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Abstract

Full Text

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ON CHEMICAL REACTIONS OF ATOMS WITH ENERGY COMPARABLE TO THE ACTIVATION ENERGY

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In the case when the energy of an atom is comparable with the activation energy of a chemical reaction, the probability of a chemical reaction can be expressed in terms of the specific rate of the chemical reaction. The specific rate of the chemical reaction $K(T)$ can be calculated by the activated-complex method or determined from experiment.

The number of molecules C or D formed per unit time in unit volume according to the scheme $A + B \to C + D$ is equal to $K(T)n_A n_B$, where n_A is the concentration of atoms of gas A; n_B is the concentration of molecules of gas B.

On the other hand, this quantity can be expressed through the cross sections $\sigma_n(v)$ of the chemical reaction:

$$K(T)n_A n_B = n_A n_B \left(\frac{\mu}{2\pi kT}\right)^{3/2} 4\pi \int_0^\infty \exp\left(-\frac{\mu v^2}{2kT}\right) \frac{\sum_n \omega_n \sigma_n(v) \exp\left(-\frac{\varepsilon_n}{kT}\right)}{\sum_n \omega_n \exp\left(-\frac{\varepsilon_n}{kT}\right)} v^3\, dv, \tag{1}$$

if we assume that the distribution over velocities of particles A and B is Maxwellian. Here m_A is the mass of atom A, m_B is the mass of molecule B,

$$\mu = \frac{m_A m_B}{m_A + m_B},$$

ε_n, ω_n are the energy and statistical weight of the n-th quantum state of molecule B, $\sigma_n(v)$ is the cross section of the chemical reaction in the case when the molecule is in quantum state n, averaged over all directions of the relative velocity. We shall regard atom A as being in the ground quantum state, in accordance with the large excitation energy of the electronic levels of an individual atom.

Generally speaking, for each reaction channel in expression (1) the threshold reaction energies may be different. This difference should be of the order of

ε_n. In the case when $\varepsilon_n \gg kT$, the gas will practically not contain molecules with such excitation energy. In the case when $\varepsilon_n \lesssim kT$, this difference may be neglected, since $E_0 \gg kT$, and the threshold energy may be taken to be the same for all channels. Expression (1) in this case is rewritten as

$$K(T) = \left(\frac{\mu}{2\pi kT}\right)^{3/2} 4\pi \frac{\sum_n \omega_n \exp\left(-\frac{\varepsilon_n}{kT}\right) \int_{v_0}^{\infty} \sigma_n(v) \exp\left(-\frac{\mu v^2}{2kT}\right) v^3\, dv}{\sum_n \omega_n \exp\left(-\frac{\varepsilon_n}{kT}\right)}. \quad (2)$$

Here

$$v_0 = \sqrt{\frac{2E_0}{\mu}}$$

is the threshold energy of the reaction. Usually $K(T)$ has the form

$$A(T) \exp\left(-\frac{E_0}{kT}\right),$$

where $A(T)$ is a function slowly varying with temperature. This means that the functions $\sigma_n(v)$ vary slowly in the region

$$v - v_0 \sim \sqrt{\frac{2kT}{\mu}}.$$

Taking $\sigma_n(v)$ outside the integral and taking into account that $E_0 \gg kT$, we obtain

$$\frac{\sum\limits_n \omega_n \exp\left(-\frac{\varepsilon_n}{kT}\right) \sigma_n(v_0)}{\sum\limits_n \omega_n \exp\left(-\frac{\varepsilon_n}{kT}\right)} = \left(\frac{\pi kT}{2\mu}\right)^{1/2} \frac{k(T)}{v_0^2} \exp\left(\frac{E_0}{kT}\right). \quad (3)$$

It is seen from formula (3) that, because of the presence under the integral of the factor $\exp\left(-\frac{\mu v^2}{2kT}\right)$, the quantity $K(T)$ is determined through the cross sections $\sigma_n(v_0)$.

Below we shall show that also in the case when atom A has a definite velocity $v_A \ll v_0$, the probability of a chemical reaction can be expressed in terms of the same quantities $\sigma_n(v_0)$.

Indeed, the distribution with respect to relative velocities has the form

$$w(\mathbf{v}) = \left(\frac{m_B}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m_B(\mathbf{v} - \mathbf{v}_A)^2}{kT}\right).$$

Using this expression, we obtain for the probability of a chemical reaction per unit time

$$\alpha(v_A) = n_B \int_{v_0}^{\infty} w(\mathbf{v})\, v \, \frac{\sum\limits_n \omega_n \exp\left(-\frac{\varepsilon_n}{kT}\right) \sigma_n(v)}{\sum\limits_n \omega_n \exp\left(-\frac{\varepsilon_n}{kT}\right)} \, d\mathbf{v}$$

or, after averaging over the angle between the direction of the relative velocity $\mathbf{v}$ and the velocity $\mathbf{v}_A$,

$$\alpha(v_A) = \left(\frac{m_B}{2\pi kT}\right)^{3/2} n_B 4\pi \exp\left(-\frac{m_B v_A^2}{2kT}\right) \int_{v_0}^{\infty} \exp\left(-\frac{m_B v^2}{2kT}\right) \frac{\operatorname{sh} \frac{m_B v_A v}{kT}}{\frac{m_B v_A v}{kT}} \times$$

$$\times \frac{\sum\limits_n \omega_n \exp\left(-\frac{\varepsilon_n}{kT}\right) \sigma(v)}{\sum\limits_n \omega_n \exp\left(-\frac{\varepsilon_n}{kT}\right)} v^3 \, dv. \qquad (4)$$

For $v_A \ll v_0$ the region of velocities making the main contribution to the value of the integral will be determined by the factor $\exp\left(-\frac{m_B v^2}{2kT} + \frac{m_B v_A v}{kT}\right)$, i.e. the width of this region will still be of order $\sim \sqrt{\frac{2kT}{m_B}}$; therefore we can again take the cross sections $\sigma_n(v_0)$ outside the integral sign, which gives, after taking relation (3) into account,

$$\alpha(v_A) = K(T) \exp\left(\frac{E_0}{kT}\right) n_B \left(\frac{m_A + m_B}{m_B}\right)^{1/2} \frac{\exp\left(-\frac{m_B v_A^2}{2kT}\right)}{v_0^2 v_A} \times$$

$$\times \int_{v_0}^{\infty} \exp\left(-\frac{m_B v^2}{2kT}\right) \left(\operatorname{sh} \frac{m_B v_A v}{kT}\right) v^2 \, dv. \qquad (5)$$

Since $v_0 \gg \sqrt{\frac{2kT}{m_B}}$, for $\left(\frac{2kT}{m_B}\right)^{1/2} < v_A \ll v_0$

$$\alpha(v_A) K(T) \exp\left(\frac{E_0}{kT}\right) n_B \left(\frac{m_A + m_B}{m_B}\right)^{1/2} \frac{kT}{m_B v_A v_0} \exp\left(-\frac{m_B v_0^2}{2kT}\right) \operatorname{sh} \frac{m_B v_A v}{kT}. \qquad (6)$$

As is evident from formula (6), $\alpha(v_A)$ increases as $\exp\left(\frac{m_B v_A v}{kT}\right)$ with increasing v_A. For $v_A = v_0$, from (4) one readily obtains

$$\alpha(v_0) = K(T)\exp\left(\frac{E_0}{kT}\right) n_B \left(\frac{m_A + m_B}{m_B}\right)^{1/2} \frac{kT}{m_B v_0^2}.$$

With a further increase in v_A, the dependence $\alpha(v_A)$ will be determined by the dependence of the cross sections $\sigma_n(v)$ on the velocity, and in order to calculate it it is necessary to know the specific form of the function $\sigma_n(v)$.

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