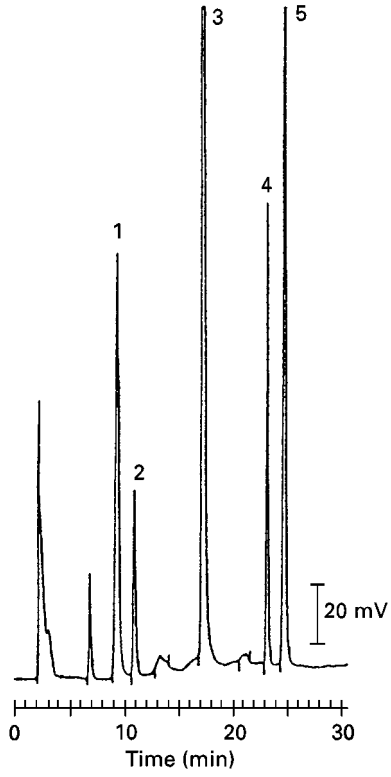

Figure 8 Coupled-column analysis of antiepileptic drugs in serum. Precolumn: 25 mm × 4 mm i.d., LiChrospher RP-18 ADS (particle size, 25 μm); analytical column: 250 mm × 4 mm i.d., LiChrospher 60 RP-Select B (particle size, 5 μm); loading mobile phase: 0.5 M monobasic sodium phosphate (pH 4.0) for 0 min at 0.5 mL min^{-1}; transfer mobile phase: 5 : 95 (v/v) acetonitrile–water for 5 min at 0.5 mL min^{-1}; separation mobile phase: acetonitrile–water with a linear acetonitrile gradient from 5% to 34% in 34 min at 0.5 mL min^{-1}; detection: UV absorbance at 205 nm; sample: 100 μL of analyte-spiked serum. Peaks: 1 = ethosuximide (10.3 nmol), 2 = primidone (1.8 nmol), 3 = phenobarbital (6.6 nmol), 4 = carbamazepine (1.3 nmol), 5 = phenytoin (2.5 nmol). (Reproduced with permission from Boos K-S and Rudolphi A (1997) The use of restricted-access media in HPLC. Part I. Classification and review. *LC–GC* 15: 602–611.)

drugs on a conventional analytical reversed-phase HPLC column. The precolumn (25 mm × 4 mm i.d.) packed with one of ISRP materials (particle size, 25 μm) can tolerate 2000 injections or more of 50 μL of human plasma.

Future Trends

Since the invention of the ISRP–GFF materials, various RAM materials have been developed for direct serum injection assays of drugs with single- and coupled-column modes. However, they are lacking in selectivity because hydrophobic or ion-exchange ligands are used as the analyte binding ligands. In the future, more selective ligands such as immunoaffinity or chemoaffinity ligands or molecularly imprinted polymers have the potential to further improve selectivity and sensitivity in bioanalysis.

Further Reading

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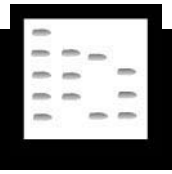
REVERSED-FLOW GAS CHROMATOGRAPHY



N. A. Katsanos, University of Patras, Patras, Greece
F. Roubani-Kalantzopoulou, National Technical University of Athens, Zografou, Greece

Introduction

Gas chromatography (GC) is a technique that is used not only to separate substances from each other, but also to 'separate' physicochemical quantities by

measuring the value of one in the presence of another, e.g. the rate of a chemical reaction in the presence of diffusion phenomena. Several books, reviews and original papers have been published dealing with physicochemical measurements by GC. Some of the properties measured pertain to the moving gas phase, e.g. diffusion coefficients of solutes into the carrier gas, and the emphasis is on determining the properties of the solutes. However, the majority of physicochemical properties studied by GC relate to the stationary phase and its interaction with well-known probe solutes, e.g. the catalytic properties of the solid stationary phase for reactions between gases. This is termed inverse gas chromatography and has the stationary phase of the system as the main object of investigation. The procedures employed are the same as those used in direct GC, but the results are used to derive properties of the stationary phase. The main source of information obtained experimentally is the broadening of the chromatographic elution peaks, mainly due to nonfulfilment of the assumptions under which the central chromatographic equation is derived, namely: (1) negligible axial diffusion of the solute gas in the chromatographic column; (2) linearity of the distribution isotherm; and (3) instantaneous equilibration of the solute between the mobile and the stationary phase. Classical chromatographic systems are not usually in true equilibrium during the retention period, so that extrapolation to infinite dilution and zero carrier gas flow rate is required to approximate true equilibrium parameters.

Another approach to extracting information about the physicochemical properties of the stationary phase from the elution peaks is based on the analysis of the statistical moments of the peaks. Both of these approaches, i.e. measurement of the broadening of the peaks and analysis of their statistical moments, are dynamic measurements because of the convective movement of the carrier gas inside the chromatographic column. In many cases achieving an acceptable precision for the quantities determined is a difficult, if not impossible, task. The reversed-flow gas chromatography (RF-GC) technique offers an additional route from experimental measurements to the properties of the stationary phase, as described below.

Physical Description and Experimental Arrangement of the System

Although there would be no GC without a mobile gas phase, i.e. a carrier gas, in most studies its flow rate remains constant throughout a single experiment. The magnitude of the flow rate is usually treated as an adjustable parameter. There are, however, two flow rate perturbation methods, the *stopped-flow* and the *reversed-flow* techniques. Both are very simple to apply and consist of either *stopping* the carrier gas flow for short time intervals, or *reversing* the direction of its flow from time to time. Experimentally, this is easily done by using shut-off valves in the first technique and a four-port valve in the second, as shown in **Figure 1**. By switching the valve from the position shown by the solid lines to that indicated by the broken lines, the carrier gas, flowing initially from end D_1 to D_2 of the sampling column, now flows in the opposite direction, i.e. from D_2 to D_1. The sampling column is a usual 1/4 in (6.35 mm) stainless-steel or glass chromatographic tube of total length $l' + l$ ranging from 40 + 40 cm to 100 + 100 cm, either straight or bent and empty of any solid or liquid material.

The system also contains two other columns: a separation column and a diffusion column.

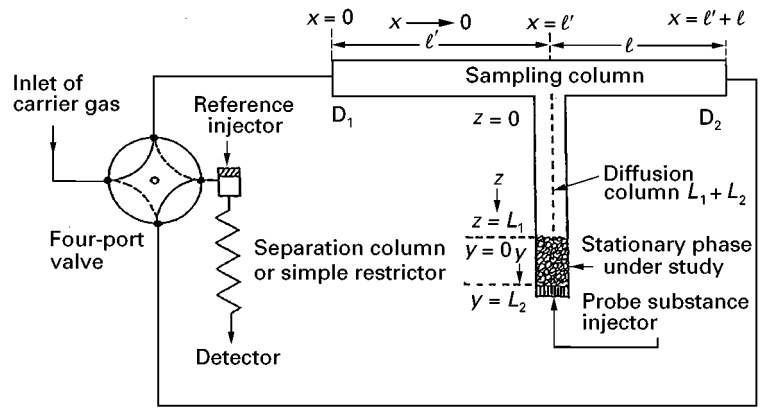


Figure 1 Schematic representation of columns and gas connections showing the principle of RF-GC. Reprinted from *Journal of Chromatography A* 775; 1997, 211–224, with permission from Elsevier Science.

A separation column of any suitable diameter and length is placed before the detector. The carrier gas flows normally in one direction through this column without any reversal, as shown by the gas connections of the valve. The separation column is filled with ordinary stationary-phase material and is used to effect the separation of two or more substances reaching the valve from the sampling column. A reference injector at the inlet end of the separation column is used for identification purposes. If only one substance reaches the detector, a simple restrictor suffices.

A diffusion column of the same diameter as the sampling column and length 30–100 cm is connected perpendicularly at about the middle of the sampling column; it is closed at the other end, and therefore no carrier gas flows through it.

The whole system of the three columns described above is placed within the oven of an ordinary gas chromatograph, with the columns and the connection tubes properly bent. The question naturally arising is: what happens when the direction of the carrier gas flowing through the sampling column is reversed, if it is not reversed in the separation column and there is no flow at all through the diffusion column? If the diffusion column does not contain any stationary phase, but only stagnant carrier gas, nothing would happen. If a probe gas is introduced through the injector into the empty diffusion column, the repeated flow reversals of duration 10–100 s would create narrow and symmetrical peaks like those shown in **Figure 2** (*sample peaks*). From the height H of these peaks in arbitrary units, measured as a function of time, t, that elapses between the injection of probe substance and the respective flow reversal, the diffusion coefficient of the substance into carrier gas can be calculated. Finally, if a certain length L_2 (3–12 cm) of the diffusion column is filled with a stationary phase, the *diffusion band* obtained by plotting H or $\ln H$ against t is different from before, owing to the interactions of this phase with the gaseous probe. This is a way of separating the pure chromatographic process from the rate or equilibrium processes involving the stationary phase.

The RF-GC method was first introduced in 1982, after preliminary studies on heterogeneous catalysis. It was later developed for measuring various physicochemical quantities pertaining to both, substances contained in the moving gas phase and stationary-phase behaviour. The technique was reviewed in 1988 and again more recently. It does not have any of the disadvantages connected with the carrier gas flow and the instrumental spreading of the chromatographic bands, because the phenomena being studied take place inside the diffusion column $L_1 + L_2$ (cf. Figure 1), with no carrier gas flowing through it. The flow reversals are used merely as a means for repeated sampling of the concentrations at the point $x = l'$, i.e. at the exit of the section L_1. This sample is transported to the separation column (containing another stationary phase for separation purposes only), and then to the chromatographic detector, without measuring the elution velocity of the sample peaks or the carrier gas flow rate, provided it is steady. An obvious difference between conventional elution gas chromatography and RF-GC is that in the former longitudinal gaseous diffusion currents are parallel to the chromatographic current, while in the second method diffusion is, from the outset, physically separated from the chromatography by placing the diffusion process perpendicular to the chromatographic process.

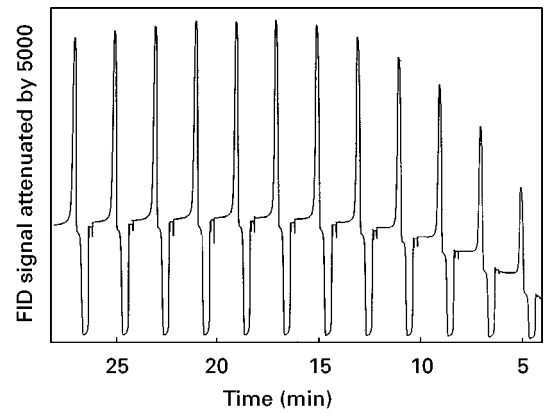


Figure 2 Sample peaks of propene in nitrogen carrier gas, with section L_2 (9.6 cm) containing 0.67 g TiO_2, at 323.2 K. FID, flame ionization detector.

Mathematical Models

Inverse gas chromatography has been used for studying many properties of solids, such as the glass transition of polymers, their crystallinity and melting point, and the thermodynamics of their solutions. The RF-GC technique is a useful tool for inverse chromatographic studies, particularly when gas–solid interfaces are involved. Several such studies have been published. Here a short outline of its possibilities is given using some characteristic examples. Take for instance the determination of diffusion parameters, adsorption–desorption rate constants and isotherms, and catalytic rate constants of some gaseous probes on typical solid catalysts, supported or not. All these physicochemical properties can be determined simultaneously in a single gas chromatographic experiment lasting a few hours. The experiment resembles those conducted with a plug flow reactor, but without a gas flowing through it, as Figure 1 shows. It is only gaseous diffusion of the reactant(s) and product(s) that

causes the movement of these substances through the solid bed along the length coordinate y, and then along length coordinate z to the junction $x = l'$ of the sampling column. Two diffusion coefficients of the probe molecules are involved in these movements: D_1 in section L_1 and another D_2 in section L_2 influenced by the bed obstruction factor γ. These are taken care of implicitly in the mathematical analysis, without using the actual values of D_1 and D_2 from the literature.

The mass balance equation of the probe reactant A in the region y (cf. Figure 1) filled with the stationary phase under study is:

$$\frac{\partial c_y}{\partial t} = D_2 \frac{\partial^2 c_y}{\partial y^2} - k_{-1} \frac{a_s}{a_y} (c_s^* - c_s) \qquad [1]$$

where c_y is the gaseous concentration of the probe A in region y; t is the time measured from the moment of injection of A as an instantaneous pulse (delta function, δ) onto the solid bed, at $y = L_2$; k_{-1} is the rate constant for desorption of A from the bulk solid; a_s is the amount of stationary phase per unit length of solid bed; a_y is the cross-sectional area of the void space in region y; and c_s, c_s^* are the concentrations of A adsorbed on the solid at time t and at equilibrium, respectively.

An analogous mass balance equation is valid for the gaseous concentration c_z of A in diffusion column z:

$$\frac{\partial c_z}{\partial t} = D_1 \frac{\partial^2 c_z}{\partial z^2} \qquad [2]$$

It is noteworthy that the usual convective terms $-v(\partial c_y/\partial y)$ and $-v(\partial c_z/\partial z)$ of gas chromatographic mass balances (v being the average linear velocity of the carrier gas) are missing from both the above equations, since no carrier gas flows through column sections y and z. This makes the solution of differential eqns [1] and [2] much easier, and all disadvantages connected with the carrier gas flow mentioned before disappear. No 'competition' between v and rate processes on the gas–solid interface takes place. No corrections of v are required, not even the measurement of its approximate value is needed, except only to calculate a calibration factor g which is needed in the isotherm determinations. Both eqns [1] and [2] have the form of Fick's second law for diffusion in one dimension, the first equation being modified only by inclusion of the far right-hand side term describing the overall rate of adsorption of the probe gas A onto the surface of the stationary phase.

The system of partial differential equations, eqns [1] and [2], is complemented by:

1. the rate of change of the adsorbed concentration c_s:

$$\frac{\partial c_s}{\partial t} = k_{-1}(c_s^* - c_s) - k_2 c_s \qquad [3]$$

now including a rate constant k_2 of a possible first- or pseudofirst-order surface reaction of the adsorbed substance A; and

2. a local experimental adsorption isotherm:

$$c_s^* = \frac{n_s}{a_s}\,\delta(y - L_2) + \frac{a_y}{a_s}\,k_1 \int_0^t c_y(\tau)\,\mathrm{d}\tau \qquad [4]$$

where n_s is the initially adsorbed amount of A, k_1 is a dynamic adsorption rate constant, and τ is a dummy variable for the time t. The adsorption equilibrium is local and instantaneous, the adsorption parameter k_1 transforming the area under the c_y versus t curve into c_s^*.

Equation [4] describes the actual experimental isotherm, not necessarily a linear one, without the help of an *a priori* isotherm equation (Langmuir, BET, etc.). The graphical experimental isotherm can be constructed in detail if desired, but this is not necessary. Only the basic definition by eqn [4] suffices to incorporate the exact isotherm into the mathematical calculations. The nonlinearity in general is automatically taken into account.

The use of a dummy variable τ for the time t simply facilitates the notation in the integral of eqn [4] without any special meaning attached to τ.

The system of eqns [1]–[4] is solved under the initial conditions:

$$c_z(0, z) = 0, \qquad c_y(0, y) = \frac{n_A}{a_y}\,\delta(y - L_2)$$

and:

$$c_s(0, y) = 0 \qquad [5]$$

where n_A is the total amount of A injected. The solution is effected by using double Laplace transforms of all terms with respect to time and length coordinates, under the given initial conditions and the isotherm eqn [4], and subject to the appropriate boundary conditions at $z = 0$, $z = L_1$ and $y = L_2$. By means of various approximations this leads to the expression:

$$H^{1/M} = g\,c_z(0, t) = A_1 \exp(B_1 t) + A_2 \exp(B_2 t) + A_3 \exp(B_3 t) + A_4 \exp(B_4 t) \qquad [6]$$

where H is the height (in arbitrary units, say cm) of sample peaks measured from the ending baseline of the chromatogram, like that of Figure 2, M is the response factor of the detector ($M = 1$ for the FID), and g is a calibration constant for the detector, transforming cm of H to mol cm^{-3} of the concentration $c_z(0, t)$ of probe substance A at $z = 0$ and time t.

A steady-state approximation for c_s in eqn [3], $dc_s/dt = 0$, leads to:

$$H^{1/M} = gc_z(0, t) = A_5 \exp(B_5 t) + A_6 \exp(B_6 t) + A_7 \exp(B_7 t) \quad [7]$$

instead of eqn [6].

The detailed assumptions on which the derivation of eqns [6] and [7] was based have been published (see Further Reading).

It is seen from eqns [6] and [7] that $c_z(0, t)$, i.e. the gaseous concentration of the probe A at the point $z = 0$ of the diffusion column (cf. Figure 1), as measured by H, should be fitted to the sum of four or three exponential functions of time. This can be achieved by a nonlinear least-squares PC program in the *Journal of Chromotography A* (1998) papers listed in the Further Reading, by entering the pairs H (peak height), t (time of reversal) in the DATA lines. The exponential coefficients of time B_1, B_2, B_3 and B_4 of eqn [6] and B_5, B_6 and B_7 of eqn [7], are calculated, together with the respective pre-exponential factors A_1, A_2, A_3 and A_4 of eqn [6], and A_5, A_6 and A_7 of eqn [7]. This PC program is based on the so-called exponential stripping method of Sedman and Wagner. The calculation of the B_i and A_i values ($i = 1, 2, \ldots, 7$) is guided by the overall goodness of fit expressed by the square of the correlation coefficient r^2. This universally accepted criterion, calculated and printed, is in the range 0.990–0.999 in most cases, showing a remarkable goodness of fit for a nonlinear regression analysis. A 't' test of significance for the smallest r^2 usually found shows that it is highly significant, with a probability smaller than 0.05% of being exceeded. The program also prints, together with the B values, their standard errors, which are usually reasonable for physicochemical measurements.

The question naturally arises as to the meaning and physical content of the parameters A_i and B_i so determined. These are given directly and explicitly by the solution of the system of eqns [1]–[5] that led to eqns [6] and [7]. They are written below:

$$\alpha_2(1 + V_1) + k_{-1} + k_2 = -(B_1 + B_2 + B_3 + B_4) = X \quad [8]$$

$$\alpha_2(1 + V_1)(k_{-1} + k_2) + \alpha_1\alpha_2 + k_1k_{-1} = B_1B_2 + B_1B_3 + B_1B_4 + B_2B_3 + B_2B_4 + B_3B_4 = Y \quad [9]$$

$$\alpha_1\alpha_2(k_{-1} + k_2) + \alpha_2V_1k_1k_{-1} + k_1k_{-1}k_2 = -(B_1B_2B_3 + B_1B_2B_4 + B_1B_3B_4 + B_2B_3B_4) = Z \quad [10]$$

$$\alpha_2V_1k_1k_{-1}k_2 = B_1B_2B_3B_4 = W \quad [11]$$

$$\alpha_2(1 + V_1) = -(B_5 + B_6 + B_7) = X_1 \quad [12]$$

$$\alpha_1\alpha_2 + \frac{k_1k_{-1}k_2}{k_{-1} + k_2} = B_5B_6 + B_5B_7 + B_6B_7 = Y_1 \quad [13]$$

$$\frac{\alpha_2V_1k_1k_{-1}k_2}{k_{-1} + k_2} = -(B_5B_6B_7) = Z_1 \quad [14]$$

$$\alpha_1 = 2D_1/L_1^2, \quad \alpha_2 = 2D_2/L_2^2,$$
$$V_1 = 2V'_G(\text{empty})\varepsilon/V_G + L_2^2/L_1^2 \quad [15]$$

where V_G and V'_G are the gaseous volumes of the void spaces in regions z and y, respectively and ε the external porosity of the solid bed. The X, Y, Z, W, X_1, Y_1 and Z_1 are just auxiliary parameters to facilitate the calculation of the primary kinetic parameters k_1, k_{-1} and k_2 from B_i. This is done as follows: the sum $k_{-1} + k_2$ is obtained from the difference $X - X_1$, from the ratio W/Z_1, or as a mean value of these two. Subtraction of $k_{-1} + k_2$ from X gives the value of $\alpha_2(1 + V_1)$. From this, α_2V_1 is easily computed since V_1 is given by the relation [15]. The calculation of k_1k_{-1} follows from the relation:

$$k_1k_{-1} = \left\{Y - \alpha_2(1 + V_1)(k_{-1} + k_2) - \frac{Z}{k_{-1} + k_2} + \frac{W}{\alpha_2V_1(k_{-1} + k_2)}\right\} \Big/ \left(1 - \frac{\alpha_2V_1}{k_{-1} + k_2}\right) \quad [16]$$

Then, dividing W by α_2V_1 and by k_1k_{-1} gives the value of k_2. The value of k_{-1} follows from the difference $(k_{-1} + k_2) - k_2$, and that of k_1 from the ratio k_1k_{-1}/k_{-1}.

The pre-exponential factors A_1, A_2, A_3 and A_4 of eqn [6] and A_5, A_6 and A_7 of eqn [7] are explicit functions of $gm\alpha_1\alpha_2/\dot{V}$, where $\dot{V}$ is the volumetric flow rate of the carrier gas, and of B_1, B_2, B_3, B_4, k_{-1}, k_2, m and m_s, but the analytical form of this dependence is not required in the calculations.

It is well known that the values of the three rate constants k_1, k_{-1} and k_2, especially determined at various temperatures, are of primary importance in characterizing solid adsorbents and catalysts. The experimental data, i.e. the H, t pairs from the chromatogram, can be analysed by using a linear adsorption isotherm, instead of the real experimental isotherm (eqn [4]) without bothering whether it is linear or nonlinear. Both methods lead to the

simultaneous determination of three primary kinetic parameters, namely, k_1, k_{-1} and k_2. From these primary rate constants, the method based on the linear isotherm calculates the overall mass transfer coefficients K_G and K_S for the gaseous and the solid phases, respectively, while the real isotherm method computes also the deposition velocity V_d and the overall reaction probability γ of the solute with the stationary phase, by means of the relations:

$$V_d = \frac{k_1 V'_G(\text{empty})\varepsilon}{A_s} \times \frac{k_2}{k_{-1} + k_2} \qquad [17]$$

$$\frac{1}{\gamma} = \left(\frac{R_g T}{2\pi M_B}\right)^{1/2} \times \frac{1}{V_d} + \frac{1}{2} \qquad [18]$$

where R_g is the ideal gas constant, T the absolute temperature, A_s the total surface area of the solid, and M_B the molar mass of the probe gas. The original definition of V_d was the flux of gas to the solid surface divided by the concentration difference between the bulk gas-phase and the surface. The values of k_1, k_{-1}, k_2, V_d and γ are calculated and printed directly by running the PC program mentioned before.

It is clear from the definitions of V_d and γ that both parameters are independent of molecular diffusion, being related only to the local adsorption isotherm (k_1), the desorption rate constant (k_{-1}) and the surface reaction rate constant (k_2).

The only physicochemical assumptions made concerning the gas–solid interactions are that all parameters measured directly or calculated indirectly refer to elementary steps at equilibrium. Thus the ratio k_1/k_{-1} represents the equilibrium distribution constant K, according to the principle of microscopic reversibility. Note that it is not easy to measure simultaneously rate constants of adsorption (k_1) and desorption (k_{-1}) at a dynamic equilibrium state like that justified experimentally in the experiments described here.

Finally, the explicit calculation of the isotherms has been described in the literature. However, eqn [6] provides an easy route to the calculation of the distribution of surface adsorption energies, ε, the local monolayer capacities, i.e. the maximum adsorbed concentrations, c^*_{max}, of the probe substance on each kind i of adsorption sites, and the local adsorption isotherms $\theta_i(p, T, \varepsilon)$ on heterogeneous surfaces of solids. Many papers and books have recently been published on this subject. From c^*_{max}, in mol per g of adsorbent, multiplying by the Avogadro number N_A and the cross-sectional area of the probe molecules in m^2, one can find the specific surface area of the stationary phase in $m^2\,g^{-1}$.

Table 1 Adsorption, desorption and surface reaction parameters for various hydrocarbons on four metal oxides, at 323.2 K, based on a linear and a nonlinear isotherm model

C_xH_y	k_1 (10^{-4} s^{-1})		k_{-1} (10^{-4} s^{-1})		k_2 (10^{-4} s^{-1})		K_G (10^{-9} cm s^{-1})	V_d (10^{-9} cm s^{-1})	γ (10^{-13})
	Linear	*Nonlinear*	*Linear*	*Nonlinear*	*Linear*	*Nonlinear*	*Linear*	*Nonlinear*	*Nonlinear*
Metal oxide: Fe_2O_3									
C_2H_2	1.56	16.0	3.51	47.8	6.17	21.6	16.4	16.3	12.7
C_2H_4	131	0.0182	1.26	397	3.41	444	1380	0.561	0.454
C_2H_6	92.0	13.4	4.99	11.3	3.25	20.3	969	28.3	23.7
C_3H_6	1.47	0.0094	3.16	521	4.13	560	15.4	0.448	0.444
1-C_4H_8	2.64	527	2.94	0.0821	2.67	0.338	27.8	2280	2610
Metal oxide: Cr_2O_3									
C_2H_2	6.76	15.5	2.69	99.9	0.340	0.383	0.196	0.132	0.151
C_2H_4	7.55	14.2	2.38	167	0.270	0.385	0.219	0.0733	0.0839
C_2H_6	6.06	9.4	3.04	81.5	0.211	0.429	0.176	0.110	0.126
C_3H_6	3.94	9.02	2.20	62.5	0.016	0.133	0.114	0.0428	0.0490
1-C_4H_8	4.91	2.63	1.08	33.4	0.218	0.805	0.142	0.138	0.158
Metal oxide: ZnO									
C_2H_2	11.8	6.90	3.52	54.3	0.211	0.936	0.440	0.374	0.291
C_2H_6	7.76	7.80	2.85	124	0.370	0.695	0.295	0.137	0.114
Metal oxide: PbO									
C_2H_2	0.180	5739	0.280	0.0322	4.52	28.9	21.2	244 800	190 900
C_2H_6	45.3	10.0	11.9	64.5	3.18	15.9	5250	84.5	70.8
C_3H_6	0.510	6.37	7.61	35.2	3.33	14.9	58.5	81.0	80.3
1-C_4H_8	1.51	5.11	3.59	5.75	2.13	23.6	138	289	331

Some Representative Results

Applying the previous theoretical analysis for the characterization of some metal oxides used as solid catalysts gave the values of the physicochemical parameters k_1, k_{-1}, k_2, K_G, V_d and γ for five probe hydrocarbons. These are given in **Table 1**, calculated for both the linear and nonlinear isotherm models. It is seen that the values of some physicochemical parameters are significantly different for the two models; it is clear that for an inorganic solid of the kind used as a catalyst the linear isotherm model is inadequate, due to the nonuniformity of the surface. The two physicochemical parameters k_1 and k_{-1} characterize any newly prepared catalyst. These constants can be measured easily and accurately and their values supply a reliable catalyst characterization.

An *a priori* acceptance of an adsorption isotherm equation is not needed, which is preferred to the Langmuir or the BET isotherms for this purpose. Any new catalyst sample can be tested by measuring adsorption and desorption rate constants before utilization. From Table 1, it can be seen that many values obtained from the nonlinear isotherm model are 1–4 orders of magnitude different from those corresponding to the linear model. All physicochemical quantities based on the nonlinear model are intended to characterize newly prepared catalysts, on the basis of accurately defined physicochemical concepts.

In some cases in Table 1 the ratios of the same parameters determined with linear and nonlinear isotherms are inverted in going from one gas–solid system to another. This is probably due to the fact that solid surfaces are very heterogeneous as regards adsorption energy distribution and this heterogeneity may differ greatly from one solid to another for the same hydrocarbon, and from one hydrocarbon to another for the same solid. The local adsorption isotherm of eqn [4] is very sensitive to the energy distribution function on the surface, whereas simple overall linear isotherms are not.

Of course, it is not possible from the measurements at one temperature to conclude whether the gas–solid interactions represent physical adsorption or chemisorption. Experiments at various temperatures, however, will give heats of adsorption and activation energies, from which it may be possible to draw conclusions about the nature of the adsorption processes.

Conclusion

The RF-GC technique is a useful tool in inverse GC studies. It has also some advantages for adsorption isotherm determinations in that: (1) the gaseous diffusion and resistance to mass transfer are not neglected, (2) the sorption effect in dynamic chromatographic systems is nonexistent, (3) the pressure gradient is negligible along the solid bed, and (4) the experimental isotherm can be determined in the presence of a surface reaction of the adsorbate. This is very important when dealing with catalysts, when many determinations based on chemisorption must follow every catalyst preparation.

The method briefly outlined here has been used for several published physicochemical measurements. Results have also been obtained for deposition parameters of air pollutants on solid surfaces with a simultaneous determination of the apparent rate constant of gaseous reactions above the solid, and also for the measurement of various rate coefficients and equilibrium constant by utilizing the solid phase as an internal wall coating of denuder tubes in place of the diffusion column.

See also: **II/Chromatography: Gas:** Theory of Gas Chromatography.

Further Reading

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