INTERRELATION OF THE PROCESSES OF VIBRATIONAL RELAXATION AND DISSOCIATION OF DIATOMIC MOLECULES

PHYSICAL CHEMISTRY

1965

SovietRxiv

Abstract

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UDC 511.10

PHYSICAL CHEMISTRY

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INTERRELATION OF THE PROCESSES OF VIBRATIONAL RELAXATION AND DISSOCIATION OF DIATOMIC MOLECULES

(Presented by Academician V. N. Kondrat' ev, March 27, 1965)

Thermal dissociation of molecules, which, as is known, takes place with overwhelming probability from the upper vibrational levels lying in the energy interval $D - T$ near the dissociation threshold D ($^{1-3}$), leads to a decrease in the population $\sum x_n$ of the latter. This, in turn, decreases the dissociation rate constant k^- relative to its equilibrium value $k^-(T)$. The decrease in $\sum x_n$ may be associated with a disturbance of the Boltzmann distribution of vibrational energy or with a decrease in the temperature T^* of the Boltzmann distribution relative to the temperature T of the translational-rotational motion of the molecules. The disturbance of the Boltzmann distribution over the upper vibrational levels was considered in ($^{2-4}$). In the general case this factor does not lend itself to exact quantitative accounting. In (^{3}) it was shown that in molecular gases (in collisions of molecules with molecules) it may appear at temperatures of the order of the characteristic ones or higher, and to a considerably lesser degree than in the case of collisions of a molecule with atoms. However, at such high temperatures, as we shall see below, it is in any case necessary to take into account that in the process of dissociation $T^* \neq T$. (At high temperatures dissociation proceeds so rapidly that the limiting process for it is the process of excitation of the several lower vibrational levels, on which the main fraction of the vibrational energy of the molecules falls.)

The degree of deviation of T^* from T is determined by solving the system of equations (^{5})*:

$$\frac{dE^*}{dt} = \frac{E - E^*}{\tau_0}\,\delta + (D - E^*)\,\frac{d\alpha}{\alpha dt}, \tag{1}$$

$$\frac{d\alpha}{dt} = -k^-\alpha\delta + k^+(1-\alpha)^2\delta^2, \tag{2}$$

where E and E^* are the values of the energy of the vibrational degree of freedom at temperatures T and T^*, respectively; t is time; α is the ratio of the number of molecules to their number in the undissociated gas; k^- and k^+ are the rate constants of dissociation and recombination; δ is the ratio of the gas density to its density under normal conditions; τ_0 is the vibrational relaxation time at $\delta = 1$.

In this work, using equations (1), (2), the dependence of the ratios T^*/T and $k^-/k^-(T)$ on T is investigated in a rapidly heated dissociating gas. The use of equations (1), (2) presupposes the existence of a Boltzmann distribution of the vibrational energy of the molecules. Thus, of the two factors leading to a decrease in $\sum x_n$ (the difference of T^* from T and disturbance of the Boltzmann distribution), only the first is taken into account.

* In equations analogous to (1), in $(^5)$, instead of D there enter other quantities, whose difference from D is insignificant if it is taken into account in $(^5)$ that dissociation occurs from the upper vibrational levels.

The relatively rapid establishment of the Boltzmann distribution (with $T^* \neq T$) in diatomic and polyatomic gases, on the one hand, and the substantial influence, as will be seen below, of the factor $T^* \neq T$, on the other, make it possible to suppose that, at least in molecular gases, the factor taken into account here is the principal one at high temperatures. The results of the numerical calculation of the dynamic model problem obtained in (6) also support this assertion.

The method of further investigation is analogous to that set forth in (5), where the problem of oxygen dissociation in argon was considered. However, in contrast to (5), model assumptions are not used here (a Morse oscillator, an exponential dependence of the dissociation probability on the energy of the vibrational level), since there is essentially no need for them in the present application. Moreover, abandoning such assumptions makes it easier to analyze the causes of the decrease of $k^-/k^-(T)$ and, by greatly simplifying the computational operations, makes it possible to solve the problem without using computers. We also note that in (5) a non-diatomic gas (argon) was considered, although, as noted above, the assumption that a Boltzmann distribution exists during dissociation is more justified in the case of a molecular gas.

To solve the system of equations (1), (2) for known values of τ_0 and $k^-(T)$, one must know the dependence of $k^-/k^-(T)$ on T^* and T. This dependence follows directly from the fact that dissociation occurs preferentially from the upper vibrational levels and has the form*

$$\frac{k^-}{k^-(T)} = \frac{\sum x_n(T^*)}{\sum x_n(T)} \approx \frac{T}{T^*} \exp\left[D\left(\frac{1}{T} - \frac{1}{T^*}\right)\right]. \tag{3}$$

Here it has been taken into account that the dissociation rate constant is proportional to the population of the upper vibrational levels and that the vibrational statistical sum $z(T)$ at high temperatures is proportional to T. (Since T^* will not differ greatly from T, it may be assumed that the numbers of upper vibrational levels lying in the intervals $(D - T) \div D$ and $(D - T^*) \div D$ are equal.)

Introduce the dimensionless variables $x = D/T$ and $y = T^*/T - 1$, and write equation (1) far from dissociation equilibrium (where the recombination reaction may be neglected) in the form

$$\frac{dy}{dt} = -\frac{y^\delta}{\tau_0} - \frac{x-y-1}{1+y}\,\delta k^-(T)\exp\frac{xy}{y+1},$$

or, taking into account that the values of τ_0 and $k^-(T)$ are known in the best case to within a factor of $1.5 \div 2$, and that in the practically interesting temperature range $x \gg y+1$,

$$dy/dt = -y^\delta/\tau_0 - x\delta k^-(T)\exp[xy/(y+1)]. \qquad (4)$$

Here relation (3) has been taken into account, as well as the fact that, in energy units at high temperatures, $E = T$, $E^* = T^*$. We shall assume $x = \text{const}$. This makes it possible to investigate the influence of the finite relaxation rate on the magnitude of k^- in pure form, not obscured by the disturbance of equilibrium due to a change in T in some gas-dynamic process. In the general case, if $x \neq \text{const}$, it is necessary to know in advance the law of variation of the temperature $T(t)$, or else to solve equations (1), (2) together with the equations of gas dynamics.

*

[*] The relation between k^- and $k^-(T)$ under various assumptions about the probabilities of vibrational transitions was investigated in (6,7). It can be shown that the model representation of a strong exponential increase in the probability of dissociation with increasing vibrational-level energy (6) leads to a relation close to (3).

The process of vibrational relaxation and dissociation far from dissociation equilibrium can be divided into a stage of attainment of a quasi-stationary regime, during which the vibrational temperature changes from the initial value T_1^* to the value T^*, determined from equation (4) when

$$dy/dt = 0, \qquad (5)$$

and a quasi-stationary stage of dissociation, during which T^* does not change. The subsequent convergence of T^* and T occurs only where the rates of dissociation and recombination become quantities of the same order, i.e., near dissociation equilibrium.

It will be shown below that during the time required to attain the quasi-stationary regime α decreases approximately by $\exp(-y/x)$ times. This means that for $x \gg 1$ (and, moreover, $x/y \gg 1$) the dissociation process takes place under the quasi-stationarity condition (5).

The relation between y and x in the quasi-stationary regime is determined by the transcendental equation

$$-y = xk^{-}(T)\tau_0 \exp\left[xy/(1+y)\right]. \tag{6}$$

It follows from this that $k^{-}/k^{-}(T)$, identically equal to $\exp[xy/(1+y)]$, differs from unity when

$$x^2 k^{-}(T)\tau_0 \approx 1, \tag{7}$$

and not when

$$k^{-}(T)\tau_0 \approx 1, \tag{8}$$

as might appear at first sight. Since $x \gg 1$, condition (7), considerably stronger than (8), bounds from above the temperature region in which $k^{-}/k^{-}(T) \approx 1$. Solving equation (6) for a given $k^{-}(T)\tau_0$ presents no difficulty.

To preserve the greatest possible generality of the subsequent results, let us substitute in (6) the theoretical values τ_0 (^{8}) and $k^{-}(T)$

$$\tau_0 = A\exp(BT^{-1/3}), \qquad k^{-}(T) = C\exp(-x), \tag{9}$$

neglecting the weak temperature dependence of the pre-exponential factors A and C.

The theoretical expression for B has the form (^{8})

$$B = (54\pi^4\nu^2a^2M)^{1/3},$$

where, according to generally accepted notation, ν is the frequency of the vibrational quantum; a is the radius of action of the exchange forces; M is the reduced mass. Using the approximate relation between a, M, ν, and D, $2\pi\nu a \approx \sqrt{2D/M}$, we find

$$\tau_0 \approx A\exp(\beta x^{1/3}), \tag{10}$$

where β is a quantity calculated from experimental data.

Equation (6), with (9) and (10) taken into account, assumes the form

$$-y = ACx\exp\left[x(y-1)/(y+1) + \beta x^{1/3}\right]. \tag{11}$$

Fig. 1

Figure 1: Fig. 1

Processing the experimental data on τ for oxygen, nitrogen (^{9}), and carbon monoxide (^{10}), to within a factor of $1.5 \div 3$, leads to the expression

$$\tau_0 \approx 10^{-10} \exp(2.9x^{1/3}) \text{ sec.} \tag{12}$$

The experimental values of τ_0 for halogen molecules (^{11}) at the same x are approximately an order of magnitude smaller and correspond to $A \approx 10^{-10}$, $\beta \approx 1.7$. The value of C, in order of magnitude, is equal to the gas-kinetic number at normal gas density $z \approx 2 \cdot 10^8 \sqrt{T} \approx 10^{10}$, multiplied by the number of vibrational levels $-\sum x_n$ in the interval $(D - T) \div D$. For $x \sim 5 \div 20$, $\sum x_n \approx 10$, and consequently

$$C \approx 10^{11} \text{ sec}^{-1}. \tag{13}$$

(The comparatively small contribution to the value of C is associated with the centrifugal stretching of excited molecules. In the case of halogens, the value of C may be several times larger owing to the increased statistical weight of electronically excited states (^{1,12}).)

After substituting into (11) the numerical values (12) and (13), we find

$$-y = 10x \exp[x(y-1)/(y+1) + 2.9x^{1/3}]. \tag{14}$$

The results of solving equation (14) are presented in Figs. 1 and 2 (curves *I*). Also shown there, to give an idea of the sensitivity of the calculation results to a possible error in the values of $k^-(T)\tau_0$, are the results of analogous calculations with the value of the pre-exponential factor in (14) multiplied by 3 (curves *II*). From Fig. 1 it is seen that an error in $k^-(T)\tau_0$ leads to an approximately two times smaller error in $k^-/k^-(T)$. For $x < 5$, the solution of equation (14) is not of much interest, since, owing to the anharmonicity of the vibrations, the advisability of using the initial equation (1) becomes doubtful. The results obtained make it possible to find k^- for diatomic molecules if $k^-(T)$ is known. (An estimate of $k^-(T)$ at high temperatures is given by (9) and (14). More accurate calculations of $k^-(T)$ can be found in the works (^{1,13,14}).)

The comparatively rapid decrease of $k^-/k^-(T)$ with increasing x leads to the so-called negative temperature dependence[15]

Fig. 1

Fig. 2

Fig. 2

Figure 2: Fig. 2

of the pre-exponential factor k^-, which is especially pronounced in the interval $7 < x < 13$.

In conclusion, let us show that during the time required for establishing the quasistationary regime, α changes by no more than a factor of $\exp(-y/x)$. The time for establishing the quasistationary regime is $\approx \tau$. The quantity α, initially equal to unity, at the time τ, according to (2), where only dissociation need be taken into account, is equal to

$$\exp\left[-\int_0^\tau \delta k^- \, dt\right] > \exp[-\delta k^- \tau]\Big|_{t=\tau};$$

but, according to (6), $\delta k^- \tau = -y/x$.

I express my gratitude to E. E. Nikitin for a useful discussion.

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Received
25 III 1965

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Note: Figure translations are in progress. See original paper for figures.