Measurement of Adsorption Isotherms for Mixed Vapors

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A great deal of work has been done in the measurement of adsorption isotherms of pure gases and vapors, but very little of the measurement of adsorption isotherms of mixed gases or vapors and much of this has been unintentional, being due to impurities in the adsorbate. Papers dealing with measurements of this type include those of Richardson and Woodhouse\(^\text{(*)}\) and Bakr and King.\(^{(*2)}\) The method of Bakr and King has the objection that each experiment yields an isolated value. Richardson's and Woodhouse's method requires extensive gas analysis and yields an isotherm in which the composition of the adsorbate changes.

Pressure data obtained where the composition of both the adsorbate and the vapor in equilibrium with it are unknown are difficult to interpret and reproduce. Because of this we have attempted to develop a method of measurement so that the composition of the adsorbed phase could be known and kept constant throughout the isotherm. Also we wished to know the composition of the vapor phase in equilibrium with the adsorbate in order to obtain the partial pressures as well as the total pressures.

A schematic diagram of the apparatus developed for this purpose is given in figure 1. The measurement of an isotherm is carried out in the following manner. A relatively large amount of liquid mixture of known composition is introduced into the liquid reservoir by means of tube (2). Considerable excess over the amount actually adsorbed is used so that the change in composition of the liquid in the reservoir is negligible during an experiment. After sealing off tube (2) the dissolved air is removed by repeated freezing and evacuation until no bubbles are visible on thawing. Stopcock (3) is then closed and the tube containing the adsorbent (7) is sealed on to the apparatus. The adsorbent (activated cocoanut charcoal was used in this work) is then outgassed by evacuation at the desired temperature (525°C.) until the McLeod gauge (8) gives a pressure of less than $2 \times 10^{-4}$ mm. Hg. The vacuum system employed consists of a mercury condensation pump backed up by a Hyvac oil pump.

The introduction of the adsorbate into the adsorbent is accomplished by first opening stopcock (3) and allowing the liquid at 20°C. to equilibrate with its vapor phase in the vapor reservoir.
Figure 1. Schematic diagram of apparatus.

(5) at the air bath temperature (25°). (The temperature of the liquid reservoir (1) is maintained at 20° by immersion in a large vacuum bottle containing water at this temperature. The composition of the vapor corresponding to a known composition of liquid at 20° for the system employed is known from other work.\(^\text{1}\).) The mercury in the vapor reservoir (5) is raised to a point corresponding to the amount of vapor which is to be introduced into the adsorbent (7). After equilibrium is established, the mercury in the cutoff (4) is raised and the levels of the mercury in (4), (5) and (6a) adjusted to fixed marks, thus confining the sample in a known volume. Since (6b) is connected to the vacuum system, the pressure of the sample in the vapor reservoir (5) can be determined by measuring the difference in the mercury levels (6a) and (6b) by means of a cathetometer. Since the volume of the vapor
reservoir is known from a previous calibration when the levels are at fixed marks and the pressure has been determined, the number of moles of gas present in the reservoir can be calculated if the perfect gas law is assumed.

To completely transfer this vapor to the adsorbent the mercury in (6) is lowered until the mercury in (a) is below the connecting piece between (a) and (c). (This type of valve proved very satisfactory and was capable of handling pressure differences as large as 12 cm. Hg.) All the vapor, except for a negligible amount in the connecting tubes, is then forced out of the vapor reservoir by displacing it with mercury and by immersing the charcoal tube in a carbon dioxide snow-acetone mixture. After completion of this operation the mercury in (6) is raised and the carbon dioxide snow-acetone mixture is removed from the charcoal and the system allowed to equilibrate at bath temperature (25°). The pressure in the adsorption chamber is then read by measuring the difference between levels (6b) and (6c), the levels (6c) and (8) being at fixed marks so that the volume of the dead space is known. The amount of dead space is such that the vapor in this volume is small compared with the amount of material adsorbed on 2 grams of charcoal, varying from 0 to 3 per cent as the equilibrium pressure increases. Hence, except for the last part of the isotherm, it is justifiable to say that the composition of the adsorbate is the same as the introduced vapor. Even at higher pressures of the isotherm this would be a good approximation. By measurement of the composition of the vapor in the dead space, knowing the volume of the dead space and the composition and amount of vapor introduced, the exact composition of the adsorbate can be calculated if desired.

To determine the composition of the vapor in the dead space the modified McLeod gauge (8) is employed. The volume in the gauge is a known function of the height of the mercury in (8a) and by measuring the heights of the mercury levels in (8a) and (8b) (making necessary capillary corrections) the pressure of the vapor in the gauge can be determined. By making a series of measurements and plotting $pv-p$ a break is obtained at the condensation pressure. Since the condensation pressure may already be known as a function of composition of the vapor or can be independently determined, the composition of the vapor can be found if the condensation pressure is known. If the composition of the vapor and the total pressure are known, the partial pressures can be calculated if all vapors are assumed to be perfect.
To obtain further points on the adsorption isotherm, the process described can be repeated until condensation of the vapor phase in the dead space occurs without compression. The condensation pressure tells the composition of the liquid and vapor phases that would be in equilibrium with the adsorbate of known composition. Therefore, the selective adsorption, which is a measure of the difference in composition between the adsorbate and the liquid phase and which can be defined as $n (n_a - N_a)$, can be determined. This definition can be shown to be related to the definition of selection adsorption, $(N \triangle N_a)$, used by Bartell and coworkers by the following relationship.

$$n (n_a - N_a) = (N - n) \triangle N_a$$

$n = \text{total moles present in the adsorbed phase.}$

$n_a = \text{mole fraction of the first component in the surface phase.}$

$N_a = \text{mole fraction of the first component in the liquid phase.}$

$N = \text{moles of adsorbate plus moles of liquid phase.}$

$\triangle N_a = \text{change of moles fraction of the first component in the liquid phase due to selective adsorption.}$

For measurements of very low pressures the McLeod gauge can be employed. Another alternative for the low pressure range is also possible. If adsorption equilibria is established with the connection between the charcoal tube and reservoir open, a fifteen fold magnification in pressure can be obtained by raising the mercury in (5) and (6) and reading the difference between levels (5a) and (6b).

To illustrate the results obtained in a particular case the isotherm for a mixture containing a mole fraction of 59% carbon tetrachloride and 41% methanol on activated charcoal is plotted in figure 2 together with the isotherms obtained for the pure components on the same material. Partial pressures were not determined for this run. The mole composition of the liquid phase which would be in equilibrium with this adsorbate as determined from the condensation pressure is 59% carbon tetrachloride. Hence, the selective adsorption per gram of adsorbent from a liquid phase having this equilibrium composition is:

$$n (n_a - N_a) = n (0.59 - 0.59) = 0$$

This mole fraction of adsorbate happens to correspond with zero selective adsorption, but this was not found to be true for other adsorbate compositions. For example for $n_a = 0.24$, $N_a$ was found to be 0.07.
Figure 2. Adsorption isotherms for carbon tetrachloride, methanol, and a mixture containing a mole fraction of 59% carbon tetrachloride and 41% methanol. The amount adsorbed, \( x/m \) is expressed in cc. of vapor at n.t.p. adsorbed per gram of charcoal (corrected for ash content and loss of weight on outgassing).

Data obtained by measurements of this nature can be used for some interesting thermodynamic calculations including the evaluation of the reversible work of wetting both for the pure liquids and their mixtures and for checking the Gibb's adsorption equation, as we hope to show in future work.

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References
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