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Abstract

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ON THE DETERMINATION OF INTERMOLECULAR INTERACTION FORCES FROM THE RESULTS OF A STUDY OF VIBRATIONAL RELAXATION IN OXYGEN

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Experimental studies of the elastic scattering of a neutral beam of particles moving at high speed make it possible in a number of cases to obtain, with a definite accuracy, the parameters of the potentials of intermolecular interaction forces (^{1}). Bearing in mind the great importance of knowing the character of the forces acting between molecules at sufficiently high thermal velocities, it is necessary, however, to seek other experimental possibilities. For this purpose it is appropriate to try to use the results of studies of the relaxation of molecular vibrations, since it is known that the excitation of molecular vibrations in a collision is closely connected with the character of the intermolecular forces (the slope of the potential curve of repulsive forces, etc.) ($^{2-6}$). Another advantage of this method is that the most effective collisions for the excitation of vibrations are those in which the relative velocity of the colliding particles v^* exceeds the mean thermal velocity $\bar{v}$ by several times. This makes it possible to obtain results referring to still higher temperatures than those at which the study of vibrational relaxation was carried out. Under these conditions the kinetic energy of the colliding molecules $\varepsilon^* = \mu v^{*2}/2$ is much greater than the vibrational quantum ΔE. In accordance with this, the classical, quasiclassical, and quantum-mechanical solutions of the problem of excitation of molecular vibrations ($^{3-6}$) lead to identical results (for identical models) and make it possible to obtain a sufficiently well-founded relation for the dependence of the relaxation time τ on temperature.

On the other hand, experimental determination of such a dependence requires a high purity of the gas under study, sufficient accuracy of measurements, and also the performance of experiments over a wide temperature interval. Pursuing these aims, we carried out a series of experiments to determine the time of vibrational relaxation in oxygen by the previously described method (^{7,8}). In these experiments the oxygen was subjected to careful purification by repeated fractionation through liquefaction; the shock tube in which the experiments were carried out was twice "flushed" with purified gas before the experiment. The remaining impurities in the oxygen amounted to less than 0.01%; further purification did not change the results. The results obtained refer to the temperature range 1200—6600° K and indicate that Blackman' s data (9) at $T < 2000°$ K are substantially too low because of the large influence of impurities; the question of the influence of impurities on the value of τ in oxygen was considered by one of the authors in (10).

For the calculations we use a model of two colliding diatomic molecules in which the center of the repulsive forces is located at the center of the atoms and their potential is equal to $V = V_0 \exp(-\alpha R)$, while the center of the attractive forces is at the center of the molecules and the attraction is characterized by the usual potential "well," described by the Lennard-Jones potential (6–12) and having depth ε/k. In this case, in accordance with (4,6), for the value of the vibrational relaxation time we obtain

$$\tau = \frac{\sqrt{3}}{64\pi^3}\left(\frac{L}{r_c}\right)\frac{h\alpha^3}{p\chi^2}\frac{\exp\left\{3\chi - \frac{\Delta E}{2kT} - \frac{3L^2\alpha}{8r_c} - \frac{4}{\pi}\sqrt{\frac{\chi}{T} - \frac{\varepsilon}{k}}\right\}}{[1 - \exp(-\Delta E/kT)]}, \tag{1}$$

where L is the equilibrium internuclear distance in the molecule; r_c is the distance between the centers of mass of the molecules at the classical turning point for ener-

energy ε^*; p is the gas pressure; $\chi = [(2\pi^4\mu\Delta E^2)/(\alpha^2\hbar^2 kT)]^{1/3}$; μ is the reduced mass of the colliding molecules, and α characterizes the interaction between atoms belonging to different colliding molecules. We shall assume that further refinement of the expression for τ will not appreciably affect the character of the temperature dependence $\tau(T)$, i.e., we shall take relation (1) to be valid to within a certain factor A, independent of temperature.* Then, retaining in the right-hand side of (1) only the principal factor $\exp(3\chi)$, transferring all the rest to the left and taking logarithms, we obtain a relation of the form

$$\varphi[\alpha, r_c, T, \tau(T)] = \frac{c}{\alpha^{2/3}}T^{-1/3}, \tag{2}$$

where c is a quantity constant for the given type of molecule. In what follows, for each experimentally obtained value of $\tau(T)$, we shall construct φ as a function of $T^{-1/3}$. The values of α and r_c entering into φ will be selected by the method of successive approximations, beginning, for example, with the values obtained in (12) by calculation. The values of α for the next step will then be determined by the slope of the straight line that can be drawn through the obtained points in the $(\varphi, T^{-1/3})$ plane by the least-squares method (Fig. 1). The value of $\ln A$ is determined by the point of intersection of the straight line

$$\varphi - \ln A = (c/\alpha^{2/3})T^{-1/3}$$

with the φ-axis. This makes it possible to determine the value of r_c in the next approximation. For this purpose, following (12), we find the so-called "effective" interaction potential O_2—O_2, reduced to a spherical one by averaging over the

Fig. 1. Experimental values of the quantity φ as a function of $T^{-1/3}$. The position of the straight line corresponds to the equation $\varphi = 233.2\,T^{-1/3} - 1.88$, determined by the least-squares method.

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angles θ_1, θ_2 of the mutual arrangement of both molecules. Taking this potential in exponential form $U = U_0 \exp(-\alpha_M r)$, where r is the distance between the centers of the molecules and α_M is a parameter characterizing the "effective" interaction between O_2 molecules, we obtain (^{12})

Fig. 1. Experimental values of the quantity φ as a function of $T^{-1/3}$. The position of the straight line corresponds to the equation
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$$\frac{1}{(4\pi)^2}\int_0^\pi 2\pi \sin\theta_1\, d\theta_1 \int_0^\pi 4V_0 e^{-\alpha R}\, 2\pi \sin\theta_2\, d\theta_2 =$$

$$= \frac{4V_0 e^{-\alpha r}}{\alpha^3 r L^2}\left[2(\alpha r + 2)(\operatorname{ch}\alpha L - 1) - 2\alpha L \operatorname{sh}\alpha L\right] = U_0 e^{-\alpha_M r}. \tag{3}$$

This relation makes it possible to obtain the value of α_M corresponding to the previously determined value of α. The pre-exponential factor U_0 is calculated from the relation following from the definition of the classical turning point r_c:

$$U_0 \exp(-\alpha_M r_c) = \frac{\mu v^{*2}}{2}. \tag{4}$$

The quantity r_c entering here is first determined from the first approximation by relation (1), taking into account the constant obtained above factor A, but with a new value of α. In doing so, putting $\exp(3L^2\alpha/8r_c) \simeq 3eL^2\alpha/8r_c$ (e is the base of natural logarithms)*, we obtain

$$r_c = A\frac{\sqrt{3}}{24\pi^3 e}\frac{h\alpha^2}{\tau p \chi^2}\frac{\exp\left\{3\chi - \frac{\Delta E}{2kT} - \frac{4}{\pi}\sqrt{\frac{\chi}{T} - \frac{\varepsilon}{k}}\right\}}{[1 - \exp(-\Delta E/kT)]}. \tag{5}$$

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* Consideration of the vibrational-rotational interaction and allowance for the transition of rotational energy into vibrational energy, which leads to a decrease in τ, indeed gives a factor independent of temperature (^{11}). The authors express their gratitude to E. E. Nikitin, who acquainted them with the work (^{11}) before its publication.

Fig. 2. Form of the potential curves of intermolecular interaction O_2—O_2: 1 –this work, 2 –according to the calculations of Vanderslice et al. (^{12}), 3 –according to the calculations of Meador (^{13}), 4 –from the results of viscosity measurements by Row and Ellis (^{14}).

Figure 2: Fig. 2. Form of the potential curves of intermolecular interaction O_2—O_2: 1 –this work, 2 –according to the calculations of Vanderslice et al. (^{12}), 3 –according to the calculations of Meador (^{13}), 4 –from the results of viscosity measurements by Row and Ellis (^{14}).

The effective velocity entering (4), according to (^{3}), is equal to $v^* = (4\pi^2 kT\Delta E/\alpha h\mu)^{1/3}$. The indicated procedure makes it possible to obtain the value of r_c in the next approximation; then the quantities α and A, etc., are again determined. The calculation showed that the sequence converges sufficiently rapidly. As a result, for the interaction of O–O atoms belonging to different colliding molecules, the value $\alpha = 4.17 \pm 0.07$ Å^{-1} was obtained; the quantity A is equal to 0.154 ± 0.031. The corresponding value for the interaction of molecules proved to be $\alpha_M = 3.97 \pm 0.07$ Å^{-1}, and the average value of U_0 from the results of all measurements of $\tau(T)$ is close to 20300 eV. This value can be regarded as accurate only to within a factor of ~ 1.5, since τ depends comparatively weakly on r_c (inversely proportionally).

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Thus, the "effective" potential of the forces of intermolecular interaction for O_2—O_2 is obtained in the form

$$U = 20300 \exp(-3.97\, r) \text{ eV}. \tag{6}$$

In accordance with (4), the expression obtained should be assigned to the energy range $0.66 \leqslant \varepsilon^* \leqslant 2.25$ eV, or to intermolecular distances $2.28 \leqslant r \leqslant 2.60$ Å. Relation (6) agrees quite satisfactorily with the results obtained from measurements of the viscosity of oxygen for energies below 0.11 eV (Fig. 2). The calculated curves for the potentials (^{12,13}) give somewhat overestimated values at small energies.

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* This expansion is quite satisfactory, since in our case the value $3L^2\alpha/8r_c$ at $r_c \sim 2.5$ Å is close to unity.

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

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