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Experiments on Molecular Association.

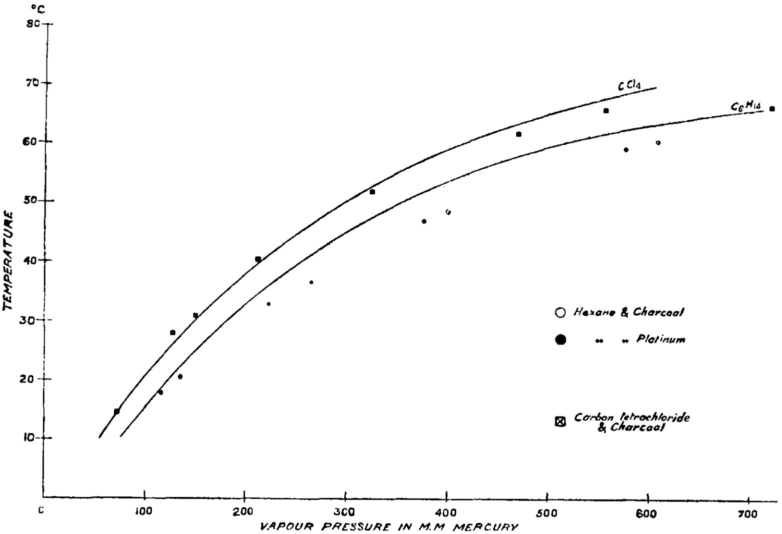
THE molecular constitution of liquids has been the subject of much investigation. It is known that in acetic acid we have molecules which have double the simple formula, and that this complex is stable even when the liquid is converted into vapour. In water, the association is even greater than this at low temperatures, but the larger molecules are less stable and can scarcely persist when the liquid is vaporised. Bromine shows some evidence of association in the vapour, but owing to experimental difficulties, little is known as to the constitution of the liquid. On the other hand, liquids such as benzene and the lower-boiling paraffins have been considered as containing only the simplest molecules. It was shown, however, some five years ago that if liquids of very diverse types were subjected to prolonged drying, the boiling points were raised to a considerable extent. This is ascribed to the increase in complexity of the molecules when the catalyst, water, is removed. Since this rise of boiling point has been shown to take place both with benzene and with hexane, two typically unassociated liquids, it is probable that, instead of associated liquids being exceptional, all liquids may be capable of association. It is supposed that there is a continual combination and dissociation of the molecules in an ordinary liquid. It is known that water can promote, not only chemical combination, but also dissociation. If water is removed as completely as possible, its absence might conceivably work in two directions: the molecular equilibrium might be reached when the molecules were much more complex owing to absence of dissociation, or, in a liquid which was normally associated, the molecules might be much less complex owing to their inability, in absence of water, to combine together. The latter state has not yet been attained; we have not been able to obtain dry liquids which boil at a lower temperature than the normal. It is true that in the very fruitful week when Prof. Smits was working with me in my laboratory, dried benzene was fractionally distilled and the first fraction which came over boiled at 80°, leaving the higher-boiling fraction (118°) behind. If instead of benzene, which is normally associated only to a small extent, we had been dealing with bromine, which is much more associated in its normal condition, it is possible that we should have been able to distil off a fraction boiling below 59°.

It was with the hope of throwing some light on this question of the equilibrium of complex and simple molecules in a liquid that a new series of experiments was undertaken, with the object of finding out if catalysts other than water had a disturbing influence. I wish to acknowledge here the invaluable help given in their performance by my assistant, Miss M. Carlton.

Two main methods of attack on the problem were chosen, the determination of the vapour pressure and the measurement of surface tension.

In the first series of experiments on vapour pressures, charcoal was used as the catalyst. Barometer tubes were made of hard Jena glass, one end of which dipped under mercury. The upper ends were furnished with bulbs in which very pure sugar charcoal could be heated to redness while the tube was being exhausted. After admission of the liquid, the tube connecting the bulb with the pump was sealed off and the tubes were surrounded by a jacket of circulating water.

Fig. 1.



The continuous curves are the normal vapour pressure–temperature curves.

The results of these preliminary experiments left no doubt as to the influence of the presence of charcoal on the vapour pressure. With ether at 16°, the vapour pressure was 25 mm. greater than with the liquid alone. With methyl alcohol at 18°, the vapour pressure was 6 mm., and at 35° 12 mm., greater in the presence of the catalyst. With benzene, the increase with the charcoal was

2 mm. only, and this excess of vapour pressure was unaltered whether the temperature was 23° or 37°.

It was found, however, that quantitative measurements of the vapour pressures of each of the liquids showed considerable variations and a lengthy series of experiments was made using the two methods devised by Smith and Menzies (*J. Amer. Chem. Soc.*, 1910, **32**, 907, 1412). Some of the results are given in Fig. 1. These experiments again failed to give results which were concordant when the same liquid and the same catalyst were used in successive experiments. They did, however, lead to two important conclusions. We had ascribed our failure to obtain concordant results in the first series to the difficulty of obtaining the catalysts in the same condition of activity; different methods of treatment, different temperatures of treatment, and even age alone might have influenced their catalytic power.

The first fact which became clear in these preliminary experiments was that a catalyst in a liquid acts very slowly and sometimes at first even in a contrary direction to that shown in the final equilibrium. That is, in any liquid there is a balance between the large and the small molecules, for in all the liquids, ten in number, which we have examined there is evidence of some association. The presence of certain catalysts can influence the equilibrium, under different temperature conditions, in the direction of producing more complex molecules and so lowering the vapour pressure, and then, under different conditions, especially long time of contact, may produce increased dissociation and higher vapour pressure.

The second difficulty was caused by the fact that a pure liquid appears to have no constancy in its composition. For instance, pure bromine, without any catalyst, gave vapour pressures which showed considerable variations according to the history of the particular specimen. If bromine were boiled for some time and the measurement taken as soon afterwards as possible, it was found that the vapour pressure was very sensibly higher than it had been before the boiling took place. The recovery of the old vapour pressure was quite slow and many days elapsed before the effect of the boiling had disappeared.

In order to eliminate the effect of this change in the liquid alone, the next series of experiments was designed. In them the vapour pressure of the liquid was balanced against the pressure of the liquid with the catalyst, through a pressure gauge. The form of the apparatus is seen in Fig. 2.

To each of the upper ends of a U-shaped tube containing mercury was sealed a pair of bulbs, which were connected with each other by a capillary tube. Into one bulb was introduced the catalyst, and the liquid was placed in the second of the pair. The same liquid was then introduced into one of the bulbs of the other pair, the second one being left empty. All the entrance tubes but one were sealed off. The remaining tube was connected to a Hyvac pump. The liquid in the two bulbs was allowed to boil in the evacuated space in order to get rid of dissolved air : the liquid was then frozen and thereafter the bulb containing the catalyst was suitably heated with the same object. The tube connected with the pump was now sealed off, and the apparatus allowed to stand for an hour. Finally, the capillary tube connecting the two sets of bulbs was sealed with a fine-pointed flame. On transferring the apparatus to a thermostat it was found that the mercury level was the same in both limbs of the U-tube, showing that the apparatus was in order. By cooling the bulb containing the catalyst, the liquid was distilled over from the adjoining bulb. In this way, the two lots of liquid could be treated in exactly the same way, and a direct determination could be made of the difference in vapour pressure brought about by the catalyst. The results are in the table on p. 953.

FIG. 3.

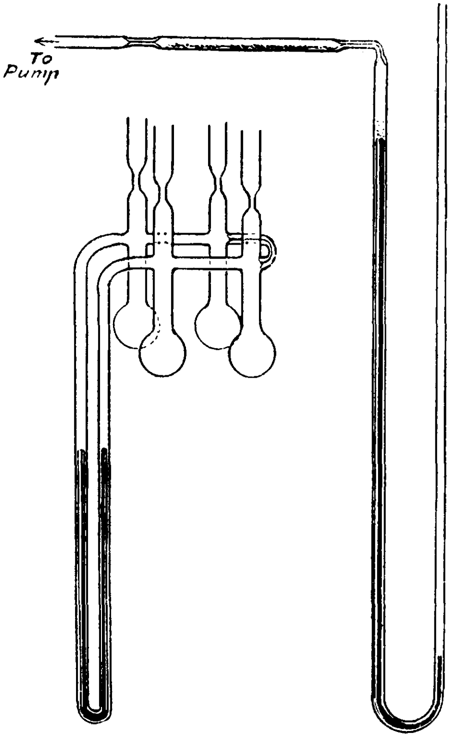


FIG. 2.

In each of the systems investigated there was an increase in the vapour pressure of the liquid in contact with the catalyst over the vapour pressure of the liquid alone. This difference increased with time up to a certain point and then became constant. The effect of the increase of vapour pressure produced by a catalyst was always seen with this apparatus, for, on standing, the liquid evaporated away from the catalyst and condensed in another part of the apparatus, although the whole was kept at a constant temperature in a thermostat.

The effects of heating and of cooling on this difference of vapour pressure were investigated and it was found that heating increased the difference and cooling diminished it. On standing, however, the original value of the difference was restored, although in some cases the time needed was some weeks.

Acetic acid and charcoal.

Time.	Diff. in mm. Hg.
Day of sealing	2·15
2 Days later ...	1·5
After heating at 80° for 4 hrs....	2·95
6 Days later ...	2·0
After keeping at 15° for 24 hrs.	2·05
2 Days later ...	2·4
5 Months later	1·9

Acetic acid and platinum black.

Time.	Diff. in mm. Hg.
Day of sealing	0·3
1 Day later ...	0·25
After heating at 80° for 4 hrs....	0·5
1 Day later......	0·75
6 Days later ...	0·8
After cooling at 15° for 1 day	1·05
3 Days later ...	1·6
After heating at 90° for 4 hrs.	1·75
5 Months later	2·2

Acetic acid and thoria.

Time.	Diff. in mm. Hg.
Day of sealing	0·4
3 Weeks later...	0·25
3 Weeks later...	1·27
Heated at 90° for 4 hrs.	1·32

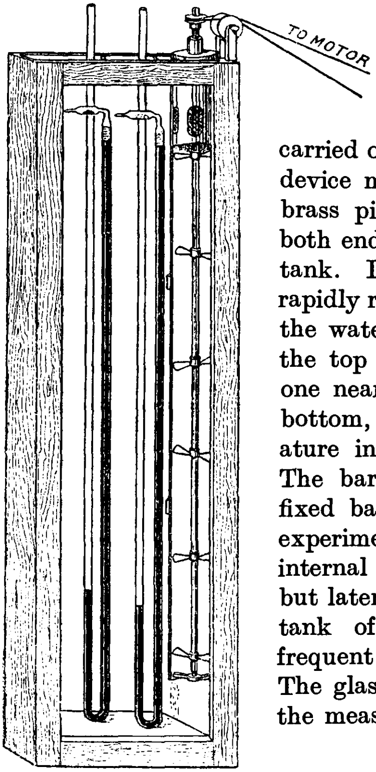
Benzene and nickel. Diff. in mm. Hg.	Methyl alcohol and charcoal. Diff. in mm. Hg.	Ether and charcoal. Diff. in mm. Hg.
3·4	5·5	40·0
3·3	6·3	41·3
3·3	6·2	41·2
3·5	6·5	39·2
3·1	6·1	40·2

Bromine and charcoal.

Time.	Diff. in mm. H_2SO_4 satd. with bromine.	Time.	Diff. in mm. H_2SO_4 satd. with bromine.
—	38·5	Interval of 2 days ...	95·2
Interval of 2 days ...	50·9	Interval of 14 days ...	125·1
Interval of 1 day	51·7	Interval of 16 days ...	133·75
Interval of 1 day	52·8	Interval of 3 days ...	142·3
Interval of 6 days ...	85·2		

In order to investigate the effect of heating on the vapour pressure of the liquid alone as well as in presence of catalysts, a return was made to the barometer tube method, with greatly improved apparatus (Fig. 3). The tube was U-shaped and made of Jena glass. The upper end of one limb was bent into a horizontal position, and by drawing it out to a capillary a bulb was formed, about 2 inches in length, to hold the catalyst. The liquid was introduced into the main barometer tube, and the catalyst into its bulb. The tube was then exhausted through the capillary and, after the liquid had been allowed to boil to expel dissolved air, the part of the vertical tube containing it was frozen and the catalyst was heated. As it was found difficult to obtain charcoal in the same state of activity in successive experiments, it was necessary to give this substance the same heat treatment. This was accomplished by slipping over the horizontal bulb a small electric furnace which maintained the charcoal at 450° for 1½ hours, the pump being kept running during the whole period. The capillary tube was then sealed, and the tube transferred to a large thermostat (Fig. 4). This was 1 sq. ft. in section and 3 ft. 6 in. in height. It was built of heavy teak, with thick plate-glass windows on opposite sides. It was filled with water and the stirring was carried out most effectively by an ingenious device made by Mr. W. J. Colebrook. A brass pipe, 5 inches in diameter, open at both ends, extends the whole height of the tank. In it is a screw propeller which, rapidly rotated by an electric motor, pumps the water continually from the bottom to the top of the tank. Two thermometers, one near the top and the other near the bottom, indicate the constancy of temperature in the different parts of the tank. The barometer tubes were clamped to a fixed bar inside the tank. In the earlier experiments, heating was effected by an internal coil carrying superheated steam, but later this was carried on in a separate tank of galvanised iron, owing to the frequent fracture of the glass windows. The glass-fronted thermostat was kept for the measurements alone.

FIG. 4.



Acetic Acid.

Catalyst.	Before heating.	Heated at 80° for 24 hrs., then cooled to 20°.	One week after heating at 20°.
None.	Normal.	+2 mm.	Normal.
Charcoal.	+1·8 mm. After an interval of 6 weeks, +6·0 mm.	+2·3 mm	+6·8 mm.
Thoria.	+0·65 mm. After an interval of 6 weeks, +7·3 mm.	+1·5 mm.	+7·3 mm.
Platinum.	+2·72 mm. After an interval of 6 weeks, −1·2 mm.	−3·8 mm.	+1·1 mm.

Water.

Catalyst.	Before heating.	Heated at 80° for 48 hrs., then cooled to 20°.	Two weeks after, at 20°.
None.	Normal.	Normal.	Normal.
Charcoal.	+2·5 mm.	+4·3 mm. 1 Day later, +0·75 mm.	+2·5 mm.
Thoria.	+2·4 mm.	+4·0 mm. 1 Day later, +1·2 mm.	+0·9 mm.
Platinum.	+1 mm.	+3·2 mm. 1 Day later, +0·6 mm.	+0·5 mm.

Measurements of the vapour pressure of water in the presence of the catalysts charcoal, platinum, and thoria show that in each instance heating has the same ultimate effect, but the interval between the actual heating and the appearance of the effect of the heating varies with the different catalysts. With thoria and platinum, heating at 80° for 24 hours produces an increase in vapour pressure, at the ordinary temperature, but if the time of heating be prolonged to 48 hours the vapour pressure within 24 hours of the heating shows a decrease from the constant value, this decrease disappearing if the tubes be allowed to stand for a few days at room temperature.

The charcoal and water, when heated at 80° for 24 hours, shows an increase in vapour pressure, if the readings be made within 24 hours of the heating; but two days after the heating the value of the vapour pressure diminishes and becomes less than before heating. This low value slowly changes back to the constant value when the barometer tubes containing the water and charcoal are allowed to stand at the ordinary temperature for a few days.

With acetic acid, charcoal as catalyst produces a decrease after 24 hours' heating; after 72 hours' heating, there is a decrease which temporarily increases for a day or two, the normal value finally returning. Thoria causes a decrease in vapour pressure when heated with acetic acid, the amount of the decrease being greatest a day or two after the heating has taken place. With platinum, a diminution in vapour pressure is caused by heating, the normal value returning after a short while.

Surface Tension Measurements.

The vapour pressure determinations having shown that the presence of catalysts produces a change in liquids, experiments were undertaken to find the molecular weights of some liquids by the method of Ramsay and Shields. Although the absolute accuracy of this method has been disputed, the differences we have found between the molecular weights of liquids alone and in the presence of catalysts are so marked that any small deviations from the true values are probably unimportant.

The determinations of the diameters of the capillary tubes were made with a microscope, kindly lent by Professor Fowler, which reads directly to the 1/1000th of a millimetre. These capillaries were sealed to glass sinkers and cleaned with a mixture of nitric and chromic acids. The containing tubes were made of special resistant glass, the formula of which was worked out by myself and the late Mr. H. J. Powell, of the Whitefriars Glass Works. The liquids were shown to have taken up no weighable amounts either from the glass or from the catalyst even after a year's contact.

The measurements were taken in a large thermostat provided with an electrically driven stirrer. Half an hour before the heights of the liquids in the capillaries were measured, the tubes were taken out and tilted to see that the liquids ran freely in the capillaries. There was always a danger that the finely powdered catalyst might block the minute opening at the bottom of the capillary. The catalysts and the liquids used were from the same preparations as those which were used in the vapour pressure experiments.

The study of surface tension was directed chiefly to the effect of three catalysts—pure charcoal, platinum black, and oxide of thorium—on the three liquids water, acetic acid, and bromine.

In all cases, comparative tubes were used containing the liquid alone, without the presence of any catalyst, so that a direct estimation of the effect of the catalyst could be made under various conditions of temperature, etc.

It has been found that the catalyst does not seem to produce its maximum effect on the complexity of the molecules at once. This is seen by the following table : the temperature interval was about 20°, the higher temperature being 40°.

Acetic Acid and Charcoal.

	Time.	Mol. wt.
After	1 day	1·541 × 60
,,	2 days	1·952 × 60
,,	3 weeks	2·525 × 60
,,	12 months	2·492 × 60

Acetic Acid alone.

	Time.	Mol. wt.
After	1 day	1·546 × 60
,,	2 days	1·568 × 60
,,	3 weeks	2·097 × 60
,,	9 months	2·097 × 60

Acetic Acid and Platinum Black.

	Time.	Mol. wt.
After	2 weeks	2·40 × 60
,,	3 months	2·273 × 60
,,	8 months	2·976 × 60

Acetic Acid and Thoria.

	Time.	Mol. wt.
After	1 day	2·538 × 60

The table for acetic acid alone shows that the acid does not reach its normal value in 2 days after filling. This points to the conclusion that in the process of filling the tube, which involves the boiling of the liquid for some time to get rid of air, dissociation of the molecules of liquid takes place, and that in 3 weeks the normal molecular weight is restored. With charcoal the same phenomenon is observed, but the molecular weight is greater by 24. With platinum black, the molecular weight is greater by 52, whilst with thoria the increase in molecular weight due to the catalyst is 29.

A similar effect is seen with water and the same catalysts.

Water and Platinum.

Time.	Mol. wt.
Day of filling	3·352 × 18
After 6 months	4·442 × 18
Heated at 40° for 16 hrs.	3·948 × 18
1 Week later	3·713 × 18
2 Weeks later	3·047 × 18
1 Day later	2·915 × 18

Water and Thoria.

Time.	Mol. wt.
3 Weeks after filling	3·125 × 18
5 Weeks after filling	3·612 × 18
9 Weeks after filling	3·866 × 18

Ramsay and Shields' value for this temperature interval is 3·259 × 18.

This method, as used, appears to have a disadvantage because the heating, even to only 40°, seems to disturb the equilibrium and this is not restored at once on cooling to the ordinary temperature. It was therefore decided to make a study of the effect of temperature on the constitution of these liquids in presence and in absence of catalysts. It must be pointed out that, after heating or cooling, the liquids were allowed to stand at the ordinary temperature for the time specified, so that the effects shown are those not measured at the high or low temperature, but through the usual interval 17—40°.

Acetic Acid.

Catalyst.	Before heating.	After heating at 80° for 2 hrs.	After heating at 80° for 48 hrs.	After 24 hrs. at the ordinary temperature.
None	2·168 × 60	2·32 × 60	1·97 × 60	1·666 × 60
Platinum black	1·872 × 60	2·527 × 60	1·782 × 60	1·586 × 60
Charcoal	2·492 × 60	2·552 × 60	1·690 × 60	2·490 × 60
Thoria	1·992 × 60	2·538 × 60	2·218 × 60	2·452 × 60

Attention may be directed, not only to the effect of the catalysts on the complexity of the molecules of the different liquids, but also to the different effects of heating for various lengths of time. Except in the cases of bromine alone and of charcoal in acetic acid, heating for only a short period seems to increase the molecular complexity, whilst heating for a long period decreases it, as would be expected. The recovery to normal is slow, but even after 3 days' standing at the ordinary temperature the molecular weight is often considerably above or below that at the beginning of the experiments.

The agreement between the vapour-pressure and the surface-tension results is not quantitative. This could not be expected, since, by the surface tension method the *average* complexity of the molecules is estimated, whilst the vapour pressure measured will be, very largely at all events, that of the smaller molecules present.

The view of the constitution of liquids which is indicated by these experiments is that all liquids may be regarded as analogous to a dissociable gas such as nitrogen tetroxide. At low temperatures the heavy molecules are more numerous; at higher temperatures the lighter ones predominate, and dissociation and combination are probably both increasing. Liquids differ, however, in this respect, that dissociation and association are much slower in liquids than in gases. Equilibrium in liquids may be profoundly disturbed by even a comparatively slight change of temperature, and complete recovery of the normal condition may be a question of weeks or even months.

The effect of the presence of a solid catalyst is, as would be expected, produced much more slowly in a liquid than in a gas, and it is not easy to understand how the catalyst comes to exert its special influence. All one can say at present is that this influence is exerted in the case of all the liquids on which experiments have been made.