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Abstract

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ON THE MECHANISM OF INTERMOLECULAR ENERGY EXCHANGE IN THE DISSOCIATION OF A DIATOMIC GAS

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Recently, a number of reactions of the thermal decomposition of diatomic molecules in shock waves have been studied. The shock-wave method makes it possible to measure the true rate constant of decomposition at the initial moments of time, since the concentration of undecomposed molecules is determined experimentally. In this respect the shock-wave method differs substantially from other methods of determining the rate of decomposition (for example, the calculation of the decomposition rate from the recombination rate, discussed in work ([1])). The experimental results obtained indicate that the dissociation of molecules behind the front of a shock wave in a pure diatomic gas sometimes proceeds considerably faster than dissociation in an atmosphere of an inert monatomic gas. In the present work it is shown that this finds a natural explanation within the framework of the previously developed concepts of the mechanism of thermal dissociation ([2], [13]).

For definiteness, let us consider the following two reactions

$$O_2 + A \to O + O + A, \qquad \mu = m/2; \tag{1}$$

$$O_2 + O_2 \to O + O + O_2, \qquad \mu = m/2, \tag{2}$$

whose rates were measured in work ([3]) in the temperature range 3000–5000°K. It was found that k_2 exceeds k_1 by an order of magnitude. On the right in (1) and (2) are indicated the relations between the reduced masses of the dissociating molecule μ and of the colliding pair m. It is essential that the undissociated molecules in (1) and (2) differ only in their internal structure, since the corresponding reduced masses m_1 and m_2 may be regarded as equal. The rate of (1), calculated earlier ([4]) in accordance with the method of work ([2]), agrees satisfactorily with experiment. In order to determine the relative rate of (1) and (2), let us consider the mechanism of vibrational excitation of the dissociating molecule.

Let ε denote the vibrational quantum of the O_2 molecule, and let ε_0 denote its first vibrational quantum; evidently $0 \leq \varepsilon \leq \varepsilon_0$. Further, let ΔE denote the mean energy of vibrational excitation transferred in one collision. At large ε, corresponding to the lower vibrational levels, the probability of vibrational excitation is described by the Landau—Teller formula; in this case ΔE is very small and decreases exponentially with increasing ε. Conversely, at very small ε the quantization of vibrations becomes insignificant (nonadiabatic collisions), and, in accordance with classical mechanics, ΔE must be of the order of kT (of course, only in the case where the masses of the atoms under consideration are quantities of the same order). The boundary between these two regions, corresponding to the quantum ε^*, is determined by the well-known relation

$$\varepsilon^*/\hbar\bar{v}\alpha \simeq 1, \tag{3}$$

in which $\bar{v}$ denotes the mean velocity of the colliding molecules, and α^{-1} the characteristic radius of action of the exchange forces. For $\varepsilon > \varepsilon^*$

mainly one-quantum transitions occur, while for $\varepsilon < \varepsilon^*$ multi-quantum transitions occur. For $\varepsilon \simeq \varepsilon^*$ the probability of a one-quantum transition is close to unity, so that $\Delta E \simeq (\varepsilon^*) \simeq \varepsilon^*$.

If the nondissociating molecule in (2) can, with appreciable probability, transfer at each collision part of its internal energy ε_1 to the vibrationally excited molecule, then the magnitude of the quantum ε^* is determined by the relation

$$(\varepsilon^* - \varepsilon_1)/\hbar\omega\alpha \simeq 1. \tag{4}$$

It was shown in Ref. (2) that the violation of the Boltzmann distribution over the vibrational states of the decaying molecule leads to the result that the rate of decay is determined by the rate of vibrational excitation in the region of vibrational energies $E \simeq E^*$, corresponding to the vibrational quantum ε^*. In this case the quantity E^* in fact acts as the dissociation energy. It follows from the foregoing that any increase in ε^* associated with the transfer of energy ε_1 decreases the value of E^* and thereby increases the rate of decay. However, if the effective dissociation energy E^* is strongly lowered, it may turn out that, owing to the increase in the population of vibrational levels as the vibrational energy E is reduced, vibrational excitation in the region $E \simeq E^*$ will no longer limit the rate of decay. In this case the rate of decay will be determined by the rate of transition of vibrationally excited molecules from an energy interval of order kT, adjacent to the dissociation boundary, into states with a continuous energy spectrum. Naturally, the probability of such a transition is already determined by the laws of classical mechanics. Such a mechanism of dissociation was proposed by Rice (^{5,6}), and was discussed recently by Rice (^{7})* and Widom (^{8}). Thus we arrive at the conclusion that the increase in the pre-exponential factor associated with a decrease in the effective dissociation energy is limited by some value, which can be calculated in accordance with Rice' s theory. The results of Refs. ([5,8]) show that the maximum value of the pre-exponential factor may be approximately two orders of magnitude larger than the collision number Z.

In case (1) $\varepsilon_1 = 0$, and the magnitude of E^* can be estimated if one uses some definite dependence $E = E(\varepsilon)$. In particular, for a linear dependence of ε on the vibrational quantum number v (Morse oscillator), it is easy to obtain

$$D - E(\varepsilon) = D\varepsilon^2/\varepsilon_0^2. \tag{5}$$

The quantity α in (3) is approximately constant for all molecules and can be determined from the known Morse potentials of diatomic molecules. Taking into account that α is connected with the fundamental frequency of vibrations and the dissociation energy of diatomic molecules by the relation $\omega \simeq \alpha\sqrt{2D/\mu}$, on the basis of (3) and (5) we have

$$D - E(\varepsilon^*) = \frac{D(\varepsilon^*)^2}{\varepsilon_0^2} = \gamma^2 \frac{\mu}{2m} kT. \tag{6}$$

Here, instead of unity on the right-hand side of (3), a dimensionless quantity γ has been introduced, which makes it possible to write (6) in the form of an exact equality. Using (6), it is not difficult to verify that in case (1) the effective dissociation energy is lowered by an amount $\sim kT/4$, which makes an altogether negligible contribution to the rate constant of decay.

In case (2) $\varepsilon_1 \neq 0$, and it is necessary to consider the possible contributions of the internal energy of the nondissociating molecule O_2 to the constant k_2. The vibrational degree of freedom of the unexcited O_2 molecule cannot make a contribution, since the quantities ε^* and ε_0 differ very greatly from each other. Transfer of a significant energy of electronic excitation is also improbable, since among electronically excited states, similar belonging to a single dissociation limit, there are none that would combine spectroscopically with high intensity. The only degree of freedom making an additional substantial contribution to the constant k_2, as compared with k_1, is the rotation of the nondissociating O_2 molecule (the rotation of the dissociating molecule has already been taken into account in the formulas of work ([2])). It is not difficult to see that the energy ε_1, corresponding to two mean rotational quanta of O_2, can without difficulty be transferred to a vibrationally excited O_2 molecule. The experimental time τ of rotational relaxation of O_2, measured in shock waves and corresponding to the conversion of translational energy into rotational energy, is of order $1/10Z$ (see, for example, ([9])). The time of multistep relaxation (successive excitation of rotational states) is related to the probability P of a two-quantum transition and the energy ε_1 by the relation

* The author is grateful to Prof. O. K. Rice for a copy of Ref. (7), sent before its publication.

$\tau \simeq (ZP\,\frac{\varepsilon_1}{kT})^{-1}$. Substituting here $\varepsilon_1 =\sim 4\sqrt{BkT}$ (B is the rotational constant of O_2, equal to 1.4 cm^{-1}), $T = 2000°K$, and comparing with the experimental value of τ, we find $P \simeq 1$. On the other hand, the amplitude of the vibrations of a strongly vibrationally excited molecule is of the same order as the parameter characterizing the asymmetry of the intermolecular interaction and responsible for excitation of rotational states. It follows from this that the probability of transfer of part of the rotational energy ε_1 to the vibrations of the dissociating molecule must be of the same order as the probability of exchange of rotational and translational energy. We note that the possibility of conversion of rotational energy into vibrational energy must also be taken into account in calculating the vibrational relaxation time of the lower vibrational levels of diatomic molecules in accordance with the theory of Schwartz and Herzfeld ([10]). From the Landau–Teller formula it is easy to obtain that transfer of the rotational energy ε_1 leads to an increase in the probability of vibrational excitation by a factor $\exp(2\chi\varepsilon_1/\varepsilon_0)$, which for typical values $\chi \simeq 10$ ([10]) gives an additional factor of order 3-5. In this connection it should be borne in mind that the energy ε_1 depends on the velocity of the colliding molecules and, consequently, on χ, so that under ordinary conditions of strong nonadiabaticity of collisions with respect to rotational excitation ε_1 can substantially exceed twice the energy of the mean rotational quantum. It is obvious that neglect of rotation should lead to poorer agreement between experimental and calculated quantities at large values of χ. From Table 1 of work ([10]) it is seen that this is indeed so.

Equality (4) can now be rewritten in the form

$$\varepsilon^* = \gamma\left[\hbar v\alpha + 4\sqrt{BkT}\right] = \gamma\hbar\sqrt{\frac{kT}{m}}\,[\alpha + 4/r_e], \tag{7}$$

where r_e is the equilibrium internuclear distance in the O_2 molecule. Taking here $r_e = 1.2$ Å and $\alpha^{-1} = 0.5$ Å, in accordance with (5) we obtain

$$E(\varepsilon^*) = D - \frac{9}{4}\gamma^2 kT. \tag{8}$$

Thus, the effective dissociation energy decreases by $\sim \frac{9}{4}kT$, while the magnitude of the vibrational quantum limiting the decomposition rate increases, in going from (1) to (2), by ~ 3 times. The combined influence of these two effects leads, according to expression (7) of work ([2]), to an increase in the relative rate (2) by approximately $3\gamma\exp(2\gamma^2) \simeq 20$ times. This factor naturally does not affect the temperature dependence of k_2.

Another relation between the constants k_1 and k_2 appears in the case when the masses of the atoms of the inert gas and of the dissociating molecule are different. An example is the decomposition of bromine, studied by Palmer and Hornig ([11])

$$\mathrm{Br}_2 + \mathrm{A} \to \mathrm{Br} + \mathrm{Br} + \mathrm{A}, \qquad \mu = m; \tag{9}$$

$$\mathrm{Br}_2 + \mathrm{Br}_2 \to \mathrm{Br} + \mathrm{Br} + \mathrm{Br}_2, \qquad \mu = m/2. \tag{10}$$

The rate constant for the decomposition reaction (9) was calculated in Ref. (2). The experimental pre-exponential factor in (9) at $T = 2000$°K is equal to $4Z$, while Widom’ s calculation (8), in accordance with Rice’ s mechanism, gives $\sim 50Z$. In accordance with (6) and (7) we find $E_9^* = D - \frac{\gamma^2}{2}kT$ and $E_{10}^* = D - \gamma^2 kT$ ($r_e(\mathrm{Br}_2) = 2.28$ Å). The magnitude of the vibrational quantum ε^* increases in going from (9) to (10) by only a factor of $\sqrt{2}$, so that the relative rate (10) is equal to $\simeq \sqrt{2e}$. The experimental value of the ratio k_{10}/k_9 varies in the range 1.5–2.4 when the temperature changes from 1600 to 1200°K (11).

In conclusion we note the following. Expressions (3) and (4), on the basis of which the estimates were made, were written in the form of approximate equalities. As a result, a dimensionless constant $\gamma \simeq 1$ enters the final expression. It is therefore of interest to make an independent estimate of the magnitude of γ and to test relations (3) and (4). This is possible to some extent on the basis of a study of the forced infrared absorption of molecules caused by deformation of the molecular electron shell during collisions. Expressions analogous to (3) and (4) determine the half-widths of various bands in the spectrum; it turns out that the value of γ is very close to unity (12). In addition, the form of the bands $k = k(\omega)$ (k is the absorption coefficient) qualitatively corresponds to the dependence considered here, $\Delta E = \Delta E(\varepsilon)$. As for the linear dependence of ε on v assumed in (5), the often observed more rapid decrease of ε on approach to the dissociation limit does not change the qualitative conclusions. In the case of oxygen dissociation, for example, taking this circumstance into account leads to a certain increase in the calculated value of the ratio k_2/k_1.

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CITED LITERATURE

1. E. E. Nikitin, N. D. Sokolov, DAN, **124**, 336 (1959).
2. E. E. Nikitin, DAN, **119**, 526 (1958).
3. M. Camac, J. Camm et al., *Chemical Relaxation in Air, Oxygen and Nitrogen*, Preprint No. 802, Inst. Aeronaut. Sci., 1958.

4. E. E. Nikitin, Dissertation, Inst. Chem. Phys., Academy of Sciences of the USSR, 1958.
5. O. K. Rice, J. Chem. Phys., **9**, 258 (1941).
6. O. K. Rice, J. Chem. Phys., **21**, 750 (1953).
7. O. K. Rice, Monatsh. Chem., **90**, 330 (1959).
8. B. Widom, J. Chem. Phys., **31**, 1027 (1959).
9. J. C. McCoubrey, M. D. McGrath, Quart. Rev., **11**, 87 (1957).
10. R. N. Schwartz, K. F. Herzfeld, J. Chem. Phys., **22**, 767 (1954).
11. H. B. Palmer, D. F. Hornig, J. Chem. Phys., **26**, 98 (1957).
12. E. E. Nikitin, Optics and Spectroscopy, **7**, No. 6 (1959); E. E. Nikitin, N. D. Sokolov, J. Chem. Phys., **31**, 1369 (1959).

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