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Constitution of Liquids : Some New Experiments.

LAST year I had the honour of presenting to the Society an address in which an account was given of experiments on the effect of catalysts on the molecular association of liquids. It was shown that these catalysts modified the union of the molecules of liquids, in the same way as they modify ordinary chemical actions. The inference was drawn that in liquids an equilibrium, depending on the temperature and the nature of the liquid, is established between the association and dissociation of molecules, which can be disturbed by the presence of catalysts. I propose in what follows to give an account of experiments which have been in progress during the last few years, extending our knowledge of dried liquids, and, secondly, of experiments which seem to indicate the reason for the great changes which take place in liquids when moisture is removed as completely as possible.

In the first place, a number of determinations of the density of the vapours of dried liquids have been made. The liquid was sealed up with purified phosphorus pentoxide in a tube to which was joined a capillary tube in which a series of ten or twelve bulbs, of about 1·5 c.c. capacity, was blown. The liquid was frozen in liquid air and the whole exhausted. From time to time, as the drying progressed, liquid was distilled into the end bulb, which was then sealed off and used for a determination of vapour density by the method of Victor Meyer, the apparatus being modified as described in a paper on gaseous nitrogen trioxide (J., 1907, **91**, 1865). The following results were obtained :

Substance.	Time of drying (years).	Temp. of detern.	Mol. wt.	Normal mol. wt.
Bromine	2	86°	234·3	160
,,	3	93	242·4	,,
Carbon disulphide	2	90	127·0	76
,, ,,	4	90	137·4	,,
Carbon tetrachloride	3	100	191	154
,, ,,	5	100	201	,,
Ethyl ether	5	102	173·1	74
Methyl alcohol	5	103	90·6	32
n-Hexane	4	100	160·5	86
Benzene	3	100	102·4	78
,,	5	100	125·9	,,
Nitrogen tetroxide	10 + 1	80	101·9	92
,, ,,	10 + 5	40	130·7	,,

The molecular aggregation of the main mass of the liquid is probably greater than is represented by the vapour density, since, as was shown in 1924, fractional distillation of the dried liquid takes place. If it were possible to distil most of the liquid away and then seal up a bulb containing the last fraction, the vapour density would probably show a much higher value.

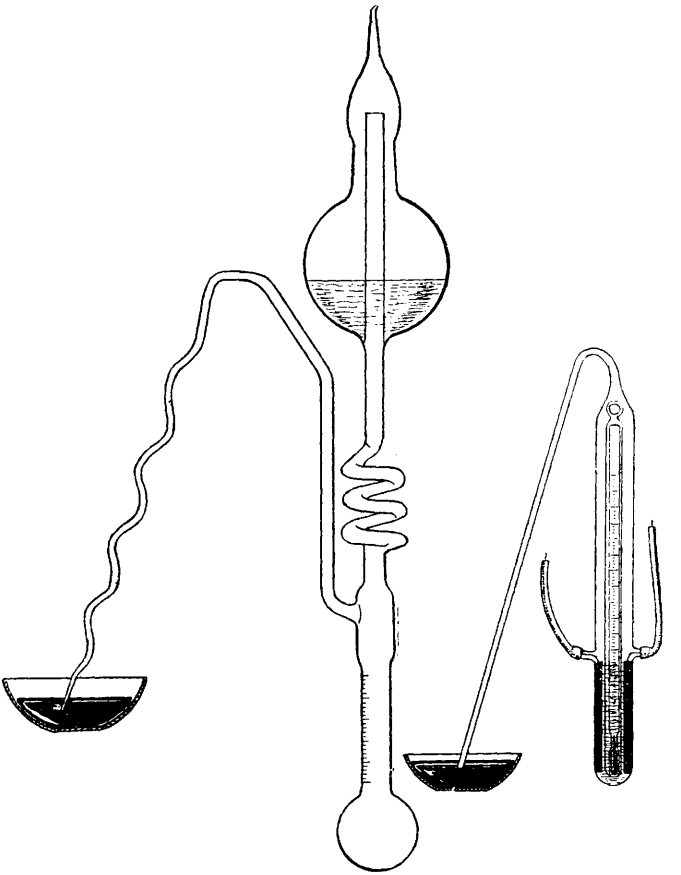

FIG. 1. FIG. 3.

It was thought that if association takes place in a dry liquid there must be a change in the latent heat of evaporation. This determination presents peculiar difficulties, since the liquid must not come into contact with the atmosphere. A modification of Berthelot's method was employed, which will be understood from the diagram (Fig. 1). Benzene, carefully purified and distilled from phosphorus

pentoxide, was contained together with phosphorus pentoxide in the upper bulb. After standing for $3\frac{1}{2}$ years, it was distilled by means of a ring burner, into the lower graduated tube, immersed in a known weight of water contained in a Dewar vessel. The boiling point of the liquid was then determined. From the volume of liquid distilled and the rise in temperature of the water, the latent heat of evaporation could be calculated. Two experiments were made with two different pieces of apparatus. The latent heats for 1 gram of benzene were 57·2 and 58, respectively, instead of 83, the normal value. The boiling point of the dried benzene was 94°, and to bring this into conformity with Trouton's rule the molecular weight of the benzene must be 136 instead of 78.

We have, therefore, in favour of the view I have repeatedly expressed, that the removal of water from liquids leads to increased molecular complexity, four separate classes of experimental data : (1) Increase of boiling point, (2) change of surface tension (J., 1922, **121**, 568), (3) increase of vapour density, and (4) for one liquid, decrease in latent heat of evaporation.

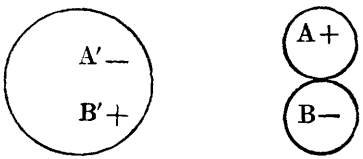

FIG. 2.

As to the reason why the withdrawal of water should bring about the displacement of equilibrium in the direction of larger molecules, there is only one hypothesis, that of Sir J. J. Thomson (*Phil. Mag.*, 1893, **36**, 320), which offers a reasonable explanation of the phenomenon.

Imagine a molecule AB, the atoms of which are held together by electrical attraction (Fig. 2). If a drop of a liquid, with high specific inductive capacity, were adjacent to it, charges would be induced in the drop and the attraction of the atom A to the atom B would be lessened. Therefore the molecule would be more easily dissociated. In the presence of liquid drops of water, therefore, molecules should be less stable. We do not know how many molecules are required to form an effective drop, but single molecules of water would probably not serve. It has been demonstrated by C. T. R. Wilson that the presence of ions in a gas determines the condensation on them of water vapour to form liquid drops. It would seem, therefore, that if we could increase the amount of ionisation in the presence of a small quantity of water vapour, we ought to get a number of drops formed and a decrease in the stability

of the surrounding molecules. In the case of gases which can react, the atoms of their molecules should be less firmly held together and reaction between the gases should be increased. This deduction has been tested as follows. It is known that ionisation is produced in a gas by heated lime, more by thoria, and most, of course, by radium bromide. Silica tubes containing a mixture of hydrogen with nitrous oxide, dried to such an extent that the moisture content was only a few milligrams to a million litres, were heated in a resistance furnace in pairs. One tube contained lime and the other powdered Jena glass. When the combining point was reached, the rate of union in the lime tube was five times that in the tube containing the powdered glass. Another tube containing thoria in place of the lime gave a rate of union twenty times that in the tube with glass alone. After 15 minutes' heating, when a large amount of water had been formed in the reaction, the rate of union became the same, whether powdered glass, lime, or thoria was present. In a third experiment, 2 milligrams of radium bromide were used, and as soon as the combining temperature of the gases was reached the mixture exploded and the tube burst. Thus, increasing the ionisation produced a greater rate of reaction, as we should expect if the formation of liquid drops assisted chemical union.

It has been shown that, in absence of water, liquids are associated, even those, such as hexane and benzene, which are ordinarily taken to be typical non-associated liquids. In my address of last year the condition of all liquids was compared to the gas nitrogen tetroxide, which only at $-20°$ consists entirely of N_2O_4 molecules. Above this temperature we conceive of the gas as a mixture of NO_2 molecules and unaltered N_2O_4 molecules. It is probable that a perpetual dissociation and recombination is taking place, equilibrium changing with temperature. The condition of the molecules in liquids is probably the same, some liquids tending to contain more of the large molecules, such as water and acetic acid, and some less, such as the two liquids mentioned above. In absence of water the large molecules are stable. If the theory outlined above is true, we ought to be able, even in presence of water, but in absence of facilities for its condensation into drops, to stabilise the large molecules and increase the number of them above the normal number corresponding to a given temperature. This I have attempted to do with three liquids, hexane, benzene, and carbon disulphide. They were chosen as supposedly non-associated liquids, though I have shown that in the dry state they are associated to such an extent that the average size of the molecules is at least twice the size of the single molecule. The liquids were dried only as far as concentrated sulphuric acid could do so, *i.e.*, there would still be a large number of water

molecules diffused through the molecules of the liquid. The boiling point of the benzene was 79·6°. Tubes of 1 cm. diameter were prepared with two platinum plates, about 7 cm. long, fixed facing each other at the lower end of the tube. A thermometer was placed between them. Benzene was introduced just to cover the plates (Fig. 3). By connecting the platinum plates with a 400-volt battery for some hours, the boiling point of the benzene was raised to 91°. A precisely similar tube containing the same benzene and similar electrodes, but without the applied voltage, was placed in the same bath; the benzene boiled at 79·6°. This effect was not destroyed when the apparatus stood for a few days with the plates disconnected from the battery; the boiling point was 88° and the boiling was steady, not violent. While the boiling was proceeding, the voltage was again applied and in two minutes the evolution of bubbles stopped. Measurements of the surface tension of the liquid indicated a molecular weight of between two and three times that corresponding to the formula C_6H_6.

This experiment, which is confirmed by similar behaviour with hexane and carbon disulphide, may be explained by supposing that the ions were removed by the electric field and therefore the water present was incapable of collecting into drops.

I thought that the effect might possibly be due to the elimination of water by electrolysis and the consequential drying of the liquid; not a trace of gas, however, could be collected over the mercury in the trough. Moreover, if the plates were connected together and allowed to stand, the surface tension indicated a normal molecular weight, and the normal boiling point was restored.

If further work on these lines should confirm the result of these preliminary experiments, we shall have, for the first time, an explanation of the rôle played by water in changes of molecular association in liquids.

I wish, in conclusion, to express my thanks to my wife and to Miss Carlton for their help in the experiments which I have described.