Summary

1. Attention has been called to a non-electrolytic reaction between molten lithium salts and glass wherein sodium ions of the glass are displaced by lithium ions.

2. The reaction has value in analytical chemistry but, from the quantitative standpoint, its application is limited.

3. The nature of the phenomenon was studied in some detail.

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NOTES

Comparison of Viscosity Data

BY FRANCIS T. MILES[1]

In a recent paper[2] Miss Mary D. Waller calculates for a number of compounds the ratios of the viscosities at the melting and boiling points and correlates the values of this ratio, η_f/η_b, with the molecular symmetry of the compounds. Molecules of high symmetry are found to have low values of η_f/η_b, and *vice versa*. In a preliminary paper[3] the same author states that the melting and boiling points can be used as comparison temperatures. It is well known, however, that the melting point of a compound is influenced by the symmetry of the molecule. Dietz and Andrews[4] have pointed out that in the series, benzene, dihydrobenzene, tetrahydrobenzene, cyclohexane, the melting points of the two symmetrical compounds, benzene and cyclohexane, are 100° higher than those of the unsymmetrical compounds, while the boiling points of all four compounds lie in a range of only 2°. These authors have proposed an explanation for this influence of molecular symmetry on the melting point. If a pair of compounds had the same boiling points and equal viscosities at equal temperatures, the less symmetrical of the two compounds, having the lower melting point, would have a higher viscosity at the melting point and therefore a higher ratio, η_f/η_b. It is interesting to calculate whether the changes of η_f/η_b in a series of similar compounds are due primarily to the variation of viscosity with temperature or merely to the lower melting points of the unsymmetrical compounds.

The variation of viscosity with temperature can be expressed approximately by an equation of the form

$$\log \eta = A + B/T_{\text{Abs.}}$$

and this relation was used by Miss Waller to extrapolate viscosity data to the melting and boiling points. It follows from this equation that

$$\log r = \log \eta_f - \log \eta_b = B(1/T_f - 1/T_b)$$

Thus it is possible to separate log r into two factors of which one, B, represents the variation of viscosity with temperature, and the other, $1/T_f - 1/T_b$, represents the extent of the liquid range and is independent of the viscosity of the liquid, except in so far as this may be a factor in determining the melting and boiling points. Miss Waller tabulates values of $T_b - T_f$ and states that changes in this do not explain the changes in r. In view of the above equation, however, it is interesting to compare log r and $1/T_f - 1/T_b$, and this is done in Tables I and II. The first four columns in each table are taken directly from Miss Waller's paper. In the fifth column are values of log r calculated from these data. Values of $1/T_f - 1/T_b$, calculated from the melting and boiling points, are given in column six, and in the last column values of B are calculated from the relation

$$\log r = B(1/T_f - 1/T_b)$$

TABLE I

	η_f	η_b	r	log r	$(1/T_f - 1/T_b)$ $\times 10^3$	B $\times 10^{-2}$
Benzene	0.0082	0.0034	2.2	0.38	0.76	5.0
Toluene	.055	.0026	21	1.33	2.92	4.5
Ethylbenzene	.059	.0025	24	1.37	3.13	4.4
***o*-Xylene**	.019	.0026	6.6	0.86	1.67	5.2
***m*-Xylene**	.018	.0024	7.5	.88	2.14	4.1
***p*-Xylene**	.00703	.0024	3	.47	1.04	4.6

TABLE II

	η_f	η_b	r	log r	$(1/T_f - 1/T_b)$ $\times 10^3$	B $\times 10^{-2}$
Pentane	0.038	0.0021	18	1.26	3.83	3.3
Hexane	.0194	.0021	9	0.96	2.67	3.6
Heptane	.0279	.0021	13	1.12	2.77	4.05
Octane	.0189	.0021	9	0.96	2.11	4.55
Nonane	.025	.0021	12	1.08	2.14	5.05
Decane	.0232	.0021	11	1.04	1.90	5.5
Undecane	.0295	.0020	16	1.17	1.92	6.1

Table I gives the results for benzene and some of its homologs. Examination of the last two

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[2] Waller, *Phil. Mag.*, **18**, 579 (1934).

[3] Waller, *ibid.*, **18**, 505 (1934).

[4] Dietz and Andrews, *J. Chem. Phys.*, **1**, 62 (1933).

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.

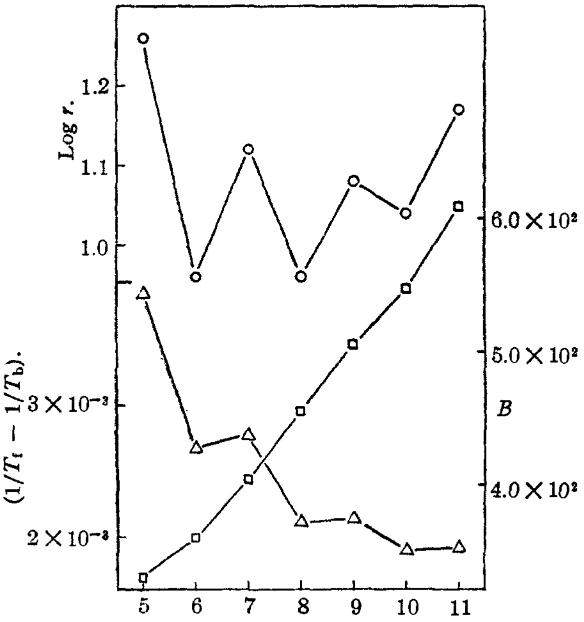

Fig. 1.—Log r, ⊙; $(1/T - 1/T)$, △; B, □.

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.

ANSTALT FÜR ANORGANISCHE CHEMIE
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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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[5] Dunn, *Trans. Faraday Soc.*, **22**, 401 (1926).

[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, 5^{te} 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).

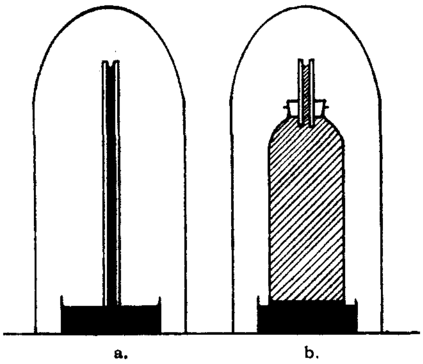

Fig. 1.

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.

[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 trifluoride were made as soon after filling the bulbs as possible since it slowly attacks glass with the formation of silicon tetrafluoride. The other substances used were of the best grades obtainable.

A number of determinations were made on both reactions and five values for each were finally selected as being the best. The average of these for reaction (1) is $\Delta H_1 = -64{,}500$ cal. with a mean error of 760 cal., and for reaction (2) $\Delta H_2 = -10{,}700$ cal. with a mean error of 800 cal.

The following heats of formation[1] were used in the calculations. NaOH(1 N), 112,210 cal.; H_2O(l), 68,387 cal.; As_2O_3(s), 156,000 cal.;[2] NaF(s), 137,600 cal. When these thermal data are combined with those determined for reactions (1) and (2), the following thermochemical equation may be written

$$\mathrm{As(s)} + 3/2\mathrm{F_2(g)} = \mathrm{AsF_3(l)} \qquad (3)$$
$$\Delta H = -198{,}300 \text{ cal.}$$

Although no experimentally determined value for the heat of vaporization of arsenic trifluoride (b. p. 63°) is available, a fairly reliable value of −7000 cal. results if Trouton's constant is taken as 21 cal./deg. This, combined with equation (3), yields 191,300 cal. as the heat of formation of AsF_3(g).

It is now possible to calculate a provisional value for the standard free energy of formation of gaseous arsenic trifluoride at 25°. The standard virtual entropies of As(s),[2] F_2(g)[3] and AsF_3(g)[4] at 25° are 8.4 cal./deg., 48.0 cal./deg. and 69.2 cal./deg., respectively. The free energy equation is then

$$\mathrm{As(s)} + 3/2\mathrm{F_2(g)} = \mathrm{AsF_3(g)} \qquad (4)$$
$$\Delta H = -191{,}300 \text{ cal.} \quad \Delta F^{\circ}_{298} = -188{,}000 \text{ cal.}$$

Rough measurements on the vapor pressure of AsF_3(l) showed it to be about 150 mm. at 23.5° and therefore the free energy of vaporization is about 1000 cal. When combined with equation (4) there results the rough value −189,000 cal. for the free energy of formation of AsF_3(l). Inasmuch as arsenic trifluoride is of considerable importance in reactions used for the preparation of other fluorides, these free energy values may find application in determining beforehand whether a proposed reaction is possible.

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(1) "International Critical Tables," Vol. V, pp. 161, 177, 180, 200.

(2) C. T. Anderson, *This Journal*, **52**, 2296 (1930).

(3) Yost and Hatcher, *J. Chem. Educ.*, **10**, 350 (1933).

(4) Yost and Anderson, *J. Chem. Phys.*, **2**, 624 (1934); Yost and Sherborne, *ibid.*, **2**, 125 (1934).

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[CONTRIBUTION FROM THE FLEISCHMANN LABORATORIES]

A General Method for Determining the Concentration of Enzyme Preparations[1]

BY W. R. JOHNSTON AND S. JOZSA

It is generally recognized that the "enzyme unit" method as introduced by Willstätter and Kuhn[2] is the most satisfactory way we have of measuring enzyme quantity.

In applying the method, however, a number of authors have defined their enzyme units in terms of the monomolecular "constants" for the reactions being studied. This application is not strictly correct since it has been established by numerous workers that in general the unimolecular law does not apply to enzyme reactions and the "constants" cannot be used as an accurate measure of enzyme quantity. This is true in the case of invertase, urease, alpha-amylase and many other enzymes.

Other investigators have defined units in terms of time values required for a definite percentage hydrolysis of the substrate by a given amount of enzyme. These units lead to sufficiently accurate measures of enzyme quantity but are not very satisfactory because of the relatively long time required for measurement and calculation.

In attempting to measure the concentration of α-amylase in various malt preparations we developed an enzyme unit method which is of general applicability and which permits rapid, accurate measurements of enzyme quantity. The method is based upon the fact that in the case of several enzymes the initial rate of action on a given substrate is directly proportional to the amount of enzyme acting. We have found this to be true in the case of α- and β-amylase and yeast invertase and other workers have demon-

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(1) Presented before the Division of Biological Chemistry at the 86th meeting of the American Chemical Society, Chicago, Ill., September 10–15, 1933.

(2) Willstätter and Kuhn, *Ber.*, **56**, 509 (1923).