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MEASUREMENT OF DIFFUSION COEFFICIENTS BY REVERSED-FLOW GAS CHROMATOGRAPHY INSTRUMENTATION

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SUMMARY

A method is reported for measuring mutual diffusion coefficients in gases. It is a gas chromatographic method, but not a broadening technique. Two short empty columns are placed perpendicular to one another: a diffusion column through which no carrier gas flows, and a chromatographic column. The carrier gas which flows through the latter carries over to the detector the diffusion flux established in the diffusion column. Analysis of the concentration–time curve recorded gives the value of the diffusion coefficient of an injected solute into the carrier gas. More reliable results are obtained by the so-called "chromatographic sampling", *i.e.* reversing the direction of flow of the carrier gas at definite known times. The analytical mathematical expression, describing the elution curves when the gas flow is reversed, is derived and used to determine diffusion coefficients for fifteen gas pairs. The results are of high precision, and comparison with the theoretical values shows that they have also high accuracy.

INTRODUCTION

The measurement of diffusion coefficients of a gas A into another gas B by gas chromatography has been reviewed by Maynard and Grushka[1]. It has been solely based on zone broadening by diffusion of a narrow pulse of component A (the solute) introduced into a long empty chromatographic column, through which component B continuously flows as a carrier gas. Obviously, these methods use the superposition of two fluxes in the same direction x: one diffusional flux, $-D(\partial c/\partial x)$, which is added to a much higher "chromatographic" flux, vc. This addition results in two undesirable features. First, long columns are required to make the diffusional flux manifest itself in the chromatographic signal, and second, the precision of the method is relatively low. It occurred to us that both can be improved if the two fluxes are separated by placing them perpendicular to one another, as shown schematically in Fig. 1. The component B enters at point D_2 and meets the detector at D_1, or *vice versa*, flowing continuously through the "chromatographic column" $l' + l$, either in direction F (forward) or in direction R (reverse). It does not flow, however, through the "diffusion column", length L, at the closed end of which the solute A is introduced, as a gas or vapour, in the form of a pulse (by means of a syringe or a gas valve).

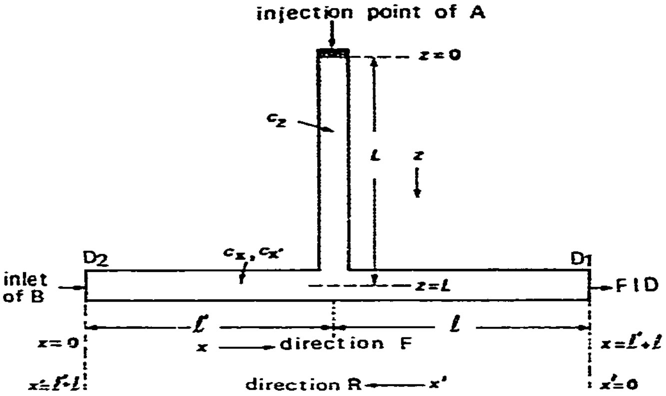

Fig. 1. Schematic representation of the diffusion (L) and the chromatographic ($l' + l$) columns for determining diffusion coefficients by the reversed-flow method.

A pure diffusion flux of A into B is set up inside column L and the result of this at $z = L$ is carried over to the detector by the carrier gas B, being recorded there as a concentration–time curve. Analysis of this curve permits calculation of the diffusion coefficient D_{AB}. Even more precise results are obtained by repeatedly sampling the chromatographic column and recording the amount of A entering it at $z = L$ within a small time interval t_M. This sampling is accomplished by repeatedly reversing the direction of the flow of B at definite known times.

It must be noted that the arrangement of Fig. 1 is free of "secondary flow" phenomena due to coiled tubes, since the diffusion column L is relatively short (0.5–1 m) and can be made straight.

EXPERIMENTAL

Apparatus

The experimental set-up for the application of the reversed-flow method is very simple. A conventional gas chromatograph with a high-sensitivity detector, *e.g.* a flame-ionization detector (FID) is modifed as shown diagrammatically in Fig. 2. The solute A is injected into the diffusion column L (61 cm × 4 mm I.D.) while the carrier gas B flows through the chromatographic column $l' + l$ (40 + 40 cm × 4 mm I.D.), either entering at D_2 with the detector placed at D_1 or *vice versa*. The reversing of the flow direction is effected by means of valve S (four-port or six-port with two alternate ports connected through a small piece of 1/16 in. tube). A restrictor can be placed at H to increase the pressure within the whole system.

Materials

The carrier gases used (nitrogen, hydrogen, helium) were of gas chromatographic grade (Linde, or Aga Chropei, ≥ 99.99% purity). The various solutes injected were purchased either from Matheson Gas Products (methane 99.99, ethylene 99.98, propylene 99.7%), or from Fluka (ethane puriss grade, *n*-butane practical grade).

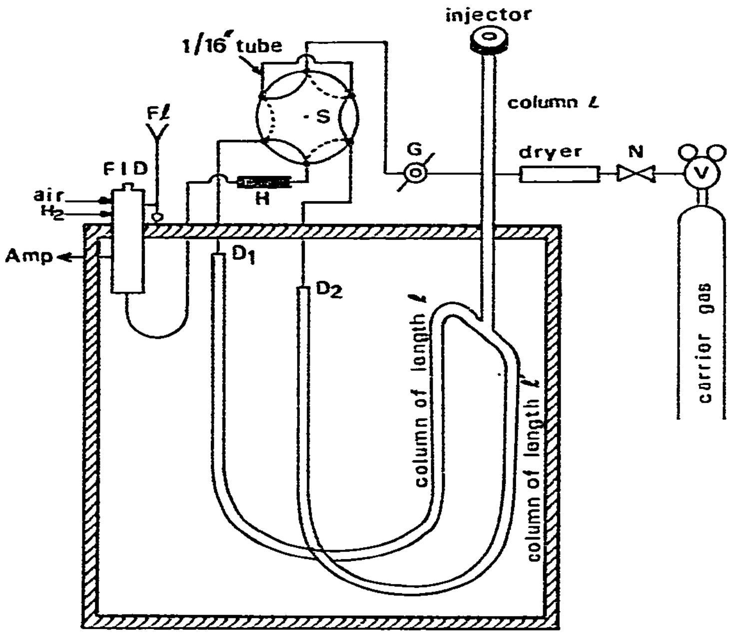

Fig. 2. Gas lines and important connections for measuring diffusion coefficients by reversed-flow gas chromatography. V = two-stage reducing valve and pressure regulator; N = needle valve; G = gas flow controller for minimizing variations in the gas flow-rate; S = six-port gas sampling valve with a short 1/16 in. tube connecting two alternate ports; H = restrictor, which can be omitted; Fl = bubble flow meter; Amp = signal to amplifier.

Procedure

While carrier gas B is flowing through the chromatographic column in direction F (Fig. 2, valve S in position indicated by the solid lines), a small amount of solute A (usually 0.5 cm^3 of gas at atmospheric pressure) is injected into the diffusion column L. After a certain time, during which no signal is noted, an asymmetric concentration–time curve for the solute is recorded, which rises slowly and then decays even more slowly. At a time (measured from the moment of injection) greater than the gas hold-up time in the column length l, the direction of the carrier gas is reversed by switching valve S to the other position (dotted lines). After a certain dead time, when no signal is recorded by the detector, the chromatographic elution curve rises steeply, then slowly and finally returns abruptly to the original concentration–time curve (Fig. 3, R-peak). After a time (from the moment of reversal) greater than the total gas hold-up time in the total column length $l + l'$, the carrier gas is again turned to the direction F. This is followed by a new extra signal (Fig. 3, F-peak). The procedure is repeated several times, until a whole series of peaks is obtained. If the two column lengths l and l' are equal, no distinction can be made between peaks obtained in direction F or R.

The pressure drop along the whole column $l' + l$ was negligible, and the diffusion coefficients were considered to have been determined at that pressure, which was measured at the injection point, by means of an open mercury manometer.

No temperature regulation was made, and the temperature reported in the

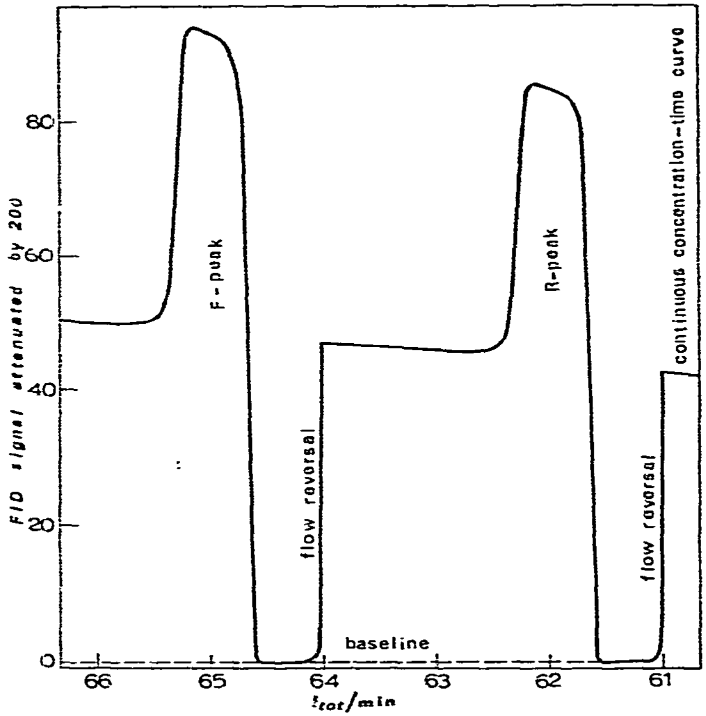

Fig. 3. A reversed-flow chromatogram for measuring the diffusion coefficient of C_2H_6 (0.5 cm^3) into N_2 ($\dot{V}$ = 0.267 cm^3 sec^{-1}) at 293°K and 1.99 atm.

results was the ambient temperature, the variation of which was small during each experiment.

THEORETICAL ANALYSIS

The analytical mathematical expressions which describe the concentration–time curve of the solute A at the detector, as well as the elution curves of peaks resulting from the reversal of the flow (R- and F-peaks, Fig. 3) are derived by reference to Fig. 1, under the following assumptions:

(a) Radial diffusion in all columns is negligible.

(b) Axial diffusion of A along coordinate x or x', *i.e.* in the chromatographic column, is negligible. This seems reasonable for a high enough flow-rate of B.

(c) The solute A is introduced in an very small section of column L, so that its total mass m is concentrated initially in the plane z = 0.

Notation

a = cross sectional area of the columns (cm^2)

c_b = concentration defined by the last term of eqn. 32 (mol cm^{-3})

c_x, $c_{x'}$ = concentrations of the solute vapour A in the chromatographic column with the carrier gas B flowing in direction F or R, respectively (mol cm^{-3})

c_z = concentration of the solute vapour A in the diffusion column L (mol cm^{-3})

$\bar{c}_x$ = Laplace transform of c_x with respect to t'
$\bar{\bar{c}}_x$ = double Laplace transform of c_x with respect to t' and t
$C_{x'}$, C_z = Laplace transforms of $c_{x'}$ and c_z with respect to t_0
$\bar{C}_{x'}$ = double Laplace transform of $c_{x'}$ with respect to t_0 and t'
$D \equiv D_{AB}$ = mutual diffusion coefficient of A and B (cm^2 sec^{-1})
f = area under the curve of F- and R-peaks (mol)
h = height above the baseline defined by eqn. 36 (mol cm^{-3})
l, l' = lengths of the two sections of the chromatographic column depicted in Fig. 1 (cm)
L = length of diffusion column depicted in Fig. 1 (cm)
m = mass of injected solute A (mol)
N = constant defined by eqn. 13
p_0, p', p = transform parameters with respect to t_0, t' and t, respectively
q = parameter defined by eqn. 3
t_0 = time measured from the injection of solute A (sec)
t_{tot} = total time passed from the injection of A to the last reversal of the gas flow (sec)
t, t' = time measured from the last reversal of the gas flow, in direction F or R, respectively (sec)
t_M, t'_M = gas hold-up time of column section l or l', respectively (sec)
v = linear velocity of the carrier gas B in the chromatographic column (cm sec^{-1})
$\dot{V}$ = volume flow-rate of carrier gas (cm^3 sec^{-1})
x, x', z = distance coordinates defined in Fig. 1 (cm)
θ, θ' = time parameters defined by eqns. 16 and 22, respectively (sec)
τ, τ' = time measured from the last reversal of the flow diminished by the gas hold-up time in the flow direction, eqns. 31 and 27 (sec).

The problem will be considered separately in the chromatographic columns, in which the concentrations of A as functions of time and distance are determined by certain differential equations with certain initial and boundary conditions.

Diffusion column L

The concentration in this column $c_z(z, t_0)$ obeys the diffusion equation (Fick's second law):

$$\frac{\partial c_z}{\partial t_0} = D\frac{\partial^2 c_z}{\partial z^2} \tag{1}$$

Laplace transformation with respect to t_0 of this equation, under the initial condition $c_z(z,0) = (m/a)\delta(z)$, where $\delta(z)$ is the Dirac delta function, gives the linear second-order equation

$$\frac{d^2C_z}{dz^2} - q^2C_z = -\frac{m}{aD}\,\delta(z) \tag{2}$$

where

$$q^2 = p_0/D \tag{3}$$

Eqn. 2 can be solved by using z Laplace transformation and, after taking the inverse transform, replacing sinh (qz) and cosh (qz) by exponential functions, and collecting terms with the same exponential, one obtains:

$$C_z = \left[C_z(0) - \frac{C_z'(0)}{q} + \frac{m}{aDq}\right]\frac{\exp(-qz)}{2} + \left[C_z(0) + \frac{C_z'(0)}{q} - \frac{m}{aDq}\right]\cdot \frac{\exp(qz)}{2} \tag{4}$$

where $C_z(0)$ and $C_z'(0)$ is the t_0 transform of the concentration c_z and its first z derivative, respectively, at $z = 0$. For the approximation of a semi-infinite cylinder, the pre-exponential factor in brackets [...] of the last term would normally be set equal to zero, to assure that $C_z = 0$ as $z \to \infty$. However, this approximation is not needed here, since there are two boundary conditions at $z = L$ or $x = l'$, by means of which the relation between $C_z(0)$ and $C_z'(0)$ can be found. These conditions, in the form of their t_0 Laplace transforms, are

$$(C_z)_{z=L} = (C_x)_{x=l'} \tag{5}$$

and

$$-D\left(\frac{\partial C_z}{\partial z}\right)_{z=L} = v(C_x)_{x=l'} \tag{6}$$

By combining eqns. 4, 5 and 6, one finds

$$C_z = \left[\frac{m}{aDq} - \frac{C_z'(0)}{q}\right]\cdot\frac{(1 + v/Dq)\exp(-qz) + (1 - v/Dq)\exp[-q(2L - z)]}{(1 + v/Dq) - (1 - v/Dq)\exp(-2qL)} \tag{7}$$

With $v = 0$, *i.e.* no flux across the boundary $z = L$ (*cf.* also eqn. 6), eqn. 7 is multiplied by the volume element $a\,dz$ and integrated between the limits 0 and L, the result being $m/p_0 - C_z'(0)aD/p_0$. Since this integration must yield m/p_0, *i.e.* the t_0 Laplace transform of the total mass of A injected, it follows that $C_z'(0) = 0$. Using this in eqn. 7, and the approximation of neglecting $\exp(-2qL)$ compared to 1 in the denominator (this is justified for not too short diffusion columns and not too long times), the above equation becomes

$$C_z = \frac{m}{aDq}\exp(-qz) + \frac{m}{aDq}\exp[-q(2L-z)]\left(\frac{2}{1 + v/Dq} - 1\right) \tag{8}$$

This equation provides a simple way to find the solution of the diffusion equation in a cylinder of *finite* length L, without the need of using reflections on boundaries, superpositions etc. It is done by putting $v = 0$, when the last term in parentheses becomes unity, and inverse Laplace transformation with respect to p_0 gives c_z as a function of time and distance:

$$c_z = \frac{m}{a(\pi D t_0)^{\frac{1}{2}}} \exp\left(-\frac{z^2}{4Dt_0}\right)\left\{1 + \exp\left[-\frac{L(L-z)}{Dt_0}\right]\right\} \tag{9}$$

For $L \rightarrow \infty$ the last exponential vanishes and eqn. 9 reduces to the well-known expression for a semi-infinite cylinder, as expected. At $t_0 = 0$ eqn. 9 vanishes everywhere except at $z = 0$, where it becomes infinite, in agreement with assumption (*c*).

Finally, eqn. 8 with $z = L$ gives $(C_x)_{x=l'}$, according to condition 5:

$$(C_x)_{x=l} = \frac{2m}{aDq} \cdot \frac{\exp(-qL)}{1 + v/Dq} \tag{10}$$

which, for high enough flow-rates, becomes

$$(C_x)_{x=l'} = \frac{2m}{\dot{V}} \exp(-qL) \tag{11}$$

since then $v \gg Dq$ and 1 can be omitted from the denominator of eqn. 10. Inverse Laplace transformation of eqn. 11 gives

$$(c_x)_{x=l'} = \frac{N \exp(-L^2/4Dt_0)}{t_0^{3/2}} \tag{12}$$

where

$$N = mL/\dot{V}(\pi D)^{1/2} \tag{13}$$

Chromatographic column $l' + l$

If the carrier gas B flows in the direction F, the concentration of A at $x = l'$, as given by eqn. 12, spreads out in the column section l towards the detector at D_1 (Fig. 1) according to the following mass balance equation, under assumption (b):

$$\frac{\partial c_x}{\partial t_0} = -v \frac{\partial c_x}{\partial x} + v(c_x)_{x=l'}\, \delta(x-l') \tag{14}$$

where $\delta(x-l')$ is the Dirac delta function.

Taking the t_0 Laplace transform of eqn. 14, with the initial condition $c_x(x,0) = 0$, we find an ordinary differential equation for C_x as a function of x. This can be integrated by means of its x Laplace transform, the result being

$$C_x = (C_x)_{x=l'} \exp(-p_0\theta) \cdot u(x-l') \tag{15}$$

where

$$\theta = (x-l')/v \tag{16}$$

and $u(x-l')$ is the Heaviside unit step function, which equals 0 for $x < l'$ and 1 for $x \geqslant l'$. At the detector, *i.e.* at $x = l' + l$, $u(x-l')$ becomes $u(l) = 1$ for $l > 0$, and θ becomes $l/v = t_M$, *i.e.* the gas hold-up time in the column section l. Thus eqn. 15 reduces to

$$C_x = C_x(l', p_0)\exp(-p_0 t_M) \tag{17}$$

and, according to a well known property of Laplace transformations ("translation"), the inverse transform of eqn. 17 for $t_M \geqslant 0$ is

$$c_x = c_x(l', t_0 - t_M)\cdot u(t_0 - t_M)$$

Using eqn. 12 for $c_x(l', t_0)$, one finds for the concentration–time curve at the detector

$$c_x = \frac{N \exp\left[-L^2/4D\,(t_0 - t_M)\right]}{(t_0 - t_M)^{3/2}} \cdot u(t_0 - t_M) \tag{18}$$

From this curve the diffusion coefficient can be computed if the height of the detector signal h (which is proportional to c_x) is multiplied by $(t_0 - t_M)^{3/2}$ and the logarithm of this product is plotted against $1/(t_0 - t_M)$. According to eqn. 18, this plot should be linear with a slope equal to $-L^2/4D$, from which D is found. An example of this type of plot is shown in Fig. 4.

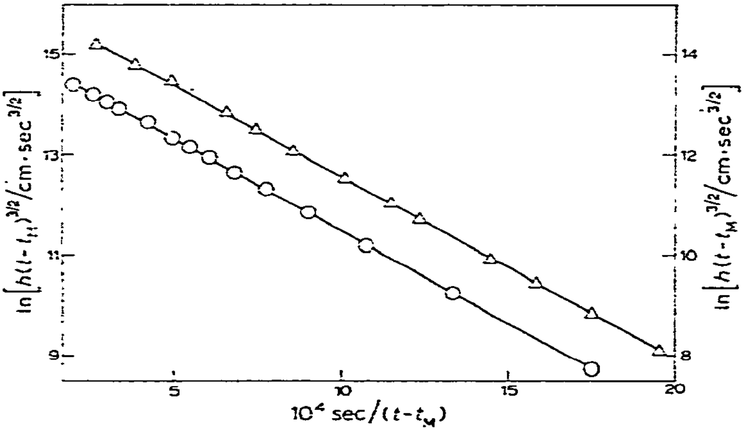

Fig. 4. Examples of plotting eqn. 18 (△, right-hand ordinate) and eqn. 36 (○, left-hand ordinate) for the diffusion of CH_4 (0.5 cm^3) into He ($\dot{V}$ = 0.283 cm^3 sec^{-1}), at 296°K and 2.03 atm.

The above method based on eqn. 18, however, presupposes that: (1) a negligible distortion of the concentration–time curve due to longitudinal diffusion along the column l takes place, and (2) the baseline of the recording system is precisely adjusted and corrected during each determination, so that nothing is added or subtracted from c_x. It is not always easy to substantiate the above requirements, and another version free of these is based on what we term "chromatographic sampling" at known times. This is very simply done by reversing the direction of the flow of B at definite times. Each reversion of the flow takes the amount of solute A which has entered the chromatographic column at $z = L$ from the diffusion column between the times $t_{tot} - t_M$ and t_{tot}, and exhibits it as an extra peak on the otherwise continuous chromatographic signal (see Fig. 3). This is predicted by the mathematical analysis which follows.

Chromatographic sampling

While the carrier gas is flowing in direction F giving the curve described by eqn. 18, its flow is reversed to the direction R at a time $t_0 > t_M$. The time measured from the moment of reversal is called t'. The distance co-ordinate x is now changed to x' defined by the relation

$$x' = l' + l - x \tag{19}$$

and the concentration $c_{x'}(x', t')$ in this time interval is given by the following equation, analogous to eqn. 14:

$$\frac{\partial c_{x'}}{\partial t'} = -v \cdot \frac{\partial c_{x'}}{\partial x'} + v(c_{x'})_{x'=l}\delta(x'-l) \tag{20}$$

As with eqn. 14, one proceeds by taking Laplace transforms of this equation with respect to time, but now the t_0 transform is taken first, followed by the t' transform. The initial condition for the latter is the expression

$$C_{x'}(x', p_0, 0) = C_{x'}(l, p_0, 0) \cdot \exp(p_0\theta')\,[1 - u(x'-l)] \tag{21}$$

obtained from eqn. 15 by writing $C_{x'}(l,p_0,0)$ for $(C_x)_{x=l'}$, substituting $1 - u(x'-l)$ for $u(x-l')$ and replacing θ, as defined by eqn. 16, by its equivalent

$$\theta = (l - x')/v = -(x'-l)/v = -\theta' \tag{22}$$

The result of the above double Laplace transformation is

$$\frac{\mathrm{d}\bar{C}_{x'}}{\mathrm{d}x'} + \frac{p'}{v}\cdot\bar{C}_{x'} = \frac{C_{x'}(l,p_0,0)}{v}\cdot\exp(p_0\theta')\cdot[1 - u(x'-l] + \bar{C}_{x'}(l,p_0,p')\cdot\delta(x'-l) \tag{23}$$

This ordinary differential equation is easily integrated by using x' Laplace transforms, giving $\bar{C}_{x'}(x',p_0,p')$:

$$\bar{C}_{x'} = \frac{C_{x'}(l,p_0,0)}{p'+p_0}\{\exp(p_0\theta')\,[1 - u(x'-l)] + \exp(-p'\theta')\cdot u(x'-l) +$$

$$-\exp[-(p_0 l + p'x')/v]\} + \bar{C}_{x'}(l,p_0,p')\cdot\exp(-p'\theta')\cdot u(x'-l) \tag{24}$$

At the detector, *i.e.* for $x' = l' + l$, $u(x'-l)$ becomes $u(l') = 1$ for $l' > 0$, and θ' becomes $l'/v = t'_M$, *i.e.* the gas hold-up time in the column section l'. Then eqn. 24

simplifies to

$$\bar{C}_{x'} = \frac{C_{x'}(l,p_0,0)}{p' + p_0}\{\exp(-p't_M)-\exp[-p'(t'_M + t_M)]\cdot\exp(-p_0t_M)\} + \bar{C}_{x'}(l,p_0,p')\exp(-p't'_M) \quad (25)$$

Taking now the inverse transforms, first with respect to p' and then with respect to p_0, one finds $c_{x'}$ at the detector as a function of t' and t_0:

$$c_{x'} = c_{x'}(l,t_0-\tau')\cdot[u(\tau')-u(\tau'-t_M)]\cdot u(t_0-\tau') + c_{x'}(l,t_0+\tau')\cdot u(\tau') \quad (26)$$

where

$$\tau' = t'-t'_M \quad (27)$$

The behaviour of eqn. 26 for various values of τ' is interesting. For $\tau' < 0$, *i.e.* for $t' < t'_M$, $c_{x'} = 0$ and no signal is recorded by the detector, until the gas hold-up time t'_M is reached, when $u(\tau') = 1$ and the chromatographic signal rises abruptly to $c_{x'}(l,t_0-\tau') + c_{x'}(l,t_0+\tau')$. It falls again to $c_{x'}(l,t_0+\tau')$ when $\tau' \geqslant t_M$, *i.e.* when $t' \geqslant t'_M + t_M$, because the square function in braces [ ] becomes zero. Then the $u(t_0-\tau')$ factor remains unity in the above interval on account of the condition that the flow is reversed at $t_0 > t_M$. Thus, the function described by eqn. 12, *i.e.* the concentration of A at $x = l'$ or $x' = l$ (*cf.* Fig. 1) which can be denoted by $c_x(l',t_0)$ or $c_{x'}(l,t_0)$, is shifted in time on reversing the flow direction. This time-shift takes place in two opposite directions, "forwards" to $c_{x'}(l,t_0 + \tau')$ and "backwards" to $c_{x'}(l,t_0-\tau')$. The first shift starts at $t' = t'_M$ and continues uninterrupted. It is nothing more than the continuation of eqn. 18 at the other end of the chromatographic column. The backward shift is barred in the interval $0 \leqslant \tau' \leqslant t_M$ or $t'_M \leqslant t' \leqslant t'_M + t_M$, and therefore starts with the concentration $c_{x'}(l,t_0)$ and ends with that of a preceding time, namely $c_{x'}(l,t_0-t_M)$. This extra signal (R-peak) adds to the forward shift and constitutes the "chromatographic sampling" signal. Thus, the experimental behaviour exhibited in Fig. 3 is predicted.

At a time $t' > t'_M + t_M$ the carrier gas flow is again turned to the direction F, the time from this moment being denoted by t. The distance coordinate is changed from x' back to x, according to eqn. 19, and the concentration $c_x(x,t)$ is again described by eqn. 14 with t substituted for t_0. To solve this equation by the method of Laplace transformations, we need the initial condition at $t = 0$. This, in the form of its t' transform, is obtained from the last term of eqn. 24, since all other terms of this equation disappear at $\tau' > t_M$. The remaining term, after taking the p_0 inverse transform, changing θ' to $-\theta$ and $u(x'-l)$ to $1 - u(x-l')$, gives the desired condition at $t = 0$ as

$$\bar{c}_x(x,t_0,p',0) = \bar{c}_x(l',t_0,p',0)\cdot\exp(p'\theta)\,[1 - u(x-l')] \quad (28)$$

The rest of the solution in the t interval follows the same procedure as that outlined for eqn. 20, namely the t' Laplace transform is taken first, then the t transform with initial condition eqn. 28. This leads to a differential equation in x similar to eqn. 23, which in turn gives the equivalent of eqn. 24, and finally the counterpart of eqn. 25 is obtained as

$$\bar{\bar{c}}_x = \frac{\bar{c}_x(l',t_0,p',0)}{p + p'} \{\exp(-pt_M) - \exp[-p(t_M + t'_M)] \cdot \exp(-p't'_M)\} + \\ + \bar{c}_x(l',t_0,p',p) \cdot \exp(-pt_M) \tag{29}$$

Successive inverse transformations with respect to p and p' then give the c_x value at the detector:

$$c_x = c_x(l',t_{tot} - \tau) \cdot [u(\tau) - u(\tau - t'_M)] \cdot u(t' - \tau) + c_x(l',t_{tot} + \tau) \cdot u(\tau) \tag{30}$$

where

$$\tau = t - t_M \tag{31}$$

and $t_{tot} = t_0 + t'$.

This equation is symmetrical with eqn. 26 and its behaviour is analogous. It predicts that $c_x = 0$ for $\tau < 0$, and at $\tau > 0$ two functions are recorded as a sum. One is given by eqn. 12 with the total time t_{tot} in place of t_0 and shifted forwards by τ. This continues uninterrupted as the last term of eqn. 30 shows. In the other function the t_{tot} is shifted backwards by τ and this function vanishes when $\tau \geqslant t'_M$. Thus, an extra signal (F-peak) appears in the interval $0 \leqslant \tau \leqslant t'_M$ "sitting" on the otherwise continuing chromatographic curve. The function $u(t' - \tau)$ in eqn. 30 is kept at unity in the above interval on account of the condition that the new reversal was at $t' > t'_M + t_M$.

Repeating the reversal of the carrier gas flow in the direction R for a second time at $t > t_M + t'_M$, then in the direction F for a third time at $t' > t'_M + t_M$, and so on, two series of peaks are produced. The R-peaks are described by eqn. 26 with t_{tot} in place of t_0, while the F-peaks are given by eqn. 30. Since the definitions "forward" and "reverse" are arbitrary, and the two above equations have the same form, one of them suffices to describe both kinds of peaks. In what follows we make use only of eqn. 30. This can be written explicitly using eqn. 12 in place of $c_x(l',t_{tot} - \tau)$ and $c_x(l',t_{tot} + \tau)$, the resulting expression describing the concentration–time curve at the detector:

$$c_x = \frac{N \exp[-L^2/4D(t_{tot} - \tau)]}{(t_{tot} - \tau)^{3/2}} \cdot [u(\tau) - u(\tau - t'_M)] + \\ + \frac{N \exp[-L^2/4D(t_{tot} + \tau)]}{(t_{tot} + \tau)^{3/2}} \cdot u(\tau) \tag{32}$$

Here, N is given by eqn. 13, t_{tot} is the total time passed from the injection of A to the *last* reversal of the gas flow, τ the time measured *from* the last reversal of the flow diminished by the gas hold-up time in the direction of the flow (*cf.* eqns. 27 and 31) and t'_M the hold-up time in the opposite direction of the flow. The function $u(t' - \tau)$ in eqn. 30 has been assumed unity, because the time elapsing between any two successive reversals is greater than the total hold-up time $t_M + t'_M$, as mentioned before.

Two other relations are useful. The first is that which gives the area under the F- and R-peaks, taking the last term of eqn. 32 as baseline. For this purpose one can use eqn. 25 and the well known relation

$$\mathscr{L}_{t_0} f = \int_0^\infty C_{x'} \mathrm{d}V = \dot{V} \int_0^\infty C_{x'} \mathrm{d}t' = \dot{V} \lim_{(p' \to 0)} (\bar{C}_{x'}) \tag{33}$$

where in place of $\bar{C}_{x'}$ we use only the first term on the right-hand side of eqn. 25, the last term giving rise to the baseline. The result is

$$\mathscr{L}_{t_0} f = \dot{V} \cdot \frac{C_{x'} (l, p_0, 0)}{p_0} \cdot [1 - \exp(-p_0 t_M)] \tag{34}$$

The area under the peaks is simply found by substituting eqn. 11 for $C_{x'}(l,p_0,0)$ and taking the p_0 inverse transform:

$$f = 2m \left[\operatorname{erfc} \frac{L}{2D^{1/2} t_0^{1/2}} - \operatorname{erfc} \frac{L}{2D^{1/2} (t_0 - t_M)^{1/2}} \cdot u(t_0 - t_M) \right] \tag{35}$$

A second useful relation is that giving the height of the F- or R-peaks above the continuous chromatographic signal (the latter being taken as baseline) at $\tau = t'_M$, which is the maximum value of τ before returning to the baseline. Denoting by c_b the last term of eqn. 32 (baseline), one finds for this height

$$h \equiv (c_x - c_b)_{\tau = t'_M} = \frac{N \exp\,[-L^2/4D(t_{\mathrm{tot}} - t'_M)]}{(t_{\mathrm{tot}} - t'_M)^{3/2}} \tag{36}$$

Thus, the plotting of $\ln[h(t_{\mathrm{tot}} - t'_M)^{3/2}]$ against $1/(t_{\mathrm{tot}} - t'_M)$ should result in straight lines with slope $-L^2/4D$. Knowing L, D can be calculated. An example of such a plot is shown in Fig. 4.

RESULTS AND DISCUSSION

Using eqn. 36, values for the diffusion coefficient of five gaseous hydrocarbons in three carrier gases have been determined and are collected in Table I. The values and their standard errors found by regression analysis using standard least-squares procedures, are reduced to 1 atm after multiplication by the pressure of the experiment. This pressure is given in Table I, so that one can find the actual values determined from the ratio D/p. For the pair ethylene–nitrogen the diffusion coefficient was determined at three different pressures, and for the pair methane–helium at two pressures. In both cases the variation of the results with small changes in pressure (and in $\dot{V}$) was small.

The precision of the method, defined as the relative standard deviation (%), can be judged from the data given for methane–helium. From the five values quoted, a precision of 0.9% is calculated.

TABLE I

DIFFUSION COEFFICIENTS OF VARIOUS SOLUTES INTO THREE CARRIER GASES AT AMBIENT TEMPERATURES AND REDUCED TO 1 atm PRESSURE

The actual values found at the pressure of the experiment, p, are simply D/p. All errors given are "standard errors", calculated by regression analysis.

Carrier gas	*Solute gas*	*T (°K)*	$\dot{V}$ *(cm³ sec⁻¹)*	*p* (atm)	*10³ D (cm² sec⁻¹)*			*Accuracy**** *(%)*
					Present work	*Calcd.*	*Lit.*$^{ref.}$	
N_2	CH_4	296.0	0.260	1.96	272 ± 4	214	–	21.3
	C_2H_6	293.0	0.267	1.99	142 ± 0.03	144	148^2	1.4 (2.7)
	n-C_4H_{10}	295.5	0.300	2.15	98 ± 0.2	98.6*	96^2	0.3 (2.7)
	C_2H_4	296.0	0.120	1.49	168 ± 2	156	163^2	7.1 (4.3)
		292.0	0.268	2.00	156 ± 0.4			0
		292.0	0.538	2.71	161 ± 0.4			3.1
	C_3H_6	298.0	0.260	1.96	124 ± 0.4	120*	–	3.2
H_2	CH_4	293.0	0.287	1.70	699 ± 3	705	730^3	0.9 (3.4)
	C_2H_6	297.0	0.267	1.56	548 ± 5	556	540^3	1.5 (3)
	n-C_4H_{10}	296.0	0.273	1.60	386 ± 3	373	400^3	3.4 (6.8)
	C_2H_4	293.0	0.300	1.75	525 ± 5	559	602^2	6.5 (7.1)
	C_3H_6	296.0	0.273	1.60	485 ± 3	486	–	0.2
He	CH_4	295.7	0.250	1.78	527 ± 3	669	–	26.9
		295.0	0.283	2.03	520 ± 1			28.7
		296.0	0.283	2.03	522 ± 1**			28.2
		296.0	0.283	2.03	514 ± 0.2			30.2
		296.7	0.283	2.03	522 ± 3			28.2
	C_2H_6	295.6	0.300	2.15	518 ± 3	507	–	2.1
	n-C_4H_{10}	290.0	0.283	2.03	333 ± 3	330	364^4	0.9 (9.3)
	C_2H_4	296.0	0.283	2.03	558 ± 4	544	–	2.5
	C_3H_6	291.0	0.283	2.03	412 ± 4	440	–	6.8

* The necessary parameters σ and ε/k were obtained from ref. 6.

** This value was determined by using eqn. 18, without reversing the flow.

*** This is defined by eqn. 38. Numbers in parentheses are the accuracies of the respective literature values.

The values of the present work are compared in Table I with those calculated theoretically by the equation[5].

$$D_{AB} = 0.0018583\, T^{3/2}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)^{1/2}\Big/ p\sigma^2_{AB}\Omega_{D,AB} \tag{37}$$

where M_A and M_B are molar masses, and $\Omega_{D,AB}$ is a dimensionless function of the temperature and of the intermolecular potential field for one A and one B molecule. Combining the Lennard–Jones parameters σ and ε/k of A and B, as given in Table B-1 of ref. 5, σ_{AB} and ε_{AB}/k are found:

$$\sigma_{AB} = (\sigma_A + \sigma_B)/2 \text{ and } \frac{\varepsilon_{AB}}{k} = \left(\frac{\varepsilon_A}{k}\cdot\frac{\varepsilon_B}{k}\right)^{1/2}$$

From this kT/ε_{AB} is calculated and then Table B-2 of ref. 5 gives the $\Omega_{D,AB}$ value.

The calculated values in Table I are for the temperature of the experiment, while the literature values refer to temperatures which differ from those of the present work by not more than 5°C. The accuracy given in the last column of Table I is a measure of the deviation of the present values from the calculated ones, defined as

$$\text{Accuracy}\ (\%) = \frac{|D_{\text{found}} - D_{\text{calcd}}|}{D_{\text{found}}} \cdot 100 \tag{38}$$

With the exception of two pairs containing methane as solute, this accuracy is better than 7.1% in all cases and in 8 out of the 15 pairs is better than 2.5%. The high deviation of the experimental from the calculated values for the pairs methane–nitrogen and methane–helium, in spite of the fact that the precision is 0.9% as mentioned before, is probably due to the approximations used in the calculated values. Finally, the accuracies of the present values can be compared with the accuracies of the respective literature values, given in parentheses in Table I and defined again by eqn. 38 with D_{lit} in place of D_{found}. This comparison leads to the conclusion that, with the exception of ethylene–nitrogen, the values of diffusion coefficients determined by the method reported here are closer to the theoretical calculated values than are the experimental values found in the literature, under similar conditions of temperature and pressure.

One final remark is that the D values determined by the present method are very sensitive to the precision with which L is measured, since D is proportional to L^2. Instead of measuring directly the length L, one can use a solute–carrier gas pair of accurately known diffusion coefficient, and carry out a calibration experiment for L. The value of L so calculated can now be used to estimate unknown diffusion coefficients. In the results reported in Table I, however, the actual length L was used, without any calibration.

In conclusion, with the aid of simple gas chromatography instrumentation, precise and accurate mutual diffusion coefficients in gases can be determined. The method has certain instrumental similarities with a technique reported by Desty *et al.*[7]. They used the diffusion of vapour from a liquid surface through a stagnant column of gas in a capillary tube, to maintain constant low concentrations of the vapour in a gas stream, in order to study the performance of a flame-ionization detector. They also described how to determine the rate of diffusion from the open end of the capillary by measuring the distance between this end and the liquid meniscus as a function of time.

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