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TEMPERATURE DEPENDENCE OF THE RATE OF GAS-PHASE REACTIONS

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CONTENTS

1. Introduction 872
2. Dissociation 873
3. Recombination 877
4. Exchange 877

1. INTRODUCTION

The rate constant of an elementary chemical reaction is usually expressed in the form of the Arrhenius equation:

$$k=A\exp(-E_0/kT) \qquad (1.1)$$

(where A and E_0 are constants) or of the formula

$$k = A_0T^{1/2}\exp(-E_0/kT), \qquad (1.2)$$

which follows from kinetic theory for when the activation energy is provided by the component of the kinetic energy of the relative motion of the interacting particles lying along the line of their centres[1]. Formula (1.2) can be obtained also in the more general example by assuming a particular dependence of the reaction cross-section upon the energy of relative motion[2]. Kassel[3] proposed also an empirical formula of the type:

$$k = CT^m\exp(-E_0/kT) \qquad (1.3)$$

($m > 0$), and gave some theoretical justification for it.

The dissociation rate constant is also frequently expressed in the form

$$k_d = A_0T^{-n}\exp(-D/kT), \qquad (1.4)$$

which takes account of the contribution of internal degrees of freedom to the activation of the molecule undergoing dissociation[1].

The rate constant of the recombination process, which is the reverse of the dissociation process, is most often described by the formula:

$$k_r = A_0T^{-m}. \qquad (1.5)$$

Whereas the formulae describing the rate constants of the dissociation and recombination processes have recently achieved some—but far from complete—theoretical justification, as discussed below, exchange processes on the other hand have hardly been investigated at all in spite of the fact that they are the commonest type of elementary reaction. Yet, it is possible to introduce some significant advances into the quantitative kinetics of exchange processes on the basis of the (still imperfect) theory of the transition state alone, and also on the basis of quantum statistics.

The main problem in the theoretical calculation of the rate constant is to evaluate the contribution of the various degrees of freedom and to make allowance for the perturbation of the equilibrium distribution brought about by the reaction itself. The transition state method avoids both these difficulties by assuming that the complicated energy exchange process can be described by the motion of the representative point along some reaction coordinate q_r whose choice is not strictly unique, whilst completely ignoring the perturbation of the equilibrium distribution of the reactants over the states. To some extent, correct allowance for these two factors can be made independently. First, we calculate the reaction cross-section σ_r as a function of the dynamic parameters of the partners during a collision—the initial vibrational states n_i and rotational states j, and also the relative velocity v of the colliding molecules. As a second step, the reaction rate R is calculated by averaging σ_r over all the n, j, v initial states by means of the expression

$$R = \int \sigma_r(n, j, v)\, v f(n, j, v)\, d\Gamma. \qquad (1.6)$$

Here $f(n, j, v)$ is the distribution function (in general, non-equilibrium) of the colliding molecules, normalised for the total number of reacting molecules. If the concentrations of the initial molecules are taken out of f as common factors, the reaction rate R can be expressed in the form

$$R = k(C_A)^\alpha(C_B)^\beta \qquad (1.7)$$

where k now has the significance of the rate constant of a reaction of order α with respect to reactant A, of order β with respect to reactant B, etc. The calculation of the

function f in expression (1.6) becomes a statistical problem which can be solved by examining the system of equations describing at the same time the relaxation (that is, the transitions between the various energy states of the reacting molecules) and the true chemical reaction (that is, the regrouping of atoms upon collision of the molecules).

Both these factors (the contribution of different degrees of freedom and the perturbation of the equilibrium distribution) influence the temperature dependence of the rate constant, and hence it is important to resolve explicitly the dynamic and the static parts of the pre-exponential factor of dissociation rate constants in order to understand the mechanism of the elementary act. In what follows, we shall briefly discuss the temperature dependence of dissociation, recombination, and exchange reactions in the gas phase.

2. DISSOCIATION

It is well established that the thermal dissociation of molecules is kinetically characterised by a first-order law at high pressures and by a second-order law at low pressures[4]. Between these two extremes is found a transition region of pressures where the reaction order varies from first to second. The pressure dependence of the dissociation rate constant arises, essentially, from the disturbance of the equilibrium distribution over the internal degrees of the reacting molecules. Since the extent of this disturbance varies with pressure, it is desirable to consider separately the possible limiting cases of the reaction

$$AB+M\rightarrow A+B+M \qquad (2.1)$$

First-Order Reactions

It is evident from physical considerations that at high pressures, when the rate of intermolecular energy transfer is greater than the rate of intramolecular energy transfer, the disturbance of the equilibrium distribution is a minimum†. Therefore we must assume that here the transition state method should lead to a satisfactory approximation for the rate constant k of the reaction. The general expression for k within the limits of this approximation is[6]

$$(k_d)_\infty = g^+\chi\frac{kT}{2\pi\hbar}\frac{F^+_{AB}}{F_{AB}}\exp(-E_0/kT), \qquad (2.2)$$

where F_{AB} and F^+_{AB} are the partition functions of the stable and the activated molecule, g^+ is the number of independent decomposition paths, and χ is the transmission coefficient.

† Throughout this paper we shall assume, when dealing with the mechanism of intramolecular energy transfer in an active molecule, that the statistical approximation is applicable. According to the modern concepts of the statistical theory[4,5] of unimolecular reactions, all the degrees of freedom of active and of activated molecules can be classified into inactive, adiabatic, and active. The first do not generally take part in energy redistribution and they do not appear explicitly in the expression for the rate constant. As regards the second, it is assumed that during the intervals between collisions the quantum numbers which characterise these degrees of freedom do not alter, but on going from an active to an activated molecule a change in these degrees of freedom is assumed—in particular, a change from vibrations to rotations[5].

The factor F^+_{AB} can be said to be known if the configuration of the activated molecule is known, or alternatively if the critical surface S^+ in (A + B) phase space is known, since its intersection with the representative point can be identified with the completion of the elementary chemical act. If we adopt a system of harmonic oscillators as a model of the molecule, and the transmission coefficient is close to unity, it follows from Eqn. (2.2) that at high temperatures ($kT \gg \hbar\omega_i$) the pre-exponential factor is of the same order as the molecular vibration frequency. Furthermore, using the theory of small vibrations it can be shown that the term $\frac{kT}{2\pi\hbar}\frac{F^+_{AB}}{F_{AB}}$ in Eqn. (2.2) always falls between the lowest and the highest frequency of the active molecule. Nevertheless, the general treatment in principle does not set an upper limit to the pre-exponential factor. However, since the frequency factor of the majority of experimentally investigated uni molecular reactions is found to be of the same order as the vibration frequency, reactions whose pre-exponential factor is greater than 10^{14} s^{-1} are often treated in the literature as having an anomalously high pre-exponential factor. High pre-exponential factors are associated with the appearance of a high degree of anharmonicity in the internal vibrations of the molecule. Anharmonicity loosens the intramolecular bonds and leads to the formation of a weakly bound activated molecule. This effect is often referred to as a large entropic contribution by the activated molecule to the partition function F^+.

The simplest (and from the quantitative aspect the most important) manifestation of anharmonicity during dissociation is the conversion of various types of vibration of the active molecule into free rotation of the activated molecule.

We can make an order-of-magnitude estimate of the contribution made by the conversion of one vibrational degree of freedom of the AB molecule into a rotational degree of freedom of the activated molecule. Under classical conditions ($kT \ll \hbar\omega_i$) we have

$$F_{vibr} = kT/\hbar\omega,\ F_{rot} = (2IkT)^{1/2}/2\pi\hbar\,. \qquad (2.3)$$

Calculation of the frequency on the basis of the Morse potential leads to $\frac{F_{rot}}{F_{vibr}} \simeq (D/kT)^{1/2}$, where D is the energy of the chemical bond.

As an example of a reaction with an anomalously large frequency factor we may consider the thermal dissociation of ethane into two CH_3 radicals. The calculation by Setser and Rabinovitch[7] uses a model of the C_2H_6 molecule in the activated state involving 12 oscillators (2 non-interacting CH_3 radicals) and 5 active rotators (free internal rotation of the CH_3 groups about the C–C axis and 4 degrees of freedom corresponding to the swing of the planes of the H_3 atoms of each CH_3 group). The C–C bond is chosen as the reaction coordinate. The calculation leads to a pre-exponential factor for the reaction of 10^{17} s^{-1} at 600°C. This figure agrees with the value derived from the experimental bimolecular recombination constant by using the relationship between the dissociation and recombination constants given by the equilibrium constant.

Formula (2.2) for the rate constant k_∞ is strictly accurate if the quantity F_{AB} is taken to be the total partition function of the activated molecule. When the problem is formulated in this way the whole of the difficulty attending the calculation of the constant is transferred to a correct definition of the critical surface. This task is generally extremely complex. Therefore in every instance when the critical surface is determined from simple qualitative

considerations a factor χ, which makes allowance for the repeated passage of a representative point through the critical surface, is introduced. Exact calculation of χ is equivalent to solving the many-body problem. An attempt to solve this problem is equivalent to denying the simplifying assumptions associated with the introduction of a reaction coordinate. However, since the latter approach is thought to be justified, we shall use the expression for χ (and discuss the temperature dependence of the transmission coefficient) which applies to the one-dimensional model.

For adiabatic reactions, assuming negligible contribution of the tunnel effect, we can put $\chi = 1$. For non-adiabatic reactions involving a change in electronic state the situation $\chi \ll 1$ is entirely possible. In this case we obtain the following expression for χ on the basis of the Landau–Zener formula[8]:

$$\chi = 2\pi W^2/\Delta F\hbar\,(kT/2\pi\mu)^{1/2}\,, \qquad (2.3a)$$

where μ is the effective mass corresponding to the motion along the reaction coordinate, ΔF is defined by the difference between the slopes of the intersecting terms U_1 and U_2 ($\Delta F = |dU_1/dq_1 - dU_2/dq_2|$); W is the matrix element which connects the relevant electronic energy levels. If the connection is through spin–orbital interaction, W is independent of T, and Eqn. (2.3a) leads to the expression

$$\chi(T) \simeq T^{-1/2}\,. \qquad (2.4)$$

If the non-adiabatic connection is due to Coriolis forces acting on the electrons, W is proportional to the speed of rotation of the molecule, so that $W^2 \simeq T$. Hence, from (2.3), we have

$$\chi(T) \simeq T^{1/2}\,. \qquad (2.5)$$

The tunnel corrections, which alter the value of χ when quasi-classical conditions cease to apply to the motion of the representative point near the critical surface, have different forms for adiabatic and non-adiabatic reactions. For the former, the tunnel correction arises from the penetration of the particle under a potential barrier which is approximately parabolic (at least, near the top of the barrier), and the approximate expression for χ is of the form[9]

$$\chi(T) \simeq (\hbar\omega^*/2kT)\sin(\hbar\omega^*/2kT)\,, \qquad (2.6)$$

where ω^* denotes the vibration frequency close to the minimum of the "inverted" potential hump.

In the second instance, penetration by the tunnel effect takes place below the point of quasi-intersection of the terms, and the shape of the barrier is nearer to triangular than to parabolic. Under these conditions χ is described[10] as the product of the over-the-barrier transmission coefficient (2.3a) and an exponential tunnel correction:

$$\chi(T) = \frac{2\pi W^2}{\Delta F\hbar\,(kT/2\pi\mu)^{1/2}}\exp\left[\frac{1}{12}(\varepsilon/kT)^3\right],\quad \varepsilon = \left[\hbar\,\frac{\partial U_1}{\partial q_1}\frac{\partial U_2}{\partial q_2}\Big/\sqrt{2\mu\Delta F}\right]^{2/3}. \qquad (2.7)$$

Evidently, a situation in which $\chi > 1$ becomes possible if tunnel transmission is taken into account. In other words, the effective activation energy becomes lower than the energy E_0 of the potential barrier. The correction for barrier lowering has a complicated temperature dependence, and it is therefore assigned to the pre-exponential factor.

Calculation of the statistical summations in (2.2) leads to the following formulae for the temperature dependence of the pre-exponential term if the model of the dissociating molecule is set up in terms of a system of s oscillators and r rotators and that of the activated molecules in terms of s^+ oscillators and r^+ rotators:

$$A(T) \simeq \chi(T)\,T^{(r^+-r/2)+1},\ \hbar\omega_i,\ \hbar\omega_i^+ \gg kT \qquad (2.8)$$

$$A(T) \simeq \chi(T)\,T^{(r-r^+)/2},\ \hbar\omega_i,\ \hbar\omega_i^+ \ll kT \qquad (2.9)$$

with $r^+ > r$ in most cases. Thus, leaving aside the transmission coefficient χ, the quantity A is characterised by a positive temperature dependence at low temperatures and a negative (or zero for $r^+ = r$) temperature dependence at high temperatures.

Second-Order Reactions

At low pressures the rate of decomposition is substantially influenced by the disturbance of the Boltzmann distribution over the internal degrees of freedom of the decomposing molecule. Hence the transition state method cannot be used to calculate the rate constant k of the reaction. For the same reason, the temperature dependence of $A(T)$ can be calculated only if the detailed excitation mechanism of the molecule AB to the dissociation threshold is known, since in the low-pressure region the rate of decomposition is limited by the rate of vibrational relaxation of excited vibrational states. Since we still lack adequate information on the probability of energy exchange during the collision of vibrationally excited molecules, we may conveniently consider the two limiting cases of activation which allow k_d to be calculated in a closed form and lead to a number of conclusions on the temperature dependence of A.

These limiting cases are known in the literature as the strong collision mechanism and the stepwise excitation mechanism[5]. The former mechanism assumes that the AB molecules which decompose at low pressures are those with energy $E_{vibr} > D$ (the active AB* molecules), and that the rate of deactivation of the active molecules does not depend on their state and is determined by the effective number of collisions between AB* and M per unit time. In this instance the principle of detailed balance requires a rate of decomposition, identical to the rate of excitation to energy states $E_{vibr} > D$, given by

$$k_d = Z\int_D^\infty \rho(E)\exp(-E/kT)\,dE/F_{AB}\,. \qquad (2.10)$$

In this excitation mechanism the dissociation produces a disturbance of the equilibrium distribution only above the threshold level. For $E_{vibr} < D$ the vibrational distribution function retains its equilibrium value.

In the stepwise excitation mechanism it is assumed that each collision between AB and M transfers an amount of energy small compared to the dissociation energy D. Thus, the molecules which react at low pressures have approached the energy threshold from below, and the concentration of active molecules is negligibly small.

If excitation of the AB molecules occurs as a result of single-step vibrational transitions ($n \to n+1$) the expression for k_d has the form

$$k_d = Z_0\left[\sum_{n=0}^{N}\exp[E_n/kT]/P_{n,n-1}\right]^{-1}\Big/F_{AB}\,; \qquad (2.11)$$

N is the number of the level corresponding to the dissociation threshold, and $P_{n,n-1}$ is the transition probability referred to a single gas-kinetic collision. For ease of comparison with (2.10), this expression can be transformed

in a way which allows generalisation to many-quantum transitions and contains as a parameter the mean square of the energy transferred at each collision $\langle\Delta E^2\rangle$. By definition we have

$$\langle\Delta E^2\rangle = (\Delta E_{n-1,n})^2 P_{n-1,n} + (\Delta E_{n,n+1})^2 P_{n,n+1} . \quad (2.12)$$

Assuming that the transition energy $\Delta E_{n,n-1}$ is an insensitive function of n, Eqn. (2.12) can be rewritten in the form

$$\langle\Delta E^2\rangle = 2\,(\Delta E^2_{n,n-1})^2\, P_n , \quad (2.13)$$

where we have used the terminology $P_n \simeq P_{n,n-1} \simeq P_{n,n+1}$. Substituting P_n from (2.12) into (2.11) and replacing the summation by an integral (which is permissible for $\langle\Delta E^2\rangle^{1/2} \ll kT$) we find

$$k_d = Z_0\Big[\int_0^D \exp(E/kT)\frac{2dE}{\rho(E)\,\langle\Delta E^2(E)\rangle}\Big]^{-1}\Big/F_{AB} . \quad (2.14)$$

It is assumed that the density of levels $\rho(E)$ is related to ΔE by $\rho(E) \simeq (\Delta E)^{-1}$. The quantity $\langle\Delta E^2\rangle$ in (2.14) is equivalent to a diffusion coefficient of the representative point over the energy levels. Hence we may suggest that Eqn. (2.14) will be correct also for many-quantum transitions provided that the excitation process can be described by the Fokker–Planck equation in energy space. Following Pitaevskii[11], we may test this assumption by direct integration of the equation as given, for example, by Nikitin[5].

The conditions under which the diffusion equation is applicable, already used above, are defined by the inequality $\langle\Delta E^2\rangle \ll (kT)^2$.

Comparing (2.14) with (2.10) we see that in the stepwise dissociation mechanism it is only molecules below the dissociation threshold ($E_{vibr} < D$) which contribute to the rate of decomposition. Thus, decomposition leads to zero population of the active molecule states and to breakdown of the equilibrium distribution below the F threshold[5]. The actual mechanism of the activation is intermediate between the two discussed above, and in general the rate of decomposition will be affected by the distribution of molecules both above and below the threshold.

By separating the exponential term from (2.10) and (2.14) we arrive at the following expressions for the pre-exponential term

$$A_1 = Z_0\int_0^\infty \rho(D+\varepsilon)\exp(-\varepsilon/kT)\,d\varepsilon/F_{AB} \quad (2.15)$$

$$A_2 = Z_0\Big[\int_{-\infty}^0 \exp(\varepsilon/kT)\frac{2d\varepsilon}{\rho(D+\varepsilon)\,\langle\Delta E^2(D+\varepsilon)\rangle}\Big]^{-1}\Big/F_{AB} . \quad (2.16)$$

Eqn. (2.15) applies to the strong collision mechanism, whereas Eqn. (2.16) applies to the stepwise excitation mechanism. In these expressions the quantity ϵ is measured from the dissociation limit; Eqn. (2.16) also assumes that the lower integration limit in (2.14) is insignificant.

We shall now turn to the temperature dependence of the pre-exponential A in the decomposition of polyatomic molecules. The calculation becomes particularly simple when the molecule can be described with acceptable precision by a model consisting of a system of s harmonic oscillators and r rotators. In the semi-classical approximation we have

$$\rho(E) = \frac{F_{rot}}{(kT)^{r/2}}\,\frac{(E+E_z)^{s+r/2-1}}{\Gamma(s+r/2)\,\Pi\hbar\omega_i} \quad (2.17)$$

where the zero-point vibration energy E_z is expressed in terms of the vibration frequency ω_i of the molecule AB by the relation

$$E_z = \frac{1}{2}\sum_i \hbar\omega_i \quad (2.18)$$

and F_{rot} denotes the rotational partition functions. Inserting (2.17) into (2.15) and taking $\rho(D+\epsilon)$ out of the integral at the point $\epsilon = 0$, we obtain

$$A_1 = \frac{Zg_{el}}{(s+r/2-1)!}\,\frac{(D+E_z)^{s+r/2-1}kT^{1-r/2}}{\prod_{i=1}^{s}\hbar\omega_i}\prod_i[1-\exp(-\hbar\omega_i/kT)]. \quad (2.19)$$

In this expression we have placed in evidence the term g_{el}, which allows for the contribution of electronically excited states lying below the dissociation threshold to the rate of decomposition. Formula (2.19) is correct within the following limitations, which are necessary to justify the use of Eqn. (2.17) and the approximation made in the integration of Eqn. (2.14):

$$D \gg skT, \quad (2.20a)$$

$$D > \sqrt{s}E_z . \quad (2.20b)$$

Formal insertion of the limit $s \to 1$ in Eqn. (2.19) leads (for $\hbar\omega/kT \ll 1$) to the well-known formula of the simplest collision theory if we put $g_{el} = 1$. This formula does not take account of the perturbation of the equilibrium distribution brought about by the decomposition.

In the classical limit Eqn. (2.19) leads to

$$A_1 \to Z_0 g_{el}\left(\frac{D+E_z}{kT}\right)^{s+r/2-1}\Big/\left(s-1+\frac{r}{2}\right)! \quad (2.21)$$

We now turn to a discussion of formula (2.16). In all real systems the functions $\langle\Delta E^2\rangle$ and $\rho(E)$ vary more slowly than exponentially for $E/kT \gg 1$. Hence, to evaluate the temperature dependence of A these functions can be taken out of the integral at the point $E = E_0$, that is, we can assign the energy transferred and the density of levels to states lying below the dissociation boundary by an amount kT. This leads to the expression

$$A_2 = Z_0 g_{el}\,\frac{\langle\Delta E^2\rangle}{(kT)^2}\,\rho(E_0-kT)\,\delta E\prod_{i=1}^{s}[1-\exp(-\hbar\omega_i/kT)]. \quad (2.23)\ddagger$$

In this expression the energy interval δE, which characterises the width of the region in which the equilibrium distribution is substantially disturbed, can be determined only by evaluating the integral in (2.16). As applied to the oscillator model of a polyatomic molecule, Eqn. (2.23) can be re written

$$A_2 = Z_0 g_{el}\,\frac{1}{2}\,\frac{\langle\Delta E^2\rangle}{kT}\,\frac{(E_0+E_r)^{s-1}}{\prod_{i=1}^{s}(\hbar\omega_i)}\prod_{i=1}^{s}[1-\exp(-\hbar\omega_i/kT)]. \quad (2.24)$$

In the classical limit ($\hbar\omega_i \ll kT$), expression (2.23) takes the form

$$A_2 = Z_0 g_{el}\,\frac{1}{2}\,\frac{\langle\Delta E^2\rangle}{(kT)^2}\left(\frac{E_0+E_n}{kT}\right)^{s-1}\Big/(s-1)! \quad (2.25)$$

Unlike formula (2.21), this expression contains the factor $\frac{1}{2}\langle\Delta E^2\rangle/(kT)^2$, which should be much smaller than unity as long as diffusion theory applies. However, if we put $\langle\Delta E^2\rangle \simeq (kT)^2$, Eqn. (2.25) is formally converted into (2.21). The temperature dependence introduced by this term cannot be established in general. A few conclusions

‡ No Eqn. (2.22) in Russian (Ed. of Translation).

are possible only if the anharmonicity of the vibrations is large, so that collisions have a high probability of leading to combination transitions in which various normal vibrations are excited and deactivated at the same time. No limits are imposed on the magnitude of the energy transferred. The only criterion which can probably be applied to evaluate $\langle\Delta E^2\rangle$ is the criterion put forward by Massey: the energy transferred with the highest probability is ΔE^*, defined by the condition

$$\Delta E^*/\hbar\alpha\bar{v}\sim 1 \qquad (2.26)$$

where $\bar{v}$ is the mean velocity of the colliding molecules and α^{-1} is the radius of action of the intermolecular potential. From (2.26) we arrive at

$$\langle\Delta E^2\rangle/(kT)^2\sim\frac{1}{T} \qquad (2.27)$$

by putting $(\Delta E^*)^2\simeq\langle\Delta E^2\rangle$ which is consistent with the condition (2.27). The stepwise excitation mechanism introduces an additional factor (T^{-1}) as compared with the strong collision mechanism.

These general ideas need to be made more precise before they can be applied to diatomic molecules. In general, there is no way of predicting which of the activation mechanisms will apply to the dissociation of diatomic molecules. Only in the simplest example—dissociation in an inert gas atmosphere—can we assert that excitation will be by the stepwise mechanism (see below). The non-equilibrium distribution function for vibrational states is zero at $E_{vibr} > D$ in the decomposition of diatomic molecules whatever the activation mechanism. Below the dissociation threshold the distribution function is close to its equilibrium value for strong collisions, and is very different from its equilibrium value (although it approaches it on moving away from the threshold) for stepwise excitation.

Expression (2.23) must be slightly modified for diatomic molecules. This is because rotation of the molecule causes significant distortion of the potential curve, thus altering the effective dissociation energy. Therefore, strictly speaking, the dissociation of a diatomic molecule cannot be described only in terms of diffusion in total energy space: we must also take into consideration diffusion in angular momentum space. In this instance, allowance for the rotational partition function F_{AB}^{rot} introduces into Eqn. (2.23) the factor g_{rot}, which has a weak temperature dependence ($g_{rot}\simeq T^{-1/2}$–$T^{-1/3}$). If the reduced mass of A and B is less than (or of the same order as) the reduced mass of AB and M, one-quantum transitions will take place up to the dissociation limit. Here we put $\langle\Delta E^2\rangle\simeq(\Delta E^*)^2$, $\rho(E_0 - kT)\simeq 1/\Delta E^*$. These lead to the expression

$$A_2\simeq Zg_{el}g_{rot}\ \frac{\Delta E^*}{kT}[1-\exp(-\hbar\omega/kT)]. \qquad (2.28)$$

In the opposite case, when dissociation of a heavy diatomic gas is proceeding in an atmosphere of a lighter gas, the average energy transferred $\langle\Delta E^2\rangle$ can be obtained (impulsive approximation) by considering the two-body collisions A–M and B–M. In this approximation we can write

$$\langle\Delta E^2\rangle\sim\frac{\mu_{AB-M}}{\mu_{AB}}E_{kin}^{AB}\,kT\,, \qquad (2.29)$$

where E_{kin}^{AB} is the mean kinetic energy of the nuclei of the AB molecules. A detailed investigation[12,13] has shown that the product $\rho(E)E_{kin}^{AB}$ close to the dissociation boundary, which appears in the general expression (2.23) for the rate constant, is relatively insensitive to the model chosen for the decomposing molecule. In particular, identical temperature dependences of A_2 are obtained for a chopped harmonic oscillator and for a Morse oscillator:

$$A_2^{harm}\sim A_2^{Morse}\sim Zg_{el}g_{rot}\ [1-\exp(-\hbar\omega/kT)]\,. \qquad (2.30)$$

Formulae (2.18) and (2.30) have been obtained for different limiting assumptions regarding the parameter which determines the effectiveness of energy transfer—the ratio of the collision time $\tau\simeq 1/\alpha\bar{v}$ to the vibration period of the nuclei $1/\omega$. Hence we may assume that in all intermediate cases the temperature dependence of the pre-exponential term A describing the dissociation of diatomic molecules will be of the form

$$A\sim T^{1/s}[1-\exp(-\hbar\omega/kT)]g_{rot}(T)\,. \qquad (2.31)$$

Experiments in shock tubes at high temperatures ($\hbar\omega/kT\ll 1$) lead to an expression of the type of (2.31) for the dissociation of diatomic molecules in an inert gas atmosphere. If, on the other hand, the dissociation takes place in an atmosphere of the diatomic gas or in an atmosphere of a monatomic gas of the same element (for example, dissociation of O_2 by O_2–O_2 and O_2–O collisions), the experimentally observed value of the factor A shows a stronger, negative temperature dependence than predicted by the above theory. A theoretical explanation of this discrepancy involves making allowance for energy transfer between the vibrational, rotational, and translational degrees of freedom of the reactants, and also evaluating possible non-adiabatic effects. Unfortunately, reliable calculations of these processes are still lacking.

Intermediate Pressure Region

In the transition region between first-order and second-order reactions the observed rate of decomposition is determined by competition between intermolecular and intramolecular energy exchange processes. Therefore, in addition to the considerations of activation and deactivation mechanisms discussed above, the theory must include assumptions on the kinetics of energy redistribution within the molecule. These kinetics are characterised by the distribution function $h(\tau)$ of active molecules over the relaxation times τ. The available information on the function $h(\tau)$ is mainly based on a theoretical study of model systems and does not allow us to relate the distribution function uniquely to the dynamic characteristics of real molecules[14]. Therefore, calculations of the constant k in the intermediate pressure region usually involve the assumption of instantaneous statistical redistribution of the energy within the molecules§. This is equivalent to assuming an exponential form of the function $h(\tau)$:

$$h(\tau)=k(E)\exp[-k(E)\tau]\,, \qquad (2.32)$$

where $k(E)$ is the rate constant of the spontaneous decomposition of the active molecule. If we adopt the hypothesis (2.32), we can find the rate constant $k(E)$ by solving the kinetic equations describing the spontaneous decomposition and relaxation in terms of the two alternative activation mechanisms. Of course, the strong collision mechanism and the stepwise activation mechanism lead to different general expressions for $k(T)$. We note only that a relatively simple formula, often used to interpret experimental

§ The term instantaneous in this context means that the characteristic time for the statistical redistribution is much smaller than the time between successive collisions.

results, can be obtained solely from the strong collision mechanism. It is of the form

$$k = \frac{kT}{2\pi\hbar}\frac{F_1^+}{F_1F_2}\exp(-E_0/kT)\int_{E^+=0}^{\infty}\frac{g^+W_2^+(E^+)\exp(-E^+/kT)\,dE^+/kT}{1+g^+W_2^+(E^+)/2\pi\hbar\rho_2(E_0+E^+)Z}, \quad (2.33)$$

where, to avoid excessive complication, the contribution of adiabatic degrees of freedom has been ignored¶ and $\chi = 1$ has been assumed.

We cannot write an explicit expression for $k(T)$ using the stepwise excitation mechanism in the transition region, because the non-equilibrium distribution function must be determined by solving a system of related equations or from the Fokker–Planck equation. A few results have been obtained for relatively simple models discussed by Nikitin[16].

3. RECOMBINATION

The rate of recombination—the reverse process to dissociation—can be calculated in terms of the rate of dissociation and the thermodynamic equilibrium constant. In spite of the fact that both dissociation and recombination produce a disturbance of the equilibrium distribution, there are conditions under which the following relation holds true:

$$k_d/k_r = K_{eq}\ . \quad (3.1)$$

We shall not discuss them here: the reader is referred to the literature[17-26]. We shall only point out that two limiting regions of pressure exist also for recombination, corresponding to third-order and second-order kinetics respectively, as well as a transition region of pressures. Since the following equality applies

$$K_{eq} = F_AF_B/F_{AB}\exp(-D/kT)\ , \quad (3.2)$$

the recombination constant can be written, in terms of the factor $A(T)$ which characterises the rate of decomposition, in the form

$$k_r = A(T)\frac{F_{AB}}{F_AF_B}\ . \quad (3.3)$$

We shall discuss this expression in greater detail for the case of recombination of atoms. Using the fact that $Z \simeq T^{1/2}$ and $F_AF_B \simeq T^3f_A^{el}f_B^{el}$, we arrive at the following expression for the temperature dependence of k_r:

$$k_r \simeq Zg_{el}g_{rot}\ \frac{\Delta E^*}{kT} = \frac{T^{3/2}T}{T^3f_A^{el}\ f_B^{el}}g_{el}g_{rot}\ \frac{\Delta E^*}{kT}\ . \quad (3.4)$$

Eqn. (3.4) assumes the single-quantum transition model, whereas Eqn. (3.5) is based on the diffusion model ignoring the temperature dependence of f_A^{el} and f_B^{el}:

$$k_r \simeq Zg_{el}g_{rot}\ \frac{\langle\Delta E^2\rangle}{2(kT)^2}\rho(E_0-kT)\frac{T^{3/2}T^2}{T^3f_A^{el}f_B^{el}} \simeq g_{el}g_{rot}\ \frac{\langle\Delta E^2\rangle}{kT}\rho(E_0-kT) \quad (3.5)$$

In many instances, however, the electronic part of the partition functions of atoms is a sensitive function of temperature because of the contribution from the lower excited states, and this must of course be taken into consideration when calculating the temperature dependence of the constant k_r by formula (3.3).

¶ The influence of adiabatic degrees of freedom, which is relatively small for polyatomic molecules, has been considered in the work of Marcus[15].

If the molecule is described approximately by means of a Morse oscillator, the quantity ΔE^* is evaluated by the Massey criterion (2.26), and account is taken of the temperature dependence of g_{el}, the following equation can be derived from Eqns. (3.4) and (3.5):

$$k_r \simeq g_{rot}\ (T)\frac{\Delta E^*}{kT} \simeq T^{-m-1/2},\ m \simeq {}^1/_2 \text{ to } {}^1/_3. \quad (3.6)$$

Thus, the theory predicts a negative temperature coefficicient for the rate constant of recombination. However, the following restrictions must be borne in mind.

Firstly, Eqns. (3.4), (3.5), and (3.6) have been derived on the assumption that the third body M is an inert gas atom. If internal degrees of freedom in M can play a significant role in the deactivation of the excited AB pair, the temperature dependence of the constant k_r may be different from Eqn. (3.6). We may assume that the main difference will be that here the quantity ΔE^* is not given by formula (2.26).

Secondly, the possibility of recombination through the formation of an intermediate complex has been ignored in the derivation of Eqns. (3.4) and (3.5):

$$A + M \rightarrow AM \quad (3.7a)$$

$$AM + B \rightarrow AB + M\ . \quad (3.7b)$$

In this recombination mechanism the constant k_r must contain the exponential term $\exp(\epsilon/kT)$, arising essentially because the recombination reaction involves bound AM pairs with a bond energy ϵ. The value of ϵ varies between 0.5 and 5 kcal mole^{-1} for different molecules†. Hence expressions of the type of (3.6) are applicable only at relatively high temperatures, when $\epsilon/kT \ll 1$.

Lastly, we should note that when recombination occurs under conditions such that three-body A + A + A collisions are significant, the temperature dependence of the recombination constant may be noticeably affected by the exchange reaction[27]

$$A_2 + A \rightarrow A + A_2\ . \quad (3.8)$$

Direct experimental evidence exists that the reaction (3.8) is important in the vibrational relaxation of diatomic molecules even at low levels[28]. Since the rate of reaction (3.8) must increase as the vibrational energy of the A_2 molecule increases, it is reasonable to expect that reaction (3.8) can provide an effective means of removing energy from the latterly formed A_2 molecule in the vibrational deactivation of the higher states.

The recombination of oxygen in an argon atmosphere[29] is one of the few examples of recombination processes for which the temperature dependence of the rate constant has been definitely characterised.

4. EXCHANGE

Exchange reactions, like dissociation and recombination, can give rise to varying degrees of disturbance of the equilibrium distribution. However, unlike the other reactions, the exchange reaction does not usually show a change in reaction order due to disturbance of the equilibrium distribution. This is because both the relaxation and particularly the redistribution of atoms occur during collisions of molecules of the same type. Perturbation of the equilibrium distribution will change the order of the reaction

† This mechanism was studied in detail by Rice[26].

with respect to the concentration of the reacting molecules only if conditions are such that relaxation and exchange occur as a result of collisions between different molecules. We shall deal later with one example of a process of this type, but first we must discuss the calculation of $k_{ex}(T)$ within the bounds of equilibrium theory. This approximation is known to be realistic for exchange reactions occurring in a dense atmosphere of inert gas, which ensures sufficiently fast relaxation.

Starting with the basic formula of the transition state method, we shall consider processes involving three or four atoms. Take the simplest exchange process, of the type

$$A + BC \rightarrow AB + C \ . \qquad (4.1)$$

We note that the critical surfaces S^+ are chosen in different ways according to whether or not the reaction involves an activation energy. For surfaces with a potential barrier the reaction coordinate is most naturally identified as the line of fastest descent from the saddle point. We assume that rotation can be separated from vibration and from motion along the reaction coordinate, both in the starting systems and in the activated complex. Then the general formula of the transition state method can be written in detail as follows:

$$k_{ex} = \frac{kT}{2\pi\hbar}\varkappa g^+ \frac{F^+_{AB}}{F_A F_B}\exp(-E_a/kT) =$$

$$= \frac{kT}{2\pi\hbar}\varkappa g^+ \frac{(F^+_{AB})_{tr}\,(F^+_{AB})_{vibr}(F^+_{AB})_{rot}}{(F_AF_B)_{tr}\,(F_AF_B)_{vibr}(F_AF_B)_{rot}}\exp(-E_a kT) \ . \quad 4.2)$$

Having thus adopted a concrete model for S^+, we find that the partition function F^+ in the general formula (4.2) acquires a definite meaning: $(F^+_{AB})_{rot}$ is calculated as the partition function of a solid with atoms fixed at the points q^+_i, and $(F^+_{AB})_{vibr}$ as the partition function of a system of harmonic oscillators with normal frequencies ω^+_i, referred to the non-rotating system of atoms with a fixed value of the reaction coordinate q^+_r.

For a reaction involving three atoms, the expression for k_{ex} takes different forms for linear and triangular complexes. In the former we have three vibrational and two rotational degrees of freedom; In the latter, two vibrational and three rotational. The temperature dependence of k is as follows:

linear complex

$$k_{ex} \simeq T^{1/2}\frac{(1-e^{-\hbar\omega_{BC}/kT})}{\prod_{i=1}^{2}(1-e^{-\hbar\omega_i^+/kT})}\exp(-E_a/kT) =$$

$$= \begin{cases} T^{-1/2}\exp(-E_a/kT), & \hbar\omega_i/kT \gg 1 \qquad (4.3a) \\ T^{3/2}\exp(-E_a/kT), & \hbar\omega_i/kT \ll 1 \ ; \qquad (4.3b) \end{cases}$$

triangular complex

$$k_{ex} \sim \frac{(1-e^{-\hbar\omega_{BC}/kT})}{\prod_{i=1}^{3}(1-e^{-\hbar\omega_i^+/kT})}\exp(-E_a/kT) = \begin{cases} \exp(-E_a/kT), & \hbar\omega_i/kT \gg 1 \ (4.4a) \\ T\exp(-E_a/kT), & \hbar\omega_i/kT \ll 1 \ (4.4b) \end{cases}$$

We can follow the transition between these two examples by taking account of the interaction between vibrations and rotation in the calculation of F^+, and by abandoning the "rigid rotator–harmonic oscillator" model used for computing the spectroscopic approximation. The rate constant expressed in the form of (4.4) is applicable only to a complex ABC^+ in which the angular departure from the linear configuration is significantly larger than the angular amplitude of the bending vibrations. As regards the temperature dependence of the pre-exponential term in (4.3) and (4.4) we note that at low temperatures the indicated dependence will apply only as long as the tunnel corrections can be ignored. The limitation at high temperatures arises from the condition that the mean vibration amplitude must be small as compared with the effective width of the potential well $1/\alpha$‡. This limitation can be expressed as a requirement that the value of the full pre-exponential factor must be substantially less than the number of collisions given by gas kinetics. If the relationship

$$\frac{kT}{2\pi\hbar}\frac{F^+_{ABC}}{F_A F_{BC}} < Z_{A-BC} \ , \qquad (4.5)$$

were formally found not to be obeyed, we would need to use as pre-exponential term the factor Z_{A-BC}, which gives a $T^{1/2}$ temperature dependence[30] to the pre-exponential term instead of $T^{3/2}$ as in (4.3) or T as in (4.4).

We shall now consider the potential energy surface in the absence of an activation barrier. The situation is typical of ion–molecule reactions, and can also arise in the reaction of various atoms with molecules.

If the interaction between the species A and BC at large enough distances corresponds to attraction, the reaction rate is in many instances determined by the rate of formation of the long-lived ABC* complex. In practice, of course, the complex ABC* can decompose either in the direction of AB + C or in the direction of A + BC, but conditions are often met when decomposition in the reverse direction can be ignored. With these assumptions, reaction (4.1) can be described by the following model: if the radial velocity of the approaching particles is sufficient to overcome the centrifugal barrier, the complex ABC* is formed, and then decomposes into the molecules AB + C. If the interaction potential is centro-symmetrical the model is described by a critical surface S^+ coinciding with a sphere of radius R_m corresponding to the coordinate of the centrifugal barrier.

Such an S^+ surface is determined not only by the characteristics of the potential, but also by the integrals describing the motion of the system under study, since R_m depends on the angular momentum of the relative motion of A and BC.

Calculations of this type[31] for potentials $U(R) \simeq R^{-s}$, with $s = 4$ (polarisation interaction) and $s = 6$ (van der Waals interaction) lead to the following expressions for the rate constants

$$k_{ex} = 2\pi e\,(\alpha/\mu)^{1/2} \ , \qquad (4.6)$$

$$k_{ex} = 2^{5/2}\,3^{1/2}\,\Gamma(2/3)\frac{\pi^{1/2}}{\sigma^+}(kT)^{1/6}\left[\frac{\alpha_1\alpha_2 I_1 I_2}{I_1+I_2}\right]^{1/2}\mu^{-1/3} \ . \qquad (4.7)$$

Here α denotes the polarisability of the neutral partner in an ion–molecule reaction characterised by the polarisation potential $U(R) = -e^2\alpha/2R^4$; α_1 and α_2 are the polarisabilities of the neutral partners, for which the long-range component of the potential can be approximated by the expression involving the ionisation potentials I_1 and I_2 of the partners $U(R) = \frac{1}{2}\frac{\alpha_1\alpha_2}{R^6}\frac{I_1 I_2}{I_1+I_2}$. It is important to note that the partition functions for the internal motion of the partners do not appear in (4.6) and (4.7). This is

‡ This limitation allows us to separate rotation from vibrations, and also to treat vibrations by the harmonic approximation.

simply because with the critical surface S^+ assumed here the reaction (that is, the intersection of S^+) occurs at such large distances that the contributions of internal motions to F and F^+ can be taken to be identical and drop out of the ratio F^+/F.

It is permissible to ignore the short-range part of the potential in the calculation of R_m only if R_m is much greater than the gas-kinetic cross-section R_0. This sets a high-temperature limit to the validity of expressions (4.6) and (4.7): the condition

$$k_{ex} > Z_0 . \qquad (4.8)$$

which states that only the long-range part of the potential contributes to the rate constant, must apply.

We shall now discuss the way in which formulae (4.3) and (4.4) are related to the expression (1.1).

If we describe the rate constant of our exchange process by the Arrhenius formula (1.1) with a constant factor, and if we express the exponential functions of temperature for the low- and the high-temperature regions in the form

$$T^n = (e\bar{T}_l)^n \exp(-nkT_l/kT), \qquad (4.9a)$$

and

$$T^m = (e\bar{T}_h)^m \exp(-mkT_h/kT), \qquad (4.9b)$$

where $\bar{T}_l$ and $\bar{T}_h$ denote some mean temperature in the low- and in the high-temperature region respectively, we obtain

$$E_l = E_0 + nk\bar{T}_l, E_h = E_0 + mk\bar{T}_h. \qquad (4.10)$$

Hence,

$$\Delta E = E_h - E_l = k(m\bar{T}_h - n\bar{T}_l) . \qquad (4.11)$$

Since, according to formulae (4.3) and (4.4), we have $n = -\frac{1}{2}$ and $m = \frac{3}{2}$ for a linear complex and $n = 0$ and $m = 1$ for a triangular complex, in the former instance expression (4.11) takes the form

$$\Delta E = \frac{k}{2}(3\bar{T}_h - \bar{T}_l) \qquad (4.12a)$$

and in the latter

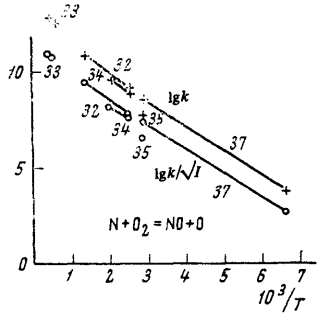
$$\Delta E = k\bar{T}_h . \qquad (4.12b)$$

We see that in both the quantity ΔE is greater than 0, that is, $E_h > E_l$. Thus, the activated complex theory requires that the activation energy should not remain constant on going from low to high temperatures but should increase with increase of temperature if the rate constant of an exchange process is described by the Arrhenius law (1.1).

The following example confirms the conclusions of the theory. One of the constants for which the numerical values obtained by different workers show the most satisfactory agreement is the rate constant of the reaction

$$N + O_2 \rightarrow NO + O + 32\ \text{kcal mole}^{-1}. \qquad (4.13)$$

Data obtained by the formulae proposed by different authors [32-37] for the appropriate temperature ranges are graphically compared in the Figure, where the quantities $\lg k_{ex}$ or $\lg[k_{ex}/\sqrt{T}]$ are plotted as ordinate and $10^3/T$ is the abscissa. It is evident from the Figure that neither $\lg k_{ex}$ nor $\lg[k_{ex}/\sqrt{T}]$ is a linear function of $1/T$. It follows that formulae (1.1) and (1.2) do not adequately describe this constant over the whole of the experimental temperature range (145-3300°K). It can also be seen from the Figure that, as the above theory requires, the effective activation energy increases with increase of temperature.



Temperature dependence of the rate constant of the reaction $N + O_2 \rightarrow NO + O$. The numbers by the points are literature references.

The following considerations also militate against the description of the rate constant of an exchange reaction by a formula of type (1.1) or (1.2) over a wide temperature range. The temperature dependence of the equilibrium constant of the reaction A + BC = AB + C is given by the expression

$$K_{eq} \simeq \frac{1-\exp(-\hbar\omega_{BC}/kT)}{1-\exp(-\hbar\omega_{AB}/kT)} \exp(-Q_0/kT). \qquad (4.14)$$

Since the equilibrium constant is the ratio of the rate constants for the forward and the reverse reaction, expressing these constants by Arrhenius formulae of the type (1.1) or (1.2) gives

$$K_{eq} = \frac{A}{A'} \exp[-(E_0 - E_0')/kT)] = \frac{A}{A'} \exp(-Q_0/kT)], \qquad (4.15a)$$

$$K_{eq} = \frac{A_0\sqrt{T}}{A_0'\sqrt{T}} \exp[-(E_0 - E_0')/kT) = \frac{A_0}{A_0'} \exp(-Q_0/kT). \qquad (4.15b)$$

Comparing these formulae with (4.10) we see that A and A' (or A_0 and A_0') can be treated as constant and temperature-independent only when $\omega_{BC} = \omega_{AB}$. Thus, if, for example, $\omega_{AB} = 2\omega_{BC}$, the quantity

$$[1-\exp(-\hbar\omega_{BC}/kT]/[1-\exp(-\hbar\omega_{AB}/kT)]$$

and therefore also the ratio A/A' or A_0/A_0', will decrease by a factor of two on going from the low-temperature to the high-temperature region.

The ratio of the pre-exponential factors should be even more clearly a function of temperature for an exchange reaction of the type

$$AB + CD \rightarrow ABC + D . \qquad (4.16)$$

The temperature dependence of the equilibrium constant, making the same assumptions as in (4.1), should now be given by the expression

$$k_{ex} \simeq T^{-1/2} \frac{(1-e^{-\hbar\omega_{AB}/kT})(1-e^{-\hbar\omega_{CD}/kT})}{\prod_{i=1}^{3}[1-\exp(-\hbar\omega_{ABC}^i/kT)]} \exp(-Q_0/kT). \qquad (4.17)$$

In the low-temperature region this leads to

$$k_{ex} \simeq T^{-1/2} \exp(-Q_0/kT) , \qquad (4.18)$$

and in the high-temperature region

$$k_{ex} \simeq T^{1/2} \exp(-Q_0/kT). \qquad (4.19)$$

The basic postulate of the transition state method, concerning the possibility of introducing a single reaction coordinate, cannot be tested by comparing theory with experiment because, on the one hand, the characteristics of the potential energy surface are not usually known, and on the other hand the degree of perturbation of the equilibrium distribution is not known. Therefore it is particularly interesting to compare the values of $k_{ex}(T)$ calculated for the same model by the transition state method and by averaging the occurrence of the reaction over the equilibrium distribution function. Calculation of σ is possible only with the help of fast computers, and only within the limits of classical mechanics for the present. Such a comparison made by Karplus and coworkers [38] for the reaction H + H_2, does not allow us to assess unequivocally the precision of the transition state method, but it provides evidence that no serious error is introduced into the temperature dependence of the rate constant $k_{ex}(T)$ by using this method. Similar investigations were recently carried out by Marcus [39,40].

Thus, it is at least possible that the transition state method will provide an acceptable estimate of the temperature dependence of $k(T)$ provided that the reaction does not significantly disturb the equilibrium distribution. It is essential, of course, to take account of the temperature dependence of the transmission coefficient for non-adiabatic reactions and reactions with light atoms, as in formulae (2.3)–(2.7).

Theoretical attempts to explain the influence of perturbation of the equilibrium distribution on the rate of an exchange reaction have concentrated not so much on calculating the non-equilibrium rate constant as on defining the conditions under which the effect is small [41-44]. It was assumed that the cross-section of the reaction depends on the relative kinetic energy, but no attempt was made to derive a concrete expression. Since the Maxwell distribution is re-established in a very short time—after a few collisions—an exchange reaction involving a sufficiently high activation energy cannot significantly affect the equilibrium distribution of velocities. This ceases to be true when the main contribution to overcoming the energy barrier is provided by the vibrational energy of the partners. We cannot exclude the situation in which the rate of vibrational relaxation is comparable with or even smaller than the rate of reaction calculated on the assumption that the Boltzmann distribution in the vibrational states is preserved. Then the true rate of the exchange reaction will be determined only by the rate of vibrational relaxation, or rather by the rate at which the reacting molecules reach the particular vibrational level which makes the largest contribution to the cross-section of the reaction. In this sense we have complete analogy with unimolecular reactions, for which the rate of decomposition at low pressures is determined by the rate of vibrational excitation of the molecules. Since the temperature dependence of the vibrational relaxation time is described not by the Arrhenius formula (1.1) but by the Landau–Teller formula [4]

$$k_{vibr} \sim \exp[-(T_0/T)^{1/3}], \qquad (4.20)$$

it may happen that the rate of an exchange reaction also will not contain an Arrhenius factor. No definite statements regarding the particular degrees of freedom which contribute most significantly to the cross-sections of various exchange reactions can as yet be made.

The study [38] of the H + H_2 → H_2 + H reaction, already mentioned, showed that the main contribution to overcoming the activation barrier comes from kinetic energy. This points to a relatively insignificant disturbance of the equilibrium distribution by the reaction. On the other hand, in a reaction of the type $H_2 + D_2 \rightarrow HD + HD$ the main contribution may come from the vibrational energy of the partners, since the decomposition of the $[H_2D_2]$ complex into two HD fragments is caused by vibrations. In this example a substantial disturbance of the equilibrium distribution can be expected. A recent investigation by Bauer and coworkers [45,46] has shown that the kinetics of this reaction do not obey a second-order law, and that the rate depends on the concentration of argon (used only as a thermal reservoir to ensure vibrational relaxation of H_2 and D_2). This change in reaction order is evidence of a disturbance in the equilibrium distribution§, and therefore that the transition state method is not applicable to the calculation of $k_{ex}(T)$. Unfortunately, no alternative method of calculating the rate constant can be suggested at present.

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CHEMICAL REACTIONS OF DIENE POLYMERS

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CONTENTS

I. Introduction 881

II. Addition to a double bond 881

1. Reactions with compounds containing a mercapto-group 881
2. Reaction with hydrogen halides 883
3. Hydrogenation 884
4. Reaction with perbenzoic acid 885

III. Reactions involving the participation of double and allyl bonds 886

1. Reaction with ethylenic monomers 886
2. Reaction with aldehydes 887
3. Reaction with molecular chlorine 888
4. Reaction with bromine and other halogenating agents 890

I. INTRODUCTION

Diene polymers are now the most widely used of all known polymeric materials. The polymerisation of dienes leads to the production of elastomers which acquire all the necessary properties during further treatment (plasticising, vulcanising). In addition to the problem of the processing and modification there is the problem of stabilising the polymer material. The effective solution of these problems is impossible without a knowledge of the chemical nature of the polymers used.

It is necessary to point out that there has not yet been any detailed investigation of the reactivity of diene polymers as a class of organic compounds. Most of the studies in the field of the chemistry of diene polymers are of an applied nature and are connected with the study of the vulcanisation and stabilisation of polymers or are directed to the study of individual reactions of diene polymers, such as chlorination, hydrochlorination, etc. At the same time, without knowing the general features of the chemistry of diene polymers it is impossible to carry out effectively work of an applied character, directed to the solution of particular practical problems.

The present review aims to be a critical consideration and systematisation of the published information on the chemistry of diene polymers up to the end of 1965. An attempt has been made to find the characteristics of the double bonds in polymers having a regular 1,5-polyene structure. The review does not attempt a detailed examination of the information on vulcanisation and oxidation that has appeared in monographs.

II. ADDITION TO A DOUBLE BOND

1. Reaction with Compounds Containing a Mercapto-Group

The reactions of hydrogen sulphide and thiols with alkenes have been studied in detail by Naylor [1]. Under the catalytic action of sulphur, hydrogen sulphide is readily added at the double bond of polyisoprene in accordance with the Markovnikov rule. The thiol formed can react with another double bond to give a sulphide. The oxidation of two thiols leads to the formation of a disulphide. As a result of the last two reactions, cross-linking of the macromolecules of the rubber takes place. In the presence of a peroxide or on ultraviolet irradiation, hydrogen sulphide adds at the double bond of polyisoprene contrary to the Markovnikov rule.

The addition of alkyl and aryl thiols to a double bond also proceeds in accordance with the Markovnikov rule in the presence of sulphur and contrary to the rule when the reaction is carried out in the presence of peroxide [2]. The easier it is for homolytic rupture of the S–H bond, the greater the acidity of the thiol, and the more active the thiol relative to the double bond. Prilezhaeva and Shostakovskii [3] give the following series for the activity of thiols in relation to alkenes:

$$C_6H_5SH > HOOC.CH_2SH > RCH_2SH > R_2CHSH > R_3C.SH.$$

Electron-donating groups in the thiyl [mercapto-] radical reduce its reactivity towards double bonds; electron-withdrawing groups, on the other hand, increase its activity. A drop in the electron density of the double bond leads to a decrease in its reactivity towards thiols.