Thermal Diffusion Factor of Hydrogen-Nitrogen Mixture

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Introduction

Recently it becomes easy to discuss intermolecular potential by the theoretical and experimental development. Considering the fact that the effect of thermal diffusion is affected more sensitively by the intermolecular potential than any other transport phenomena, such as viscosity, ordinary diffusion, etc., it will be interesting to treat the effect in relation to this standpoint. Actually, several authors have already attacked the problem theoretically1), but it seems to us that they did not extend their research in such details so far as to check whether or not the experimental data agree with their theory over the entire range of composition. It was, therefore, attempted in the present paper to treat the problem from another direction, adopting hydrogen-nitrogen mixture as the system to be studied, because it has been the most studied of all the binary mixtures.

Theoretical Consideration

To begin with, thermal diffusion factors α of this system were collected from the reports hitherto published, instead of k_t, for

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1) S. Chapman, *Proc. Roy. Soc.*, A **177**, 38 (1940). R.C. Jones, *Phys. Rev.*, **58**, 111 (1940); **59**, 1019 (1941). M. Kotani, *Proc. Math.-Phys. Soc. Japan*, **24**, 76 (1942). T. Kihara and M. Kotani, *ibid.* **25**, 602 (1943). Hirschfelder, Bird, and Spotz, *Chem. Rev.*, **44**, 205 (1949). K. E. Grew, *Proc. Roy. Soc.*, A **189**, 402 (1947), K. E. Grew, *Proc. Phys. Soc.*, **62**, 655 (1949). E. R. S. Winter, *Trans. Faraday Soc.*, **46**, 81 (1950), etc.

the reason that the former constant varies less against composition than the latter[*].

All these values, except those which were obtained at the mean temperatures much lower than 0°C, are plotted in solid circles against molar fraction of hydrogen (c), as shown in Fig. 1, where some of them had to be determined by evaluating from the data of original papers. The four points designated in the triangle are those determined under 1–12.6 atm. pressure recently by Hirota and Kobayashi[2], using the Clusius-Dickel column, and the numerals attached to them indicate the pressure under which the experiment was carried out. It will be important that these data at high pressure also coincide with those obtained at ordinary pressure, though, according to Becker, it will increase to some extent under 80 atmospheric pressures[3].

If we exclude, for the time being, the values marked by the triangle and the open circle which will be explained in the present paper, it is evident that the observed α's increase linearly with hydrogen concentration[**], but there is a tendency for their mutual difference to increase more greatly at the same time, especially in the concentration above $c=0.80$. Such a dispersed state of the results cannot be caused by the temperature difference among the measurements, because the difference is too small to be explained on both theoretical and experimental grounds, while also it cannot be caused by the slight pressure difference[4], as described above.

On the other hand, the first approximate values[5] of α were calculated by using the Lennard-Jones 12:6 potential:

$$V(r)=4\epsilon\left\{\left(\frac{r_0}{r}\right)^{12}-\left(\frac{r_0}{r}\right)^{6}\right\}$$

(ϵ is the depth of the potential energy minimum and r_0 is the low velocity collision diameter). The difficult numerical calculation could be avoided by use of the tables given by Hirschfelder, et al.[1,6], the basic constants required in the procedure are as follows:

$\epsilon(H_2)/k=33.3°K$,
$r_0(N_2)=2.968Å$ (from viscosity),
$\epsilon(N_2)/k=91.46°K$,
$r_0(N_2)=3.681Å$ (from viscosity),
and $\epsilon(N_2\sim H_2)/k=47.8°K$,
$r_0(N_2\sim H_2)=3.325Å$.

(k is the Boltzmann constant.) The temperature was assumed to be 321.6°K in the calculation.

The calculated result is shown by the full line in Fig. 1, where the dotted is the one when a rigid sphere potential is adopted in calculation, using 2.730Å, 3.756Å and 3.243Å as the collision diameter of hydrogen, nitrogen and nitrogen-hydrogen, respectively. It is clearly shown, as ought to be, that the latter cannot reproduce the experiment, while that of the Lennard-Jones potential can reproduce the experimental values better. But even this potential cannot give the decreasing tendency of α in high hydrogen concentration.

Experiment and Discussion

Considering the situation, thermal diffusion

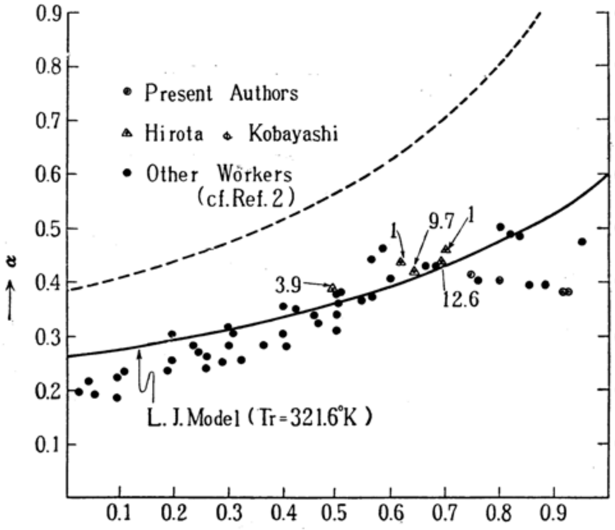

Fig. 1

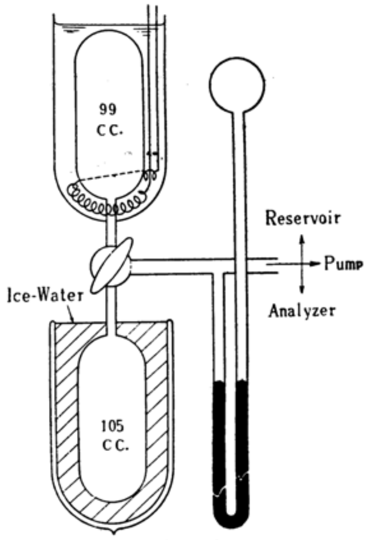

Fig. 2

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[*] Between a and kt, there is a relation: $kt=ac(1-c)$, where c is the concentration in molar fraction.

[**] The present data of Hirota and Kobayashi differ slightly wih those of the former report, due to the accurate determination done later.

[2] K. Hirota and Y. Kobayashi, *J. Chem. Phys.*, **21**, 246 (1953).

[3] E.W. Becker and A. Schulzeff, *Naturw.*, **35**, 219 (1948).

[4] Regarding this system, E. Whalley (private communication) obtained the result that separations at one atmosphere and 1 mm.Hg. seem to be identical within a few percent, if two bulbs were maintained for a sufficient time at 295°K and 427°K, respectively.

[5] Chapman and Cowling, "Mathematical Theory of Non-Uniform Gases" (1939).

[6] Hirschfelder, Bird and Spotz, *J. Chem. Phys.*, **16**, 968 (1948).

factors of relatively high hydrogen concentration were determined by the two-bulb-method. The main apparatus consisted of two bulbs (about 100 cc.) as shown in Fig. 2. Higher and lower temperatures were kept at 0°C. and 100°C. by ice-water and boiling water, respectively. The purity of the samples was tested mass-spectrometrically, and the impurity, being mostly oxygen, was found to be less than 0.1%. The concentration of hydrogen in the samples was analyzed by the volume decrease, oxidizing it with CuO heated at 300°C. During sampling care was taken that no concentration change should occur due to the difference of the diffusion rate of hydrogen and nitrogen through the tubing. Each experiment was carried out for a much longer time—five or more times —than the relaxation time (ca. 1.5 hours) defined by

$$t_r=\left(\frac{L}{\rho DS}\right)\left(\frac{mm'}{m+m}\right)\cdot\frac{1}{2}\cdot\left(\frac{T+T'}{T-T'}\right)\cdot\ln\left(\frac{T'}{T}\right),^{7)}$$

where L, length of the connecting tube = 11 cm;
ρ, density;
D, diffusion coefficient;
S, cross section of the tube = (π/4.0 cm^2);
$m(m')$, mass in the reservoir of higher (lower) temperature;
$T(T')$, higher (lower) temperature.

The experimental data and α obtained from them are shown in table 1 and by the open circles in Fig. 1 (c=0.74, 0.79, 0.88 and 0.89). It is shown that the experimental points are still lower than the theoretical line. Therefore, the discrepancy already mentioned in the region of higher concentration does not disappeared, but rather seems to be confirmed. Considering the fact that the potential adopted by the present paper holds fairly well to other transport phenomena, such an unexpected disagreement between theory and experiment may be brought out by the use of Chapman's first approximate formula of α besides as well as becauce of the incompleteness of the intermolecular potential adopted.

Table I

Mean hydrogen conc. (molar fraction)	Separation (molar fraction)	Thermal diffusion factor α
0.741_4	0.023_8	0.39_7
0.792_8	0.020_4	0.39_8
0.879_5	0.010_7	0.32_5
0.890_0	0.010_5	0.34_4

Summary

The thermal diffusion factor of the nitrogen-hydrogen system has been discussed theoretically. It has been found that the Lennard-Jones potential can reproduce the experimental result, if the hydrogen concentration is below 0.8 in molar fraction. Each experiment done by use of the two-bulb-method in hydrogen concentration 0.74−0.89 has given similarly smaller value than expected theoretically. Such discrepancy may be caused by the theoretical formula of α as well as by the incomplete intermolecular potential.

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7) H. Brown, *Phys. Rev.*, **58**, 661 (1940).