CHROM. 15,352

TEMPERATURE VARIATION OF GAS DIFFUSION COEFFICIENTS MEASURED BY THE REVERSED-FLOW SAMPLING TECHNIQUE

N. A. KATSANOS* and G. KARAISKAKIS

Physical Chemistry Laboratory, University of Patras, Patras (Greece)

(Received August 16th, 1982)

SUMMARY

The temperature dependence of mutual diffusion coefficients in the binary gas mixtures $C_2H_6 + He$, $C_2H_4 + He$, $C_3H_6 + He$, $C_2H_6 + N_2$, $C_2H_4 + N_2$ and $C_3H_6 + N_2$ has been studied experimentally, using the reversed-flow gas chromatography sampling technique reported earlier. An improved sampling procedure was developed theoretically and applied, giving reversal-peaks twice the height of those obtained previously, thus increasing the sensitivity and precision of the method. The 43 diffusion coefficients determined for the above six binary gas mixtures at various temperatures show an average difference of 4.4 % from those calculated using the Fuller–Schettler–Giddings equation. The mean exponents in T^n, giving the temperature dependences of gas diffusion coefficients, were in accord with results given in the literature.

INTRODUCTION

The temperature dependence of diffusion coefficients in binary gas mixtures has been the subject of many theoretical investigations, all of which lead to a power dependence T^n, but with different values of n. No systematic experimental study seems to have been carried out in order to verify the various theoretical or semi-empirical equations describing the above dependence. A possible reason for this was the lack of a simple and accurate enough experimental method for measuring diffusion coefficients at relatively high temperatures. One such method, however, has been reported recently[1], which uses the detector and the gas lines (modified) of a conventional gas chromatograph to pass one component B (the carrier gas) through an empty chromatographic column. About midway along this column a diffusion column is connected perpendicularly to the first. This diffusion column is a straight, relatively short (*ca.* 60 cm) piece of empty tubing (4 mm I.D.), closed at the other end with a conventional rubber septum. Through this the other gaseous component A (the solute gas) is introduced by injection with a syringe.

Gas A is now allowed to diffuse into B inside the latter column, establishing a diffusion flux at the junction of the two columns. The pure carrier gas B passing over this junction carries to the detector the flux of A set up in the diffusion column. The

amount of A entering the chromatographic column within a small fixed time interval is recorded as a function of time, by repeatedly sampling this column. This so-called "chromatographic sampling" is accomplished by reversing the direction of the flow of B from time to time, using a suitably connected simple six-port gas valve.

The chromatographic sampling creates at the detector extra peaks, the heights of which vary with time. The analytical mathematical expression describing this variation has been derived[1] and used to determine the diffusion coefficient of A into B. Using this method the diffusion coefficient in fifteen pairs of gases was determined[1] and compared with the corresponding theoretical values, and with eight literature values obtained by other methods. It was shown that the reversed-flow method described above has a precision of 0.9 % and gives values of diffusion coefficients closer to the theoretical calculated values than the literature ones.

All of the diffusion coefficients reported in the earlier paper[1] are referred to ambient temperature (*ca.* 23°C). In this work, we used the oven of the chromatograph to study the temperature variation of diffusion coefficients in six binary gas mixtures.

THEORETICAL

The basic equations describing the concentration in space and time of the solute A in the mixture of A and B have been derived. At the junction of the two columns ($z = L$, $x = l'$) this concentration is (*cf.*, eqn. 12 and Fig. 1 in ref. 1):

$$c_x(l', t_0) = \frac{N \exp(-L^2/4Dt_0)}{t_0^{3/2}} \tag{1}$$

where

$$N = mL/\dot{V}(\pi D)^{1/2} \tag{2}$$

However, the chromatographic sampling equation (eqn. 30 in ref. 1),

$$c_x = c_x(l', t_{tot} - \tau) \cdot [u(\tau) - u(\tau - t'_M)] \cdot u(t' - \tau) + c_x(l', t_{tot} + \tau) \cdot u(\tau) \tag{3}$$

where

$$\tau = t - t_M \tag{4}$$

and $t_{tot} = t_0 + t'$, was found only for the case $t' > t'_M + t_M$, *i.e.*, when the time passing between two successive reversals was greater than the total gas hold-up time in both sections $l' + l$ of the chromatographic column. In this paper we take a further step and generalize the sampling theory so that it includes also the case $t' < t'_M + t_M$. As before, we start from the mass balance equation (eqn. 14 in ref. 1) with t substituted for t_0:

$$\frac{\partial c_x}{\partial t} = -v \cdot \frac{\partial c_x}{\partial x} + v(c_x)_{x=l'} \delta(x - l') \tag{5}$$

This is integrated by taking successive Laplace transformations with respect to t_0, t' and t, but now with a different initial condition at $t = 0$ than before, as the inequality $t' > t'_M + t_M$ does not necessarily hold true. The new initial condition (in the form of its t_0 and t' double transform) is obtained from the whole of eqn. 24 in ref. 1 instead only from its last term. By making the necessary coordinate transformations from x' to x, the desired condition at $t = 0$ reads:

$$\bar{C}_x(x,p_0,p',0) = \frac{C_x(l',p_0,0)}{p' + p_0} \{ \exp(-p_0\theta) \cdot u(x - l') +$$

$$+ \exp(p'\theta) \cdot [1 - u(x - l')] - \exp[- (p_0 + p') l/v + p'\theta] \} +$$

$$+ \bar{C}_x(l',p_0,p') \cdot \exp(p'\theta) \cdot [1 - u(x - l')] \tag{6}$$

where

$$\theta = (x - l')/v \tag{7}$$

The result of the above procedure is an ordinary differential equation in x, which is easily integrated by using x Laplace transforms, giving $\bar{C}_x(x,p_0,p',p)$:

$$\bar{C}_x = \frac{C_x(l',p_0,0)}{p' + p_0} \left\{ \frac{\exp(-p_0\theta) - \exp(-p\theta)}{p - p_0} \cdot u(x - l') + \right.$$

$$- \frac{\exp(p'\theta) - \exp(-p\theta)}{p + p'} \cdot u(x - l') + \frac{\exp(p'x/v) - \exp(-px/v)}{p + p'} \times$$

$$\left. \times \exp(- p'l'/v) [1 - \exp(- p_0 l/v) \cdot \exp(- p'l/v)] \right\} +$$

$$+ \frac{\bar{C}_x(l',p_0,p')}{p + p'} \{ \exp(p'\theta) - \exp[- (p'l' + px)/v] +$$

$$- [\exp(p'\theta) - \exp(-p\theta)] \cdot u(x - l') \} +$$

$$+ \bar{C}_x(l',p_0,p',p) \cdot \exp(-p\theta) \cdot u(x - l') \tag{8}$$

At the detector, i.e., for $x' = l' + l$, $u(x - l') = 1$ and $\theta = l/v = t_M$, whereby eqn. 8 is considerably simplified. Then, performing inverse Laplace transformations with respect to p, p' and p_0 in succession, one finds the final equation giving the c_x value at the detector:

$$c_x = c_{x,1}(l',t_0 + t' + \tau) \cdot u(\tau) +$$

$$+ c_{x,2}(l',t_0 + t' - \tau) \cdot [1 - u(\tau - t')] \cdot [u(\tau) - u(\tau - t'_M)] +$$

$$+ c_{x,3}(l',t_0 - t' + \tau) \cdot u(t_0 + \tau - t') \times$$

$$\{ u(t - t') [1 - u(\tau - t'_M)] - u(\tau - t') [u(\tau) - u(\tau - t'_M)] \} \tag{9}$$

where τ is given by eqn. 4.

Eqn. 9 is the general chromatographic sampling equation and deserves some comments. It contains on the right-hand side three concentration terms like that of eqn. 1. These terms, denoted $c_{x,1}$, $c_{x,2}$ and $c_{x,3}$, all refer to $x = l'$ but to different values of the time variable, namely $t_0 + t' + \tau$, $t_0 + t' - \tau$ and $t_0 - t' + \tau$, respectively. Each of the concentration terms is multiplied by a combination of unit step functions, so that it appears in certain time intervals and vanishes in all others. The various possibilities that exist depend on the relative values of t_0, t', t, t_M and t'_M. As a first case one takes the condition $t' > t_M + t'_M$, which reduces eqn. 9 to eqn. 3 as the term $c_{x,3}$ becomes zero for all values of t. Thus, the sampling equation of the previous paper[1] (eqn. 30) is a special case of the more general eqn. 9. This case produces two series of peaks, R- and F-peaks.

The other special case arises when $t' < t_M + t'_M$ and is analysed as follows. The first term of eqn. 9 $c_{x,1}$ appears at $t = t_M$ ($\tau = 0$) and continues uninterrupted. The second term $c_{x,2}$ appears again at $t = t_M$, but it is cut down either at $t = t_M + t'$ ($\tau = t'$) or at $t = t_M + t'_M$ ($\tau = t'_M$), whichever comes first. This, of course, depends on whether $t' < t'_M$ or $t' > t'_M$.

The third term $c_{x,3}$ appears at $t = t'$ and vanishes at the same t value as the second term. Thus, for $\tau \geqslant t'$ or $\tau \geqslant t'_M$ only $c_{x,1}$ remains as an "ending baseline".
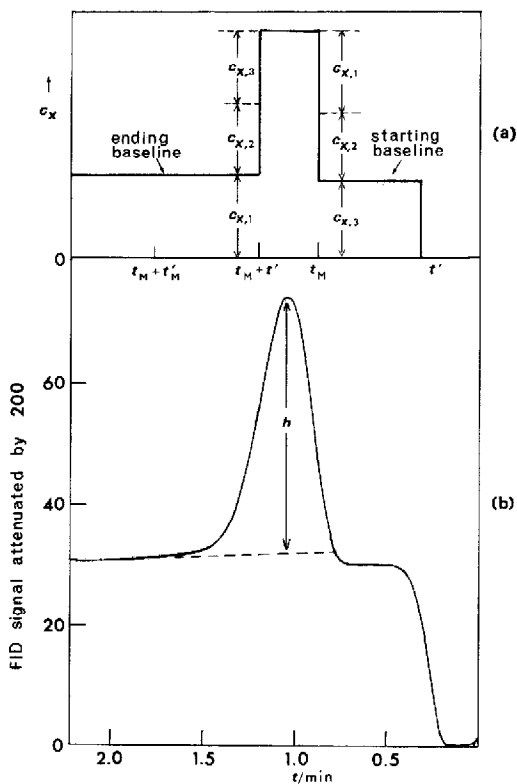

Fig. 1. (a) Elution curve predicted by eqn. 9 for $t' < t_M$ and $t' < t'_M$; (b) curve found experimentally for the diffusion of C_2H_4 into He, at 373.9°K and $\dot{V} = 0.34$ cm^3 sec^{-1} (corrected).
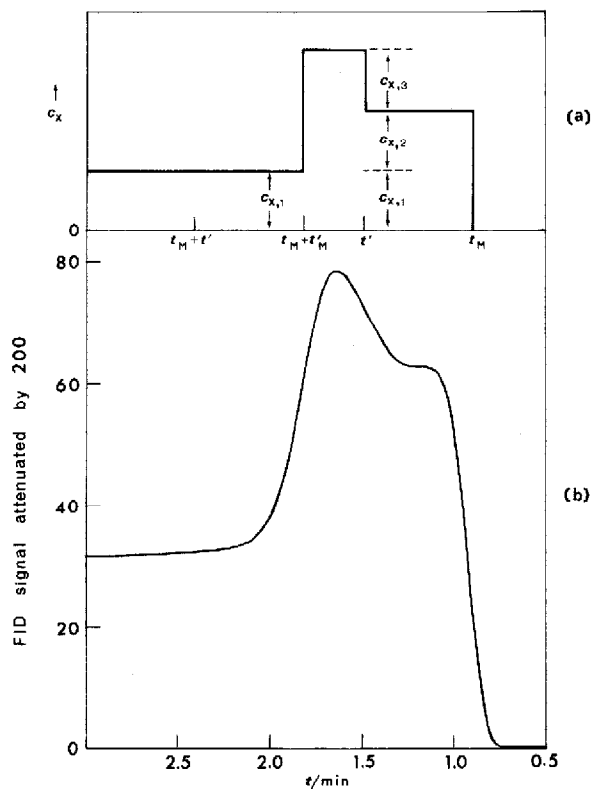
Fig. 2. (a) Theoretical elution curve for $t' > t_M$ and $t' > t'_M$; (b) experimental curve for the diffusion of C_2H_4 into He, at 373.9°K and $\dot{V} = 0.34$ cm^3 sec^{-1}.

Before that there are two possibilities: (i) $t' < t_M$, or (ii) $t' > t_M$. In case (i) the $c_{x,3}$ term appears first and then "sitting" on it the sum $c_{x,1} + c_{x,2}$. This is depicted diagrammatically in Fig. 1a, while Fig. 1b gives an actual experimental curve belonging in this situation. In case (ii) the sum $c_{x,1} + c_{x,2}$ appears first and then on it $c_{x,3}$ (Fig. 2).

As the $c_{x,1}$ and $c_{x,3}$ terms differ little in their time argument, the situation depicted in Fig. 1 has the appearance of a relatively narrow peak of two terms, with baseline the remaining term ($c_{x,3}$ as the starting and $c_{x,1}$ as the ending baseline). The smaller t' is, the narrower this peak becomes, as its width is clearly equal to t'.

The situation in Fig. 2 is less favourable for measurements, because a single term ($c_{x,3}$) appears to "sit" on a starting baseline consisted of two terms ($c_{x,1} + c_{x,2}$) and on an ending baseline of only $c_{x,1}$. The relative heights of the various concentration terms in the actual experimental curves of Figs. 1 and 2 are not exactly those predicted by eqn. 9, owing to diffusional spreading of the peaks in the chromatographic column.

In this paper the conditions of Fig. 1 were adopted, i.e., t' was smaller than both t_M and t'_M. As the extra peaks like that of Fig. 1, produced by the double flow reversals, are fairly symmetrical, their maximum corresponds to $t = t_M + t'/2$ or $\tau =$

$t'/2$. The height h of this maximum, measured from the ending baseline, gives the sum $c_{x,2} + c_{x,3}$. From eqn. 9, by putting $\tau = t'/2$ in these two terms, one obtains

$$h = c_{x,2}(l',t_0 + t'/2) + c_{x,3}(l',t_0 - t'/2) \tag{10}$$

The times in the two terms on the right-hand side differ only by t', and as this was only 30 sec, both terms can be taken at a mean time t_0. Then eqn. 10 becomes simply

$$h \approx 2c_x(l',t_0) \tag{11}$$

Thus the double flow reversal produces peaks of twice the height of those with the single flow reversal reported earlier, and consequently increases the precision of the method.

Finally, using eqn. 1 in place of $c_x(l',t_0)$, eqn. 11 gives

$$h = \frac{2N\exp(-L^2/4Dt_0)}{t_0^{3/2}} \tag{12}$$

i.e., a relationship analogous to eqn. 36 in ref. 1. Thus, by plotting $\ln(ht_0^{3/2})$ against $1/t_0$, we find D from the slope $-L^2/4D$ of this linear plot. An example is given in Fig. 3.
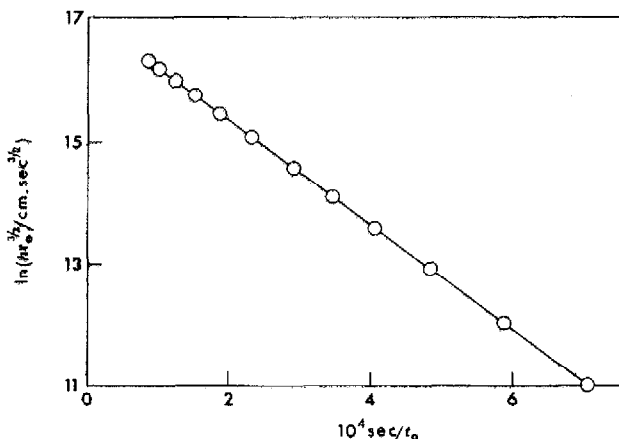

Fig. 3. Plot of eqn. 12 for the diffusion of C_2H_6 into N_2 at 388.5°K and 1 atm.

EXPERIMENTAL

Materials

The carrier gases (helium and nitrogen) were obtained from Linde (Greece) and had a purity of $\geqslant 99.99\%$. The solutes ethene (99.98%) and propene (99.7%) were purchased from Matheson Gas Products, and ethane (puriss grade) was obtained from Fluka.

Apparatus

The experimental details of the application of the reversed-flow method have been described elsewhere[1]. One modification in this work was to coil the diffusion column L (111.4 cm × 4 mm I.D.) and place it inside the chromatographic oven, with its closed end at the injector position of the chromatograph. The two lengths, l and l', of the empty chromatographic column (99.4 and 99.7 cm × 4 mm I.D.) were also inside the oven as before. Temperature variations in the oven were less than ±0.1°C. The carrier gas flow-rates (corrected tõ the column temperature) were in the range 0.29–0.47 cm^3 sec^{-1}.

Procedure

The procedure for chromatographic sampling outlined in the Theoretical section was adopted, giving reversal-peaks almost twice the height of those obtained previously, thus increasing the sensitivity and precision of the method. The details are as follows.

The carrier gas B is flowing in direction F (*cf.*, Fig. 1 in ref. 1), and 0.5 cm^3 of the solute A are injected into the diffusion column L as before. When the asymmetric elution curve of A in B starts to be recorded by the detector, the direction of the carrier gas flow is reversed for a time period *shorter* than the gas hold-up time in both column sections l and l', and then it is restored again to the original direction F. After a certain dead time an extra signal is recorded, the shape of which is shown in Fig. 1. This double reversal of the flow is repeated several times with always the same duration (30 sec) of backwards flow. This gives rise to a series of peaks corresponding to various times from the solute injection.

The pressure drop along column $l' + l$ was negligible, and the pressure at the injection point was measured with an open mercury manometer.

RESULTS AND DISCUSSION

Using eqn. 12, the mutual diffusion coefficients in six binary gas mixtures were determined at 1 atm pressure and various temperatures. These are given in Tables I and II. The precision of the values for D given in these tables is high, as judged from the associated standard errors. The accuracy given in the last column is the deviation of the experimental values from those calculated theoretically:

$$\text{Accuracy } (\%) = \frac{|D_{\text{found}} - D_{\text{calcd.}}|}{D_{\text{found}}} \cdot 100 \tag{13}$$

The theoretical values were computed using the Fuller–Schettler–Giddings (FSG) equation[2]:

$$D = \frac{0.001 \; T^{1.75} \left(\dfrac{1}{M_A} + \dfrac{1}{M_B} \right)^{1/2}}{P[(\Sigma v_i)_A^{1/3} + (\Sigma v_i)_B^{1/3}]^2} \tag{14}$$

where $(v_i)_A$ and $(v_i)_B$ are the atomic volume increments of the solute and carrier gas, respectively, referred to as "diffusion volumes". Values of the latter are listed in Table I in ref. 2.

TABLE I

DIFFUSION COEFFICIENTS OF THREE SOLUTES INTO CARRIER GAS HELIUM, AT VARI-
OUS TEMPERATURES AND 1 atm PRESSURE

The $\pm$ values in this and the following tables are "standard errors", calculated by regression analysis.

Solute gas	T $(°K)$	$10^3 D (cm^2\ sec^{-1})$		Accuracy $(\%)$
		This work	Calculated	
C_2H_6	296.7	491 $\pm$ 2	456	7.1
	322.6	556 $\pm$ 2	528	5.0
	344.0	618 $\pm$ 3	590	4.5
	364.4	684 $\pm$ 3	653	4.5
	385.3	745 $\pm$ 6	720	3.4
	407.3	807 $\pm$ 4	793	1.7
	426.3	878 $\pm$ 8	859	2.2
	447.3	941 $\pm$ 5	935	0.6
C_2H_4	296.8	525 $\pm$ 4	478	9.0
	322.9	599 $\pm$ 1	554	7.5
	336.0	649 $\pm$ 1	594	8.5
	348.1	674 $\pm$ 2	632	6.2
	361.3	726 $\pm$ 2	674	7.2
	373.9	780 $\pm$ 6	716	8.2
	399.9	860 $\pm$ 19	806	6.3
	426.9	932 $\pm$ 3	903	3.1
	476.5	1112 $\pm$ 10	1096	1.4
C_3H_6	345.0	528 $\pm$ 0.7	500	5.3
	365.5	584 $\pm$ 1	553	5.3
	388.0	642 $\pm$ 1	614	4.4
	407.7	690 $\pm$ 1	670	2.9
	428.0	750 $\pm$ 2	730	2.7
	449.4	819 $\pm$ 3	795	2.9

The FSG equation for the estimation of the theoretical diffusion coefficients was selected because it gives values closer to those found experimentally than other theoretical equations. Thus, the average accuracy for the 43 diffusion coefficients listed in Tables I and II is 4.4%, whereas it would be 7.3% if, instead of FSG, the Hirschfelder–Bird–Spotz equation[3] were used.

All of the theoretical or semi-empirical equations describing the dependence of the diffusion coefficient on temperature lead to the relationship

$$D = AT^n \tag{15}$$

where A is a complex function including molar masses or volumes, critical volumes or temperatures, volume increments, pressure, etc., depending on the special equation used. Eqn. 15 shows that the exponent n can be found from the slopes of the linear plots of $\ln D$ against $\ln T$. An example of such a plot, using experimental data from this work, is shown in Fig. 4. The various values of n calculated from these plots, denoted as n_{found}, are given in Table III. For comparison purposes, the values of n found from similar plots of calculated diffusion coefficients (using the Hirschfelder–Bird–Spotz equation[3]) are also given. We used this equation because it is the only one

TABLE II

DIFFUSION COEFFICIENTS OF THREE SOLUTES INTO CARRIER GAS NITROGEN, AT VARIOUS TEMPERATURES AND 1 atm PRESSURE

| Solute gas	T $(^\circ K)$	$10^3 D (cm^2 \ sec^{-1})$		Accuracy $(\%)$
		This work	Calculated	
C_2H_6	322.8	172 ± 0.2	170	1.2
	345.7	193 ± 0.2	191	1.0
	365.0	214 ± 0.7	210	1.9
	388.5	$242 + 0.3$	234	3.3
	407.6	256 ± 0.2	255	0.4
	427.5	282 ± 0.4	277	1.8
	449.3	303 ± 0.5	302	0.3
C_2H_4	322.8	189 ± 0.08	179	5.3
	344.7	213 ± 0.1	200	6.1
	364.2	234 ± 0.3	221	5.6
	387.6	260 ± 0.3	246	5.4
	407.5	286 ± 0.4	269	5.9
	428.9	306 ± 0.3	294	3.9
	449.8	335 ± 0.9	319	4.8
C_3H_6	322.8	143 ± 0.2	138	3.5
	344.6	164 ± 0.1	155	5.5
	387.4	202 ± 0.2	190	5.9
	406.4	220 ± 0.4	206	6.4
	428.9	243 ± 0.3	227	6.6
	459.0	266 ± 0.2	255	4.1
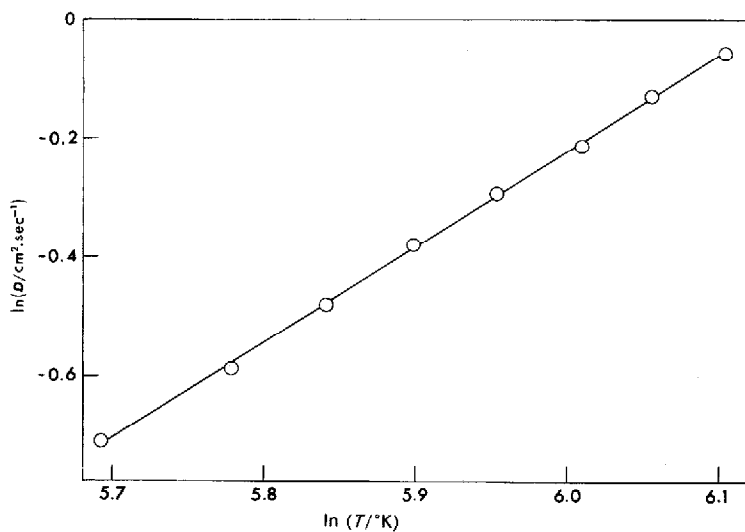
Fig. 4. Plot of eqn. 15 for the diffusion of C_2H_6 into He.

TABLE III

VALUES OF THE EXPONENT n OF EQN. 15 CALCULATED FROM THE PRESENT EXPERI-
MENTAL DATA (n_{found}) AND FROM THEORETICAL DIFFUSION COEFFICIENTS (CALCU-
LATED FROM HIRSCHFELDER–BIRD–SPOTZ EQUATION) (n_{calcd})

Carrier gas	Solute gas	n_{found}	$n_{calcd.}$
He	C_2H_6	1.60 ± 0.01	1.680 ± 0.002
	C_2H_4	1.59 ± 0.03	1.671 ± 0.002
	C_3H_6	1.63 ± 0.02	1.685 ± 0.003
	Mean	1.61 ± 0.01	1.679 ± 0.001
N_2	C_2H_6	1.73 ± 0.04	1.801 ± 0.008
	C_2H_4	1.71 ± 0.02	1.779 ± 0.005
	C_3H_6	1.77 ± 0.05	1.844 ± 0.008
	Mean	1.74 ± 0.02	1.808 ± 0.004

in which the exponent n varies from one system to another. The mean values of n_{found}
listed in Table III are somewhere between the 1.5 suggested by the Stefan–Maxwell,
Gilliland and Arnold equations[3] and 1.81 predicted by the Chen–Othmer equation[3].
A value of 1.75 is also predicted by the Huang[4] and the FSG equations.

Seager et al.[5] investigated experimentally (with a different method) the tem-
perature dependence of gas–gas and gas–liquid vapour diffusion coefficients. They
found that the value of exponent n varied rather widely from one system to another.
Their average value of n (1.70) was very close to our experimental values. Hargrove
and Sawyer[6] determined the diffusion coefficients for a variety of solutes at various
temperatures and found a value of n varying from 1.43 to 1.93, depending on the
binary system studied. Our mean values of n again lie within this range.

As a general conclusion, one can say that the method for measuring mutual
diffusion coefficients in gases reported earlier[1], and the improved sampling technique
reported here, give fairly accurate values of diffusion coefficients at relatively high
temperatures. It is therefore suitable for studying the temperature variation of gas
diffusion coefficients.

SYMBOLS

c_x	= concentration of the solute vapour in the chromatographic column (mol cm^{-3});
$C_x, \bar{C}_x, \bar{\bar{C}}_x$	= single, double and triple Laplace transforms with respect to t_0, to t_0 and t', and to t_0, t' and t, respectively;
D	= mutual diffusion coefficient of A and B (cm^2 sec^{-1});
h	= height of the maximum of extra peaks above the ending baseline (mol cm^{-3});
l, l'	= lengths of the two sections of the chromatographic column (cm);
L	= length of diffusion column (cm);
m	= mass of injected solute A (mol);
M_A, M_B	= molar masses of solute and carrier gas, respectively (g mol^{-1});
N	= constant defined by eqn. 2;

p_0, p', p = transform parameters with respect to t_0, t' and t, respectively;

P = pressure (atm);

t_0 = time measured from the injection of solute A to the last backward reversal of gas flow (sec);

t_{tot} = sum of the times t_0 and t' (sec);

t' = time interval of backward flow of carrier gas (sec);

t = time measured from the last restoration to forward direction of the gas flow (sec);

t_M, t'_M = gas hold-up time of column section l or l', respectively (sec);

v = linear velocity of carrier gas B in the chromatographic column (cm sec^{-1});

$(v_i)_A, (v_i)_B$ = atomic volume increments of solute and carrier gas, respectively (cm^3 mol^{-1});

$\dot{V}$ = volume flow-rate of carrier gas (cm^3 sec^{-1});

x, x' = distance coordinates measured from one or the other end of the chromatographic column;

θ = time parameter defined by eqn. 7 (sec);

τ = time defined by eqn. 4 (sec).

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