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Abstract

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Academician V. N. KONDRAT' EV

RATE CONSTANTS FOR THERMAL EXCITATION OF SODIUM IN MIXTURES OF SODIUM VAPOR WITH ARGON AND NITROGEN

In connection with the study of the physical and chemical properties of gases at high temperatures, electronically excited states of atoms and molecules are acquiring ever greater importance. If under thermodynamic equilibrium the concentration of these particles is determined by the laws of thermodynamics and statistics, then in the absence of equilibrium the chief role begins to be played by the laws of kinetics, above all the kinetics of thermal excitation, and also the kinetics of the reverse process (quenching of luminescence):

$$\mathrm{A} + \mathrm{M} \underset{k'}{\overset{k}{\rightleftharpoons}} \mathrm{A}' + \mathrm{M} \tag{1}$$

(A is the excited particle, M is any particle). These processes are also important because in a number of cases (if not always) thermal ionization of gases proceeds through intermediate states of electronic excitation, which may be represented schematically as follows:

$$\begin{gathered} \mathrm{A} + \mathrm{M} \rightarrow \mathrm{A}' + \mathrm{M}, \\ \mathrm{A}' + \mathrm{M} \rightarrow \mathrm{A}^+ + \mathrm{e} + \mathrm{M}. \end{gathered} \tag{2}$$

However, precisely in the kinetic respect, the processes of electronic excitation of atoms and molecules by impact of heavy neutral particles have as yet been studied very little. All available experimental data have for the most part been obtained in investigations of the excitation of atoms by impact of fast atoms possessing high energy. Measurements of excitation functions give curves which start from 0 near the excitation threshold and pass through a maximum at energies of the fast atoms of 50,000–500,000 kcal/g-atom (^{1}). The rates of impact ionization processes (or the cross sections of these processes), apparently, have not been measured at all.

Meanwhile, from the standpoint of the kinetics of thermal excitation of atoms, the greatest interest is presented by rate constants (cross sections) of excitation processes at energies close to the excitation threshold. In view of the absence of direct measurements of excitation cross sections of atoms and molecules by impact of heavy neutral particles,* it is of interest to calculate these quantities from the cross sections of the reverse process, i.e., the process of fluorescence quenching, for example the D-fluorescence of sodium

$$\mathrm{Na}' + \mathrm{Ar} \rightarrow \mathrm{Na} + \mathrm{Ar}.$$

The cross section of this process at a temperature of 860° K was measured in work (^{3}), and also in work (^{4}). Both of these works give practically coincident values: $q' = (0.32 \pm 0.2) \cdot 10^{-15}$ and $0.29 \cdot 10^{-15}$ cm^2.

The rate constant of the quenching process in the present case can be represented by the formula

$$k' = q' \left(\frac{8RT}{\pi\mu}\right)^{1/2}. \tag{3}$$

Substituting in this formula $q' = 0.3 \cdot 10^{-15}$ cm^2, $\frac{1}{\mu} = \frac{1}{23} + \frac{1}{40}$ and $T = 860°$ K, we obtain $k' = 0.33 \cdot 10^{-10}$ cm$^3 \cdot$ molecule$^{-1} \cdot$ sec^{-1}. The rate constant of the reverse process, i.e., the process of excitation of the $3p^2P$ level of the sodium atom on the basis–

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[*] As one of the few examples one may indicate the process $\mathrm{Xe} + \mathrm{Xe} \rightarrow \mathrm{Xe}' + \mathrm{Xe}$. The rate constant of this process can approximately be represented by the formula (^{2})

$$k = 1.2 \cdot 10^{-9} e^{-3.7/RT} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{sec}^{-1} \ (3.7 \text{ eV}).$$

···the relation

$$\frac{k}{k'} = K = \frac{g'}{g} e^{-A/RT}, \tag{4}$$

is expressed by the formula

$$k = q \left(\frac{8RT}{\pi\mu}\right)^{1/2} e^{-A/RT}, \tag{5}$$

where $q = \frac{g'}{g} q'$ (g' and g are the statistical weights of the $3p^2P$ and $3s^2S$ states of Na). At a temperature of 860° K we obtain $k \simeq 5 \cdot 10^{-25}$ cm$^3 \cdot$ molecule$^{-1} \cdot$ sec^{-1}.

Unfortunately, formulas (3) and (5) cannot be used to calculate the constants k' and k at other temperatures, since the cross section q' (and consequently q) itself varies with temperature. This follows from the fact that at room temperature inert gases (including argon) do not quench the D-fluorescence of sodium at all (^{5}).

It may be assumed that the temperature dependence of q', at least for a limited temperature interval, is expressed by the Arrhenius law,

$$q' = q'_0 e^{-a/RT} = 0.3 \cdot 10^{-15} e^{-\frac{a}{R}\left(\frac{1}{T}-\frac{1}{860}\right)} \text{ cm}^2. \tag{6}$$

In this case, for the temperature dependence of the rate constant of thermal excitation of sodium by argon we shall have

$$k \sim \sqrt{T} e^{-\frac{A+a}{RT}},$$

i.e.

$$-R \frac{d \ln(k/\sqrt{T})}{d(1/T)} = A + a > A.$$

In contrast to inert gases, other gases at room temperature noticeably quench D-fluorescence. In papers ($^{6-8}$), for the cross section for quenching of D-fluorescence by nitrogen at a temperature close to room temperature, the values $q' = 19.1 \cdot 10^{-15}$, $8.2 \cdot 10^{-15}$, and $4.5 \cdot 10^{-15}$ cm^2, respectively, were obtained. On the other hand, in papers (^{3,4,9}) the cross sections for quenching of sodium D-fluorescence were measured at temperatures of 828, 858, and 873° K and at different velocities of the Na$'$ atom, produced by photodissociation of sodium iodide,

$$\text{NaJ} + h\nu \rightarrow \text{Na}' + \text{J},$$

under the action of light of different frequencies. Calculating the velocity of the Na$'$ atom from the equation

$$v_{\text{Na}} = \sqrt{2 \frac{m_{\text{J}}}{m_{\text{NaJ}}} \frac{E_{\text{NaJ}} + h\nu - D_{\text{NaJ}} - A_{\text{Na}}}{m_{\text{Na}}}}, \tag{7}$$

where E_{NaJ} is the mean thermal energy of NaJ*, $D_{\text{NaJ}} = 70.6$ kcal/mol, $A_{\text{Na}} = 48.1$ kcal/g-atom, and the mean thermal velocity of a nitrogen molecule from the formula

Fig. 1. Cross section for quenching of the D-fluorescence of sodium by nitrogen at various velocities of the Na atom

Figure 1: Fig. 1. Cross section for quenching of the D-fluorescence of sodium by nitrogen at various velocities of the Na atom

$$v_{\mathrm{N}_2} = \sqrt{\frac{3RT}{m_{\mathrm{N}_2}}}, \tag{8}$$

we find the mean velocity of the relative motion of Na$'$ and N_2 as

$$v = \sqrt{v_{\mathrm{Na}}^2 + v_{\mathrm{N}_2}^2}. \tag{9}$$

The effective cross section for fluorescence quenching can be calculated from the formula

$$q' = \frac{kT}{p_{1/2} v \tau}, \tag{10}$$

where $p_{1/2}$ is the pressure of the quenching gas (N_2) at which the fluorescence intensity is equal to one half of the maximum, and τ is the mean duration—lifetime of the excited sodium atom ($1/\tau = 7.2 \cdot 10^7$ sec^{-1}). The values of q', calculated by formula (10) from the data of various authors, are presented in Fig. 1 as a function of the reciprocal velocity ($10^5/v$). This figure also gives the values of q' obtained in works ([7],[8])* for resonance excitation of sodium at room temperature. Drawing a straight line through the mean of these values ($\overline{q'} = 6.4 \cdot 10^{-15}$ cm^2) and the origin, we see that the remaining values of q' are grouped around this straight line. Hence one may conclude that the cross section for quenching of the D-fluorescence of sodium by nitrogen approximately obeys the law

Fig. 1. Cross section for quenching of the D-fluorescence of sodium by nitrogen at various velocities of the Na atom

$$q' \sim \frac{1}{v} \tag{11}$$

or

* $E_{\mathrm{NaJ}} = 5.4;\ 5.6$ and 5.7 kcal/mol respectively at 828, 858 and 873°K.

$$k' = q'v \simeq 8 \cdot 10^{-10}\ \text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{sec}^{-1}. \tag{12}$$

Further, on the basis of relation (4), for the rate constant of excitation of the sodium atom (state $3p^2P$) we obtain

$$k \simeq 8 \cdot 10^{-10} \frac{g'}{g} e^{-A/RT} \simeq 2 \cdot 10^{-9} e^{-A/RT}. \tag{13}$$

Thus, on the basis of an analysis of experimental data on the quenching of sodium fluorescence by nitrogen and argon, it may be concluded that, whereas in the case of argon the quenching constant increases with temperature (possibly according to the Arrhenius law), in the case of nitrogen it does not depend on temperature. This difference can apparently be explained by the fact that the potential-energy curves of $\text{Na}' + \text{Ar}$ and $\text{Na} + \text{Ar}$ intersect at a point whose energy is higher (approximately by the quantity a) than the energy of the atoms $\text{Na}' + \text{Ar}$. In the case of nitrogen, however, the transition $\text{Na}' + \text{N}_2 \rightarrow \text{Na} + \text{N}_2$ occurs without expenditure of additional energy, which is possibly due to the fact that a considerable fraction of the energy of the electronic excitation of sodium is converted into vibrational energy of the nitrogen molecule,

$$\text{Na}' + \text{N}_2 \rightarrow \text{Na} + \text{N}_2^*$$

(N_2^* denotes a vibrationally excited nitrogen molecule).

Vibrational energy, naturally, must also play a role in the reverse process of thermal excitation of the electronic levels of atoms and molecules. Therefore it should be expected that thermal excitation in collisions of molecules with atoms or molecules should occur with a considerably greater probability than in collisions of atoms with atoms.

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* The value $q' = 19.1 \cdot 10^{-15}$ cm^2, obtained in work (6), should be considered unlikely.