Measurement of Phase Equilibria at High Pressures by Tracer-Pulse Chromatography

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Tracer-pulse chromatography allows the accurate measurement of sorption isotherms even at elevated pressures and in systems with more than one solute. Vapor equilibria of normally liquid solutes are best measured by scintillation counting of a liquid in which the column effluent and the emergent radioactive pulse are absorbed. An example is the equilibrium adsorption of *n*-heptane by molecular sieves at 200°C. and at pressures up to 3 atm. Sorption equilibria of permanent gases are measured by use of a more conventional differential technique wherein the column effluent passes through an ion chamber. Its use is illustrated by the equilibrium adsorption of methane by activated charcoal at pressures up to 70 atm.

Tracer-pulse chromatography (*1, 2*) is a new method of measurement of phase equilibria such as gas-liquid, gas-solid, or liquid-solid sorption and vapor-liquid equilibria. Its main virtues are its combination of the speed and simplicity of chromatographic techniques with the accuracy of conventional volumetric or gravimetric methods and its unique suitability for multicomponent phase equilibria. It is well known that the use of ordinary elution chromatography for phase equilibrium measurements is limited to single solutes at very low concentrations in a nonsorbed carrier fluid. Tracer-pulse chromatography operates differently and is not subject to the same limitation; it can be used with high solute concentrations or pressures, even in multicomponent feeds, and requires no nonsorbed carrier fluid. Yet its apparatus, like that of gas chromatography, is readily adapted to operation at high pressures and temperatures, frequently making possible measurements difficult to carry out by other means.

The purpose of this note is to describe the apparatus of tracer-pulse chromatography; its use is illustrated in the measurement of gas adsorption equilibria of single solutes at elevated pressures. A new approach to such measurements for normally liquid solutes proves quite successful. The same equipment may also be used with multicomponent feeds.

TRACER-PULSE CHROMATOGRAPHIC METHOD

As with other chromatographic methods, a solid sorbent is packed directly into a column, whereas a liquid sorbent is introduced as a thin covering on an inert solid carrier. The column is brought to equilibrium throughout with a continually flowing feed fluid. A pulse of a radioisotope of any one solute of the feed in radioactively labeled form is then introduced into the ingoing fluid without otherwise altering its composition. The retention volume $V_{Ri}(C_i)$ of this tracer pulse, corrected for the void volume V_g, gives directly the concentration $\overline{C}_i$ of solute i in the stationary phase as a function of its known concentration C_i in the feed fluid and the volume of stationary phase V_s[*] (*1*):

$$V_{Ri}(C_i) - V_g \equiv V'_{Ri}(C_i) = \overline{C}_i V_s / C_i \qquad (1)$$

Equation (1) is valid for all feed components and is not limited as in ordinary chromatography to very small concentrations and linear isotherms. V_g has the usual meaning of the free volume (excluding that of the sorbent) contained between the point of pulse injection and the detector, and can be measured by a pulse addition of a nonsorbed substance to the feed fluid. Both $V_{Ri}(C_i)$ and V_g then are measured in units of feed volume at column pressure and temperature, as is the denominator of C_i. Any dimensionally consistent set of concentration and volume units may be used. All that is required is that the units of the *amount* of solute i in the mobile phase $C_i V_g$ or measured by the retention volume $C_i V_{Ri}(C_i)$ are the same as those of the *amount* of solute in the stationary phase $\overline{C}_i V_s$. Further, the units of $\overline{C}_i$ may be of amount per unit volume of sorbate, sorbent, or sorbate plus sorbent, depending on the choice of volume meant by V_s. Similarly, the units of $\overline{C}_i$ may be of amount per unit weight of stationary phase, V_s then being substituted by the weight w_s of the stationary phase. In addition, it is convenient, particularly for equilibria of vaporized liquid feeds, to make use of the corresponding quantities, $v_{Ri}(c_i)$, v_g, and c_i, which are measured at the condition, temperature, and pressure of actual observation rather than at those of the column. Then because

$$c_i(v_{Ri}(c_i) - v_g) \equiv c_i v'_{Ri}(c_i) \equiv c_i v'_{Ri}(C_i) = C_i V'_{Ri}(C_i) \qquad (2)$$

one has from Equation (1)

$$\overline{C}_i = c_i v'_{Ri}(C_i)/V_s \qquad (3)$$

In practice, the retention volumes $v_{Ri}(c_i)$ and v_g can be obtained by direct measurement as differences between wet-test meter or burette readings for gaseous or liquid feeds, respectively. This obviates the need of operating with strictly constant or precisely known flow rates and eliminates these sources of error.

The sorption isotherm of a single compound is obtained from retention volume measurements of pulses of the pure solute vapor at several pressures. The appropriate form of Equation (3) is

$$\overline{C} = c[v_R(P) - v_g(P)]/V_s \equiv c v'_R(P)/V_s \qquad (4)$$

wherein the argument of $v_g(P)$ reminds us that in units of feed volume the void volume is pressure-dependent.

A sorption isotherm of a single solute can also be closely approximated by measurements at one total pres-

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[*] A relation equivalent to Equation (1) was independently presented by Stalkup and Deans (3), who discussed its application at vanishing solute concentrations. The validity of Equation (1) at finite solute concentrations (*1*) meanwhile has already been experimentally verified (*4*).

sure, but at several partial pressures of the solute in a nonsorbed carrier. That tracer-pulse chromatography does not *require* the presence of an extraneous substance is a significant advantage over other chromatographic techniques. More important, however, is the advantage that in tracer-pulse chromatography an equilibrium loading is determined by an experimentally well-defined quantity, the retention volume. The measurement of sorption isotherms up to substantial loadings by other chromatographic procedures involves deductions from shapes of diffuse concentration boundaries (*5*) or of asymmetric peaks (*6*). The fact that the observed spreading may have many causes besides isotherm shape limits the accuracy of these methods. Further, their use is confined to mobile phases consisting of no more than two components.

Compared with ordinary volumetric or gravimetric methods of measuring sorption equilibria of single solutes, tracer-pulse chromatography offers the advantages of speed, sturdiness, and simplicity. It suffers from the need of larger amounts of sorbent and solute, from the limitation an unavoidable pressure drop places on its accuracy, and from the requirement of radioisotopes. It offers the most promise in the measurement of multicomponent equilibria, where ordinary static and flow methods can provide sorption data for individual components only indirectly, through analyses and material balances. Indeed, there appears to be no other general method of determining directly sorption of individual members of complex mixtures.

APPARATUS FOR GASEOUS FEEDS

Besides requiring a radiation detector, the equipment for normally gaseous feeds differs from that of ordinary gas chromatography in only two important respects: the feed need not include a nonsorbed carrier, and the operating pressure may be much higher. Gaseous feed of the desired equilibrium composition is charged directly from a pressure supply cylinder through a regulator to the column. In the present experiments the column was 120 cm. long and 4.9 mm. in I.D. Flow rates were about 25 cc./min. at column conditions. Adsorbent particles of 20-40 mesh were used. A tracer pulse at low pressure is introduced by means of pairs of isolation valves (see Figure 1). The flow rate is regulated by a needle valve downstream from the column. Exit of the tracer pulse, methane-C^{14} in this case, from the column is recorded with a conventional ionization chamber and vibrating reed electrometer amplifier. A thermal conductivity cell in series detects pulses of helium, by which the void volume $v_g(P)$* is determined.

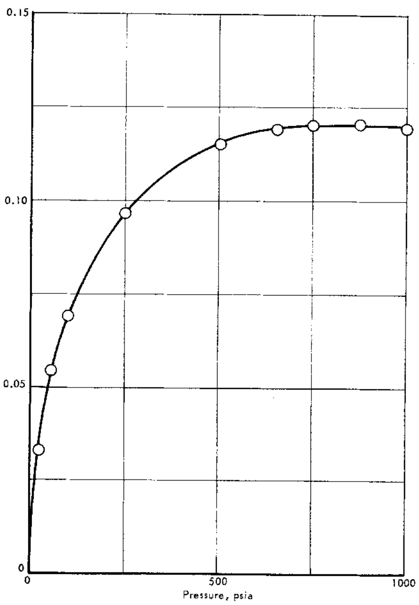

Fig. 2. Methane–PCB activated charcoal equilibrium at 25°C.

Figure 2 shows an isotherm measured by this means for methane adsorbed on a shell-based activated charcoal (Pittsburgh type PCB) at 25°C. Isotherm points are derived from the amount of adsorbent and the weights of solute contained in the corrected retention volumes. The adsorbate concentration q in units of weight solute adsorbed per unit weight of adsorbent W_s is, similarly to Equation (4)

$$q = cv'_R(P)/W_s \tag{5}$$

wherein the units of q require that the units of c be weight per unit volume. Although the isotherm in Figure 2 extends to 1,000 lb./sq. in. abs., its precision is about ± 2%.

APPARATUS FOR LIQUID FEEDS

Equilibrium between vapors of normally liquid substances and sorbents is more conveniently measured with an apparatus shown schematically in Figure 3. Liquid feed is charged from a burette to a small-volume reciprocating pump. The feed is totally vaporized before entering a column with a length of 275 cm. and an I.D. of

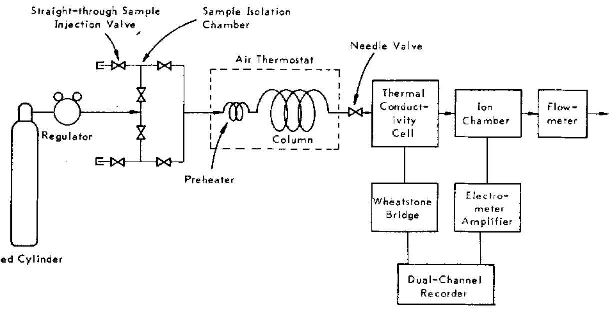

Fig. 1. Schematic diagram of tracer-pulse chromatographic apparatus for gaseous feeds.

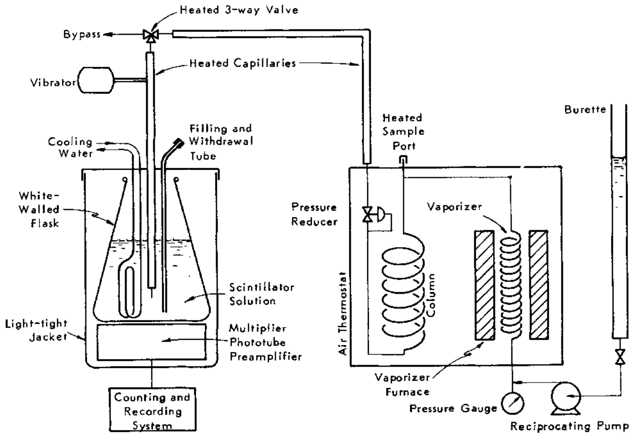

Fig. 3. Schematic diagram of tracer-pulse chromatographic apparatus for liquid feeds.

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* Measured values of $v_g(P)$ were smaller than void volumes computed from the known geometrical volume of the apparatus less the particulate volume of the adsorbent. It is possible that the use of $v_g(P)$ allows a measure of the volume of the adsorbed phase, and through Equation (*4*), its density.

8.1 mm. and packed with 20-40 mesh adsorbent particles. Vapor flow rates through the column were about 100 cc./min. After leaving the column, the vapor passes through a regulator with which the column pressure is set. A heated capillary line carries it on into the scintillator solution of the detector.

The scintillator solution [6 g. of 2,5-diphenyloxazole and 0.1 g. 1,4-bis-[2-(4-methyl-5-phenyloxazoyl)]-benzene/liter of toluene] is contained in a white-walled flask whose bottom is optically coupled to a multiplier phototube. The solution is cooled by means of tap water circulating through a stainless steel coil immersed in it, and is stirred by means of a vibrator. A tube is provided for in situ filling (by syringe) or emptying (by suction) of the flask. The flask and multiplier phototube are enclosed in a light-tight case, the interior of which is painted with a flat black paint. An O-ring seal is used between the body of this case and its cap. The vibrator shaft, which contains the heated capillary, and the filling-and-withdrawal tube enter the case through Sealastic fittings, while the cooling-water coil enters through drilled-out Swagelok fittings. This apparatus gives no evidence of increases in the background count rate due to light leaks.

Pulses from the multiplier phototube, corresponding to photoflashes resulting from radioactive disintegrations in the solution, are amplified by a preamplifier and a linear amplifier. Low-voltage pulses are rejected by a lower-level discriminator. The output is fed alternatively into a scalar coupled to a digital printer, or to a ratemeter coupled to a recorder.

Radiotracer pulses of *n*-heptane-C^{14} were injected as a liquid through a heated sample injection port of usual design. Since all the arriving vapor of each pulse is absorbed in the scintillator solution, the method gives an integral, rather than a differential, record. The directly measured experimental quantity is the volume of liquid $v_R(P)$ leaving the burette between the time of injection of the labeled pulse and that corresponding to the half-height of the resulting step signal from the detector. The void $v_g(P)$* in units of feed volume was found similarly by use of nonsorbed Kr^{85}. The weight q adsorbed per unit weight adsorbent is given by Equation (5), with c equal to the weight density of liquid *n*-heptane.

Measured equilibria for *n*-heptane adsorbed on Linde molecular sieves type 5A (with 20% wt. binder) at 200°C. are shown in Figure 4. The full curve in Figure 4 is based on measurements at subatmospheric pressures with a McBain balance (7). Again, in spite of the elevated temperature of measurement, results follow immediately through Equation (4) from directly measured retention volumes by whose precision of measurement theirs is primarily limited. This is also here about ± 2%. In both examples, however, the use of longer columns or lower gas velocities would be expected to result in higher precision.

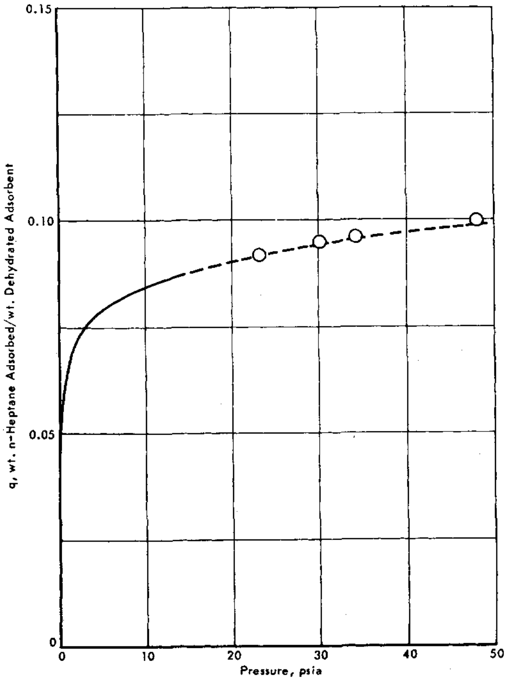

Fig. 4. *n*-Heptane—molecular sieves 5A equilibrium at 200°C.

NOTATION

c = concentration of mobile phase at conditions of volume measurement
c_i = concentration of i^{th} component in multicomponent mobile phase at conditions of volume measurement
C_i = concentration of i^{th} component in multicomponent mobile phase at conditions in column
$\overline{C}$ = concentration of a single solute in stationary phase in equilibrium with a pure solute feed
$\overline{C_i}$ = concentration of i^{th} component in stationary phase in equilibrium with multicomponent feed
P = column pressure of a gaseous mobile phase
q = weight of adsorbate per unit weight adsorbent
v_g = void volume in units of volume of mobile phase at conditions of volume measurement
v_R = retention volume in units of volume of mobile phase at conditions of volume measurement
v_{R_i} = retention volume of i^{th} component in multicomponent mixture in units of volume of mobile phase at conditions of volume measurement
v'_R = $v_R - v_g$
v'_{R_i} = $v_{R_i} - v_g$
V_g = geometrical void volume
V_{R_i} = retention volume of i^{th} component in multicomponent mixture in units of volume of mobile phase at column conditions
V'_{R_i} = $V_{R_i} - V_g$
V_s = volume of stationary phase
w_s = weight of stationary phase
W_s = weight of adsorbent

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* Measured values of $v_g(P)$ agreed within experimental error with those computed from the known geometrical volume of the apparatus less the particulate volume of the adsorbent, including the intrazeolitic volume.