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REVERSED-FLOW GAS CHROMATOGRAPHY APPLIED TO PHYSICO-CHEMICAL MEASUREMENTS

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SUMMARY

Physico-chemical measurements by reversed-flow gas chromatography can be performed by creating a diffusion current of the gaseous solute into the carrier gas, perpendicular to the chromatographic movement, and superimposing on it the effect of a rate or equilibrium process taking place at one end of the diffusion column. The reversals of the direction of the carrier gas flow give rise to a series of sample peaks which, plotted as the logarithm of their height *vs.* time, form a so-called diffusion band.

From a non-distorted diffusion band, the void fraction (porosity) of a solid bed, and the partition coefficient of a solute between a gas phase and a solid phase can be determined. From a distorted diffusion band, mass transfer and partition coefficients across gas–solid and gas–liquid boundaries are computed, and also reaction rate constants when the solute transferred to the solid reacts chemically with it. Furthermore, mass transfer coefficients, connected with the evaporation of pure liquids and liquid mixtures, and also activity coefficients of one or more components in these mixtures, can be determined.

INTRODUCTION

The use of gas chromatography (GC) for physico-chemical measurements based on the traditional techniques of elution, frontal analysis, and displacement development, is not a new field of research. Two relatively new methods are based on perturbations imposed on the carrier gas flow. One is the stopped-flow technique, used mainly for studying the kinetics of surface-catalysed reactions, and the second is the so-called reversed-flow gas chromatography (RF-GC) technique. The latter is really a sampling technique and consists basically of reversing the direction of flow of the carrier gas from time to time. If this carrier gas contains other gases at certain concentrations, recorded by the detector system, the flow reversals create perturbations on the continuous chromatographic elution curve, which take the form of extra chromatographic peaks, called sample peaks (Fig. 1). A single flow reversal creates sample peaks like that marked A, and two successive flow reversals, *i.e.* reversal of the flow for a small time period t' followed by resumption of flow in the original direction, gives rise to peaks like B. These "double reversal" sample peaks are usually

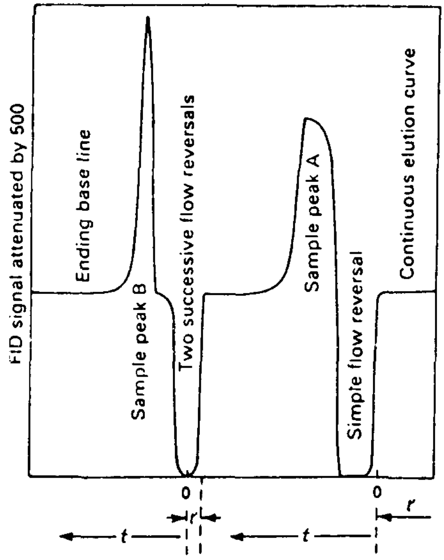

Fig. 1. Sample peaks due to flow reversals of carrier gas helium containing a small amount of heptane vapour (from ref. 2).

more symmetrical and higher, and can be made as narrow as required. It has been shown[1] that theoretically the width of the B peaks at their half-height is equal to the duration t' of the backward flow of the carrier gas.

If the concentration of a constituent in the flowing gas depends on a rate process (*i.e.* a slow phenomenon) or on a fast process leading to an equilibrium state within the chromatographic system, then, by repeatedly reversing the flow, one performs a repeated measurement of the rate or the equilibrium state of this process, *e.g.* of the rate of a chemical reaction on a catalytic surface. Appropriate equations are derived by means of which the rate or the equilibrium coefficient of the process responsible for the sample peak formation is determined, *e.g.* the rate constant of the above reaction.

So far, the process influencing the concentration of a component has been confined to a very short section near the middle of the chromatographic column, and the relevant coefficient has been extracted from the chromatographic process itself by using the chromatographic sampling equation already derived[1]. The applications of the method with this kind of arrangement have been reviewed[1], and some uses in kinetic analytical chemistry have also been briefly described[2]. However, a new group of physico-chemical measurements has been recently made by physically separating the rate process or the equilibrium state being studied from the chromatographic process, thus rendering possible the determination of physico-chemical quantities not easily or accurately measured otherwise. It is the object of this paper to review briefly this new group of applications of the RF-GC technique. The details of most of the work described have already been published[3,5–8] but are not included in the previous reviews[1,2], and some new, original work is added here.

GENERAL EXPERIMENTAL SET-UP

A schematic representation of the columns and gas connections for the application of RF-GC is given in Fig. 2. It is basically a simple set-up.

(1) A conventional gas chromatograph is used with any kind of detector capable of detecting the vapour(s) contained in the carrier gas. A high sensitivity device, such as a flame ionization detector or a flame photometric detector is to be preferred, whenever appropriate. The oven of the chromatograph must be big enough to accommodate two columns, if possible, although for most applications a single-column oven will do.

(2) The so-called sampling column is constructed from chromatographic tubing (glass, stainless steel or other material) of any diameter (usually 4 mm I.D.), and with a total length of 0.8–2.5 m, depending on the particular application. This sam-

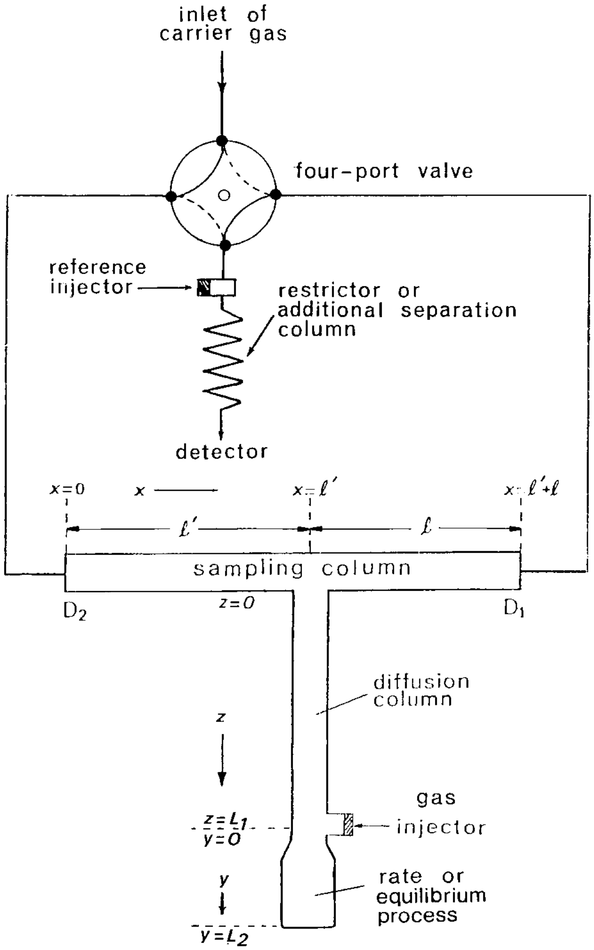

Fig. 2. Schematic representation of the columns and gas connections for measurements of physico-chemical quantities by the RF-GC technique.

pling column may be empty, or it may be packed with one of the usual chromatographic materials for separation. The sampling column is coiled and accommodated inside the oven of the chromatograph.

(3) The diffusion column is constructed from the same material as the sampling column and is connected perpendicularly to it, usually at its middle point. This column has two sections, z and y. Section z (L_1) is 30–100 cm long and is of the same diameter as the sampling column, whilst Section y (L_2) is shorter, 1–12 cm, and usually has a larger diameter (18 mm I.D.). An injector between the two regions permits the introduction of a small gaseous volume (0.5–1 ml at atmospheric pressure) of the solute being studied. The diffusion column may be empty or it may contain a liquid or a solid material in its y section. The whole column is coiled and placed inside the oven of the chromatograph. It may be also positioned outside the oven and kept at room temperature, or it may be heated by a heating band or by water circulation around it from a thermostat.

(4) The sampling and the diffusion columns form what is called the sampling cell, and this cell must be connected to the carrier gas inlet and the detector in such a way that the direction of the carrier gas flow through the sampling column (no carrier gas flows through the diffusion column) can be reversed at any time desired. This can be done by using a four-port valve to connect the ends D_1 and D_2 of the sampling column to the carrier gas supply and the detector, as shown schematically in Fig. 2. With the valve in the position indicated by the solid lines, the carrier gas (dried and regulated by a gas-flow controller) enters the column at D_2 and leaves it from D_1 towards the detector. By switching the valve to the other position (dashed lines) the direction of the carrier gas flow is reversed and enters the column at D_1.

To avoid condensation of solutes inside the valve and in the 1/16 in. connection tubes, it is preferable to place the body of the valve inside a large hole in the oven wall, and the connecting tubes should run as far as possible inside the oven. Also, the whole valve body may be placed in a heated enclosure like those commercially available.

Instead of a four-port valve, one can also use the usual six-port gas-sampling valve, with a short 1/16-in. tube connecting two alternate ports, as shown in Fig. 5 of ref. 1.

(5) Whenever a detector with a flame is used, a restrictor is placed ahead of the detector to prevent the flame from being extinguished when the valve is turned from one position to the other. A restrictor is also needed when one wishes to increase the pressure inside the sampling cell.

Separation of various components contained in the carrier gas is usually effected by packing the sampling column with an appropriate chromatographic material. Alternatively, the sampling column may be kept empty, separations being made with an additional chromatographic column connected in place of the restrictor, which is then not needed (*cf.* Fig. 2). This additional column can be accommodated either in the same oven as the sampling column or in a separate oven and heated at a different temperature.

Note that the flow reversals are "confined" to the sampling column; in the separation column the carrier gas flows always in the same direction. Reference substances for identification purposes can be introduced into the separation column through the reference injector shown in Fig. 2.

THEORETICAL

The physical separation of a rate or an equilibrium process under study from the chromatographic process itself is achieved by confining the former process to the diffusion column (preferably in Section y) while chromatographic movement occurs within the sampling column. Thus, the two processes are placed perpendicularly to one another. The flow reversals of the carrier gas at known times, t_0, during the experiment repeatedly sample the concentration, $c(l', t_0)$, of a solute vapour at the junction, $x = l'$, with the help of the sample peaks (*cf.* Fig. 1). The height, h, of these peaks above the ending baseline is[1]

$$h \approx 2c(l', t_0) \tag{1}$$

The concentration, $c(l', t_0)$, generally depends on: (1) the rate coefficients of the slow processes taking place inside the diffusion column; (2) the equilibrium constants of possible equilibrium states in the rate-process region; and (3) the diffusion coefficient of the solute into the carrier gas, since it is longitudinal diffusion along Section z that carries the solute from the rate or equilibrium process region to the junction, $x = l'$.

In the earliest use of a diffusion column, the process region (Section y) was absent and Section z was employed simply to measure the diffusion coefficient of a solute, or a mixture of solutes, into the carrier gas[1,2], and also for the calibration of detectors[2]. Now, the diffusion current is used *as a carrier* and the rate or equilibrium processes are superimposed on it. The old conventional way of measuring physico-chemical quantities by gas chromatography is mainly based on the distortion of a chromatographic elution band brought about by the processes pertaining to those quantities. In the present method, it is a *diffusion band* that is distorted by those processes. The apparent advantage of the chromatographic band, which can be made to move through the column as fast as required by changing at will the carrier gas flow-rate, is offset by the possibility of changing the apparent diffusion coefficient of the solute along Section z. This is brought about by changing the ratio of the gaseous volumes of Sections y and z, as will be shown presently.

APPLICATIONS OF THE METHOD

The diffusion band in the absence of other processes

Suppose that the diffusion column is empty and a small volume of a solute gas or vapour A is introduced through the injector of Fig. 2, while a carrier gas, B, *e.g.* nitrogen, flows through the sampling column, $l' + l$, and also fills the diffusion column, $L_1 + L_2$. A diffusion current of the injected solute into the carrier gas arises inside the latter column, creating a finite concentration of it at the junction, $x = l'$. This is sampled as a function of time by reversing the direction of the carrier gas flow for a short interval, t', as previously described, thus giving rise to sample peaks. In Fig. 3, Curve 1, the height of the sample peaks as a function of the time, t_0, of the flow reversal is plotted on a semilogarithmic scale. Such a curve is termed a diffusion band. This is solely due to the longitudinal diffusion of the solute vapour into the carrier gas along the diffusion column, $L_1 + L_2$.

The mathematical equation describing a diffusion band as an analytical function of the time has been derived[3] and is given by

$$c(l', t_0) = \frac{N_2}{1 + 1.801\ V'_G/V_G} \exp\left(-\frac{\pi^2 D/4L_1^2}{1 + 1.801\ V'_G/V_G}\ t_0\right) \tag{2}$$

where D is the diffusion coefficient of A into the carrier gas B, V_G and V'_G are the gaseous volumes in Sections L_1 and L_2 of the diffusion column, respectively, and

$$N_2 = \pi m D/\dot{V}L_1^2 \tag{3}$$

where m is the amount of solute injected, and $\dot{V}$ the volumetric flow-rate of the carrier gas in the sampling column. Since the height, h, of the sample peaks is approximately equal to $2c(l', t_0)$ according to eqn. 1, eqn. 2 describes the diffusion band ($\ln h$ *vs.* t_0) as a linear function with slope

$$-\frac{\pi^2 D/4L_1^2}{1 + 1.801\ V'_G/V_G}$$

This applies only to the descending part of the plot after the maximum (*cf.* Fig. 3), because in the derivation of eqn. 2 the term responsible for the ascending branch of the curve was ignored. The expression $D/(1 + 1.801\ V'_G/V_G)$ is the apparent diffusion coefficient previously mentioned, its value depending on the ratio V'_G/V_G.

Suppose now that the experiment is repeated with the lower part L_2 of the

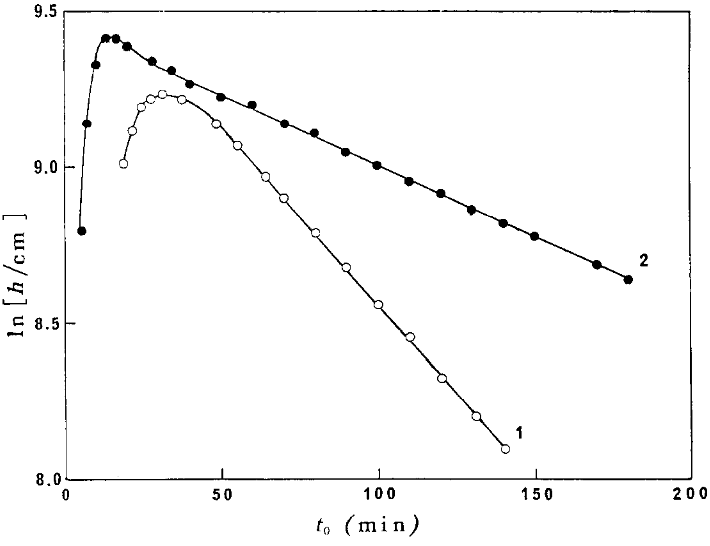

Fig. 3. Plots of $\ln h$ *vs.* t_0 for methane in carrier gas nitrogen ($\dot{V}$ = 0.357 cm³s⁻¹) at 364 K with L_1 = 46.8 cm and V_G = 10.6 cm³. (○) Vessel L_2 empty and V'_G = 1.06 cm³; (●) vessel L_2 filled with 9.596 g of γ-alumina (100–120 mesh) (from ref. 3).

diffusion column filled with solid particles on which the solute gas is not adsorbed and with which it does not react in any way, *e.g.* glass beads or alumina, with methane as a solute. The descending part of the diffusion band is again described by eqn. 2, the only difference being that V_G is now the gaseous volume of the void space in L_2, filled with the solid. An example is given by Curve 2 of Fig. 3. An obvious application of eqn. 2 is thus to determine the external porosity ε (void fraction), of the solid bed by performing two simple experiments, one with L_2 empty and another with L_2 filled with the solid. If r is the ratio of the slopes of the two diffusion bands obtained experimentally (linear parts after the maximum), it is easily found from eqn. 2 that

$$\varepsilon = r + \frac{r-1}{1.801} \frac{V_G}{V'_G} \tag{4}$$

V'_G being the gaseous volume of the empty bed.

Determination of partition coefficients from the diffusion band

If the injected solute is adsorbed on the solid filling L_2, or else dissolves in the liquid film covering the surface of the solid, the partition coefficient, K, of the solute between the gas and the solid phases can be determined, provided that the distribution equilibrium is rapidly established. In that case, the relevant equation describing the descending part of the diffusion band is derived from eqn. 27 in ref. 3 by omitting the time parameter, p_0, compared with the rate constant, k_{-1}, assumed very large, and taking the inverse Laplace transform of the remaining terms. The result is

$$c(l', t_0) = \frac{N_2}{1 + 1.801\,(1 + k)V'_G/V_G} \exp\left[-\frac{\pi^2 D/4L_1^2}{1 + 1.801\,(1 + k)V'_G/V_G}\, t_0 \right] \tag{5}$$

where k is the partition ratio of the solute between the two phases.

Four experiments are required to calculate k and K.

(1) A diffusion band with a non-adsorbed gas, such as methane, and an empty diffusion column with known values of V_G and V'_G. These can be found, for example, by filling L_1 and L_2 with water at a known temperature and weighing it. From the slope of this band, using eqn. 2, the diffusion parameter, $\alpha = \pi^2 D/4{L_1}^2$, is determined.

(2) A diffusion band with the same non-adsorbed gas, but with L_2 filled with the solid material. From the slope of this band, using the α value from the previous experiment, the value of V'_G/V_G for the filled bed is easily found, together with the void fraction ε, using eqn. 4.

(3) A diffusion band with the solute gas under study and an empty column to calculate α for this solute.

(4) A diffusion band with the examined solute gas and L_2 filled to find k by means of eqn. 5, knowing $\pi^2 D/4L_1^2$ from the third experiment and V'_G/V_G from the second. Lastly, K is found from the relation $K = k\varepsilon/(1 - \varepsilon)$.

Experiments (1) and (3) can be omitted by using diffusion coefficient values from other sources and the length L_1 to calculate α for the two gases.

Mass transfer and partition coefficients across phase boundaries from a distorted diffusion band

If the equilibrium state of the interaction between the solute, A, and the solid is established slowly, there is a finite value for the overall mass transfer coefficient, K_s, of A between gas and solid phases, and the diffusion band is no longer linear (after the maximum), but distorted, as shown in Fig. 4. This distortion is described by the equation[3]

$$c(l', t_0) = \frac{N_2/2}{1 + 1.801\, V'_G/V_G}\left[\left(1 + \frac{Z}{Y}\right)\exp\left(-\frac{X+Y}{2}\,t_0\right) + \left(1 - \frac{Z}{Y}\right)\exp\left(-\frac{X-Y}{2}\,t_0\right)\right] \tag{6}$$

where

$$X = \frac{\pi^2 D/4L_1^2 + 1.801\, k_1 V'_G/V_G}{1 + 1.801\, V'_G/V_G} + k_{-1} \tag{7}$$

$$Y = \left(X^2 - \frac{\pi^2 D/L_1^2}{1 + 1.801\, V'_G/V_G}\, k_{-1}\right)^{\frac{1}{2}} \tag{8}$$

$$Z = X - 2k_{-1} \tag{9}$$

and k_1, k_{-1} are the rate constants for adsorption on the solid and for desorption from the solid, respectively, given by

$$k_1 = KK_sA_s/V'_G \tag{10}$$

$$k_{-1} = K_sA_s/V_s \tag{11}$$

A_s being the total free surface area of the solid (bare or covered with a liquid), and V_s the total volume of the solid.

With the help of eqn. 6, the values of k_1 and k_{-1} can be computed from the distorted diffusion band. From these rate constants, the partition ratio, k, and the partition coefficient, K, are easily calculated:

$$k = k_1/k_{-1} = KV_s/V'_G \tag{12}$$

as well as the mass transfer coefficient, K_s, by means of eqn. 11. The k_1 and k_{-1} values are calculated from the exponential coefficients $(X + Y)/2$ and $(X - Y)/2$ of eqn. 6, using a suitable computer program or, if these two coefficients are sufficiently different, by finding first the slope, $-(X - Y)/2$, and the intercept, $\ln h_0$, of the last linear part of the $\ln h$ *vs.* t_0 plot, and then replotting the initial data after the maxi-

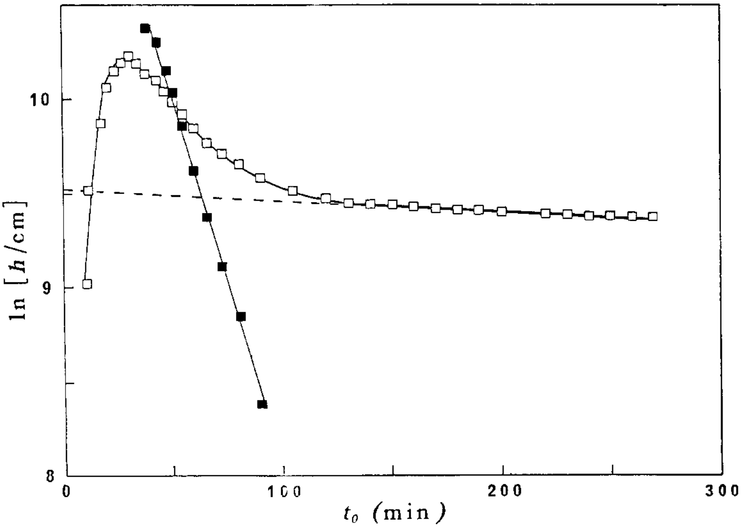

Fig. 4. The plot of ln h vs. t_0 for butane, with L_2 filled with 9.284 g of γ-alumina (10–22 mesh) (□). The points ■ (plotted as 1 + ln h) are obtained by subtracting, from the experimental points after the maximum, the points corresponding to the extrapolation (dashed line) of the linear part (from ref. 3).

mum as $\ln\{h - h_0 \exp[-(X - Y)t_0/2]\}$, as shown in Fig. 4, to find $-(X + Y)/2$ from the slope of the new plot. The product Π of these coefficients is

$$\Pi = \frac{\pi^2 D/4L_1^2}{1 + 1.801\ V'_G/V_G}\ k_{-1}$$

and thus permits the calculation of k_{-1}, while their sum equals X (given by eqn. 7), leading to the value of k_1.

Suppose now that the vessel L_2 of the diffusion column does not contain a solid but is filled with a liquid, in which the injected solute gas may dissolve. If this dissolution is fast or non-existent, eqn. 5 with $V'_G = 0$ can be applied:

$$c(l', t_0) = N_2 \exp(-\pi^2 D t_0/4L_1^2) \tag{13}$$

This predicts a diffusion band that is linear after the maximum with slope $-\pi^2 D/4L_1^2$. An example is given in Fig. 5, curve 2. But if the mass transfer of the solute across the gas–liquid boundary is slow, the diffusion band obtained is distorted, as shown by curve 3 of Fig. 5, and is again described by eqn. 6 with $V'_G = 0$ and X, Y and Z, given by expressions slightly different from eqns. 7, 8 and 9. The expression giving X is obtained by substituting eqn. 10 for k_1 in eqn. 7 and setting $V'_G = 0$ in the denominator of the latter:

$$X = \frac{\pi^2 D}{4L_1^2} + \frac{1.801\ KK_L A_L}{V_G} + k_{-1} \tag{14}$$

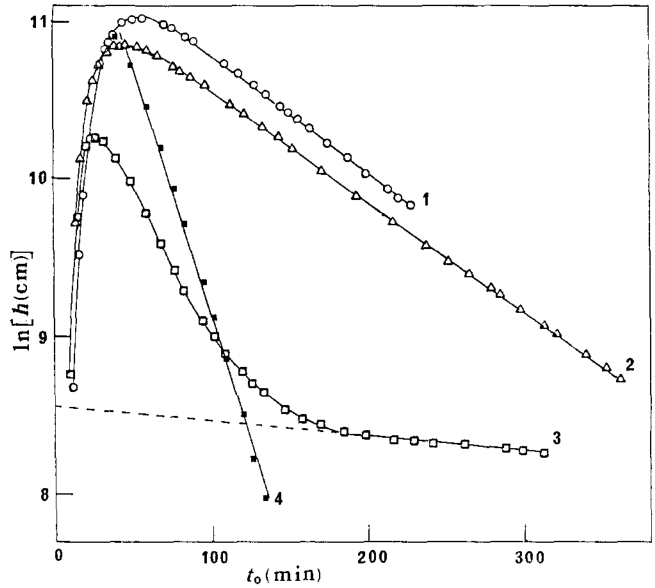

Fig. 5. Diffusion bands, obtained with butane as solute gas in carrier gas nitrogen, at 327 K. Curve 1 was obtained with a small vessel (L_2 = 2 cm) containing no liquid, curve 2 with a larger vessel containing 10.4 ml of water, and curve 3 (plotted as 1 + ln h) with L_2 containing 10.4 ml of hexadecane. Line 4 (plotted as 2 + ln h) was constructed by subtracting, from the experimental points of curve 3, the points corresponding to the extrapolation (dashed) of the linear part (from ref. 5).

where K_L is the overall mass transfer coefficient in the liquid phase (substituted for K_s), and A_L is the free surface area of the liquid (substituted for A_s). The Y function is given by eqn. 8 with $V'_G = 0$, and the Z by eqn. 9. Finally,

$$k_{-1} = \frac{K_L A_L}{V_L} \tag{15}$$

where V_L is the volume of the liquid. It is also noteworthy that the product KK_L in eqn. 14 is equal to the overall mass transfer coefficient in the gas phase, K_G, according to the two-film-theory of Whitman[4].

From the exponential coefficients $(X + Y)/2$ and $(X - Y)/2$, calculated from the distorted diffusion band as described before, one can find the value of k_{-1} by multiplying them

$$\Pi = \frac{\pi^2 D}{4L_1^2} k_{-1} \tag{16}$$

and dividing the product, Π, by the coefficient $\pi^2 D/4L_1^2$, found in the absence of liquid. Adding the two exponential coefficients gives X as before, and subtraction of $\pi^2 D/4L_1^2$ and k_{-1} according to eqn. 14 leads to the value of 1.801 $KK_L A_L/V_G$. From this, $KK_L = K_G$ is found, and from k_{-1}, using eqn. 15, K_L is calculated. Finally, the partition coefficient, K, is determined from the ratio K_G/K_L. From K, the Henry's law constant in Nm/mol $H^* = RT/K$ is also computed.

The above relations referring to a gas–liquid boundary have been derived previously[5] in a slightly diffferent way and have been successfully applied in the case of three hydrocarbon solutes (butane, propene and methane), with nitrogen as the carrier gas and hexadecane as the liquid stationary phase. The mass transfer coefficients, the partition coefficient, and the Henry's law constant were determined in the same experiment[5]. The Henry's law constants were not appreciably different from those calculated from literature data.

Mass transfer combined with a chemical reaction

An interesting variation of the case when vessel L_2 contains a solid is the mass transfer phenomena of the solute across the gas–solid boundary, followed by a chemical reaction with the solid. Analysis of the distorted diffusion band obtained can lead to the simultaneous determination of the reaction rate constant, k_2, the adsorption rate constant on the solid, k_1, the desorption rate constant, k_{-1}, from the solid, and from the last two rate constants, the partition ratio, k, the partition coefficient, K, and the overall mass transfer coefficient, K_s.

The relevant mathematical equation describing the diffusion band in this case can be derived in a way analogous to that followed for eqn. 6, and it has the same general form, except for the expressions describing the functions X, Y and Z, which, instead of eqns. 7–9, are given by the relations

$$X = \frac{\pi^2 D/4L_1^2 + 1.801\ k_1 V'_G/V_G}{1 + 1.801\ V'_G/V_G} + k_{-1} + k_2 \tag{17}$$

$$Y = \left[X^2 - \frac{(\pi^2 D/L_1^2)\,(k_{-1} + k_2) + (7.204\ V'_G/V_G)k_1 k_2}{1 + 1.801\ V'_G/V_G}\right]^{\frac{1}{2}} \tag{18}$$

$$Z = X - 2(k_{-1} + k_2) \tag{19}$$

The three rate constants, k_1, k_{-1}, and k_2, are calculated from the sum Σ and the product Π of the two exponential coefficients, $(X + Y)/2$ and $(X - Y)/2$, of eqn. 6:

$$\Sigma - \frac{\alpha}{1 + V} = k_{-1} + k_2 + \frac{V}{1 + V} k_1 \tag{20}$$

$$\Pi \frac{1 + V}{\alpha} = k_{-1} + k_2 + \frac{V}{\alpha} k_1 k_2 \tag{21}$$

where

$$\alpha = \pi^2 D/4L_1^2 \tag{22}$$

and

$$V = 1.801\ V'_G/V_G \tag{23}$$

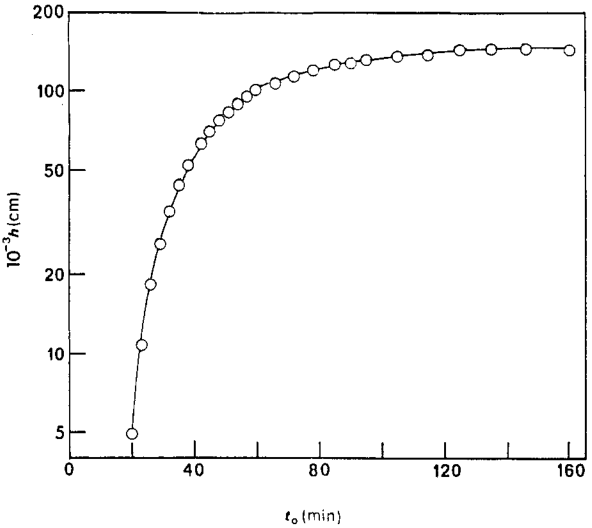

Fig. 6. Diffusion band obtained from the evaporation of ethanol into helium ($\dot{V}$ = 0.543 cm^3s^{-1}), at 336.8 K and 1 atm (from ref. 6).

At least two experiments are required, conducted with two different values of L_1 (*cf.* Fig. 2). Thus, a pair of equations like eqn. 20 is obtained, the subtraction of which gives the value of k_1, and this, being substituted back in one of them, yields the value of the sum $k_{-1} + k_2$. Also, a pair similar to eqn. 21 is obtained, and when these two are subtracted, the value of the product k_1k_2 is computed. This can be substituted back into one of the eqn. 21 pair to find $k_{-1} + k_2$ again. Having calculated k_1, $k_{-1} + k_2$ and k_1k_2, we can easily find k_1, k_{-1} and k_2. Now, using eqn. 12 we calculate k and K, and finally by means of eqn. 11 we compute K_s.

Instead of only two values of L_1, one can use more values of L_1 and plot the left-hand sides of eqns. 20 and 21 *vs.* $V/(1 + V)$ and V/α, respectively, to find k_1 and k_1k_2 from the respective slopes, and $k_{-1} + k_2$ from both intercepts. Finally, note that the V value can be changed by changing L_2 instead of L_1, a more difficult task, however, since the amount of the solid filling L_2 must also change.

Mass transfer connected with evaporation of liquids

Another rate process that can be studied with the arrangement of Fig. 2 is the evaporation of liquids[6]. For this purpose, no solute is injected, but L_2 is filled with a volatile liquid, the vapour of which diffuses into the carrier gas. The flow reversals again create sample peaks, similar to those of Fig. 1. This time, the diffusion band obtained has a different shape, as exemplified by Fig. 6. Mathematical analysis[6] permits the measurement of the diffusion coefficient, D, of the vapour from the liquid into the carrier gas, and at the same time the determination of the mass transfer coefficient, K_L, of the vapour across the liquid–vapour boundary, which can be termed the rate coefficient for the evaporation of the liquid. The equation derived[6] for a long-time approximation is

$$\ln (h_\infty - h) = \ln h_\infty - \frac{2(K_L L_1 + D)}{L_1^2} t_0 \qquad (24)$$

where h_∞ is the constant infinity height of the sample peaks after a long time, given by the relation

$$h_\infty = \frac{2K_L D c_0}{\upsilon(K_L L_1 + D)} \tag{25}$$

where υ denotes the linear velocity of the carrier gas, and c_0 the equilibrium concentration of the vapour at the temperature of the experiment.

A plot based on eqn. 24 is shown in Fig. 7. From the slope of such plots, which is $-2(K_L L_1 + D)/L_1^2$, and a theoretically calculated value of D, a first K_L value can be computed. This can be used to plot the short-time data according to a short-time approximation, which is

$$\ln\left[h\left(\frac{L_1}{2t_0^{1/2}} + K_L t_0^{1/2}\right)\right] = \ln\left[\frac{4K_L c_0}{\upsilon}\left(\frac{D}{\pi}\right)^{\frac{1}{2}}\right] - \frac{L_1^2}{4D} \cdot \frac{1}{t_0} \tag{26}$$

Fig. 7 shows an example. From the slope of the new plot, $-L_1^2/4D$, a first experimental value for D is found. This can be used with the slope of the first plot to find a better approximation for the K_L value, and this, in turn, to replot eqn. 26 for a better approximation of the D value. A further iteration is not usually required, because it does not improve the values of K_L and D.

Mass transfer coefficients for evaporation can be measured, not only in pure liquids, but also in liquid mixtures such as alcohol–water[7].

Measurement of activity coefficients in liquid mixtures

In a binary liquid mixture, such as alcohol–water, in which only the vapour of the one component (the alcohol) is recorded by a flame ionization detector, the height of the sample peaks is proportional to the concentration, c_0, of that component, in equilibrium with the liquid. This is given by rearrangement of eqn. 25:

$$c_0 = \frac{\upsilon h_\infty}{2}\left(\frac{L_1}{D} + \frac{1}{K_L}\right) \tag{27}$$

and can be calculated from it, since all quantities on the right-hand side are known from measurements described earlier.

If the same experiment is performed with the pure liquid component in vessel L_2, *e.g.* pure alcohol, it gives the respective concentration, $c_0^{\bullet}$, of the pure component. The ratio of the two concentrations is the activity, a_A, of the alcohol in the liquid mixture

$$\frac{c_0}{c_0^{\bullet}} = \frac{p}{\overset{\bullet}{p}} = a_A = \gamma_A X_A \tag{28}$$

assuming that the deviation of the solute vapour from ideal behaviour is small. The activity coefficient, γ_A, can be found[8] from c_0, $c_0^{\bullet}$ and the molar fraction in the liquid, X_A. From the activity coefficients measured and their variation with temperature, excess partial molar thermodynamic functions of mixing can be calculated[8].

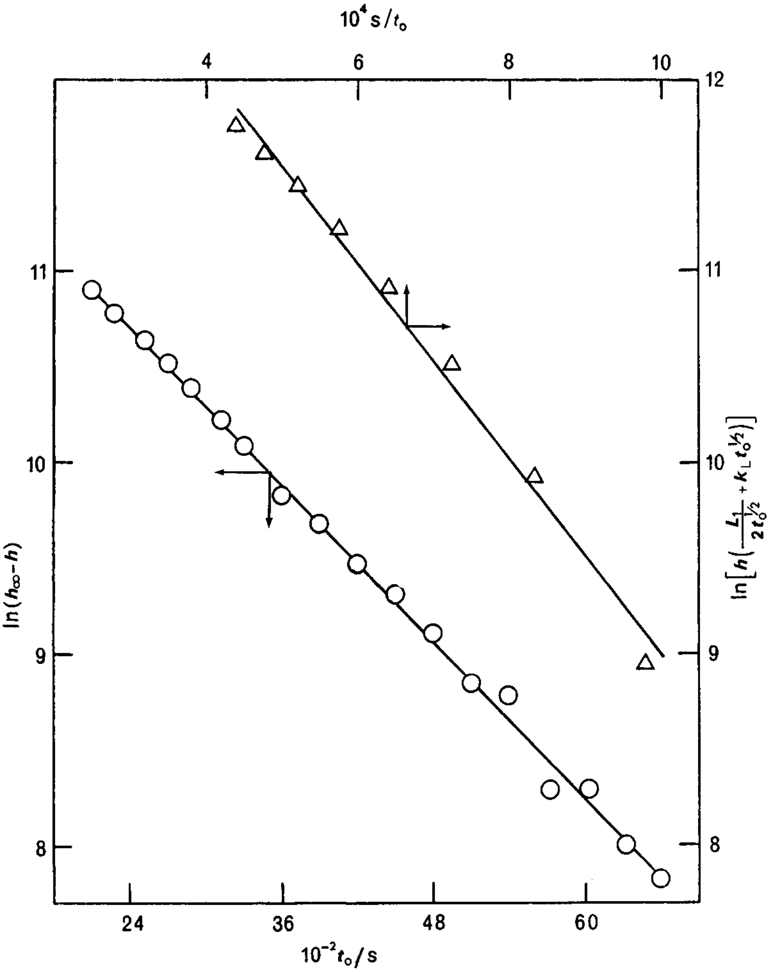

Fig. 7. Data from evaporation of methanol into helium at 322.5 K, plotted according to (○) eqn. 24 and (△) eqn. 26.

If both components of the liquid mixture are recorded by the detector system, the sample peaks can be separated into two-component sample peaks by filling the sampling column (*cf.* Fig. 2) with a suitable chromatographic packing material, or by using an additional separation column, as shown. Each series of sample peaks will obey eqns. 24–28, yielding diffusion coefficients, mass transfer coefficients, and activity coefficients for both components of the liquid mixture.

CONCLUSION

The RF-GC technique offers the possibility of determination of physico-chemical quantities that are not easily or accurately measured by the traditional methods of elution, frontal analysis, and displacement development. The new method uses a very simple experimental set-up based on a slight modification of a usual gas chromatograph. It is a relatively fast and sensitive technique, particularly for catalytic studies, where it can lead to the simultaneous determination of the adsorption rate constant of the reactant on the catalyst, the reaction rate constant on the catalyst's surface, and the desorption rate constant from the catalyst; from these rate constants, the partition ratio, the partition coefficient, and the overall mass transfer coefficients of the reactant and/or the product(s) can also be computed. In the absence of a chemical reaction, the method can be useful for determining all the above physicochemical quantities other than the reaction rate constant[3]; in the absence of adsorption–desorption phenomena, only the external porosity of the solid bed can be determined; and in the absence of a solid, the diffusion coefficient of the solute in the carrier gas is found[1].

If a liquid is used in place of the solid, the mass transfer and the partition coefficient across the gas–liquid boundary[5–7], as well as the activity coefficient of a solute dissolved in the liquid, can be determined[2,8].

Experiments on the practical applications of eqns. 4, 5, 17, 18, 20 and 21 are well under way.

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