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## MEASUREMENTS OF DIFFUSION COEFFICIENTS BY THE METHOD OF GAS CHROMATOGRAPHY

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SUMMARY

Experimental diffusivities have been obtained for several gas-gas, gas-liquid vapor and gas-solid vapor systems, using the method of gas chromatography. On the basis of the experimental results, a generalized semi-empirical equation has been developed to predict the diffusivity of binary systems as a function of pressure and temperature. A comparison of this equation with data appearing in the literature yields an average error of 3.5 %, which is smaller than that predicted by many other methods.

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## INTRODUCTION

In the prediction of gas-vapor binary diffusivity, it has been a common practice to assume that the diffusivity is inversely proportional to the total pressure of gas atmosphere. This assumption, however is not always justified. The present work was, therefore, undertaken to investigate effects of pressure and temperature on the diffusivity in gas phases.

Numerous techniques are available in the literature for measurements of diffusion coefficients. Most of these methods, however, are quite time-consuming in the evaluation of quantitative results<sup>1</sup>. Recent advancement in the theory of chromatography has made it possible to develop methods<sup>1-3</sup> for rapid and accurate determinations of diffusion coefficients. In addition, a commercially available gas chromatography unit, with an empty tube replacing the packed column, can be utilized for such a study. This method has been applied by the authors in a previous study<sup>3</sup> with satisfaction. Therefore, it was another objective of the present work to extend this method to other systems.

Experimental diffusivities were obtained for several gas-gas, gas-vaporized liquid and gas-vaporized solid binary systems using the method of gas chromatography. Experimental results and factors affecting the diffusivity will be discussed. On the basis of the experimental data, a semi-empirical equation has been developed to predict the gas phase diffusivity as functions of pressure and temperature. A

comparison of the equation proposed with that appearing in the literature also will be made in this paper.

#### THEORETICAL CONSIDERATIONS

The mechanisms of band broadening in linear, nonideal chromatography have been examined by many investigators. Two basically different approaches, the plate theory and the rate theory, have been employed in the development of chromatographic theories. By combining these two lines of thought, relationships between the height equivalent to a theoretical plate and various parameters of the rate theory can be obtained.

In the plate theory<sup>4-6</sup>, the separating efficiency of a chromatographic column is characterized by the height equivalent to a theoretical plate. The column is conceived as consisting of a number of plates or vessels. A volatile solute is introduced into the first vessel, where it dissolves in a nonvolatile liquid which is present there and exerts a vapor pressure above it. A constant flow of a gas, not soluble in the liquid, is passed through the vessels and carries the vapors above the liquid from one vessel to another. In this procedure, it is assumed that the volume of the inert gas phase and the volume of the nonvolatile liquid is the same in each vessel and that these volumes remain constant during the stripping process. In each vessel, the two phases are considered to be equilibrium at any moment. Furthermore, the equilibrium constant is assumed to be independent of the concentrations (linear isotherm). On the basis of these assumptions, the concentration of the solute in the inert gas phase of any given vessel can be derived<sup>5</sup>; the distribution obtained with this continuous flow is of the Poisson type. With the aid of this concentration equation, the number of vessels or plates for a given column can be calculated from the elution diagram. The height equivalent to a theoretical plate,  $H$ , is then derived to be<sup>5</sup>,

$$H = \frac{L}{n} = \frac{L}{d^2} \left( \frac{w}{4} \right)^2 \quad (1)$$

In the above equation,  $L$  denotes the length of the column consisting of  $n$  plates. The peak width and the retention time of the chromatogram are represented by  $w$  and  $d$ , respectively.

In the application of the rate theory, the column is visualized as a continuous medium in which transport phenomena are taken into account. This approach was used by VAN DEEMTER *et al.*<sup>7</sup>, to derive an expression for the height equivalent to a theoretical plate. These authors considered that longitudinal eddy and molecular diffusions and non-equilibrium effect are the most important factors contributing to the efficiency of gas chromatographic columns. Their equation was modified by GIDDINGS<sup>8</sup>, JONES<sup>5</sup>, and others to include other effects. The generalized expression for the height equivalent to a theoretical plate is<sup>5</sup>,

$$H = 2\lambda d_p + \frac{2\gamma D_g}{v} + \frac{2}{3} \frac{k}{(1+k)^2} \frac{d_1^2}{D_l} v + C_1 \frac{k^2}{(1+k)^2} \frac{d_g^2}{D_g} v + C_2 \frac{d_p^2}{D_g} v \\ + 2\rho \sqrt{C_1 C_2} \frac{k d_g d_p}{(1+k) D_g} v + \frac{7\nu r_0^4}{48 R_0^2 D_g} \quad (2)$$

where  $C_1$ ,  $C_2$ , and  $\rho$  and  $\lambda$  are the correlation factors. The average diameter of the solid particles and the average thickness of the liquid film are denoted by  $d_p$  and  $d_l$ , respectively. The average thickness of the gas phase is expressed by  $d_g$ . The diffusion coefficients of a sample in the gas phase and in the liquid phase are represented by  $D_g$  and  $D_l$ , respectively. In eqn. 2,  $k$  is the ratio of the time in the liquid phase to the time in the gas phase,  $v$  is the flow velocity of the carrier gas,  $\gamma$  is the Labyrinth factor,  $R_0$  is the radius of curvature at the center of the coiled tube, and  $r_0$  is the inside radius of the circular cross section tube.

In the right hand side of eqn. 2, the first term arises from lateral diffusion, that is, the eddy effect of multiple paths in gas, and the second term represents the effect of longitudinal diffusion of the sample in gas. The resistances to mass transfer in the liquid and gas phases are shown in the third and fourth terms. The fifth term denotes the contribution of the gas velocity distribution and the sixth term represents the correlation associated with the fourth and fifth terms. The smearing effect of a solute zone due to column bonding<sup>9</sup> is given in the last term.

In a circular cross section tube, we have<sup>10,11</sup>  $C_1 = 1/4$ ,  $C_2 = 1/24$ , and  $\rho = (2/3)^{1/2} = 0.817$ . If an empty column is used, the distribution coefficient  $k$  and  $\lambda$  are all equal to zero,  $\gamma$  is equal to 1, and the lateral diffusion path in the mobile phase,  $d_p$ , is correspondent to  $r_0$  (ref. 10). Thus, eqn. 2 can be simplified to

$$H = \frac{2D_g}{v} + \frac{r_0^2 v}{24D_g} + \frac{7vr_0^4}{48R_0^2 D_g} \quad (3)$$

In the present work,  $r_0$  and  $R_0$  are equal to 0.25 and 4.20 cm, respectively. By substituting these values in eqn. 3, we obtain

$$D = \frac{v}{4} [H \pm (H^2 - 0.0298)^{1/2}] \quad (4)$$

Eqns. 1 and 4 imply that only three quantities, the peak width, the retention time, and the flow velocity, are required to calculate the gas phase diffusivity.

## EXPERIMENTAL

A gas chromatograph (Shimadzu Model GC-1C) with a thermal conductivity detector was utilized in this study. Hydrogen was used as carrier gas as well as a component of the gas-vapor binary system. About 1 cc each of  $N_2$  and  $CO_2$  were injected separately into the diffusion column by a gas sampler. Liquid samples, about 0.05  $\mu$ l each, were injected by a Hamilton syringe. The technique for the control of sample size was discussed in the previous paper<sup>3</sup>.

Small quantities of naphthalene and camphor were injected by a solid sampler. In order to facilitate the control of sample size, and to keep it away from mixing with air, solid sample was packed in a small hole at the top of a copper alloy carrier in the solid sampler. About a 20-min interval was required for the injection of the solid sample to ensure that the air in the injection port was completely removed.

The column, having a length of 968.83 cm, was treated with dilute hydrochloric acid, and then washed with distilled water prior to each experiment. Thus, the effect of active copper film in the inner copper surface on experimental diffusivity can

be neglected<sup>3</sup>. A standard manometer and a soap film flow meter were connected to the outlet of the carrier gas to measure pressure and flow rate for each run. A needle valve which lies between the outlet of the carrier gas and the manometer was used to adjust the flow rate. The flow rate of the carrier gas in the column was controlled within  $1.0 \pm 0.05$  cm/sec for the gas-gas and gas-vaporized liquid binary systems to eliminate the tailing effect and to yield a good reproducibility. Experiments were carried out at temperatures ranging from 25 to 250° and at pressures varying from 770 to 1560 mm Hg.

In each experiment, the pressure, the temperature, and the flow velocity of the carrier gas were recorded. The peak width,  $w$ , and the retention time,  $d$ , of the chromatogram were also measured. Thus, the height equivalent to a theoretical plate,  $H$ , and in turn, the diffusivity,  $D$ , can be calculated from eqns. 1 and 4, respectively.

Although the plate model was originated from discrete systems, it can be applied to continuous flow systems by considering that the height equivalent to a theoretical plate is the length of a vessel whose mean concentration is in equilibrium with its own effluent<sup>4,6</sup>. The use of the plate height as a parameter for the characterization of chromatographic zone spreading is then acceptable as discussed by GIDDINGS<sup>4</sup>. The assumption of linear isotherm in the development of eqn. 1 is valid for low concentration region; the non-linearity of the distribution isotherm at high concentrations can cause the band to become asymmetric<sup>6</sup>. In the absence of a stationary phase in the present work by using an empty column as mentioned earlier, such a possible complication is virtually eliminated.

Eqn. 1 is developed by considering that the sample is introduced into the first plate only. This is an important factor which may cause the state of affairs to be much more involved in the calculation of  $H$ . It takes a certain time interval,  $\Delta t$ , for vaporization of a sample after it is introduced into the column. The larger the sample, the longer the time is required. A criterion used successfully in the previous work<sup>3</sup> to avoid the complication of large samples is to maintain  $v\Delta t < H$ . This implies that it is desirable to carry out an experiment with a small sample and at a small flow velocity of the carrier gas. In addition to these, the time for the syringe to remain in the injection port should be kept at a minimum period. If the amount of sample introduced is larger than that can be contained in the first vessel, the actual peak becomes broader<sup>6</sup>; the calculated diffusivity is larger than the true value in this case. Therefore, each diffusivity reported in the present work is an average value from at least three measurements. This will ensure that the above mentioned criterion is followed and that the error caused by sample size can be neglected. The average deviation among these three determinations for each reported diffusivity is 2.7%. Other methods of eliminating errors caused by finite sample size also have been discussed by KEULEMANS<sup>6</sup>.

The effect of lateral diffusion or the eddy effect of multiple paths in gas phase is another important factor<sup>5,8</sup> to be considered in applying eqn. 4 to calculate the molecular diffusivity. Although all experiments were carried out under laminar flow condition (Reynold number is less than 2), turbulence could occur in the vicinity of the connecting section of the U-shaped column. This is demonstrated by the fact that the calculated diffusivity increases with the flow velocity of the carrier gas if this velocity exceeds a certain value, as illustrated in the previous paper<sup>3</sup>. To eliminate

this possible error due to eddy diffusion, experiments were conducted at various flow velocities under the same pressure and temperature. The true molecular diffusivity was then determined at zero velocity by extrapolating from curve obtained in a plot of calculated  $D$  value *versus*  $v$ .

The sensitivity of the conductivity detector was also examined before the diffusivities were obtained. The linearity of response was checked by varying the sample size. The response was found to be linear over the range of concentration employed. This indicates that the error caused by the detector is negligible.

As mentioned earlier, the observed diffusivities can be reproduced within an average deviation of 2.7%. This value is probably a good reflection of the precision of the chromatographic method and is reasonable compared with that found by other investigators<sup>1, 3, 9, 12, 13</sup>.

## RESULTS AND DISCUSSIONS

Experimental results were obtained for the gas-gas, gas-liquid vapor and gas-solid vapor systems at pressures ranging from 770 to 1560 mm Hg. The gas-gas binary diffusivities were determined for  $H_2$ - $CO_2$  and  $H_2$ - $N_2$  at temperatures varying from 25 to 150°C. The gas-liquid vapor cases studied include  $H_2$ -methanol,  $H_2$ -benzene,  $H_2$ -*n*-hexane,  $H_2$ -ethanol,  $H_2$ -cyclohexane,  $H_2$ -*n*-butanol,  $H_2$ -toluene,  $H_2$ -isooctane,  $H_2$ -*sec.*-butanol, and  $H_2$ -oxylyene at 100°. For the gas-solid vapor systems of  $H_2$ -naphthalene and  $H_2$ -camphor, experiments were conducted at temperatures from 160 to 240°C. In each run, the temperature and the flow velocity were maintained at constant values. This would eliminate adverse effects due to fluctuation of pressure and flow velocity during the experiment. The pressure and temperature dependences of the diffusivity are illustrated in Figs. 1 and 2 for some typical runs. The complete results are shown graphically in Figs. 3-8 for all cases studied.

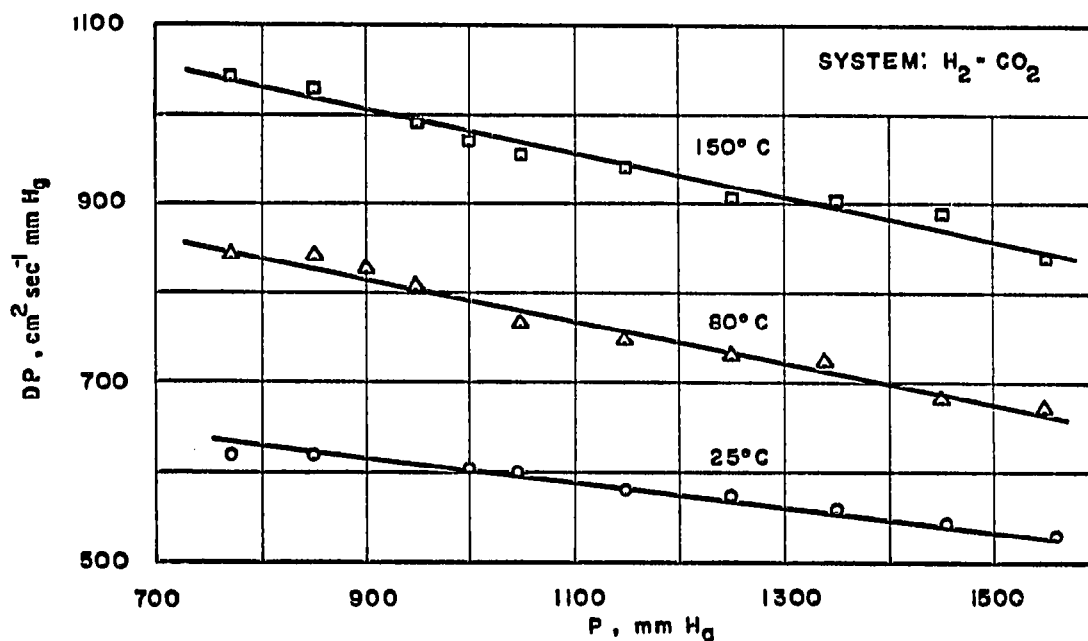


Fig. 1. Effect of pressure on diffusivity.

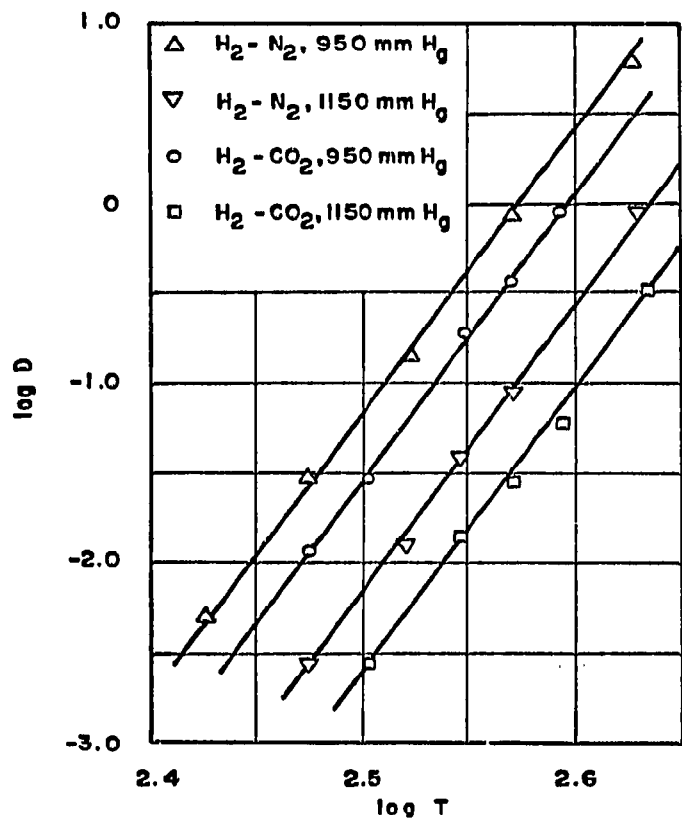


Fig. 2. Effect of temperature on diffusivity.

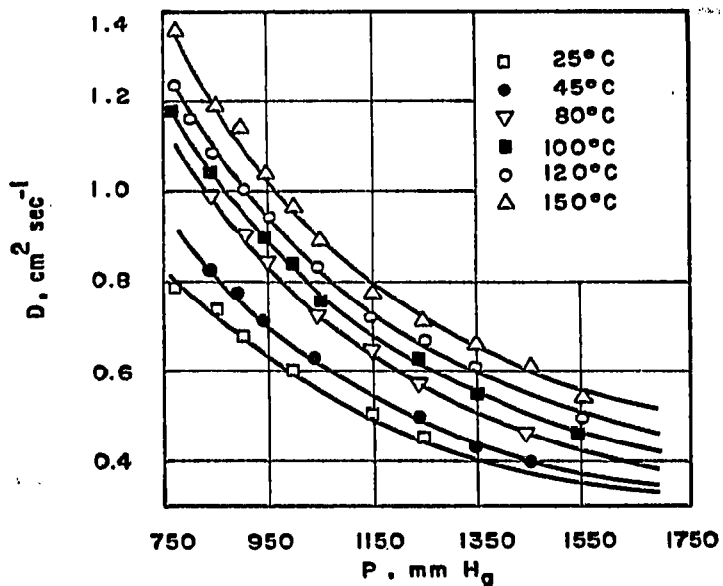


Fig. 3. Diffusivity of hydrogen-carbon dioxide system.

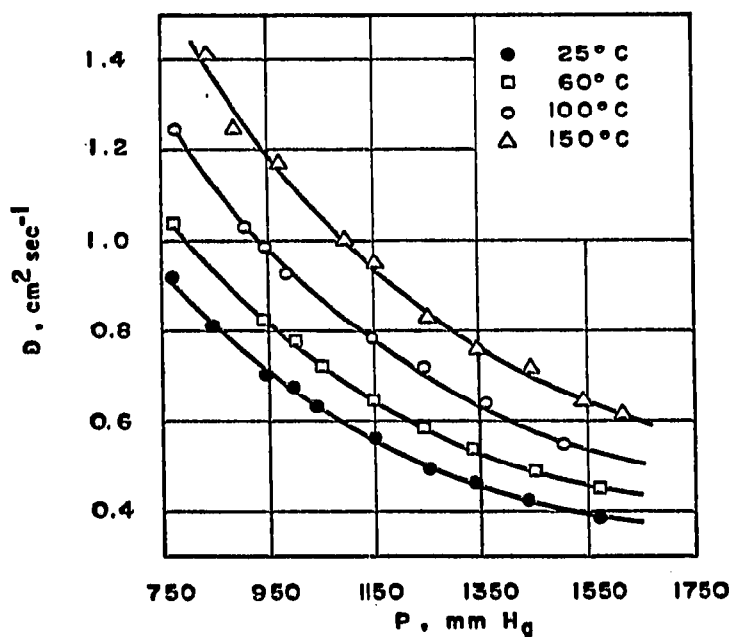


Fig. 4. Diffusivity of hydrogen-nitrogen system.

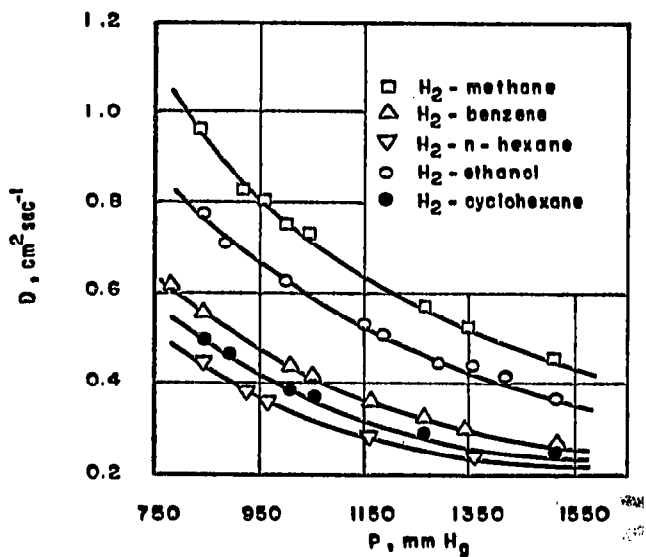


Fig. 5. Diffusivity of gas-liquid vapor systems at 100°C.

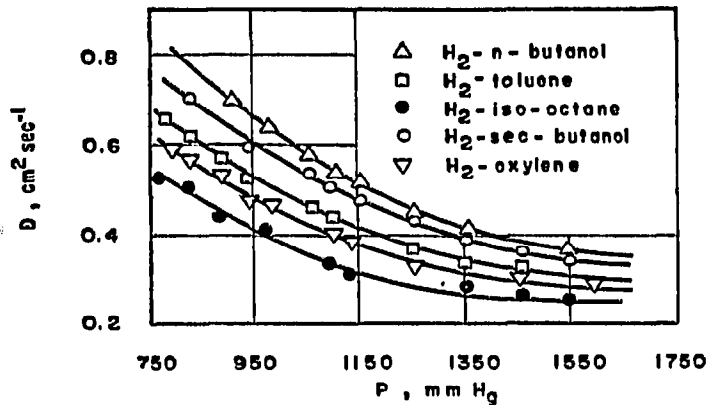


Fig. 6. Diffusivity of gas-liquid vapor systems at 100°C.

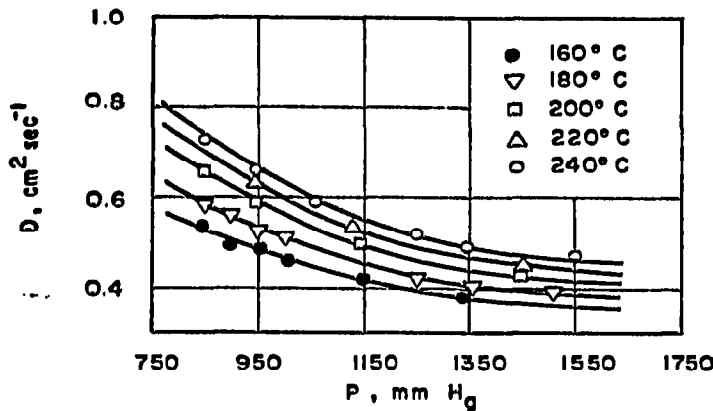


Fig. 7. Diffusivity of naphthalene in hydrogen.

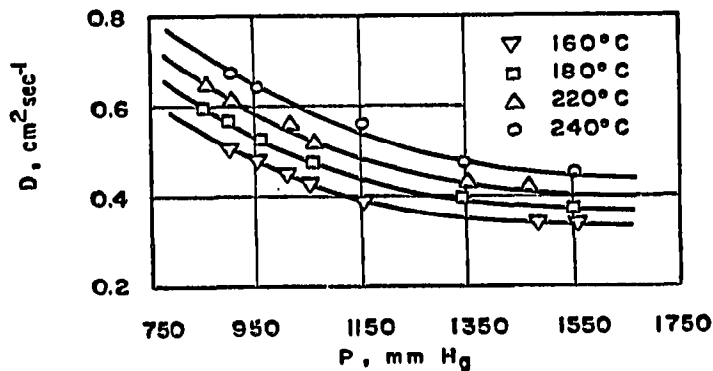


Fig. 8. Diffusivity of camphor in hydrogen.

In the plots of  $D$  versus  $P$ , we find that the slopes obtained for the gas-gas and the gas-liquid vapor systems are smaller than that for the gas-solid vapor cases. This is because the Van der Waals force and the lattice force that existed in solid molecules are larger than those in liquid and gas molecules. In other words, the effect of pressure on the molecular concentration gradient is less important in the vaporized naphthalene and camphor than in the gas or in the vaporized liquid samples. Fig. 1

also illustrates that over the pressure range of experiments, the  $DP$  value decreases linearly with the pressure at a given temperature. In accordance with the argument of kinetic theory, the gas diffusivity should be inversely proportional to the pressure ( $DP = \text{constant}$ ). However, SLATTERY AND BIRD<sup>14</sup> showed that the theory is not valid at high pressures. Their measurements of self-diffusivities of dense gases indicated that below the critical pressure, the diffusivity decreases as the pressure increases. Hence, our experimental results are in agreement with the general trend of pressure dependence reported by SLATTERY AND BIRD<sup>14</sup>. We find that the diffusivity is inversely proportional to  $P^{1.286}$  for the gas-gas and gas-vaporized liquid binary systems and to  $P^{0.865}$  for the gas-vaporized solid binary systems.

The temperature dependence of diffusion coefficient is shown in Fig. 2. Our calculated results indicate that the gas-vaporized solid systems are more sensitive to temperature than any other binary systems. The reason might be the forces between the molecules are different from each other in such a system. For all cases, the average value of the exponent for the gas-gas and gas-vaporized liquid binary systems is 1.75, and that for the gas-vaporized solid binary systems is 1.71. These values agree well with those obtained by other investigators<sup>9, 12, 13</sup>.

From the values obtained, a generalized equation for the diffusion coefficient of gas-gas and gas-vaporized liquid binary systems can be derived from the Maxwell equation.

$$D = \frac{AT^{1.75}}{S^2 P^{1.286}} \left[ \frac{1}{M_A} + \frac{1}{M_B} \right]^{\frac{1}{2}} \quad (5)$$

Following the modification of ARNOLD<sup>15</sup> and assuming that the collision diameters are proportional to the cubic roots of the molar volumes of the components at the normal boiling point, the above equation can be modified to yield,

$$D = \frac{AT^{1.75}}{(V_A^{\frac{1}{3}} + V_B^{\frac{1}{3}})^2 P^{1.286}} \left[ \frac{1}{M_A} + \frac{1}{M_B} \right]^{\frac{1}{2}} \quad (6)$$

where  $T$  is the absolute temperature,  $P$  is the total pressure, and  $M_A$  and  $M_B$  are the ordinary molecular weights. The volume of one mole of liquid compound at the boiling point is denoted by  $V$ . For several elements and simple molecules the  $V$  values are available<sup>12</sup>. The correlation factor,  $A$ , is found to be 5.06 from a plot of eqn. 6 using the experimental data.

The percentage errors calculated by eqn. 6 are listed in Table I. The comparison of this equation with 134 data points appeared in the literature gives an average error of 3.51%. As shown in Table II, the present correlation gives a better result compared with most of the other techniques. These include the methods of FULLER *et al.*<sup>12</sup>, ARNOLD<sup>15</sup>, GILLILAND<sup>2</sup>, ANDRUSSOW<sup>16</sup>, HIRSCHFELDER *et al.*<sup>17</sup>, WILKE AND LEE<sup>18</sup>, SLATTERY AND BIRD<sup>14</sup>, CHEN AND OTHMER<sup>19</sup>, and OTHMER AND CHEN<sup>20</sup>. Furthermore, the method proposed is simple and has wide application. Eqn. 6 can be applied to estimate gas-gas and gas-vaporized liquid binary gas-phase diffusivities provided that the diffusion volume is known.

It should be noted that eqn. 6 yields values smaller than that obtained from the experiments for gas-vaporized solid binary systems. The deviation might be



TABLE I

PERCENTAGE ERROR CALCULATED BY EQUATION 6

Obs. = experimentally observed diffusivity reduced to 1 atm pressure; calc. = diffusivity calculated by eqn. 6.

Systems	Ref.	Temp. (°K)	Obs. (cm <sup>2</sup> /sec)	Calc. (cm <sup>2</sup> /sec)	Error <sup>b</sup> (%)
H <sub>2</sub> -D <sub>2</sub>	21	288.2	1.240	1.270	2.41
H <sub>2</sub> -D <sub>2</sub>	22	295.5	1.250	1.330	6.40
H <sub>2</sub> -N <sub>2</sub>	23	193.0	0.368	0.355	- 3.53
H <sub>2</sub> -N <sub>2</sub>	23	200.0	0.401	0.377	- 5.98
H <sub>2</sub> -N <sub>2</sub>	23	253.0	0.600	0.569	- 5.17
H <sub>2</sub> -N <sub>2</sub>	23	273.0	0.708	0.652	- 7.90
H <sub>2</sub> -N <sub>2</sub>	24	287.5	0.743	0.712	- 2.82
H <sub>2</sub> -N <sub>2</sub>	25	294.0	0.763	0.741	- 2.88
H <sub>2</sub> -N <sub>2</sub>	1	297.2	0.779	0.756	- 2.82
H <sub>2</sub> -N <sub>2</sub>	23	300.0	0.800	0.768	- 4.00
H <sub>2</sub> -N <sub>2</sub>	25	322.0	0.903	0.869	- 3.76
H <sub>2</sub> -N <sub>2</sub>	25	398.0	1.289	1.258	- 2.41
H <sub>2</sub> -N <sub>2</sub>	26	400.0	1.270	1.270	0.00
H <sub>2</sub> -N <sub>2</sub>	25	450.0	1.541	1.559	1.16
H <sub>2</sub> -N <sub>2</sub>	25	506.0	1.883	1.914	1.61
H <sub>2</sub> -N <sub>2</sub>	25	573.0	2.417	2.382	- 1.44
H <sub>2</sub> -Ar	23	287.9	0.828	0.738	-10.86
H <sub>2</sub> -Ar	23	354.2	1.111	1.063	- 4.32
H <sub>2</sub> -Ar	23	418.0	1.714	1.422	-17.04
H <sub>2</sub> -CO <sub>2</sub>	24	289.2	0.619	0.609	- 1.61
H <sub>2</sub> -CO <sub>2</sub>	11	298.0	0.646	0.642	- 0.61
H <sub>2</sub> -H <sub>2</sub> O	27	307.3	1.020	0.934	- 8.43
H <sub>2</sub> -H <sub>2</sub> O	27	328.6	1.121	1.048	- 6.51
H <sub>2</sub> -H <sub>2</sub> O	27	352.7	1.200	1.188	- 1.00
H <sub>2</sub> -NH <sub>3</sub>	25	273.0	0.745	0.715	- 4.21
H <sub>2</sub> -NH <sub>3</sub>	25	293.0	0.833	0.812	- 2.60
H <sub>2</sub> -NH <sub>3</sub>	22	296.8	0.856	0.826	- 3.50
H <sub>2</sub> -NH <sub>3</sub>	25	333.0	1.021	1.008	- 1.07
H <sub>2</sub> -NH <sub>3</sub>	25	413.0	1.435	1.472	2.57
H <sub>2</sub> -NH <sub>3</sub>	25	533.0	2.149	2.300	7.02
H <sub>2</sub> -methane	11	298.0	0.726	0.679	- 6.47
H <sub>2</sub> -ethane	11	298.0	0.537	0.494	- 8.01
H <sub>2</sub> - <i>n</i> -butane	23	287.9	0.361	0.342	- 5.23
H <sub>2</sub> - <i>n</i> -butane	23	354.2	0.507	0.492	- 2.88
H <sub>2</sub> - <i>n</i> -butane	23	430.0	0.763	0.691	- 9.43
H <sub>2</sub> - <i>n</i> -hexane	28	288.7	0.290	0.285	- 1.72
H <sub>2</sub> -cyclohexane	28	288.5	0.319	0.311	- 2.38
H <sub>2</sub> - <i>n</i> -heptane	29	303.2	0.283	0.298	5.22
H <sub>2</sub> - <i>n</i> -octane	29	303.2	0.277	0.271	- 2.16
H <sub>2</sub> - <i>n</i> -decane	28	364.1	0.306	0.335	9.47
H <sub>2</sub> -benzene	30	311.3	0.404	0.391	- 3.12
He-N <sub>2</sub>	18	293.0	0.705	0.679	- 3.69
Ne-N <sub>2</sub>	18	298.0	0.688	0.699	1.59
He-N <sub>2</sub>	1	298.2	0.687	0.701	2.20
He-N <sub>2</sub>	18	300.0	0.743	0.708	- 4.71
He-N <sub>2</sub>	13	323.2	0.766	0.807	5.35
He-N <sub>2</sub>	13	353.2	0.893	0.941	5.37
He-N <sub>2</sub>	13	383.2	1.077	1.085	0.74
He-N <sub>2</sub>	13	413.2	1.200	1.240	3.33
He-N <sub>2</sub>	13	443.2	1.289	1.402	8.78
He-N <sub>2</sub>	13	473.2	1.569	1.565	0.255
He-N <sub>2</sub>	13	498.2	1.650	1.720	4.24
He-N <sub>2</sub>	18	600.0	2.400	2.381	- 0.792

(Continued on p. 22)

TABLE I (continued)

Systems	Ref.	Temp. (°K)	Obs. (cm <sup>2</sup> /sec)	Calc. (cm <sup>2</sup> /sec)	Error <sup>a</sup> (%)
He-N <sub>2</sub>	18	900.0	4.790	4.840	1.68
He-N <sub>2</sub>	18	1200	7.740	8.020	3.36
He-CO <sub>2</sub>	31	276.2	0.531	0.502	- 5.50
He-CO <sub>2</sub>	13	298.2	0.612	0.574	- 6.21
He-CO <sub>2</sub>	31	317.2	0.661	0.641	- 2.98
He-CO <sub>2</sub>	13	323.2	0.678	0.663	- 2.42
He-CO <sub>2</sub>	31	346.2	0.765	0.744	- 2.69
He-CO <sub>2</sub>	13	353.2	0.800	0.772	- 3.50
He-CO <sub>2</sub>	13	383.2	0.884	0.891	0.729
He-CO <sub>2</sub>	13	413.2	1.040	1.017	2.21
He-CO <sub>2</sub>	13	443.2	1.133	1.150	1.50
He-CO <sub>2</sub>	13	473.2	1.279	1.283	0.313
He-CO <sub>2</sub>	13	498.2	1.414	1.412	0.141
He-O <sub>2</sub>	1	298.2	0.718	0.722	0.557
He-O <sub>2</sub>	13	323.2	0.809	0.831	2.72
He-O <sub>2</sub>	13	353.2	0.987	0.968	- 1.92
He-O <sub>2</sub>	13	383.2	1.120	1.117	- 0.268
He-O <sub>2</sub>	13	413.2	1.245	1.276	2.49
He-O <sub>2</sub>	13	443.2	1.420	1.442	1.55
He-O <sub>2</sub>	13	473.2	1.595	1.611	1.003
He-O <sub>2</sub>	13	498.2	1.683	1.767	4.76
He-Ar	31	276.2	0.646	0.628	- 2.78
He-Ar	23	287.9	0.697	0.677	- 2.79
He-Ar	32	298.0	0.725	0.719	- 0.827
He-Ar	31	317.2	0.797	0.803	0.772
He-Ar	13	323.2	0.809	0.831	2.72
He-Ar	31	346.2	0.924	0.933	0.932
He-Ar	13	353.2	0.978	0.968	- 1.12
He-Ar	23	354.2	0.979	0.973	- 0.613
He-Ar	13	383.2	1.122	1.123	0.089
He-Ar	13	413.2	1.237	1.276	3.15
He-Ar	13	443.2	1.401	1.441	2.85
He-Ar	13	473.2	1.612	1.610	- 0.124
He-Ar	13	498.2	1.728	1.747	1.11
He-Ar	32	500.0	1.860	1.778	- 4.41
He-Ar	32	1000	6.250	5.980	4.32
He-Ar	32	1100	7.380	7.070	- 4.2
He-Air	31	276.2	0.624	0.582	- 6.77
He-Air	31	317.2	0.765	0.744	- 2.77
He-Air	31	346.2	0.901	0.865	- 4.09
He-H <sub>2</sub> O	33	298.2	0.908	0.837	- 7.82
He-H <sub>2</sub> O	27	307.2	0.902	0.881	- 2.33
He-H <sub>2</sub> O	27	328.5	1.011	0.992	- 8.99
He-H <sub>2</sub> O	27	352.2	1.121	1.122	0.89
He-CH <sub>4</sub>	12	373.0	1.005	0.949	- 5.57
He-n-heptane	29	303.2	0.265	0.250	- 5.65
He-n-octane	29	303.2	0.248	0.233	- 5.85
He-benzene	13	423.2	0.610	0.578	- 5.25
He-benzene	13	298.2	0.384	0.314	- 18.2
He-benzene	13	463.2	0.715	0.679	- 5.03
He-benzene	13	503.2	0.815	0.783	- 3.93
He-benzene	13	523.2	0.861	0.839	- 2.55
He-methanol	13	423.2	1.032	1.022	- 0.96
He-methanol	13	463.2	1.218	1.198	- 1.64
He-methanol	13	503.2	1.389	1.384	- 0.36
He-methanol	13	523.2	1.475	1.482	0.47
He-ethanol	33	298.2	0.494	0.415	- 16.0

TABLE I (continued)

Systems	Ref.	Temp. (°K)	Obs. (cm <sup>2</sup> /sec)	Calc. (cm <sup>2</sup> /sec)	Error <sup>a</sup> (%)
He-ethanol	13	423.2	0.821	0.764	- 6.93
He-ethanol	13	463.2	0.925	0.896	- 3.14
He-ethanol	13	503.2	1.048	1.053	0.477
He-ethanol	13	523.2	1.173	1.110	- 5.37
He-propanol	13	423.2	0.676	0.681	0.74
He-propanol	13	463.2	0.761	0.798	4.860
He-propanol	13	523.2	0.959	0.987	2.920
He-2-propanol	13	463.2	0.784	0.798	1.785
He-2-propanol	13	523.2	0.988	0.987	- 0.101
He-butanol	13	463.2	0.689	0.678	- 1.6
He-butanol	13	523.2	0.841	0.840	- 0.119
He-pentanol	13	463.2	0.578	0.608	5.19
He-pentanol	13	523.2	0.729	0.752	3.15
He-hexanol	13	463.2	0.531	0.542	2.07
He-hexanol	13	523.2	0.686	0.670	- 2.33
He-propanol	13	503.2	0.896	0.921	2.790
He-2-propanol	13	423.2	0.677	0.681	0.592
He-2-propanol	13	503.2	0.882	0.921	4.420
He-butanol	13	423.2	0.587	0.579	- 1.360
He-butanol	13	503.2	0.792	0.783	- 1.14
He-pentanol	13	423.2	0.507	0.519	2.37
He-pentanol	13	503.2	0.666	0.702	5.4
He-hexanol	13	423.2	0.469	0.463	- 1.28
He-hexanol	13	503.2	0.631	0.625	- 0.95

<sup>a</sup> Percentage error =  $((D_{\text{calc}} - D_{\text{obs}})/D_{\text{obs}}) \times 100\%$ .

TABLE II

## AVERAGE PERCENTAGE ERROR OF VARIOUS METHODS

Methods	% error
This work	3.51
FULLER <i>et al.</i> <sup>13</sup>	3.40
ANDRUSSOW <sup>16</sup>	27.79
HIRSCHFELDER <i>et al.</i> <sup>17</sup>	18.99
CHEN AND OTHMER <sup>19</sup>	10.85
OTHMER AND CHEN <sup>20</sup>	4.53
GILLILAND <sup>2</sup>	6.64
ARNOLD <sup>15</sup>	11.75
WILKE AND LEE <sup>18</sup>	15.26
SLATTERY AND BIRD <sup>14</sup>	19.95

attributed to the effects of pressure and temperature on the diffusion coefficients of different phases. The diffusion coefficient is proportional to  $T^{1.71}$  as mentioned earlier and the correlation factor  $A$  is found to be 0.585 for the gas-solid vapor systems studied in this work.

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