

STRETCHING AND THE DIFFERENCE IN THE INTERMOLECULAR POTENTIALS OF H_2 AND D_2 FROM LOW TEMPERATURE DATA

A. K. GHOSH AND A. K. BARUA

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, CALCUTTA-32.

(Received September 15, 1966)

ABSTRACT. By analysing the low temperature viscosity data of H_2 and D_2 the effect of stretching on the intermolecular potentials of H_2 and D_2 has been considered. In the calculations quantum effects have also been taken into account. The results confirm the suggestion by Barua and Saran regarding the temperature dependence of the difference in the intermolecular potentials of H_2 and D_2 .

INTRODUCTION

In recent years, the difference in the intermolecular potentials of H_2 and D_2 has received attention from a number of workers. Previously, the general convention was to assume the potentials of isotopes to be identical. However, Michels, de Graaf and Seldam (1960) from an analysis of the accurate second virial coefficient data of Michels *et al.* (1959) first observed a definite difference in the intermolecular potentials of H_2 and D_2 . This was corroborated by Saran and Barua (1965) from an analysis of the viscosity data of H_2 and D_2 reported by Barua, Afzal, Flynn and Ross (1964). From the theoretical side, Knaap and Beenakker (1961) suggested that difference in the intermolecular potentials of H_2 and D_2 was due to the difference in their polarizabilities. Subsequently, Barua and Saran (1963) from an analysis of the second virial coefficient data (Michels *et al.*, 1960) obtained a regular temperature dependence of the difference in the intermolecular potentials of H_2 and D_2 which they explained as due to the temperature dependence of the polarizabilities of these gases. This temperature dependence of the polarizability comes mainly due to the stretching of the molecules with the increase of temperature. More recently, Mason, Amdur and Oppenheim (1965) have analysed various transport properties data including viscosity data for H_2 and D_2 and confirmed the results obtained by Michels *et al.* (1960) and Saran and Barua (1965). Due to the non-availability of quantum corrections for the transport properties which become prominent for H_2 and D_2 for temperatures below the room temperature, Saran and Barua (1965) had to limit their calculations to 300°K. However, recently quantum corrections for the transport properties have been calculated for the Lennard-Jones (12 : 6) model (Imam-Rahajoe, Curtiss and Bernstein 1965). In this paper we have examined the viscosity data of H_2 and D_2 as reported by Rietveld, Itterbeek, and Velds (1959) down to 14.4°K.

THEORETICAL FORMULAE

For all our calculations we shall use the Lennard-Jones (12:6) potential, which may be written as,

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad \dots (1)$$

where $\phi(r)$ is the potential energy between two molecules separated by a distance r , ϵ is the depth of potential minimum and σ is the value of r for which $\phi(r) = 0$. The Lennard-Jones (12:6) potential holds strictly for spherically symmetrical molecules, i.e. it is incapable of taking into account inelastic collisions. However, as pointed out by Mason *et al.* (1962), viscosity is unaffected (to the first approximation) by inelastic collisions and at least for this particular property it is justified to use spherically symmetric potential.

The reduced coefficient of viscosity, η^* (Saran and Barua, 1965) may be written as

$$\eta^* = \eta\sigma^2/\sqrt{(m\epsilon)} \quad \dots (2)$$

which is a function of $T^* = kT/\epsilon$

From Eq. (2) we can obtain the expression,

$$\frac{\eta_H - \eta_D}{\eta_H} = 1 - \frac{\sqrt{m_D \epsilon_D}}{\eta_H} \sigma_D^{-2} \eta^*(T^*_D) \quad (3)$$

where the subscripts H and D stand for H_2 and D_2 respectively and m represents the mass.

Let $\rho = (\sigma_H - \sigma_D)/\sigma_H$,

then neglecting the higher terms,

$$\sigma_D^{-2} = \sigma_H^{-2} (1 + 2\rho) \quad \dots (4)$$

By developing $\eta^*(T^*_D)$ around the corresponding values of $\eta^*(T^*_H)$, we get

$$\begin{aligned} \eta^*(T^*_D) &= \eta^*(T^*_H) + (T^*_D - T^*_H) \partial \eta^* / \partial T^*_H \\ &= \eta^*(T^*_H) + T \cdot \delta \cdot \partial \eta^* / \partial T, \end{aligned} \quad \dots (5)$$

where $\delta = (\epsilon_H - \epsilon_D)/\epsilon_D$

The magnitude of ρ is small (Knaap and Boenakker, 1961) and we shall neglect it in our considerations. Eq. (3) may thus be written as,

$$\frac{\eta_H - \eta_D}{\eta_H} = 1 - \frac{\sqrt{m_D \epsilon_D}}{\eta_H} \sigma_H^{-2} \left[\eta^*(T^*_H) + T \cdot \delta \cdot \frac{\partial \eta^*}{\partial T} \right] \quad \dots (6)$$

Since, $m_D = 2m_H$ and $\sqrt{\epsilon_D/\epsilon_H} \approx (1 - \frac{1}{2}\delta)$... (7)

We obtain finally,

$$\frac{\eta_H - \eta_D}{\eta_H} = 1 - \sqrt{2} \left(1 - \frac{\delta}{2} \right) \left[1 + \frac{T \cdot \delta}{\eta_H} \frac{\partial \eta_H}{\partial T} \right]$$

$$\simeq 1 - \sqrt{2} + \delta \left[\frac{1}{\sqrt{2}} - \frac{\sqrt{2}}{\eta_H} \cdot T \cdot \frac{\partial \eta_H}{\partial T} \right] \quad \dots (8)$$

neglecting higher orders in δ .

From the theoretical side, following the procedure of Knaap and Beenakker (1961) and neglecting the difference in the repulsive energy of H_2 and D_2 , we obtain

$$\delta = \left[\left(1 - \frac{2\Delta\alpha(T)}{\alpha_H(T)} \right)^{-1} \left\{ \left(1 - \frac{2\Delta\alpha(T)}{\alpha_H(T)} \right)^{-1} - 1 \right\} \frac{\alpha_H(T)}{2\Delta\alpha(T)} \right] - 1 \quad \dots (9)$$

where $\Delta\alpha(T) = \alpha_H(T) - \alpha_D(T)$, $\alpha(T)$ being the polarizability at temperature T .

However, polarizability of molecules depends on internuclear distance and the stretching of the molecules with the increase of temperature will affect polarizability and consequently the intermolecular potentials. For a diatomic molecule the stretching due to vibrations and rotations may be expressed as (Bell, 1942)

$$\Delta r = \frac{kT}{2\pi^2\mu r_e v^2} + \frac{1}{2\pi^2\mu r_e v^2} \frac{\sum k(k+1)(2k+1)\sigma e^{-k(k+1)\sigma/kT}}{\sum (2k+1)e^{-k(k+1)\sigma/kT}} \quad \dots (10)$$

where μ is the reduced mass, v the frequency of vibration, r_e the equilibrium internuclear distance and $\sigma = h^2/8\pi^2\mu r_e^2$. By knowing $\alpha' = (d\alpha/dr)$, the change of polarizability due to stretching can be calculated. α'_H has been calculated accurately by Ishiguro *et al.* (1952) α'_D can be obtained from the relation,

$$\alpha'_D = \frac{(I_R/I_0)_D}{(I_R/I_0)_H} \left\{ \frac{(\nu_0 - \nu)^4_H}{(\nu_0 - \nu)^4_D} \frac{\mu_D \nu_D}{\mu_H \nu_H} \frac{(\alpha'_H + \frac{7}{48} \gamma'_H)^2 (\alpha_D^2 + \frac{7}{48} \gamma_D^2)}{(\alpha_H^2 + \frac{7}{48} \gamma_H^2)} - \frac{7}{48} \gamma'_D \right\} \quad \dots (11)$$

where I is the intensity of the incident radiation of frequency ν_0 , I_0 the intensity of Rayleigh scattering and I_R the intensity of Raman line of frequency $\nu_0 - \nu$, γ denotes the anisotropy and $\gamma' = d\gamma/dr$. We have taken $\alpha_H, \gamma_H, \gamma_D$ and α'_H as obtained by Ishiguro *et al.* (1952). From the measurements of I_R/I_0 for H_2 and D_2 by Bhagabantam (1931, 1932), α'_D can be calculated from Eq. (11). Taking the value of $\alpha'_H = 1.411 \times 10^{-16}$ we get $\alpha'_D = 3.354 \times 10^{-16}$.

METHOD OF CALCULATION

Since we are concerned with low temperature data, it is necessary to account for quantum effects for the application of the theoretical formulae given above. These quantum corrections arise from symmetry and quantum effects and are particularly prominent for the lighter gases at low temperatures. Recently, Imam-Rahajoe, Curtiss and Bernstein (1965) have calculated from the phase-shifts

the quantum mechanical collision integrals for the Lennard-Jones (12 : 6) potential. In order to correct the experimental viscosity data for the quantum effects we have utilized the relation

$$\Delta\eta = \eta_c - \eta_q = C \left[\frac{1}{\Omega_c^{(2,2)*}(T^*)} - \frac{1}{\Omega_q^{(2,2)*}(\Lambda^*, T^*)} \right] \quad (12)$$

where the subscripts c and q stand for classical and quantum mechanical values, $\Omega^{(2,2)*}$'s are the collision integrals, $T^* = kT/\epsilon$, $\Lambda^* = h/\sigma\sqrt{2\mu\epsilon}$, is the quantum parameter, C is a function of the molecular weight, collision cross-section and temperatures (Hirschfelder, Curtiss and Bird, 1954). The force constants required for the calculation were obtained by fitting the experimental viscosity data to the Lennard-Jones (12 : 6) potential by the method of translation of axes (Mason and Rice, 1954). The results obtained are shown in Table II and are in

TABLE I
Experimental and calculated values of δ

| T °K. | η_D/η_H | δ_{exp} | δ_{calc} |
|-------|-----------------|----------------|-----------------|
| 20.4 | 1.455 | 0.067 | 0.058 |
| 71.5 | 1.446 | 0.061 | 0.056 |
| 90.1 | 1.441 | 0.054 | 0.055 |
| 196.0 | 1.418 | 0.013 | 0.051 |
| 229.0 | 1.413 | -0.004 | 0.051 |

TABLE II
Force constants of H_2 and D_2

| | This work | | | Diller and Mason (1966) | | |
|-------|-------------------|--------------|-------------|-------------------------|--------------|-------------|
| | ϵ/k (°K) | σ (Å) | Λ^* | ϵ/k (°K) | σ (Å) | Λ^* |
| H_2 | 38.9 | 2.89 | 1.71 | 37.2 | 2.97 | 1.70 |
| D_2 | 35.08 | 2.959 | 1.24 | 35.0 | 2.976 | 1.238 |

good agreement with those reported by Diller and Mason (1966). It was, however, observed that the viscosity data of D_2 as reported by Rietveld *et al.* (1959) are systematically lower than the more precise data of Kestin and Nagashima (1964) at 20°C and 30°C and those of Barua, Afzal, Flynn and Ross (1964) in the range -50°C to 150°C. It appears that the lower viscosity values of Rietveld *et al.* (1959) may be due to the presence of hydrogen as impurity. In order to correct

for this we have calculated the percentage of hydrogen from the simple formula for the viscosity of gas mixtures

$$\frac{1}{\sqrt{[\eta_{mix}]_1}} = \frac{x_H}{\sqrt{[\eta_H]_1}} + \frac{1-x_H}{\sqrt{[\eta_{D_2}]_1}} \quad \dots \quad (13)$$

By taking the viscosity data (at zero density) of Barua *et al.* (1964) as the correct data for D_2 and η_{mix} as the experimental values of viscosity of D_2 , we have x_H the molefraction of H_2 in D_2 from Eq. (13). From three overlapping temperatures the average percentage of H_2 in D_2 comes out to be 2.67. We have corrected the experimental values of the viscosity of D_2 for the presence of H_2 according to the rigorous formulac for the viscosity of gas mixtures on the Chapman-Enskog theory. In order to obtain $\partial\eta_H/\partial T$ we have fitted the viscosity data to the polynomial

$$\eta_H = a + bT + cT^2, \quad (14)$$

by the least square, the coefficients being $a = 2.8195\mu P$ $b = 0.43\mu P^\circ K^{-1}$ $c = -0.4584 \times 10^{-3}\mu P^\circ K^{-2}$. The polynomial fit the data within an average deviation of 2% and for the viscosity value at 14.4°K, the deviation is about 10% which may very well be due to experimental error. Consequently, we shall leave the data at 14.4°K out of our consideration. Experimental values of δ can be calculated from Eq. (8) and are recorded in column 3 of Table I. The theoretically calculated values of δ are also shown in the same table.

DISCUSSION OF RESULTS

It may be seen from Table I that the calculated and the experimental values of δ show the same trend of variation with temperature. At the lower temperatures the agreement is quantitative. It must be pointed out that in view of our approximations and the small magnitude of δ , even qualitative agreement between experimental and the calculated values of δ should be considered as satisfactory. The results confirm the previously observed temperature dependence of Barua and Saran (1963). It is relevant here to refer to the suggestion of Mason *et al.* (1965) that the temperature dependence of δ (Barua and Saran, 1963) may be due to the limitations of the Lennard-Jones (12:6) model. However, it has been shown that both viscosity and second virial data show a temperature dependence of δ (Saran and Barua, 1965). From physical principles as well, intermolecular potentials should change with temperature as polarizability changes with temperature. That this effect plays a prominent role in diatomic molecules has also been shown by Saran and Deb(1966). Consequently a variation in δ with temperature is expected. Since Lennard-Jones (12 : 6) potential gives results which are consistent from the experimental and theoretical viewpoints it is perhaps not quite justified to ascribe the temperature dependence of δ (Barua and Saran, 1963) as due to an artifact of the model used for intermolecular forces. If the potential

model fails to give expected results then perhaps one of the reasons for the failure may be ascribed to the limitation of the model used.

ACKNOWLEDGMENT

The authors like to thank Prof. B. N. Srivastava, D.Sc., F.N.I., for his kind interest.

REFERENCES

- Barua, A. K., Afzal, M., Flynn, G. P. and Ross, J., 1964, *J. Chem. Phys.*, **41**, 374.
Barua, A. K. and Saran, A., 1963, *Physica*, **29**, 1393.
Bell, R. P., 1942, *Trans. Faraday Soc.*, **38**, 422.
Bhagabantam, S., 1931, *Indian J. Phys.*, **6**, 319,
———, 1932, *Indian J. Phys.*, **7**, 549.
Diller, D. E., and Mason, E. A., 1966, *J. Chem. Phys.*, **44**, 2604.
Hirschfelder, J. O., Curtiss, C. F. and Bird, R. B., 1954, *Molecular Theory of Gases and Liquids*, John Wiley & Sons, Inc., N. Y.
Imam-Rahajoo, S., Curtiss, C. F. and Bernstein, R. B., 1965, *J. Chem. Phys.*, **42**, 530.
Ishiguro, E., Arai, T., Kotani, M., and Mizushima, M., 1952, *Proc. Phys. Soc., Japan*, **A 65**, 178.
Kestin, J., and Nagashima, A., 1964, *Phys. Fluids*, **7**, 730.
Knaap, H. F. P., and Beenakker, J. J. M., 1961, *Physica*, **27**, 523.
Mason, E. A., Amdur, I. and Oppenheim, I., 1965, *J. Chem. Phys.*, **43**, 4458.
Mason, E. A., and Rice, W. E., 1954, *J. Chem. Phys.*, **22**, 522.
Mason, E. A., and Monchick, L., 1962, *J. Chem. Phys.*, **36**, 1622.
Michels, A., de Graaf, W., Wassenaar, T., Lovelt, J. M. H., and Louwerse, R. 1959, *Physica*, **25**, 25.
Michels, A., de Graaf, W., and Ten Seldam, C. A., 1960, *Physica*, **26**, 393.
Rietveld, A. O., Van Itterbeek, A., and Velds, C. A., 1959, *Physica*, **25**, 205.
Saran, A., and Barua, A. K., 1965, *Canad. J. Phys.*, **43**, 2374.
Saran, A., and Deb, S. K., 1966, *Mol. Phys.*, **10**, 221.