Ternary Diffusion Coefficients in Gases[*]
$-C_6H_6-H_2-N_2$ System $-$

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Abstract: $-$Binary and ternary diffusion coefficients in gases are measured by using an improved Stefanian diffusion cell or evaporation tube. The experiments are carried out for benzene-hydrogen, benzene-nitrogen and benzene-hydrogen-nitrogen systems and over the range of temperature 30°C to 77°C. For the ternary system, the concentration of hydrogen at the top of the tube is varied from 15 mol% to 92 mol%. The observed values of ternary diffusion coefficients, within the experimental errors, are in good agreement with those estimated from the Stefan-Maxwell's equations. It is also made clear that the Wilke's equation, if the concentration ratios in it are replaced by their logarithmic means, can estimate the ternary diffusion coefficients within the error less than 10%.

I. Introduction

Gases used at chemical industries are multicomponent mixtures. Most of measurements of diffusion coefficient and mass transfer rate have so far been carried out for binary systems. It is usual to treat approximately multicomponent systems as binary systems. Little is known, however, about the degree of approximation. In order to accurately design an equipment, the diffusion coefficient and mass transfer rate used must be as accurate as possible. It is neccessary, therefore, to measure with precision the diffusion coefficients and mass transfer rates in multicomponent mixtures.

The multicomponent systems (mainly, ternary systems) have been studied by many workers[4),11),13),15),16)]. For example, Wilke[16)] evaluated ternary diffusion coefficients from the evaporation rate of a liquid into a long tube. He reported that the ternary diffusion coefficients coincided with those in quasi-binary system. The equation to calculate the quasi-binary diffusion coefficients is refered to as the Wilke's equation and is in general expressed as follows[1),16)]:

$$D'_A = \frac{1 - y_A}{y_B/D_{AB} + y_C/D_{AC} + y_D/D_{AD} + \cdots} \tag{1}$$

Nagasaka et al[11)] and Onda et al[13)] used a Stefanian diffusion cell to measure ternary diffusion coefficients. They pointed out that the observed values were in good agreement with those estimated from the Stefan-Maxwell's equation, but not with those from the Wilke's equation. Since, however, their apparatus were not fine, their data contained the appreciable errors. In addition, in their experiments the ranges of temperature and concentration of gas mixtures were limited.

The systems dealt with in this paper are $C_6H_6-H_2$, $C_6H_6-N_2$ and $C_6H_6-H_2-N_2$. The diffusion coefficients are measured by an improved Stefanian diffusion cell[10)]. The experimental temperature

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extends to 77°C, at which the vapour pressure of benzene is 690 mmHg.　It is investigated what approximation to Wilke's equation is suitable to estimate the diffusion coefficient and the mass transfer rate in the ternary system.　Various kinds of approximation are examined.　The result is as follows: if the concentration ratios in the Wilke's equation are replaced by their logarithmic means, the ternary diffusion coefficents and the mass transfer rates may with considerable precision be estimated at the vapour pressures near the boiling point of evaporated liquid.　The values obtained are in good agreement with experimental values.

2. Theory

The evaporation tube in Stefanian device is schematically shown in **Fig. 1**.　The vapour of liquid A diffuse upward through the stagnant binary mixture of B and C, which is hereafter denoted by BC.　At the top of the tube the vapour pressure of A is zero, but the bottom or the gas-liquid interface is saturated with vapour A.　The following conditions are assumed.
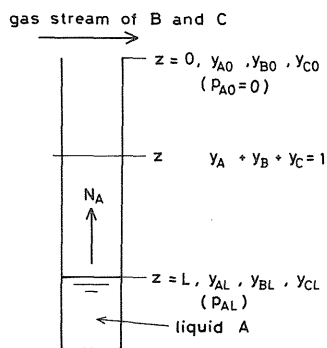
i) flow of vapour A through BC is in steady state.

ii) gas phase is ideal.

iii) diffusion rate is uniform over the cross-section of tube.

iv) cooling effect associated with evaporation is negligible.

v) binary diffusion coefficient is independent of gas composition.

Fig. 1　Diffusion of A through stagnant layer of B and C in steady state

Then, the Stefan-Maxwell's equation for the ternary mixture are written as[1]

$$\frac{dy_A}{dz} = - \frac{N_A}{cD_{AB'}} y_B - \frac{N_A}{cD_{AB}} y_C$$

$$\frac{dy_B}{dz} = \frac{N_A}{cD_{AB}} y_B$$

$$\frac{dy_C}{dz} = \frac{N_A}{cD_{AC}} y_C$$

$$\tag{2}$$

which are under the boundary conditions,

$$z=0, \quad y_A=y_{AO}(=0), \quad y_B=y_{BO}, \quad y_C=y_{CO}$$
$$z=L, \quad y_A=y_{AL}, \quad y_B=y_{BL}, \quad y_C=y_{CL}$$

$$\tag{3}$$

The solutions of the set of Eqs. (2) satisfying the boundary conditions (3) are given by

$$y_A = 1 - y_{BO} \exp(-N \cdot z/L)$$
$$\qquad - y_{CO} \exp(-Nr \cdot z/L)$$
$$y_B = y_{BO} \exp(-N \cdot z/L)$$
$$y_C = y_{CO} \exp(-Nr \cdot z/L)$$

$$\tag{4}$$

where the dimensionless mass transfer rate N and the ratio of binary diffusion coefficients r have been introduced;

$$N = - \frac{LN_A}{cD_{AB}}, \quad r = \frac{D_{AB}}{D_{AC}}$$

$$\tag{5}$$

It is convenient for later discussion that the component B and C are chosen as that $r>1$.　Furthermore, it should be noted that the mass transfer rate N is negative as understood easily from Fig. 1.　The concentration of vapour A on the gas-liquid interface corresponds to the vapour

pressure of liquid A and is written in the form

$$y_{AL} = 1 - y_{BO} \exp(-N) - y_{CO} \exp(-Nr) \tag{6}$$

The dimensionless mass transfer rate N and the theoretical mass transfer rate $-N_A$ can be calculated from Eqs. (5) and (6). The concentration ratio in gas phase and that on gas-liquid interface, respectively, are given by

$$y_C / y_B = (y_{CO} / y_{BO}) \exp\{-N(r-1)\cdot z / L\} \tag{7}$$

$$y_{CL} / y_{BL} = (y_{CO} / y_{BO}) \exp\{-N(r-1)\} \tag{8}$$

The Wilke's equation (1) is an empirical equation for estimating the diffusion coefficients in multicomponent gas mixture. For the ternary system it takes the form

$$D'_A = \frac{D_{AB}\{1 + (y_C / y_B)\}}{1 + (D_{AB} / D_{AC})(y_C / y_B)} \tag{9}$$

It is obvious from Eqs. (4) and (7) that y_A, y_B, y_C and y_C / y_B are the function of distance z from the top of tube. To the y_C / y_B itself in Eq. (9), however, an approximation is done. According to the kind i of approximation adopted, the above equation is rewritten as

$$(D'_A)_i = \frac{D_{AB}\{1 + (y_C / y_B)_i\}}{1 + r\cdot(y_C / y_B)_i} \tag{10}$$

Four kinds of approximation are chosen:

0) constant

$$(y_C / y_B)_0 = y_{CO} / y_{BO} \tag{11}$$

1) arithmetic mean

$$(y_C / y_B)_1 = (1/2)\{(y_{CO} / y_{BO}) + (y_{CL} / y_{BL})\} \tag{12}$$

2) logarithmic mean

$$(y_C / y_B)_2 = \frac{(y_{CO} / y_{BO}) - (y_{CL} / y_{BL})}{ln(y_{BL}\cdot y_{CO} / y_{BO}\cdot y_{CL})} \tag{13}$$

3) integral mean

$$(y_C / y_B)_3 = \frac{1}{L} \int_0^L (y_C / y_B) \, dz \tag{14}$$

It is directly seen that Eq. (13) is identical with Eq. (14). Hence, the approximations (0), (1) and (2) will be examined.

On the other hand, the mass transfer rate of A through BC, $[N_A]_{1i}$, can be easily calculated in the same way as for binary system;

$$[N_A]_{1i} = \frac{(D'_A)_i P}{LRT} \cdot \frac{p_{AL} - p_{AO}}{p_{BCM}} \tag{15}$$

By using the ideal gas law and Eqs. (10) and (15), the dimensionless mass transfer rate N_{1i} is defined similarly to N in Eq. (5);

$$N_{1i} = \frac{L[N_A]_{1i}}{cD_{AB}}$$

$$= \frac{1 + (y_C / y_B)_i}{1 + r\cdot(y_C / y_B)_i} \cdot \frac{P_{AL} - P_{AO}}{P_{BCM}} \tag{16}$$

The ratio K_{1i} of $[N_A]_{1i}$ to $-N_A$ is introduced to examine the degree of approximation;

$$K_{1i} = \frac{[N_A]_{1i}}{-N_A} = \frac{N_{1i}}{N} \tag{17}$$

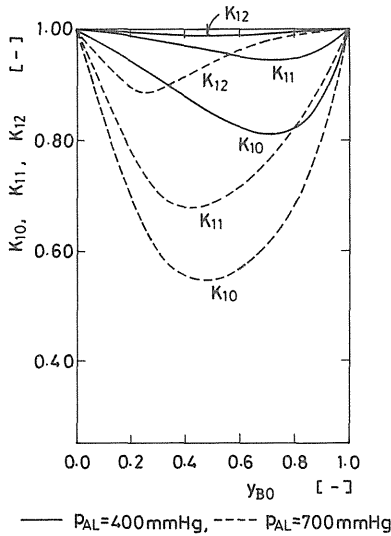The $K_{1i}(i=0, 1, 2)$ varies with the concentration and the ratio of diffusion coefficients. Its behaviour

Fig. 2　Relationship among the ratios of the mass transfer rates (K_{1i}) and the concentration of B, (y_{BO}), at $r=4.0$

—— $p_{AL}=400\,mmHg$, ---- $p_{AL}=700\,mmHg$

is shown in **Fig. 2**, where the ternary diffusion coefficients have been evaluated by substituting either of Eqs. (11), (12) and (13) into Eq. (10).

The procedure to obtain experimentally ternary diffusion coefficient D_{obs} and mass transfer rate $[N_A]_2$ must be also considered.　The $[N_A]_2$ is related to the variation in time of diffusion path length L :

$$[N_A]_2 = \frac{D_{obs}P}{LRT} \cdot \frac{p_{AL}-p_{AO}}{p_{BCM}} = \frac{\rho_L}{M_L} \cdot \frac{dL}{d\theta} \tag{18}$$

Integrating this differential equation and rearranging its result, we obtains as the diffusion coefficients,

$$D_{obs} = \frac{L_\theta^2 - L_O^2}{2\theta} \cdot \frac{RT\rho_L}{M_L P} \cdot \frac{p_{BCM}}{p_{AL}-p_{AO}} \tag{19}$$

The ratio K_2 of $[N_A]_2$ to $-N_A$ is introduced in the same manner as K_{1i}.　That is,

$$K_2 = \frac{[N_A]_2}{-N_A} = \frac{D_{obs}}{D_{AB} \cdot N} \cdot \frac{p_{AC}-p_{AO}}{p_{BCM}} \tag{20}$$

The theoretical diffusion coefficient D_{theor} to be compared with the observed one D_{obs} is obtained by the procedure described below.　Assuming the ternary system as quasi-binary system, we can write the following equation similar to Eq. (18),
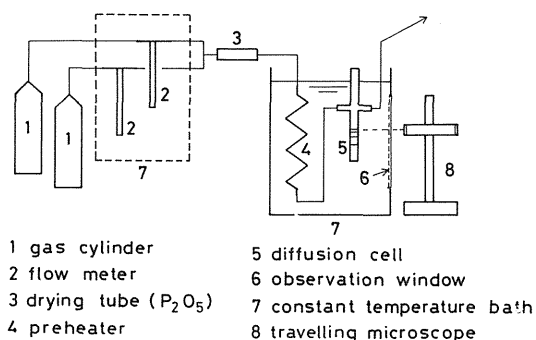
$$-N_A = \frac{D_{theor}P}{LRT} \cdot \frac{p_{AL}-p_{AO}}{p_{BCM}} \tag{21}$$

Since the $-N_A$ can be evaluated from Eqs. (5) and (6), the diffusion coefficient D_{theor} is determined by ;

$$D_{theor} = \frac{(-N_A)LRT}{P} \cdot \frac{p_{BCM}}{p_{AL}-p_{AO}} \tag{22}$$

On the other hand, the D_{theor} can be connected with the dimensionless mass transfer rate N ;

$$D_{theor} = D_{AB} \cdot N \cdot \frac{p_{BCM}}{p_{AL}-p_{AO}} \tag{23}$$

3. Experimental

The benzene used is of pure grade (99mol% minimum purity).　Hydrogen and nitrogen have been supplied by Hitachi Oxygen Co., Ltd. (99.9 mol% minimum purity).

The schematic diagram of apparatus is shown in **Fig. 3** and the details of the improved Stefanian diffusion cell are shown in **Fig. 4.**

It has been pointed out that the Stefanian method is simple but inaccurate[7].　The experimetal errors result from the instrumental imperfection and the cooling effect associated with the evaporation of liquid.　The former is mainly from lack of the uniformity in inner diameter of the tube and of that in thickness of the observation window.　Therefore, the inner and outer diameters of the capillary tube are to be made as uniform as possible by use of specially-made Pyrex-glass. Two kinds of tube are used.　One is 0.10 cm in inner diameter, 0.65 cm in outer diameter and about 10 cm long, and the other is the same in diameters and about 23 cm long.　The observation

Fig. 3 Schematic diagram of experimental apparatus

1 gas cylinder
2 flow meter
3 drying tube (P_2O_5)
4 preheater

5 diffusion cell
6 observation window
7 constant temperature bath
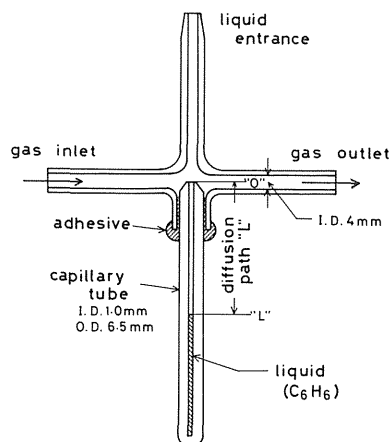8 travelling microscope

Fig. 4 Diffusion cell

window is also made uniform in thickness to avoid parallax. It is a polished Pyrex-glass plate of 0.50 cm in thickness.

The cooling effect depends on the inner diameter of the tube and on the evaporation rate. It is experimentally confirmed that if the tube with the inner diameter of 0.10 cm and with the diffusion path long enough is used, the cooling effect becomes negligible[12]. Other effects have in detail been elsewhere[10]. The composition of gas mixtures varies with the flow rates of hydrogen and nitrogen and affects significantly the diffusion coefficients. The flow rates of both gases, therefore, must be carefully controlled. The flow meters of capillary type are used and the capillary is immersed in the constant temperature bath. As a result, the deviation from the average gas composition is less than ±0.3%. The overall flow rate is 250 cm³/min. The temperature of the constant temperature bath, in which the diffusion cell is immersed, is controlled within ±0.03 °C and measured to a precision of 0.01 °C with a calibrated mercury thermometer. The temperature is read by a magnifying glass. The measuremets is carried out at the interval of 5 °C over the range of 30 °C to 70 °C and also at 73 °C, 75 °C and 77 °C.

The time duration of experimetal run varies from 2 to 25 hours, depending on the temperature and gas composition. The total pressure in tube is taken as barometric pressure in the laboratory at the time of the experimental run. Since the barometric pressure sometimes changes during a run, the arithmetic mean of barometric pressures at the start and finish of the run is taken as the pressure of the system. The largest variation of barometric pressures during a run is 3.0 mmHg. The pressure is measured on a standard barometer to a precision of 0.1 mmHg. The observed diffusion coefficients are corrected to 1 atm.

4. Results and Discussion

4.1 Binary systems. $C_6H_6-H_2$ and $C_6H_6-N_2$

When the diffusion cell of Stefanian type is used, the binary diffusion coefficient can be calculated from the following equation[14],

$$D_{AB} = \frac{L_\theta^2 - L_0^2}{2\theta} \cdot \frac{RT\rho_L}{M_L P} \cdot \frac{p_{BM}}{p_{AL} - p_{AO}} \tag{24}$$

The values of density ρ_L and vapour pressure p_{AL} in Eq. (24) are quoted from the literatures[3),5)]. The diffusion coefficients obtained in the range of 30 ℃ to 77 ℃, together with those reported by other authors[2)], are plotted in **Fig.5**. The values obtained in this work are in good agreement with the others within ±1.0%. The reproducibility of the experimental runs is excellent compared with that in other experiments[6),13)], because the deviation from the mean value is 0.4% on the average. The cooling effect in $C_6H_6-H_2$ system is slight at a temperature above 70 ℃.

4.2 Ternary system.　$C_6H_6-H_2-N_2$

The concentrations of hydrogen in the mixture fed into diffusion cell are 15, 30, 50, 70, 85 and 92 mol%. The experimental temperature extends from 30 ℃ to 77 ℃. The vapour pressures of benzene p_{AL} at 30, 50, 70 and 77 ℃ are 119, 271, 551 and 690 mmHg, respectively. For each concentration of hydrogen, the ternary diffusion coefficients D_{obs} (refer to Eq. (19), together with D_{theor}, $(D'_A)_0$ and $(D'_A)_2$, are shown in **Fig.6**. It is clear from Fig. 6 that the observed values
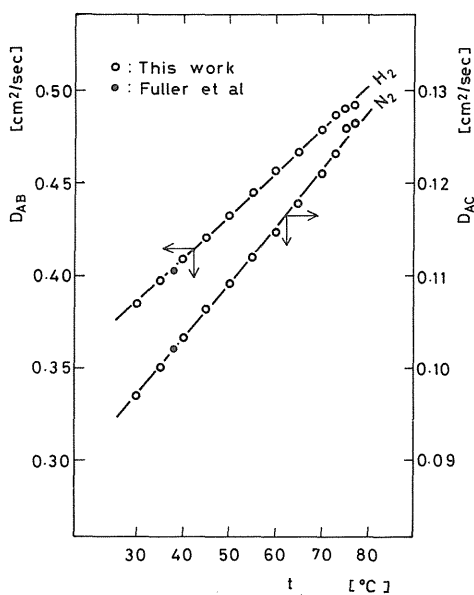

Fig. 5　Binary diffusion coefficients of $C_6H_6-H_2$ and $C_6H_6-N_2$ systems

Fig. 6　Ternary diffusion coefficients of $C_6H_6-H_2-N_2$ system

are in good agreement with theoretical ones. The deviation from the mean value is less than 0.5%. It is thus concluded that the reproducibility in each run is excellent. At a temperature above 70℃, however, the observed value deviates appreciably from the theoretical one. The change of vapour pressure causes by a little change of temperature of the bath affects considerably the diffusion coefficient D_{obs}. When the concentration of hydrogen is high, the cooling effect of vaporization on the diffusion coefficient appears to be slight.

The plots of the quantities K_{1i} and K_2 against the concentration of hydrogen are shown in
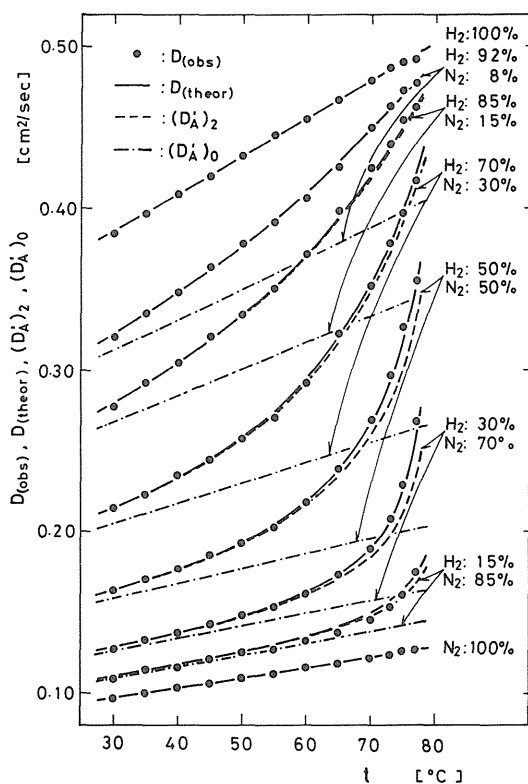
Figs. 7 to **10,** where the vapour pressure of benzene is taken as a parameter. The K_2, which denotes
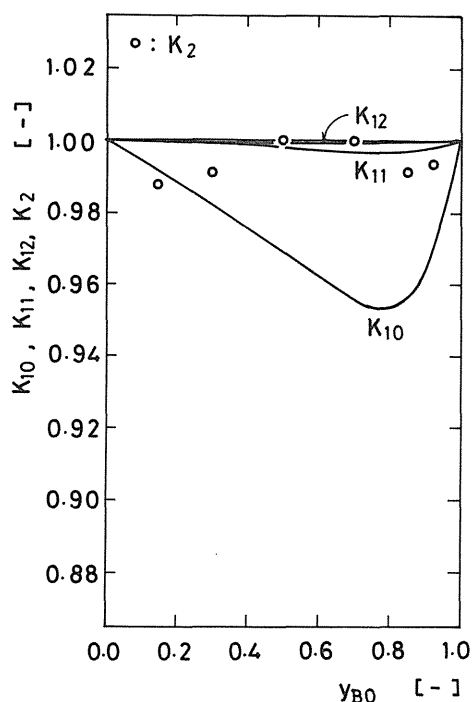
Fig. 7 Comparison of K_{10}, K_{11}, K_{12} and K_2 with the composition (y_{BO}) at 30 °C(C_6H_6-H_2-N_2 system, p_{AL}=119 mmHg, r=4.0)
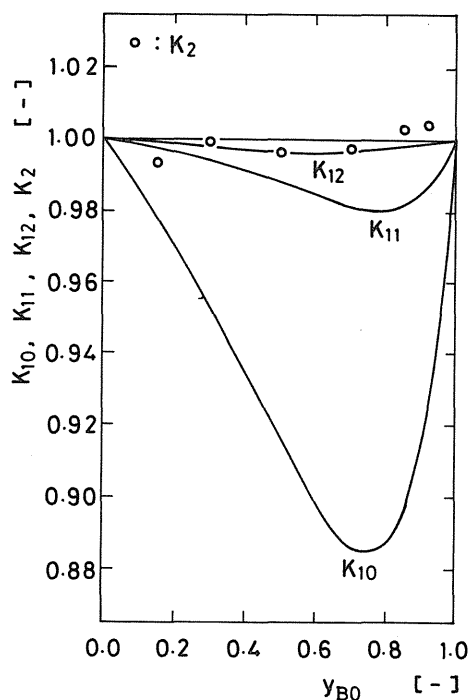
Fig. 8 Comparison of K_{10}, K_{11}, K_{12} and K_2 with the composition (y_{BO}) at 50 °C $(p_{AL}$=271 mmHg, r=3.9)

the ratio of observed mass transfer rate to theoretical one, is close to unity within ±1.0%. It may be thus concluded that the model for application of theory (see Fig. 1) is appropriate to the evaporation tube on a series of assumptions described in section 2. These figures show evidently that K_{10}, K_{11} and K_{12} are different compared with each other, depending on the vapour pressure p_{AL} and the composition y_{BO}.

The value of K_{10} falls with a rise in temperature (or vapour pressure). At 30 °C it takes 0.95 as minimum. That is, the mass transfer rate is lower than its theoretical one by 5% in maximum. The value of K_{10} at 70 °C becomes still smaller and its minimun is 0.72. At 77°C, the minimum value of K_{10} is 0.57 or about a half of theoretical value.

The value of K_{11} at 50 °C takes 0.98 as the minimum. Its error is smaller than 2% and the degree of appreximation is considerably improved. At 70 °C and 77 °C, however, the minimum values of K_{11} are 0.87 and 0.71, respectively.

The minimum value of K_{12} at 70 °C is 0.97 and at 77 °C it is 0.90. The errors are smaller than 10%. The logarithmic approximation, therefore, is much more excellent in compare with other approximations.

When the ternary diffusion coefficient at a temperature below 30 °C is estimated from the Wilke's equation applying the constant approximation, the error is smaller than 5%.

The value of r for $C_6 H_6 - H_2 - N_2$ system lies between 3.9 and 4.0 and is considered to be almost constant.   If it is much smaller than 4, say 2, the error may be considerably small and the arithmetic approximation can be also statisfactorily applied.
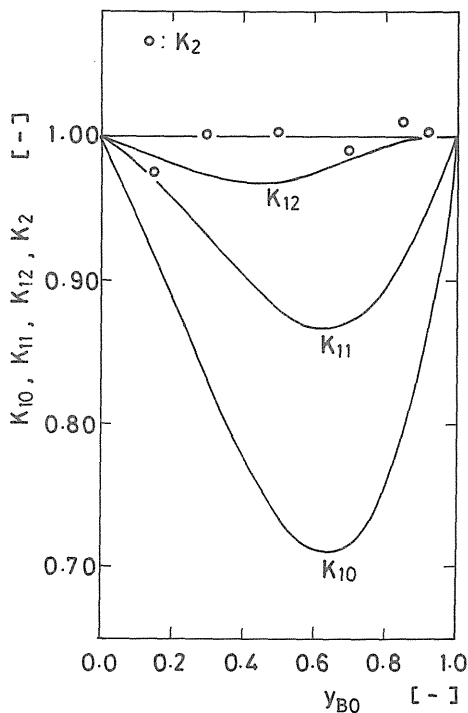

Fig. 9   Comparison of K_{10}, K_{11}, K_{12} and K_2 with the composition (y_{BO}) at 70 °C (p_{AL}=551 mmHg, r = 3.9)
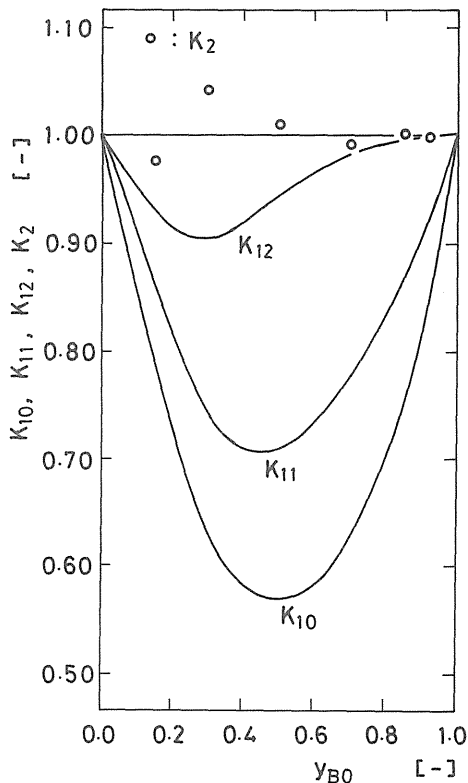

Fig. 10   Comparison of K_{10}, K_{11}, K_{12} and K_2 with the composition (y_{BO}) at 77 °C (p_{AL}=690 mmHg, r = 3.9)

When each concentration of hydrogen and nitrogen at the top of the tube is equal to 0.5 (mole fraction), the ratio of the concentration of nitrogen to that of hydrogen at the gas-liquid interface is 0.80, 0.56, 0.12 and 0.01 at 30, 50, 70, and 77 °C, respectively[8].   Such a abnormal change of concentrations at the bottom may be considered to be primarily due to the application of the constant approximation to the modified Wilke's equation.

It is evident that the values of K_{1i} depend on the ratio of binary diffusion coefficients r the vapour pressure p_{AL} and the ratio of concentration of C to that of B at the both ends of diffusion path.

5. Conclusion

The gaseous diffusion coefficients for binary systems of $C_6H_6-H_2$ and $C_6H_6-N_2$ and for ternary system of $C_6H_6-H_2-N_2$ are measured by using an improved Stefanian diffusion cell.   The range of experimental temperature is from 30 °C to 77 °C and the vapour pressure varies from 119 mmHg to 690 mmHg. For the ternary system, the concentration of hydrogen at the top of the tube

is between 15 and 92 mol%.   The observed diffusion coefficients are in good agreement with the theoretical ones calculated from the Stefan-Maxwell's equation.   It is made clear, furthermore, that the ternary diffusion coefficients, within the error less than 10%, can be estimated from the Wilke's equation to which the logarithmic mean is applied.

Nomenclature

c	: total molar concentration	(g-mol/cm^3)
D_{AB}	: binary diffusion coefficient of A in B	(cm^2/sec)
D_{obs}	: observed diffusion coefficient for ternary system (Eq.(19))	(cm^2/sec)
D_{theor}	: theoretical diffusion coefficient for ternary system (Eq.(22))	(cm^2/sec)
D'_A	: effective diffusion coefficient of A	(cm^2/sec)
$(D'_A)_i$	: effective diffusion coefficient (Eq.(10))	(cm^2/sec)
K_{1i}	: ratio of the mass transfer rate (Eq.(17))	(—)
K_2	: ratio of the mass transfer rate (Eq.(20))	(—)
L	: diffusion path length	(cm)
M_L	: molecular weight of pure liquid	(—)
N	: dimensionless mass transfer rate (Eq.(5))	(—)
N_{1i}	: dimensionless mass transfer rate (Eq.(16))	(—)
N_A	: rate of diffusion of component A	(g-mol/cm^2·sec)
$[N_A]_{1i}$	: approximate rate of diffusion (Eq.(15))	(g-mol/cm^2·sec)
$[N_A]_2$	: observed rate of diffusion	(g-mol/cm^2·sec)
P	: total pressure	(atm)
p_A	: partial pressure of component A	(mmHg)
p_{BM}, p_{BCM}	: logarithmic mean of p_{BO} and p_{BL} or p_{BCO} and p_{BCL}	(mmHg)
R	: gas constant	(cm^3·atm/g-mol·°K)
r	: ratio of binary diffusion coefficients ($r = D_{AB}/D_{AC}$)	(—)
y_A	: mole fraction of component A	(—)
z	: distance in direction of diffusion	(cm)

Greek Letter

ρ_L	: liquid density	(g/cm^3)
θ	: time	(sec)

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