}$ is the cross-section of formation of the composite system XY* (or, as we shall call it, the capture cross-section of X and Y) in the state ϵ, and $P_{\epsilon f}$ is the probability of its breakdown along the channel f. The summation in Eqn. (2.1) is made over all states ϵ which can be formed from the initial state i. The symbol v_i denotes the initial relative velocity of the molecules X and Y.

The probability of breakdown $P_{\epsilon f}$ is given by the normalised partial rate of breakdown along the specified channel:

$$P_{\varepsilon f} = k_f(\varepsilon)/[k_1(\varepsilon) + k_{-1}(\varepsilon)] \qquad (2.2)$$

where

$$k_1 = \sum_f k_f(\varepsilon), \quad k_{-1} = \sum_i k_i(\varepsilon)\ . \qquad (2.3)$$

Here the summations with respect f and i are made over all channels in forward and reverse directions. The decomposition rate constants $k_n(\epsilon)$ of the active molecule $(XY^*)_\epsilon$ are in turn calculated from the theory of unimolecular reactions.

In classical mechanics the differential capture cross-section $\delta\sigma_{i\epsilon}(v_i)$ is given by the relation

$$\delta\sigma_{i\varepsilon}(v_i) = 2\pi b_i db_i \qquad (2.4)$$

where b_i is the impact parameter, which satisfies the condition $b_i < b_i^c$, while b_i^c is the maximum impact parameter at which capture takes place. In this formulation it is assumed, of course, that formation of the composite system does not involve surmounting a potential barrier, i.e. that the first stage in the reaction takes place with zero activation energy. The relation (2.4) is conveniently expressed in terms of the relative momentum l_i of the molecules X and Y:

$$\delta\sigma_{i\varepsilon}(v_i) = \frac{2\pi}{p_i^2} l_i dl_i, \quad p_i = \mu v_i\ . \qquad (2.5)$$

Although the condition of capture is most simply formulated by the requirement $l_i < l_i^c$, it is useful to introduce into (2.5), instead of l_i, the total momentum J of the system of colliding molecules, since it alone is a complete integral of the motion. Henceforward for simplicity we shall discuss the collision of an atom A with a molecule BC, so that the total angular momentum J is given by the vector sum

$$l_i + j_i = J \qquad (2.6)$$

in which j_i denotes the intrinsic momentum of BC.

Transformation from the variable l_i to the variable J (with j_i fixed) is most simply accomplished by means of the rules of vector addition[5,6]. As a result of this transformation the differential capture cross-section $\delta\sigma_{i\epsilon}$ is written

$$\delta\sigma_{i\varepsilon}(v_i) = \frac{2\pi}{p_i^2} \varphi(J; j_i, l_i^c) J dJ \qquad (2.7)$$

where the explicit form of the function φ has been given in a previous paper[6]. Here we note merely that φ vanishes when $J > j_i + l_i^c$. In order to determine l_i^c, we must formulate the conditions of capture. If the capture of A and BC takes place at sufficiently great distances, the main contribution will be made by the isotropic polarisation interaction $W(R) = q(R_0/R)^s$, and l_i^c then depends on the relative kinetic energy of the fragments[5-7]:

$$l_i^c(v_i) = (2\mu E_t R_0^s)^{1/s} \left(\frac{sq}{2E_t}\right)^{1/s} \left(\frac{s}{s-2}\right)^{1/s-1/s} \qquad (2.8)$$

$$E_t = \mu v_i^2/2\ .$$

The energy E_i is subject, of course, to the limitations indicated below, which result from neglect of the contribution made by short-range forces[8].

We now specify the set of quantum numbers ϵ, on the assumption that the only integrals of motion of the composite system are the total energy E and the total angular momentum J[5-11]. Certain assertions must also be made concerning the electronic states between which a statistical redistribution of energy is possible. The probabilities of non-adiabatic transitions between these states are supposed to be sufficiently high for them not to limit the transfer of the representative point from one potential surface to another.

This last hypothesis cannot be regarded as valid for all reactions in which an intermediate complex is formed. Several ion–molecule reactions are now known whose very small cross-section is ascribed to the low probability of non-adiabatic transitions between the electronic states linking the initial and final terms of the partners[12].

The total cross-section σ_1 of reaction (1.1) can now be rewritten

$$\sigma_1(v_i) = \frac{\pi}{p_i^2} \int 2 J dJ \varphi(J; j_i, l_i^c) \frac{k_1(E,J)}{k_1(E,J) + k_{-1}(E,J)} \qquad (2.9)$$

where k_1 and k_{-1} are the rates of the spontaneous breakdown of ABC* in forward and reverse directions. In calculating the cross-section of reaction (1.1) into a specified channel (e.g. in a state having specified vibrational or rotational quantum numbers), we must replace $k_1(E,J)$ in the numerator of (2.9) by the corresponding partial rate constant. In most cases Eqn. (2.9) can be considerably simplified, since the relative momentum l_i usually exceeds appreciably the intrinsic angular momentum of the reactant molecules. In this case we can put $J \simeq l_i = p_i b_i$, and Eqn. (2.9) becomes

$$\sigma_1 = \frac{2\pi}{p_i^2}\int_0^{l_i^c} 2\, l_i dl_i \frac{k_1(E,J)}{k_1(E,J)+k_{-1}(E,J)} = 2\pi\int_0^{b_i^c} \frac{k_1(E,J)\, b_i db_i}{k_1(E,J)+k_1(E,J)} \quad (2.10)$$

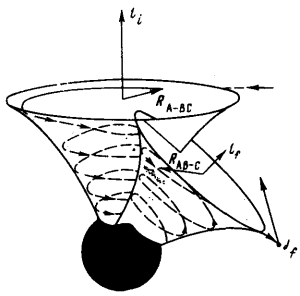


Figure 1. Energy surface for reaction involving an intermediate complex.

A reaction of this type can be represented diagrammatically by the movement of a representative point along potential-energy surfaces (Fig. 1). The relative motion of A and BC in the initial stage of capture takes place in a plane perpendicular to the relative angular momentum $\boldsymbol{l}_i$. If the energy axis lies in the direction of the vector $\boldsymbol{l}_i$, capture is represented by the trajectory described by the vector R_A–BC, as it descends spirally into the "funnel" corresponding to the potential W_{A-BC}. The representative point then reaches a region of strong interaction, where the redistribution of energy is described by statistical laws (shaded region). Finally, the representative point begins to rise along a second "funnel", which corresponds to the potential W_{AB-C} and whose axis lies in the direction of the vector of the relative motion of the products $\boldsymbol{l}_f$. The direction of the vector $\boldsymbol{l}_f$ is related to that of the intrinsic angular momentum $\boldsymbol{j}_f$ of the fragment AB and to the vector $\boldsymbol{J}$ by the conservation law $\boldsymbol{J} = \boldsymbol{l}_f + \boldsymbol{j}_f$.

If the dependence of the rates of decomposition k_1, k_{-1} on the total momentum $\boldsymbol{J}$ is neglected in the calculation of σ_1, formula (2.9) simplifies further to

$$\sigma_1 = \left[2\pi\int_0^{b_i^c} bdb\right]\frac{k_1(E)}{k_1(E)+k_{-1}(E)} = \sigma_1^{c_0}(v_i)\frac{k_1(E)}{k_1(E)+k_{-1}(E)} \quad (2.11)$$

where the first factor in the right-hand formulae gives the total capture cross-section, while second factor is the probability of breakdown in the forward direction.

Since the values of k_n are proportional to the number n of states in a channel, it is clear that the larger of the two constants k_1 and k_{-1} will be that which corresponds to the exothermic direction of the reaction. Let us assume for definiteness that reaction (1.1) is exothermic in the forward direction. Let us suppose further that the total energy E_1 of the initial state satisfies the condition $E_1 \ll Q$, where Q is the heat of reaction. Then the inequality $k_1 \gg k_{-1}$ will probably hold, and Eqn. (2.11) will give

$$\sigma_1 = 2\pi\int_0^{b_i^c} bdb = \sigma_1^c(v_i)\,. \quad (2.12)$$

Nevertheless, the cross-section σ_{-1} for the reverse reaction will contain the ratio $k_{-1}(E,J)/k_1(E,J) \ll 1$ following the integral sign. This ratio is proportional to the ratio of the number of open decomposition channels in reverse and forward directions. Provided that $E_1 < \hbar\omega$, i.e. when vibrations of BC cannot be excited on breakdown of the complex ABC*, the energetic dependence of σ_{-1} on the total energy of the partners AB and C near the threshold Q is described by the formula [8]

$$\sigma_{-1} = \text{const}\,(E-Q)^{s/4}\,. \quad (2.13)$$

This threshold dependence of the rate is related fundamentally to the law of the conservation of angular momentum. This can be seen from the argument that the first stage of the reaction involves formation of the composite system ABC*, the angular momentum of which is distributed within a certain range $0 < J < l_f^c$. On decomposition in the direction A + BC the maximum anular momentum j_i of the molecule BC is small, being determined by the excess of energy $E-Q$ over the threshold. On the other hand, l_i is also small for low values of E_i. This means that the vector sum of j_i and l_i is small, certainly much smaller than l_f^c. Thus only complexes having a small angular momentum $0 < J < l_i^c$ are actually able to break down in the direction A + BC. For complexes having $l_i^c < J < l_f^c$ only one type of decomposition is available—breakdown in the reverse direction: ABC* → AB + C.

Model Reaction $A_2^+ + A_2 \rightarrow A_3^+ + A$

As illustration of the statistical theory of bimolecular reactions we shall discuss an ion–molecule reaction of the above type. An actual example of such a reaction is the process

$$H_2^+(E_{i,n}) + H_2 \rightarrow H_3^+ + H + Q,\ Q = 1{,}1\ \text{eV} \quad (2.14)$$

in which the H_2^+ ions possess a specified vibrational excitation (quantum number n) and a relative kinetic energy E_1. The problem consists in calculating the cross-section σ of this reaction as a function of n and E_i.

Let us first consider the calculation of the total reaction cross-section for the ground state $n = 0$. An estimate based on a simplified form of the statistical theory [13] (disregarding the conservation of total momentum) shows that, with energy $E_i < 0.1$ eV, the rate of breakdown of the complex $[H_4^+]^*$ in the forward direction substantially exceeds the rate in the reverse direction. The cross-section of the reaction should then coincide with the capture cross-section σ^C, which in turn is given by the general formula (2.12) with the polarisation potential $W(R) = -\alpha e^2/2R^4$ (in which α is the polarisability of the neutral particle):

$$\sigma^c(v_i) = 2\pi e\sqrt{\frac{\alpha}{2E_i}},\ E_i = \mu v^2/2 \quad (2.15)$$

where μ is the reduced mass of the partners. An experimental investigation of the formation of H_3^+ ions (and of D_3^+

ions in the analogous reaction with deuterium) confirms the diminution in cross-section with increase in energy, the experimental absolute cross-sections being close to the theoretical values over the energy range investigated[15,16].

Let us now examine the dependence of σ on the vibrational quantum number n of the H_2^+ ion. In calculations based on the general formulae (2.9) it must be borne in mind that the initial angular momentum of this ion is quite small if it is produced by ionisation of low-energy H_2 molecules. Therefore the simplified formula (2.10) can be used to calculate σ_1, and for $n \neq 0$ the contribution of E_i to the total energy of the composite system $[H_4^+]^*$ can in general be neglected if $E_i < n\hbar\omega^+$ (where ω^+ is the vibration frequency of H_2^+). The cross-section σ_1 is conveniently written $\sigma_1 = \sigma^C P(E_{i,n})$, where $P(E_{i,n})$ is to be interpreted as the mean probability of reaction along the given channel. Different calculations of this factor[17,18] are difficult to compare directly, since the second was based on a simplified form of the theory[13], and took no account of identical channels of decomposition.

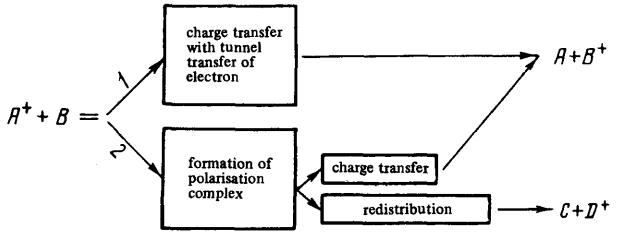


Figure 2. Competition between charge transfer with tunnel transfer of an electron, charge transfer with complex formation, and redistribution with complex formation.

Examination of the different cases of addition of the angular momenta of molecules resulting from breakdown of the composite system $[H_4^+]^*$ leads to the following estimate for the relative efficiency of decomposition in the forward direction with energy $E_i = 0.04$ eV[17]:

$$P(n=0):P(n=1):P(n=2):P(n=3):P(n=4) = 1:0.9:0.75:0.62:0.52. \quad (2.16)$$

This agrees qualitatively with the initial terms in the analogous series representing the experimental data[19]

$$1:0.5:0.4:0.5:0.0\ . \quad (2.17)$$

The discrepancy between theory and experiment, and in particular the inability of the statistical theory to explain the very marked decrease in probability of reaction for $n \geq 4$, are perhaps due to the breakdown of the main assumption of the theory, that a long-lived complex is formed at sufficiently high energies, and to the disregard of the effect of anisotropic interaction in determining the boundary between open and closed channels†. It must also be remembered that the experiment giving the series (2.17) was interpreted on the assumption that the Franck–Condon principle applied to the ionisation of H_2. It is possible, however, that this principle is not satisfied in the vicinity of the threshold[21].

In calculating the cross-sections of reactions between an ion and a molecule we must take into account the competition between the redistribution of particles and the transfer of charge[16,22]. An important aspect is that, as the kinetic energy increases, the charge-transfer cross-section diminishes more slowly than does the redistribution cross-section. Fig. 2 illustrates such competition in the case of resonance charge transfer. Along path *1* either the transfer of an electron by the tunnel effect or the formation of a polarisation complex is possible. The relative efficiency of these processes is proportional to the corresponding cross-sections, which in turn are determined by the critical values of the impact parameters.

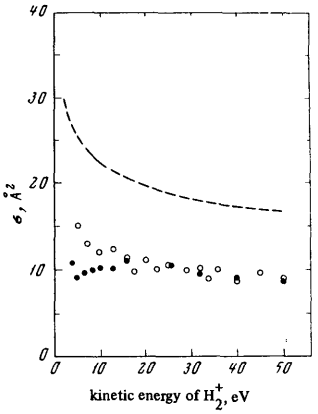


Figure 3. Charge transfer as one of the paths of the competing reactions (2.14) and (2.19). The broken curve shows the calculated charge-transfer cross-section, and the points represent experimental results.

Along branch *2* the relative efficiency of the two paths is now determined by the distribution of energy in the complex, depending mainly on the sign and magnitude of the energy evolved during the redistribution. In particular Markin and Tal'roze[23] investigated the reaction

$$H_2^+ + O_2 \rightarrow [H_2O_2^+]^* \begin{cases} HO_2^+ + H & (a) \\ O_2^+ + H_2 & (b) \end{cases} \quad (2.18)$$

which satisfies this condition. The ratio σ_a/σ_b of the cross-sections was found to diminish with increase in energy, and the cross-section of reaction (*a*) became very small at a relative energy of the ions of about 10 eV. This immediately shows that the lifetime of the composite system decreases with increase in energy, and ultimately the very concept of an intermediate complex becomes devoid of meaning.

Another example, from the work of Levental et al.[24], is illustrated in Fig. 3. The broken curve represents the calculated cross-section σ_{calc} of resonance charge transfer

$$H_2^+ + H_2 \rightarrow H_2 + H_2^+ \quad (2.19)$$

† Such anisotropy is most clearly apparent in reactions between an ion and a molecule having a dipole[20]. In this case the field of the ion retards the rotation of the molecule, and in the limiting case completely orients it in the direction of the line of collision, so that the classification of channels into closed and open should allow for interaction of the momenta l_i and j_i.

while the points give the experimental values of the cross-sections σ_{exp} for this process. The divergence between the two curves is due to reaction (2.14), which "cuts out" from the cross-section σ_{calc} the internal region σ_1 in such a way that $\sigma_{exp} = \sigma_{calc} - \sigma_1$.

3. THEORY OF DIRECT REACTIONS. MECHANISM OF DIRECT DISLODGMENT

Experimental investigation of reactions occurring in molecular beams shows that many exchange reactions, particularly those of alkali-metal atoms with halogen and hydrogen halide molecules, do not involve the formation of a long-lived intermediate complex: i.e. they take place by a direct mechanism. Henceforward we shall take "direct mechanism" to mean a mechanism of interaction of the partners in which the residence time in a volume of molecular dimensions is of the order of a few nuclear vibration periods or less. Fig. 4 shows the various possibilities for the redistribution of atoms in the simplest reaction A + BC → AB + C which has a direct mechanism. In the rebound mechanism A approaches BC, a chemical bond AB is formed, and then the atom C is repelled from the resulting molecule AB. As already mentioned, this situation is usually discussed in terms of the transition state theory.

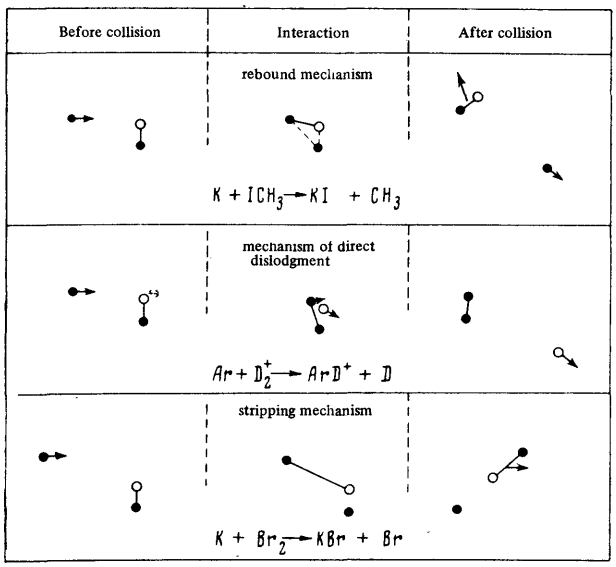


Figure 4. Diagrammatic illustration of rebound mechanism, mechanism of direct dislodgment, and stripping mechanism.

If a mechanism of direct dislodgment operates, the atom A dislodges the atom C from the molecule BC, is slowed down, and remains combined with the atom B.

With a stripping mechanism the atom A interacts mainly with atom B, and the interaction of A with C can often be neglected. The resulting diatomic molecule is scattered mainly in the direction of motion of the atom A.

Fig. 4 includes examples of reactions of the above types.

It is an extremely complicated theoretical task to calculate the cross-sections of such processes. However, the theory assumes a simple form when the time of interaction τ_{st} between the incident atom A and one of the atoms in the molecule BC can be regarded as small in comparison with the period of vibration of the initial molecule BC or the final molecule AB (the so called impulse approximation) [25-27]:

$$\tau_{st}\omega_{AB},\ \tau_{st}\omega_{BC} \ll 1 . \qquad (3.1)$$

An analytical expression can be obtained for the reaction cross-section if two additional conditions are introduced besides (3.1): it must be postulated that the amplitude of the pair scattering A_{XY} is far smaller than the interatomic distances in the molecules:

$$A_{XY} \ll R_{XY},\ X, Y = A, B, C \qquad (3.2)$$

and that the interaction potential U of three particles is additive in character:

$$U = U_{AB} + U_{BC} + U_{AC} . \qquad (3.3)$$

The pair potentials are completely arbitrary: the only limitation imposed on them is due to condition (3.1). It must be noted that the additive potential approximation (3.3) permits no description of a potential barrier or a region of breakdown, nor a region of transition from one surface to another. Therefore the approximation (3.3) can be applied only to reactions in which neither activation energy nor non-adiabatic effects play a significant part.

Condition (3.1) imposes a lower limit of 5–10 eV on the relative energy of the partners on collision. With such energies the exchange

$$A + BC \rightarrow AB + C \qquad (3.4)$$

begins to be subject to competition by the dissociation

$$A + BC \rightarrow A + B + C . \qquad (3.5)$$

The existing theory enables the reaction cross-sections for exchange σ_{exch} and dissociation σ_{diss} to be calculated with the quantum character of the motion of the nuclei in the intermediate and resulting molecules taken into account. Here we shall give merely a brief account of the classical form of the theory describing the broad features of the energy dependence of the cross-section in the range above the above lower limit [25].

Assuming for simplicity that the target molecule is at rest before collision, we shall consider that a stable molecule AB is formed if the relative energy E_{AB} of the atoms A and B after the dislodgment of C is less than the bond energy D_{AB}.

The starting point for deducing an expression for σ_{exch} is the formula for the differential cross-section of the loss of energy ΔE by the atom A incident with energy E on the stationary atom C. For a model of rigid spheres we have

$$d\sigma = \pi R_0^2 \frac{d\Delta E}{\Delta E_{max}},\quad \Delta E_{max} = E\frac{4\mu_{AC}}{m_A + m_C} . \qquad (3.6)$$

The energy E_{AB} of atom A after dispersions on C, expressed in the system of the centre of mass A–B, is

$$E_{AB} = (E - \Delta E)\frac{\mu_{AB}}{m_A} . \qquad (3.7)$$

Expressing $d\Delta E$ in Eqns. (3.6) in terms of dE_{AB}, and equating the differential retardation cross-section $d\sigma$ to the differential capture cross-section, we find that

$$d\sigma_{exch} = d\sigma(E_{AB}) = \pi R_0^2 \frac{m_A}{\mu_{AB}}\frac{dE_{AB}}{\mu_{AB}} . \qquad (3.8)$$

The total exchange cross-section is obtained from this by integrating with respect to dE_{AB}:

$$\sigma_{exch}=\pi R_0^2\frac{m_A}{\mu_{AB}\Delta E_{max}}\left[\min\begin{Bmatrix}\frac{\mu_{AB}}{m_A}E\\ D_{AB}\end{Bmatrix}-\frac{\mu_{AB}}{m_A}(E-\Delta E_{max})\right]. \quad (3.9)$$

Hence it follows that, when $E \leq D_{AB}m_A/\mu_{AB}$, the exchange cross-section is πR_0^2. This is clearly the case: right from the start the relative energy of A–C is such that every dislodgment of C enables a stable molecule to be formed. When $E > D_{AB}m_A/\mu_{AB}$, the exchange cross-section diminishes because the dissociation channel is opened:

$$\sigma_{exch}=\frac{\pi R_0^2}{4}\left[\frac{(m_A+m_C)^2(m_A+m_B)}{m_Am_Bm_C}\cdot\frac{D_{AB}}{E}-\frac{(m_A-m_C)^2}{m_Am_C}\right]. \quad (3.10)$$

When the energy has the value E^* at which the expression in square brackets vanishes, the exchange channel is completely closed, and every collision A + BC leads to the dissociation of BC.

The concepts of a mechanism of direct dislodgment cannot usually be applied, either to thermal reactions or to processes in molecular beams, if the kinetic energy of the partners does not exceed several tens of electron-volts. Nevertheless, this mechanism represents an important particular case in which a many-body problem reduces to a problem of pair interactions. The more exact quantum theory of reactions of direct dislodgment enables us to take into account the effects of repeated scattering, a sudden change in potential, preliminary rotational and vibrational excitation of the target molecule, and the dependence of the effective dissociation energy of the resulting molecule AB on its rotational state[26,27]. In particular, the quantum distribution of momenta of atoms in the vibrational ground state of the hydrogen molecule has been suggested to be responsible for the rapid fall in the cross-section of the reaction

$$Ar^+ + H_2 \rightarrow ArH^+ + H \quad (3.11)$$

in the energy range $E > E^*$, where according to classical views the cross-section of the process should have been precisely zero. A mechanism of direct dislodgment provides an explanation for the slower fall (with increase in energy) in the cross-section of the reaction

$$Ar + D_2^+ \rightarrow ArD^+ + D \quad (3.12)$$

than in that of the reaction

$$Ar^+ + D_2 \rightarrow ArD^+ + D \quad (3.13)$$

as a consequence of initial vibrational excitation[27]. Furthermore, a simple interpretation is given of the fact that the cross-section of formation of the ion ArH^+ in the reaction Ar + HD^+ exceeds that for formation of the ion ArD^+.[27]

However, the interpretation of the above reactions of direct dislodgment is not unambiguous. In many cases reactions of this type can be successfully described in terms of a stripping model[12,28,29]. Nevertheless, a mechanism of direct dislodgment should always be considered as a possible mechanism at high collision energies, especially as it permits of relatively simple theoretical treatment.

4. THEORY OF DIRECT REACTIONS. MECHANISM OF STRIPPING

Let us now discuss another type of reaction, taking place by the so called stripping mechanism. This term applies to reactions in which an incident atom A interacts mainly with the atom in the molecule BC which is directly involved in the exchange‡. The interaction of A with C in reaction (3.4) can be neglected, for example, in rapid collisions where the time of interaction of A with B is less than the time required for substantial transfer of momentum from B to C. It is possible that processes of this kind, together with those of direct dislodgment, play a part at energies exceeding 5–10 eV. With ordinary thermal reactions (below 10 000°K) the relation between the collision time and the time of intramolecular vibrations is such that there can be no question of impulse interaction of A with B. Nevertheless, there exist certain types of reaction, even at low energies, whose formal characteristics satisfy the conditions of stripping. The cross-section of these reactions is usually very large ($\sigma \geq 100$ Å), and the resulting diatomic molecule is scattered mainly ahead relative to the direction of motion of the atom A. Since large cross-sections indicate that detachment occurs at large impact parameters ($b > 6$–7 Å), a model having a short-range potential (e.g. a rigid-sphere model) cannot be used to interpret these reactions.

Examples of processes of this type are provided by the reactions

$$M + X_2 \rightarrow MX + X \quad (4.1)$$

where M is an alkali-metal atom and X a halogen atom. A "spectator–stripping" model describes approximately the kinetics of such reactions, the M atom stripping an X atom from the X_2 molecule, while the momentum of the other X atom remains almost unchanged. A suggested interpretation of the dynamics of these reaction[30–32] starts from a mechanism of "harpooning", in which the first stage of the process involves dissociative charge transfer, and the second stage the formation of a bound ion-pair:

$$M + X_2 \rightarrow M^+ + X_2^- \rightarrow M^+ + X^- + X \rightarrow M^+X^- + X \rightarrow MX + X\ . \quad (4.2)$$

The first stage—charge transfer—is the only inelastic process occurring at large distances, so that elastic processes make the chief contribution to scattering without redistribution of particles. The fact that all non-elastic channel without particle redistribution can be excluded from consideration enables the reaction and the elastic scattering to be described relatively simply in terms of a so called optical model. This model consists essentially in replacing the actual potential $W(R_{X_2-M})$, which leads to elastic scattering, by a complex potential[28] (R_{X_2-M}), the imaginary part of which (in a quantum treatment of the process of scattering) is responsible for partial absorption of the scattered particles. This absorption, which is shown in a weakening of the beam of incident particles, must be attributed, of course, to the reaction. If the elastic scattering of particles can be interpreted in terms of an optical model, therefore, it will give direct information on the probability of reaction as a function of the impact parameter. While describing reaction as absorption of the initial particles, an optical model, of course, will give no indication of the way in which energy is distributed among the degrees of freedom of the reaction

‡ The distinction between a model of direct dislodgment and a stripping model is most simply explained by comparing the limiting energies E^* of the incident atom A at which the exchange channel is closed. For the former case

$$E^*=\left(\frac{m_A+m_C}{m_A-m_C}\right)\left(\frac{m_A+m_B}{m_B}\right)D_{AB}$$

and for the latter

$$E^*=\left(\frac{m_A+m_B}{m_B}\right)D_{AB}.$$

products. In this sense it will give less information on the reaction than will detailed dynamic models. However, it possesses the advantage that it permits a simple interpretation of elastic scattering in terms of an interaction potential and an interaction responsible for charge transfer.

An energy diagram illustrating dissociative charge transfer is shown in Fig. 5. On the right are depicted the terms of the molecule X_2 and the ion X_2^- (internuclear distance r) when the intermolecular distance R is infinite. The left-hand side of the diagram shows the terms as a function of R. Term *1* corresponds to effective interaction of X_2 and M in the initial state with a fixed angle γ between the vector R and the molecular axis r of the molecule X_2. At great distances, which are of interest in the present problem, this interaction $W_C(R)$ is characterised by weak attraction. When the centrigual energy is taken into account, however, the effective potential $W_{C,\mathrm{eff}}(R) = W_C(R) + l^2/2\mu R^2$ represents repulsion. The set of effective ionic terms $W_i(R)$ corresponds to Coulombic attraction. For every value of the energy ϵ reckoned from the level of the separated system $X_2(n = 0)$ + M there is a corresponding term $W_i(\epsilon,R)$, and $W_{\mathrm{eff}}(\epsilon,R) = W_i(\epsilon,R) + l^2/2\mu R^2$. Among them Fig. 5 shows the boundary of the continuous spectrum *2* ($\epsilon = \epsilon_0$), term *3* corresponding to a vertical transition ($\epsilon = \epsilon^*$), the boundary of the Franck–Condon region *5* ($\epsilon = \epsilon^* - \Delta\epsilon$), and *6* ($\epsilon = \epsilon^* + \Delta\epsilon$), one of the terms of the continuous spectrum *4* (arbitrary ϵ).

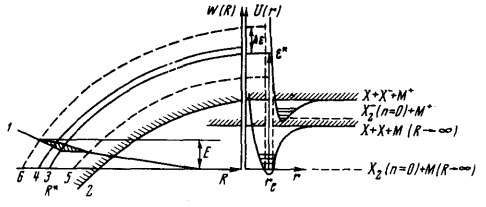


Figure 5. Electronic and vibrational terms involved in the dissociative charge transfer $M + X_2 \rightarrow M^+ + X^- + X$.

Interaction between covalent and ionic states can be described in different ways. Firstly, we can speak of non-adiabatic transitions between the covalent term and a continuous system of ionic terms. Secondly, we can speak of a broadening of a covalent term immersed in a continuum of ionic terms, and of conversion of a stationary into a quasi-stationary state. The second interpretation is illustrated in Fig. 5, where the covalent term *1* is shown broadened within the Franck–Condon region.

Let us suppose that the breakdown of each vibrational state of the molecule X_2 in the region $R \simeq R^*$ can be considered independently, and that the relative motion of X_2 and M can be described by means of classical mechanics. The first of these postulates permits a substantial simplification of the general problem, by reducing it actually to a two-body problem. The possibility of the independent description of dissociations arises only if, during passage through the Franck–Condon region, the interaction X_2–M does not induce vibrational transitions between the levels of X_2 (condition that the collisions shall be adiabatic) and if the interaction is sufficiently weak in absolute magnitude for no overlapping of the broadened vibrational levels of the X_2 molecule to occur in the region $R \simeq R^*$. These conditions can be written

$$\omega(X_2)\,\tau_{st} \gg 1 \qquad (4.3a)$$

$$\bar{\Gamma}_n/\hbar\omega(X_2) \ll 1 \qquad (4.3b)$$

where τ_{st} denotes the characteristic time of traversal of the Franck–Condon region, while $\bar{\Gamma}_n$ is the mean width of the vibrational level at $R \simeq R^*$. When conditions (4.3) are satisfied, the probability of dissociation of every level can be calculated by means of the formulae of the quasi-stationary adiabatic approximation

$$P_n = \exp\left[-\frac{1}{\hbar}\int_R \Gamma_n(R)\,dt\right] \qquad (4.4)$$

This approximation forms the basis of the so called optical model in stripping reactions[33–38]. Formula (4.4) gives the attenuation of a beam of elastically scattered particles moving along the trajectory $\mathbf{R} = \mathbf{R}(t)$. A rough estimate of the exponential (4.4) yields

$$\frac{1}{\hbar}\int \Gamma_n(R)\,dt = \frac{\bar{\Gamma}_n\tau_{st}}{\hbar} = \left(\frac{\bar{\Gamma}_n}{\hbar\omega}\right)(\omega\tau_{st}) \qquad (4.5)$$

We can see that conditions (4.3) do not restrict the value of this integral (4.5): the first factor on the right-hand side is small, while the second is large. This means that, to the approximation of independent vibrational states, a case of considerable absorption is possible, i.e. a relatively high probability of reaction. It is clear that, with sufficiently large impact parameters, the relations (4.3) will always be satisfied. However, the total contribution of those collisions for which the condition of relatively strong absorption $\bar{\Gamma}_n\tau_{st}/\hbar > 1$ is satisfied as well as conditions (4.3) will depend on the features of the interaction responsible for charge transfer.

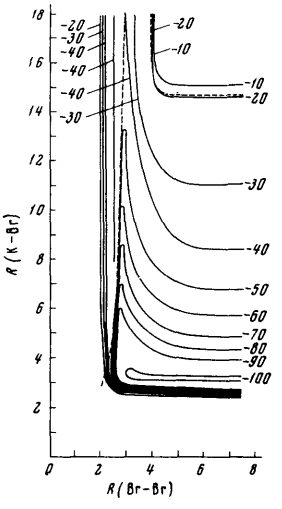


Figure 6. Energy surface for the reaction $K + Br_2 \rightarrow KBr + Br$ constructed by adiabatic mixing of covalent and ionic terms[32].

Infringement only of the first of the two conditions (4.3) implies that the channel of vibrational excitation can compete with the dissociation channel. If only the second condition is infringed, the probability of vibrational excitation is low, but the mutual influence of different vibrational states of the covalent electronic term must be taken into

account in calculating the probability of transition. However, these conditions are not fundamental, in the sense that an approximate solution of the problem can still be obtained from a consideration of two interacting particles. If neither of the conditions (4.3) is satisfied, the problem of calculating the cross-section, both of elastic scattering and of scattering accompanied by reaction, reduces to the general three-body problem, where we need consider only the one electronic term arising from the adiabatic mixing of both covalent and ionic states. The principal characteristics of the potential energy of a system for which a covalent state and an ionic state are fundamental are illustrated in Fig. 6. Here we note the main features of the motion of the representative point along a surface of this type. The presence of a sharp break on the surface, corresponding to transition from a covalent state to an ionic state of the partners, is very vividly illustrated by the concept of an "electronic harpoon"[30-32]. The atom M approaches the molecule X_2, and at quite a large distance, when the relative motion of the neutral pair M and X_2 can still be regarded as free, an electron passes from the atom M to the molecule X_2. After the electronic "harpoon" has linked the pair M^+ and X_2^- by Coulombic attraction, rearrangement of the system is possible, resulting in formation of the pair M^+X^- and X. The actual process of rearrangement can take place in various ways. In particular, the electronic term of the system X_2^- may correspond to an unstable state. If the time required for dissociation of the ion were short compared with that during which the distance between M^+ and X_2^- changed significantly, the angular distribution of the particles and the energy distribution could be calculated formally from the conservation laws for momentum and for energy. In contrast to a true stripping reaction, however, these relations should have also taken into account the change in energy and relative momentum of the pair X_2^- occurring on non-adiabatic transition of the X_2 molecule from a neutral to an ionic state. These ideas have been used to interpret experiments on the reactions of potassium, rubidium, and caesium atoms with bromine and iodine molecules[32]. If dissociation of the ion cannot be regarded as instantaneous, the general problem cannot be divided into a set of two-particle processes, and its solution requires explicit consideration of the interaction of three particles. In this way we arrive at the general problem mentioned in the Introduction.

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