Reports

Accurate Chromatographic Method for Sorption Isotherms and Phase Equilibria

Abstract. *Partition coefficients can be determined with accuracy by a "tracer-pulse" method in which the retention volume of a tracer of the respective species is measured. The method is applicable to multicomponent equilibria and can be used at elevated temperature and pressure. A less accurate "differential" method not requiring a tracer is also described.*

Gas-liquid, gas-solid, and liquid-solid sorption isotherms are usually determined by static measurements, which can be made with accuracy, but are lengthy and inconvenient at elevated temperatures and pressures. We have devised an accurate and rapid chromatographic technique which does not suffer from these disadvantages.

Of the two usual chromatographic techniques, one type consists of determining sorption equilibrium from the peak rentention volume of a small sample (*1*) and is accurate but restricted to high dilution of the sorbable substance. In the second type, the sorption isotherm is computed from the shape of the diffuse rear boundary in elution from a previously saturated column (*2*) or from asymmetric peak shapes (*3*). These methods give the isotherm up to substantial sorbent loading, but the necessary corrections for extraneous peak- or band-broadening effects and other imperfections cannot be made with accuracy and the evaluation is lengthy and subject to accumulation of errors. Our method is as accurate as the first while covering as wide a concentration range as the second.

According to elementary theory of chromatography, the partition coefficient K of a substance between the stationary and the mobile phase is related to the adjusted retention volume of the substance:

$$K \equiv \overline{C}/C \doteq V_R'/V_L \qquad (1)$$

where $\overline{C}$ and C are the amounts of the substance in the stationary and the mobile phase, respectively, per unit volume of the respective phase, V_R' is the adjusted retention volume (adjusted for mobile-phase hold-up), and V_L is the volume of the stationary phase. Equation 1 is used in the methods of the first type and is derived with the assumptions of a linear isotherm (that is, constant K), isothermal behavior, small sample size, negligible pressure drop in the column, and other minor idealizations but is, for all practical purposes, not impaired by peak-broadening effects.

The "tracer-pulse method" proposed here for accurate determinations of sorption isotherms up to higher concentrations is also based on Eq. 1 but it operates under different conditions. To determine the partition coefficient $K(C)$ at the mobile-phase concentration C of the substance under investigation, the column is brought to equilibrium with a continuous stream of the fluid phase at concentration C. Into this stream a small sample, also of concentration C, is introduced, but it is tagged with a detectable isotope of the substance under investigation; then the retention volume of the isotope is measured. Application of Eq. 1 with V_R' as the adjusted retention volume of the isotope gives the distribution coefficient $K(C)$. The measurement is repeated with a series of different concentrations C to obtain the whole isotherm.

It is readily shown that Eq. 1 indeed applies. Aside from a usually quite negligible isotope effect the sorbent does not distinguish between the normal and labeled isotopes. Except for the isotope distribution the column thus remains in equilibrium with the fluid throughout the measurement, that is, the "total" concentrations C and $\overline{C}$ of the substance (normal plus labeled) remain constant. For a constant concentration C of the substance the equilibrium distribution of a labeled species of that substance is

$$\overline{C}^*/C^* = \overline{C}/C = \text{const.} \qquad (2)$$

where quantities with asterisks are the (variable) concentrations of the labeled species and those without asterisks are the (constant) "total" concentrations. For constant C, as in the tracer-pulse measurement, the sorption isotherm of the labeled species thus is linear. Also, even at high concentrations C no heat-of-sorption effects will disturb isothermal behavior, since merely an isotopic exchange occurs which does not give rise to liberation or consumption of heat. Meeting the other conditions for validity of Eq. 1 is essentially a matter of proper choice of experimental conditions. Equation 1 can thus be applied to obtain the distribution coefficient of the isotope from its retention volume, and according to Eq. 2, this coefficient equals the distribution coefficient of the substance at the respective concentration C.

The technique is quite general and can be applied to gas-solid, gas-liquid, and liquid-solid equilibria; it can also be applied to systems with any number of sorbable components. In gas-liquid systems the liquid is supported on an inert carrier, as in gas-liquid chromatography.

Attention must be given to the definition of the volume of the stationary phase because, at high loading, sorbed molecules may add significantly to this volume. The quantities V_L, $\overline{C}$, and K may be defined in terms of either the gross or the net volume of the stationary phase, that is, including or excluding the volume occupied by the sorbed molecules. Equation 1 is correct with either definition, provided the definition is used consistently for all three quantities (*4*). Also, the three quantities may equally well be replaced by the corresponding ones defined in terms of stationary-phase weight instead of volume. Furthermore, activity coefficients and relative volatilities can be calculated from the partition coefficients in the same way as at infinite dilution (*1*).

In gas-liquid systems with liquid sorbents having appreciable volatility, the obvious difficulty of keeping the amount of liquid on the support constant can largely be obviated by operating with a gas phase which contains the components of the liquid at their respective vapor pressures. It is even possible to apply the technique to gas-liquid equilibria in the complete absence of liquid "sorbent" of low volatility. In such cases, it is convenient to measure the retention volumes of all species. For each component i one has, according to Eq. 1

$$\overline{C}_i V_L = C_i (V_R')_i \qquad (3)$$

for the amount of i in the liquid phase. Thus, from the retention volumes of all species the total amount of stationary liquid in the column is readily calculated. The relative volatility K_i of species i (defined as the ratio of the mole fractions y_i and x_i of i in the gas and liquid phases, respectively) in multicomponent gas-liquid equilibria then is readily obtained from

$$\kappa_i = \frac{y_i}{x_i} = \frac{\sum_{j=1}^{n} C_j (V_R')_j}{(V_R')_i \sum_{j=1}^{n} C_j} \qquad (4)$$

where the summations are carried out over all n components. If the mixture is not too complex, the retention volumes of all components can be determined in one single experiment, with use of different isotopes or different relative amounts of tagged species to distinguish between the various components.

Compared to other chromatographic methods in which the sorption isotherm of a substance is obtained from the peak or band shape, the tracer-pulse method has the disadvantages of requiring a separate measurement for each point on the isotherm. The evaluation, however, is simpler and more rapid since the retention volume of each peak immediately gives an isotherm point, whereas in the other methods the evaluation of the peak or band shape requires, at each point, a graphical integration or slope construction. In view of their speed, the disadvantage of a larger number of chromatographic measurements is likely to weigh little against the gain in accuracy, reliability, and ease of evaluation. Furthermore, the tracer-pulse method also permits measurements of single-component gas sorption in the absence of a carrier gas, and of partition coefficients or relative volatilities of a number of components in multicomponent systems in one single experiment.

The tracer-pulse method is, of course, restricted to substances that can be tagged with detectable isotopes. For lack of a suitable isotope a modified "differential method", based on the same principle as the differential reactor in heterogeneous catalysis, may be used. After the column is in equilibrium with solvent and solute at concentration C, this concentration is changed stepwise to a slightly higher or lower value and the retention volume of the concentration step (more accurately, of the center of gravity of the step) is measured. It is readily shown by a material balance written around the column that the adjusted retention volume of the step, V_R', at sufficient dilution is related to the slope of the isotherm by

$$d\overline{C}/dC = V_R'/V_L \qquad (5)$$

provided that the step has been made so small that the isotherm slope remains essentially unchanged by the concentration change. To verify that this condition is met, two measurements may be made by changing the concentration in the first from C to $C + \Delta C$ and in the second from C to $C - \Delta C$; both retention volumes should be the same within the tolerable error. The use of a concentration pulse instead of a step is possible and is experimentally more convenient, but has the disadvantage that, to obtain a detectable peak height $C + \Delta C$ in the effluent over the background of height C, the injected pulse must be of considerably higher concentration, a fact which puts more strain on the assumption of constant isotherm slope within the range of concentrations occurring in the column. Because it involves the more difficult detection of small concentration changes in the effluent, the assumption of invariant isotherm slope, and a slope construction in computing the isotherm from the retention volumes, the differential method is less accurate and more cumbersome than the tracer-pulse method. However, the advantage of invariance against extraneous peak or band-broadening effects is preserved.

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9 August 1963

High-Pressure Transitions in $A^{(III)}B^{(VI)}$ Compounds: Indium Telluride

Abstract. *Metallic InTe(II) has a NaCl structure with $a_0 = 6.154$ Å and becomes superconducting below 3.5°K. These results are substantially different from those previously reported. The pressure-temperature diagram to 850°C and 50 kb is presented.*

In a systematic study of the effects of high pressure on the $A^{(III)}B^{(VI)}$ compounds, a high pressure metallic phase of InTe has been discovered. The properties of this InTe(II) phase, preliminary measurements of which have been reported (*1–3*), differ in several essential respects from those observed independently and recently reported by Darnell, Libby, and coworkers (*4, 5*). Specifically, we find that InTe(II) has the NaCl (B1) structure rather than simple cubic (*4*); that its lattice constant is 6.154 Å rather than 3.07 Å (*4*); and that its superconducting transition temperature is 3.5° to 3.7°K rather than 2.18°K (*5*).

Initially InTe(II) was synthesized by fusion of the semiconductor grade elements at 40 to 50 kb and about 1000°C (*1*). It has also been obtained by transformation, at pressures above 28 kb and temperatures above 150°C, of the stoichiometric tetragonal InTe(I) phase prepared at 1 atm (*2*). When the samples are cooled to room temperature, the high-pressure phase is readily recovered at atmospheric pressure but slowly transforms (20 percent in 4 months) to InTe(I). Samples have been retained at dry-ice temperature for as long as 9 months without detectable transformation. At 100°C, the transformation to InTe(I) is 75 percent complete in 1 hour, and above 125°C InTe(II) has no appreciable stability at atmospheric pressure.

Darnell, Yencha, and Libby (*4*) proposed a simple cubic structure for InTe(II) with lattice spacing of 3.07 Å. For a 1:1 binary compound, the indices which they assign to their d-spacings can only be those of a CsCl structure. Since this structure would have one atom each of In and Te per unit cell, the calculated density would be 13.8 g/cm^3, not 6.69 as they report. Since the average density measured for several samples by liquid displacement is 6.82 g/cm^3, a simple cubic structure is eliminated. We propose that InTe(II) has the NaCl structure with $a_0 = 6.154$ Å, corresponding to a theoretical den-