columns of this table shows that while B is approximately constant (within 30%) and shows no regular dependence on molecular symmetry, $1/T_f - 1/T_b$ varies over a four-fold range and shows a definite increase with decreasing symmetry. In other words the increase of r with decreasing molecular symmetry can be largely attributed to changes in $1/T_f - 1/T_b$. In the case of the paraffins (Table II) B increases regularly with the increase in the number of carbon atoms, as has been pointed out by Dunn,[5] while $1/T_f - 1/T_b$ decreases on changing from a hydrocarbon containing an odd number of carbon atoms to one containing an even number of carbon atoms and increases on proceeding to the next (odd) hydrocarbon. This is evident from Fig. 1 in which log r, B and $1/T_f - 1/T_b$ are plotted against the number of carbon atoms in the molecule. The alternation in r, pointed out by Miss Waller, can thus be traced to an alternation in $1/T_f - 1/T_b$ which is due to the well known alternation in the melting points.

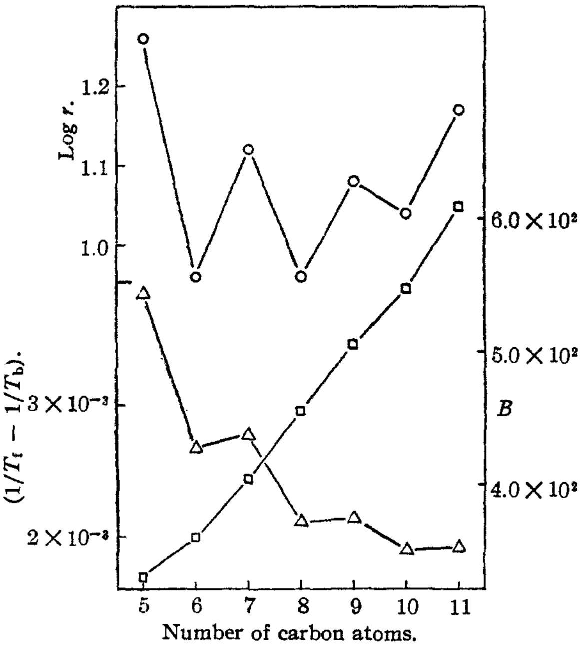

Fig. 1.—Log r, ⊙; $(1/T - 1/T)$, △; B, □.

From these calculations it appears that the correlation between values of r and molecular symmetry is due, in a large part at least, to the dependence of the melting point on molecular symmetry, which does not involve viscosity. It is doubtful, therefore, whether the melting point should be used as a standard temperature for the comparison of viscosities.

The writer is indebted to Professor Hans Erlenmeyer for advice and help on this note.

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(5) Dunn, *Trans. Faraday Soc.*, **22**, 401 (1926).

An Explanation of Hysteresis in the Hydration and Dehydration of Gels

BY JAMES W. MCBAIN

It is well known that hysteresis in the hydration and dehydration of porous gels at moderately high relative humidities is connected with the filling and emptying of pores with liquid.[1]

Such hysteresis sometimes persists even after rigorous evacuation in the attempts to eliminate other impurities.[2] An explanation is usually sought in terms of "friction in the contact angle" or the familiar "Jamin effect."

It is the purpose of this note to present an alternative mechanism, suggested in discussion with the class on Sorption at Stanford University. Figure 1a gives in well-known fashion an illustration of the fact that capillary condensation occurs in wettable pores of sufficiently small radius and relatively high humidities in accordance with the formula of Lord Kelvin[3] as used by Anderson[1]

$$\ln p/p_s = -2\sigma v/rRT$$

where p is the pressure at concave surface, p_s is the pressure of saturated vapors of liquid in bulk at that temperature, σ is the surface tension, v is the volume of 1 gram mole of condensed liquid, r the radius of the capillary, R the gas constant, T the absolute temperature, and ln represents the natural logarithm to the base e.

The applicability of the formula depends upon the liquid and is generally restricted to pores of radius from about 20 Å. up to visible dimensions.

Figure 1b gives a diagram of a lecture experiment we have used to show two possible positions of true stable reversible equilibrium, where a stoppered bell jar has a narrow capillary passing through the stopper. Either the capillary is filled to the same height as in Fig. 1a, the bell jar

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(1) McBain, "The Sorption of Gases and Vapours by Solids," George Routledge and Sons, Ltd., London, 1932; Zsigmondy, *Z. anorg. Chem.*, **71**, 356 (1911); "Kolloidchemie," O. Spamer, Leipzig, 5te Aufl., Bd. 11, p. 76, 1927; Zsigmondy, Bachmann and Stevenson, *Z anorg. Chem.* **75**, 189(1912); Anderson *Z. physik. Chem.*, **88**, 212 (1914).

(2) Lambert and Clark, *Proc. Roy. Soc.* (London), **A122**, 507 (1929); Foster, *ibid.*, **A147**, 128 (1934).

(3) Thomson, *Phil. Mag.*, [4] **42**, 448 (1871).

likewise remaining full up to this point (liquid shown by oblique lines in the diagram), or, alternatively, the meniscus is even more stably placed at a very slightly greater height inside the bell jar than outside, both the capillary and most of the bell jar thus being empty (this position is drawn in solid black).

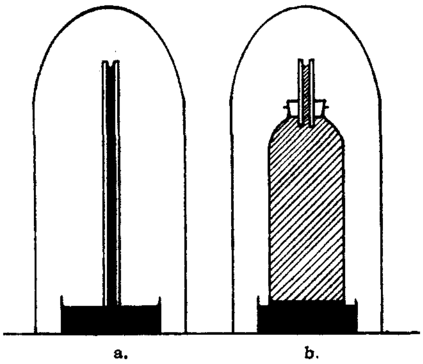

Fig. 1.

The interstices in a gel may be extremely irregular in every respect, since they are built up from the juxtaposition of myriads of ultramicrons. These irregular channels will have an equally irregular cross section but the same principles will apply as with the circular cross sections shown in Figs. 1a and 1b. A few of the pores may resemble Fig. 1a in that they are of uniform cross section and therefore will fill or empty at a definite relative humidity according as the pressure is increased or decreased. Others may be more like Fig. 1b in which the openings to the vapor phase are of different dimensions and initial and completed filling correspond to different relative humidities.

In general, however, pores may be represented diagrammatically as in Fig. 2, where the essential feature is that larger cavities are accessible only through smaller channels or orifices.

In pores of the type of Fig. 2, as the relative humidity of a vapor is gradually increased, condensation of liquid will begin at the narrowest cross section and will extend to wider cross sections only as the relative humidity is increased, until when the vapor is sufficiently nearly saturated the pore will be completely filled. Upon subsequent diminution of the relative humidity, however, in general no evaporation will occur from this particular pore until the relative humidity has fallen to the value corresponding to the largest orifice or passage leading to the larger enclosed cavities. Since chance determines the size of this largest orifice leading to any particular cavity and since this principle holds for every enlargement in each of the numerous pores, the curve representing the amount of liquid retained during dehydration will lie above that for progressive hydration and this hysteresis will be due to the mechanism here pictured.[4]

Fig. 2.

It might be thought that in the lecture experiment, Fig. 1b, the liquid in the stoppered bell jar should break and fall away. However, it is well known that a great reduction in pressure is required to initiate the formation of a bubble in a mass of liquid. Hence the liquid under slight hydrostatic tension is forever stable. If through chance a very minute bubble began to form in any particular spot, where in accordance with Maxwell's distribution law of thermal vibrations a group of adjacent molecules simultaneously acquired a sufficiently high kinetic energy, the ultramicroscopic or even microscopic bubble would be immediately crushed and eliminated by the surface tension of the liquid.

The considerations here discussed might well simulate a "Jamin effect" in the penetration of soil or sand.

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[4] Compare the alternative presented by H. Engelhard and W. Stiller in their Fig. 6 [*Z. Elektrochem.*, **40**, 835 (1934)].

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The Heat and Free Energy of Formation of Arsenic Trifluoride

BY DON M. YOST AND JOHN E. SHERBORNE

The heat of formation of liquid arsenic trifluoride was obtained indirectly by determining the heats of solution of the trifluoride, and of a mixture of arsenious oxide and sodium fluoride in about 1 liter of 1 N sodium hydroxide solution. The reactions involved are

$$2AsF_3(l) + 6NaOH(1\ N) = 6NaF\ (\text{in } 1\ N\ NaOH) + As_2O_3\ (\text{in } 1\ N\ NaOH) + 3H_2O(l) \quad (1)$$

$$6NaF(s) + As_2O_3(s) = 6NaF\ (\text{in } 1\ N\ NaOH) + As_2O_3\ (\text{in } 1\ N\ NaOH) \quad (2)$$

The arsenic trifluoride was purified by fractional distillation and then condensed into thin-walled evacuated bulbs. The bulbs, containing a known weight of the material, were broken under the sodium hydroxide solution in an adiabatic calorimeter. The same procedure was followed with the arsenious oxide–sodium fluoride mixtures. All thermal experiments with the arsenic