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Adsorption Isotherms for Hydrogen-Bonded Liquids on Charcoal

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IN van der Waal's adsorption on charcoal, a plot of the weight adsorbed as a function of the relative pressure (p/p_0) of the vapor gives a curve which is roughly the same for a large number of substances. A few exceptions are known, of which water is the outstanding example, in which marked deviations from the typical curve occur, particularly at low pressures. The underlying basis of these deviations becomes evident when it is realized that these exceptional substances all form strong hydrogen bonds in the liquid state. A stronger parallelism is then found to exist between adsorbability and condensation properties of a gas than has been realized previously.

A plot of boiling point as a function of van der Waal's a shows a region, bounded by the curves in Fig. 1, in which "normal" liquids are found. These are the substances which exhibit normal adsorption isotherms. In contrast,

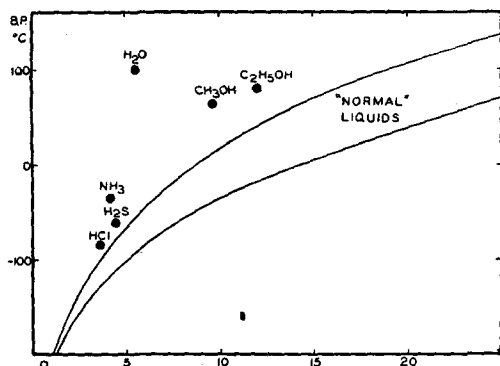


FIG. 1.

water, ammonia, and methyl alcohol, which show abnormal isotherms, also stand outside the normal region in Fig. 1, the distance being a rough measure of the deviation from the typical isotherm.

The deviation in the boiling-point curve is caused by the presence of strong hydrogen bonds in the liquid state, a condition which necessitates more energy to vaporize the molecules than would be required to overcome van der Waal's forces alone.

The deviations in the adsorption isotherm are also caused by hydrogen-bonding which may express itself in two different ways. In the region of low relative pressures (0.3–0.4), for water for example, the extent of adsorption appears to be unusually small. The apparent anomaly, is owing, however, to misleading values assigned to the relative pressure when one deals with a strongly hydrogen-bonded liquid. If there were no such bonding in liquid water, the boiling point and vapor pressure would be in line with those of the other hydrides of the sixth-group elements and would be near -80° to -100°C , and about 20,000 mm (at room temperature), respectively. On the basis of this latter value for the vapor pressure if the liquid had no hydrogen bonds, the relative pressure of 0.3–0.4 is reduced to 0.0003–0.0004 and the observed adsorption is normal even though small. Since the adsorption at low pressures on charcoal (not containing specially-prepared, surface complexes) does not reflect in any way the hydrogen-bonding properties of water, this vapor behaves as if it came from a normal liquid with a vapor pressure of 20,000 mm.

Above relative pressures of 0.3–0.4 there is a steep rise in the water isotherm. Clearly this must be owing to the formation of a network of hydrogen-bonded water molecules, anchored initially by the few adsorbed molecules. Under these conditions the adsorbed phase does reflect the properties of the liquid and hence the isotherm rapidly approaches the normal curve.

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