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Studies of diffusion and other rate processes by gas chromatography

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Abstract
Physicochemical measurements by gas chromatography are reviewed, and the carrier gas flow-rate perturbation is introduced as the stopped-flow and the reversed-flow techniques. The general principles of the latter are presented, and then the latest theoretical developments and applications for measurement of rate coefficients and distribution constants are given. These include gas diffusion coefficients, obstructive factors and external porosities in solid beds, diffusion coefficients of gases in liquids, interfacial gas-liquid resistances to mass transfer, and the simultaneous determination of adsorption, desorption and reaction rate constants of gases on solids.

INTRODUCTION

The quantitative theory of gas chromatography is based on a first-order conservation equation derived under two assumptions: (1) Axial diffusion of the solute component in the gas phase is negligible, which is not unrealistic for high enough linear velocities, and (2) equilibration of the solute between the two phases is instantaneous. The solution of this equation is usually based on: (1) A linear isotherm, (2) the initial condition that, at time = 0, the concentration of the solute vapour in the gas phase and in the stationary phase is zero along the whole column length, and (3) an input distribution described by Dirac's delta function. This solution predicts, for the elution curve of a solute component at the exit of the column, a very sharp and narrow peak at time equal to the retention time t_R.

In spite of that, the elution curve has the typical appearance of an elution chromatogram obtained after a pulse injection of a single solute, namely, it is broadened compared to that predicted by the theory, due to the so-called *broadening factors*. The most important of these factors are related to non-fulfilment of the assumptions under which the conservation equation was derived and solved, namely: (1) Non-negligible longitudinal diffusion in the gas, (2) non-instantaneous equilibration of solute between the mobile and the stationary phases, (3) non-linear isotherm, and (4) an unsharp input distribution. Summing up the variances due to the first two broadening factors and dividing them by the column length, one translates them to an apparent height equivalent to a theoretical plate, analogous to that used in fractional distillation. Adding now a term A to account for flow-independent contributions, we get the well-known van Deemter equation.

PHYSICOCHEMICAL MEASUREMENTS BY GAS CHROMATOGRAPHY

Although the broadening factors are very annoying in chemical analysis by chromatography, no physicochemical measurement by traditional methods of chromatography would be possible, if these factors were absent. It is well known today that gas chromatography offers many possibilities for physicochemical measurements, some of which lead to very precise and accurate results with relatively cheap instrumentation and a very simple experimental setup. They are widely used today, a fact emphasized by the edition of books (refs. 1,2) dealing only with such physicochemical measurements. Until a few years ago these measurements were exclusively based on the traditional techniques of elution development, frontal analysis, and displacement development, under constant gas flow rate. Studies on diffusion and rate processes were

based on the broadening factors and embraced by van Deemter equation. It was through the coefficients B and C of this equation that most diffusion coefficients in gases and liquids, as well as the coefficients of other rate processes, were calculated. Chapter 4 of ref. 3 and chapter 12 of ref. 1 describe all the above in detail. An extensive table of diffusion coefficients measured by the chromatographic broadening techniques, together with the underlying theory, was published by Maynard and Grushka (ref.4). Another approach to extract physicochemical parameters from the elution peaks is based on the analysis of the statistical moments of the peaks (ref.5). Other physicochemical measurements are adsorption studies relating to determination of adsorption isotherms and thermodynamic parameters for adsorption. Details of this application can be found elsewhere (ref.6). Here it is worthmentioning that the simple observation of a chromatographic elution peak gives qualitative information about the shape of the adsorption isotherm. Some advances on determination of gas--solid adsorption isotherms by the so-called step and pulse method have been made by Guiochon and his co-workers (refs. 7,8). Also, Jaulmes et al. (refs. 9-11) made a thorough study of peak profiles in non-linear gas chromatography.

The carrier gas flow-rate perturbation

Although there would be no gas chromatography without a mobile gas phase, i.e. a carrier gas, its linear velocity v or volume flow-rate $\dot{V}$ remains constant throughout a single experiment in most gas chromatographic studies, or analytical applications. Thus, this magnitude is usually treated as an adjustable parameter of gas chromatographic equations. Following, however, the widespread use of temperature programming in gas chromatographic analysis, the programming of the carrier gas inlet pressure, and hence its flow-rate, had also been reported and reviewed (refs. 12,13). In spite of the development of various programming modes (e.g., step programming, continuous linear and non-linear programming), and the existence of commercial units permitting the general use of the technique, flow (pressure) programming has not been used to extract information of a physicochemical nature in gas chromatography. Its uses have been limited to analytical applications.

Except flow programming, there are two other kinds of flow-rate perturbations imposed on the carrier gas. These are *the stopped-flow* and *reversed-flow* technique. Both are very simple to apply and consist in either *stopping* the carrier gas flow for short time intervals, or *reversing* the direction of its flow from time to time. Experimentally, this is most easily done by using shut-off valves in the first technique and a four- or six-port gas sampling valve in the second. Thus, sophisticated mechanical, pneumatic or other special systems are not required as in flow programming gas chromatography. To the best of our knowledge, the first who used the stopping of the carrier gas flow for varying time periods were Knox and McLaren (ref.14), with the purpose of producing extra broadening of the chromatographic peaks for measuring gas diffusion coefficients. However, the stopped-flow method was substantially introduced in 1967 by Phillips and his co-workers (ref. 15) to study chemical reactions on the chromatographic column. The reversed-flow technique was introduced in its preliminary form in 1980 (ref.16). Both these techniques have solely been used for physicochemical measurements and constitute the object of ref.17. The rest of this paper will be devoted to the latest theoretical developments and applications concerning measurement of rate coefficients and distribution constants for diffusion and other rate processes by Reversed-Flow Gas Chromatography (RF-GC).

The reversed-flow technique

General principles. Instead of basing physicochemical measurements on retention volumes of elution peaks, their broadening and their shape distortion, due to the physicochemical processes under study, one can perform such measurements accurately and easily if the chromatographic column, being at a steady-state condition , is perturbed so that it deviates from equilibrium for a short time interval and then is left to return to the original state. This is analogous to relaxation techniques. The perturbation chosen was the change in the direction of flow of the carrier gas, and it was done by using a four- or six-port valve connected as shown in Fig. 1. The carrier gas is turned to flow in the opposite direction either for a long time, or only for a short time interval t'(10-60 s), smaller than the gas hold-up time of a solute in the sections ℓ' and ℓ of the sampling column. Then, it is restored to its original direction of flow. The question arising is what would we observe on the chromatogra-

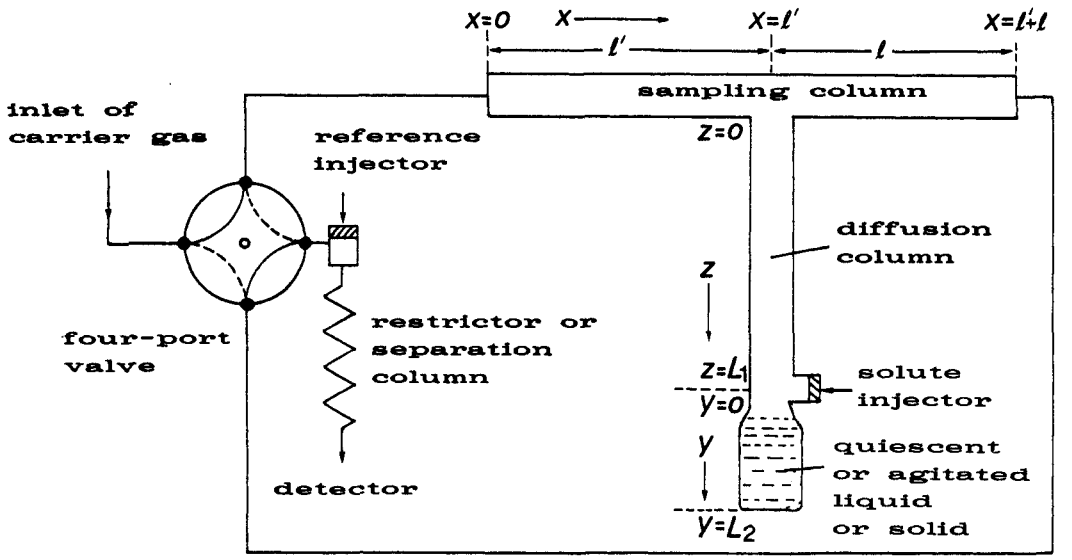

Fig. 1. Schematic representation of columns and gas connections for studying diffusion and other rate processes by Reversed-Flow Gas Chromatography.

phic elution curve? If pure carrier gas were passing through the sampling column, nothing would happen on reversing the flow. But if a solute comes out of the diffusion column L_1 as the result of its diffusion into the carrier gas, the flow reversal records its concentration in the junction $x = \ell'$. This concentration recording has the form of extra chromatographic peaks (*sample peaks*), superimposed on the otherwise continuous detector signal. An example is given in Fig. 2. The peaks can be made as narrow as we want, since the width at their half-height is equal to the duration t' of the backward flow of the carrier gas through the empty sampling column.

The sample peaks are predicted theoretically by the so-called chromatographic sampling equation, which describes the concentration-time curve of the sample peaks created by the flow reversals, and has been derived (refs. 17, 18) using mass balances, rates of change etc., and integrating the resulting partial differential equations under given initial and boundary conditions. It gives the concentration of the solute at the junction of the sampling and the diffusion column $x = \ell'$ of Fig. 1 for different values of the time variable. The sampling equation predicts the sample peaks theoretically and its predictions coincide with the experimental sample peaks shown in Fig. 2, the only difference being that the peaks predicted are square, whereas those actually found are not square owing obviously to non-ideality.

The area under the curve or the height h from the continuous signal of the sample peaks, meausred as a function of time, is proportional to the concentration of the substance under study at the junction $x = \ell'$ of the sampling cell. Therefore, it can be used for the determination of the rate or equilibrium coefficient of the phenomenon responsible for this concentration. The relation between h and $c(\ell', t_0)$ where t_0 is the time from injection of a solute, is given by the equation

$$h \approx [2c(\ell', t_0)]^m \qquad (1)$$

where m is the response factor for the detector, being unity for a flame ionization detector. There remains $c(\ell', t_0)$, and therefore h, to be found theoretically as an analytic function of time for every phenomenon under study. Then, measuring h experimentally as a function of time, one can construct what is termed a *diffusion band*. Examples are shown in Fig. 3. It is the shape and the distortion of these bands, rather than of the old elution peaks, that lead to the calculation of various physicochemical parameters. In most cases, this is done in a simple, though accurate

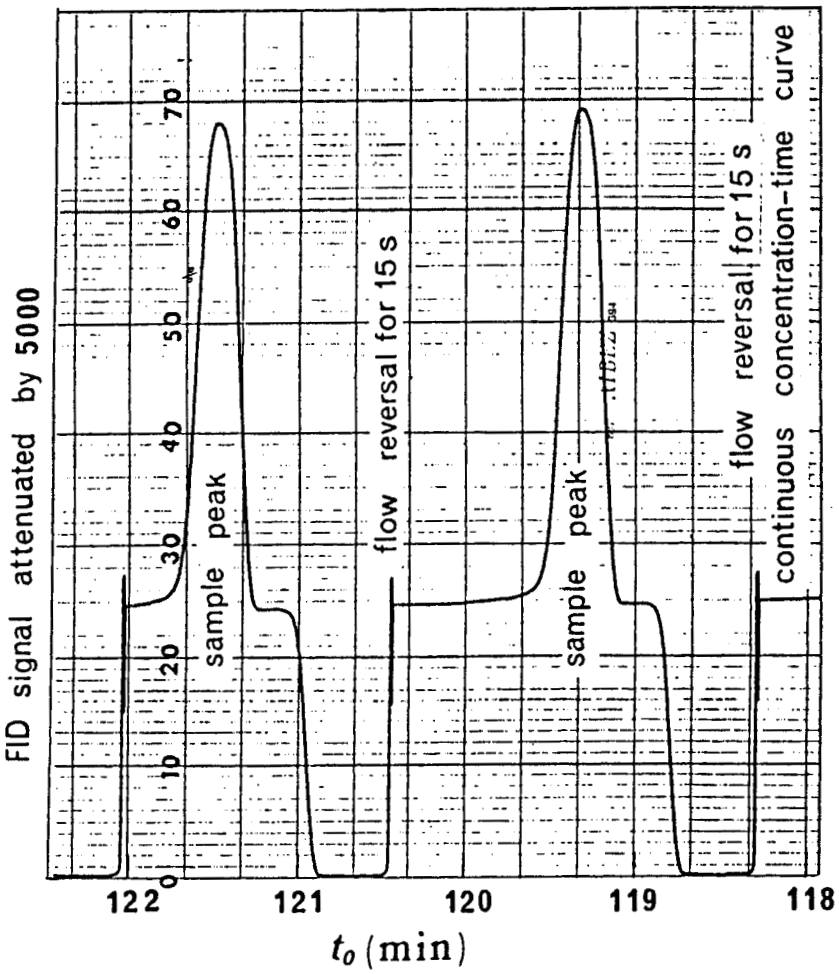

Fig. 2. A reversed-flow chromatogram with two sample peaks due to the diffusion of propene into nitrogen (corrected volume flow-rate $\dot{V} = 0.36$ cm^3 s^{-1}), at 324.7 K and 1 atm (Fig. 2 of reference 26, reproduced with permission of the American Chemical Society).

way, using cheap conventional gas chromatography instrumentation, without the need of doing any kind o proper gas chromatography operations and measurements.

Gas diffusion coefficients and related parameters. The first example of the application of RF-GC method is provided by the accurate measurement of gaseous diffusion coefficients (refs. 18-20), without bothering about the main difficulties associated with the traditional gas chromatographic methods, e.g., the disadvantages inherent in operation at low flow-rates, the difficulty of correctly allowing for the instrumental spreading of the chromatographic band outside the column, to mention only a few difficulties. The same and other problems are met in the determination of the obstructive factor γ, since it is the product $\gamma \mathcal{D}_G$ which is usually determined from plate height measurements in packed columns, employing a range of carrier gas velocities around the optimum value. Then, γ is usually found by assuming a theoretical value for the diffusion coefficient $\mathcal{D}_G$. An additional disadvantage of this method is that the experimental data are fitted to the van Deemter equation, assumed correct.
The arrested elution method of Knox and McLaren (ref.14) bypasses some of the experimental and theoretical difficulties of the standard continuous elution method, but it still lies heavily on the time of passage along the column and the accurate measurement of the outlet elution velocity.

The RF-GC technique does not have any of the disadvantages connected with the carrier gas flow and the instrumental spreading of the chromatographic bands, because

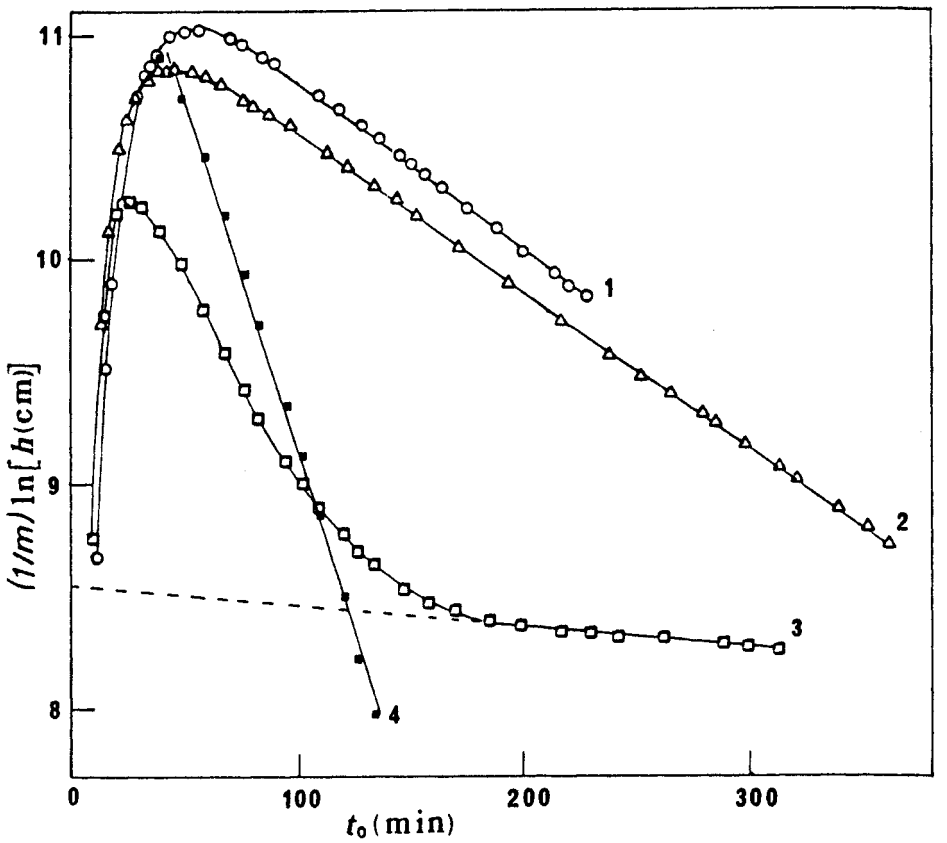

Fig. 3. Diffusion bands obtained with 1 cm^3 of butane injected into the diffusion column L_1 at 327 K. Curve 1 was obtained with an empty L_2 vessel, curve 2 with L_2 containing 10.4 cm^3 water, and curve 3 (plotted as $1+\ln h$) with L_2 containing 10.4 cm^3 hexadecane. Line 4 (plotted as $2+\ln h$) was obtained by subtracting from the experimental points of curve 3 after the maximum the points corresponding to the extrapolated (dashed line) last linear part of it. (Fig. 3 of ref. 26, reproduced with permission of the American Chemical Society).

the phenomena being studied are taking place inside the diffusion column L_1 and the vessel L_2 and no carrier gas flows through these vessels. The gas flows only through the column $\ell' + \ell$, and is merely used as a means for repeated sampling of the concentrations at the point $x = \ell'$, i.e., at the exit of the column L_1. This is done with the help of the narrow and symmetrical sample peaks mentioned before (cf. Fig. 2), without measuring their elution velocity, or the carrier gas flow-rate, provided it is steady. The experimental data recorded are the height h of the sample peaks in arbitrary units (say in cm), and the time t_0 elapsing between the solute injection and the respective flow reversal, the duration of the latter being always the same (say 30 s). If one plots $(\ln h)/M$ against t_0, a diffusion band is obtained, like curves 1 and 2 of Fig. 3. An obvious difference between the old elution gas chromatography and the RF-GC is that in the former longitudinal gaseous diffusion currents are parallel with the chromatographic current and the diffusion coefficients $\mathcal{D}_G$ or $\gamma\mathcal{D}_G$ are extracted from this mixed current by mathematical analysis. In the second method, the diffusion current is from the outset physically separated from the chromatographic current, and this is done by placing the diffusion process perpendicular to the chromatographic process. A diffusion band, rather than an elution band, is now mathematically analyzed to yield diffusion coefficients, or other physicochemical parameters from its distortion, in the same way that a distorted elution chromatographic band permits similar calculations. It must be pointed out that instrumental or other spreading of the sample peaks does not influence the results.

The mathematical function describing the diffusion band can be derived for two general situations: (1) When the gaseous solute injected at the lower end of the diffusion column L_1 (cf. Fig.1) does not interact in anyway with the solid or liquid materials filling column L_1 and/or vessel L_2 ; (2) when the injected solute interacts physically or chemically with the filling materials. For gas diffusion coefficients and related parameters measurements, situation (1) applies and the diffusion band has been derived (ref.21) for three subcases: (a) When both, column L_1 and vessel L_2, are empty of any solid or liquid material; (b) when both, column L_1 and vessel L_2, are packed with a solid material that does not interact with the injected solute; (c) when L_1 is empty and only L_2 is packed with the above solid. Case (c) gives a general solution for $c(\ell',t_o)$ comprising (a) and (b) as special cases. This solution is a sum of three exponential functions of time, $\exp(-r_i\beta t_o)$, where $\beta = \pi^2 \mathcal{D}_G / L_1^2$ and $r_i (i=1,2,3)$ are the roots of an algebraic equation incorporating the geometrical characteristics of the cell, like the lengths L_1 and L_2, and the ratio of their gaseous volumes. If the solution is substituted for $c(\ell',t_o)$ in eqn (1), the height h of the sample peaks as a function of time is obtained, i.e., the function describing the diffusion bands (cf. Fig.3), when the column L_1 is empty and the vessel L_2 is packed with a solid not interacting with the injected solute. The same equation describes the diffusion band when column L_1 and vessel L_2 are both empty of any solid material or both packed with non-reacting material. The roots r_1, r_2 and r_3 differ considerably from one another, making the exponential coefficients $-r_1\beta$, $-r_2\beta$ and $-r_3\beta$ of the three functions very different, and therefore easily determinable from the experimental diffusion band. For example, the absolutely smaller root, say $-r_3$, describes the diffusion band at long enough times, i.e., after its maximum (cf. Fig.3), when the other two exponential functions have already decayed to negligibly low values. It corresponds to the last linear part of the band, as the latter is a semilogarithmic plot. The slope of this part gives $-r_3\beta$ and, using the relation $\beta = \pi^2 \mathcal{D}_G / L_1^2$, the diffusion coefficient $\mathcal{D}_G$ of the solute in the carrier gas is easily calculated. Thus, injecting a small gaseous volume (0.5 to 1 cm^3 at atmospheric pressure) of a solute at the lower end of the diffusion column (cf. Fig.1), and then performing repeated flow reversals for 10-60 s, we obtain a series of sample peaks (cf. Fig.2). The height h of these peaks from the ending baseline are plotted as $(1/m)\ln h$ vs. the time of each reversal t_o measured from the injection moment, when a diffusion band is obtained (cf. Fig.3). The slope of the last linear part of this plot gives the diffusion coefficient $\mathcal{D}_G$ of the injected solute into the carrier gas.

Results of diffusion coefficient measurements, using this method, in binary and multicomponent gas mixtures, are collected in ref. 17 (pp. 132-140). The precision of the method, defined either as the relative standard deviation (%) or as the relative standard error (%) associated with each value, is better than 1% in most cases. Comparison of the diffusion coefficients found with those calculated theoretically, permits the calculation of the method's accuracy. With the exception of two pairs containing methane as solute and three values for the pair C_2H_4/He, the accuracy is better than 7.5% in 55 cases. Finally, a comparison with the values determined by broadening techniques (ref.4) leads to the conclusion that, with the exception of C_2H_4/N_2, the values of diffusion coefficients determined by the reversed-flow method are closer to the theoretically calculated values than are the experimental values found by broadening techniques, under similar conditions of temperature and pressure. By plotting $\ln \mathcal{D}_G$ versus $\ln T$, one can calculate the exponent n in the relationship $\mathcal{D}_G = AT^n$, to which all theoretical and semiempirical equations lead for the dependence of $\mathcal{D}_G$ on T. The reversed-flow method for measuring gas diffusion coefficients can be extended to simultaneous determination of diffusion coefficients in multicomponent gas mixtures (ref.20), an experimental problem which has practical, as well as theoretical importance.

Determination of the obstructive factor, γ. This factor is determined from two experimental plots at the same temperature, using the same cell: (a) A diffusion band with both the diffusion column L_1 and the vessel L_2 empty of any solid, and (b) a diffusion band with both L_1 and L_2 packed with the solid material under study, provided that a gaseous solute, that is not sorbed by the solid or does not interact with it in any way, is used in the diffusion experiment. If the slopes of the last linear parts after the maximum of the above bands are b (empty) and b (packed), their ratio gives directly the value of hte obstructive factor, without any other measurement or correction (ref.21).

Determination of the external porosity, ε. One more diffusion band, in addition to those described under (a) and (b) above, is required for this determination: (c) a band obtained with the diffusion column L_1 empty and vessel L_2 packed with the solid under study. The steps to be taken for calculating the porosity can be found in the original paper (ref. 21).

Other related parameters. In another work (ref.22) it was shown that, in the same experiment, one can determine, together with the diffusion coefficient, relative molar responses of the solutes to the thermal conductivity detector, collision diameters and critical volumes. Following the determination of diffusion coefficients simply and accurately, a treatment of them was undertaken (ref. 23) to successfully calculate Lennard-Jones potential parameters and parachor values.

Resistance to mass transfer and other rate processes. The RF-GC technique was applied to measure, not only parameters related to longitudinal diffusion, but also quantities pertaining to the second broadening factor, namely, non-instantaneous equilibration of solute between the mobile and the stationary phases. Upon this, one bases the determination of liquid diffusion coefficients, the interfacial resistance to mass transfer, and gas-solid adsorption/desorption kinetics. These measurements are made when the injected solute interacts physically or chemically wih the liquid or solid materials filling column L_1 and/or vessel L_2. Such interactions distort, not the sample peaks which remain narrow and symmetrical, but the diffusion band changing its shape and/or its slope (cf. Fig.3, curves 1,2 and 3). It is this distortion which is used to measure the above parameters. The function for the diffusion band with a quiescent liquid in vessel L_2 is a sum of two exponential functions of time (ref.24). From the values of the two exponential coefficients, together with the values of the respective pre-exponential factors, determined by means of a non-linear regression analysis computer programme, one can calculate the diffusion coefficient of the injected gas into the liquid, $\mathcal{D}_L$, and its partition coefficient, K, between the liquid and the carrier gas. Recently, this study was extended to chemical interactions of the dissolved gas with the liquid, being a solution of other substances (ref.25).

With an agitated liquid in L_2, the overall mass transfer coefficients of the injected solute in the gas phase, K_G, and in the liquid phase, K_L, can be determined. The function for the diffusion band has exactly the same form as with a quiescent liquid, but the physical content of the exponential coefficients and the pre-exponential factors are different. From these, K_G, K_L and K are found (ref.26). The inclusion of a chemical reaction in an agitated solution has also been studied (ref.25).

In the presence of a reactive solid in vessel L_2, adsorption/disorption kinetics, gas-solid chemical reactions and heterogeneous catalysis can be investigated, leading to the determination of rate constants for adsorption (k_1), disorption (k_{-1}) and for chemical reaction (k_2) (refs.27-30).

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