THE MELTING-POINT OF CHLORAL HYDRATE

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In a series of papers on evaporation and dissociation, Ramsay and Young have examined the behavior of chloral hydrate on heating and observed that this substance can be heated under reduced pressure to 64° without melting. Naumann¹ and others have also shown the very complete dissociation which takes place in the vapor phase. As the melting-points of this substance have been given as ranging from 48° to 57° , it has been thought advisable to examine this point more closely as it is possible that the variations observed may not be due to errors of observation, but to the changes which take place in the substance on heating.²

If one take as a general case a compound AB, made up of two components A and B, one may express the change in melting-point consequent on dissociation of the compound by the concentration-temperature diagram (Fig. 1).

The point C will then represent the melting-point of the pure compound when there is no dissociation. Should dissociation take place, the freezing-point is lowered and C_1 will represent the temperature at which the solid compound is in stable equilibrium with a melt containing both dissociation products A and B. Should dissociation take place, C is depressed and one gets a lower freezing-point. C will then represent the melting-point of the pure compound when no dissociation takes place. C_1 will represent a melting-point corresponding to a certain amount of dissociation which takes place at the temperature represented by a coordinate cutting the point C_1 .

¹ Naumann. Ber. chem. Ges. Berlin, 10, 822 (1877); Würtz. Comptes rendus, 84, 971 (1877); 88, 825 and 861 (1879); 90, 98 (1880).

² Cf. Bancroft. Jour. Phys. Chem. 3, 85 (1898).

Fig. 1

Melting-points between C and C_1 could be realized in the case of a substance which dissociates with measurable slowness. If the compound be heated up to its melting-point and be allowed to cool rapidly, the amount of dissociation would be small and one would therefore expect to obtain a freezing-point comparatively near the original melting-point. Were the substance cooled sufficiently slowly so as to allow the dissociation to proceed far, then on heating again one would obtain a melting-point lying much lower on the temperature axis. On the other hand, could one remove the product of dissociation rapidly enough, one should arrive at the true melting-point of the substance, providing a sublimation temperature was not reached first.

Ramsay and Young in their experiments on the vapor pressure of chloral hydrate, heated this substance which had been previously fused on the bulb of a thermometer in a vacuum, and observed that no melting took place at 64° , although at atmospheric pressure the identical crystals melted at 50.6° . This could be explained by assuming that under these conditions the products of dissociation were removed with such rapidity that no point on a line joining C and C_1 was realized. When however

the pressure was raised sufficiently, the substance melted and fused at once. Here one was obviously dealing with a system containing a compound and one or both of the components, with a consequent lowering of the melting-point below that of the true fusion of the undissociated substance.

On the other hand, chloral hydrate has been assumed to contain two substances whose formulæ have been variously given and should one, on heating, really deal with two isomeric modifications in the melt, together with the products of dissociation, one would then have to do with a system more complex than the foregoing, and which could be represented schematically as follows :

Fig. 2

Let C_α and C_β represent the melting-points of the two modifications and D_α and D_β the melting-points of the two isomers, lowered by the presence of the products of dissociation. Then to each of the compounds, the temperature between C_α and C_β would correspond to a line joining C and C_i on the preceding diagram. If C_α were the more stable, and it could be proven that no dissociation took place, but simply that a change of C_β into C_α took place, then one would obtain a stable freezing-point

on melting and cooling either isomer, represented by X where the one form as solid phase was in stable equilibrium with solution and vapor. On the other hand, did dissociation accompany this change into the stable form, one would get a further fall of the freezing-point corresponding to point Y on the curve D_aYN , where the one form in solid phase was in equilibrium with the dissociation products and the isomers as liquid phase. M would be a point where C_a and C_β would coexist as solid phases with liquid and vapor, and N where the components C_a and C_β would coexist with the dissociated liquid and vapor. Hence, to put the case more concretely, did one have a compound existing in two modifications, one might have the following phenomena taking place.

I. On obtaining the two isomers and heating rapidly, or in some other way inhibiting the amount of dissociation, one would obtain high melting-points corresponding respectively to C_a and C_β . Did dissociation simultaneously take place, one would obtain various melting-points between C_a and D_a , and C_β and D_β .

II. Did no dissociation take place, but simply tautomeric change, one would obtain on long heating a melting-point corresponding in temperature and in the relative concentration of the two forms to a point on the curve C_aMC_β .

III. With the two changes described as I and II taking place at the same time, viz., Tautomerism and Dissociation, one gets final equilibrium at Y on the curve D_a and ND_a .

In order to arrive at a conclusion regarding the changes which take place on heating, it would therefore be necessary to heat the compound or compounds under as many conditions as would favor or retard both changes and dissociation, and further, to perform the experiments in such ways as could bring together desired combinations of the two processes.

The chloral hydrate used for these experiments was commercial. The substance was in large transparent plates. Experiments made in this laboratory in the previous winter on the purification of the substance by fractional crystallization from chloroform, carbon disulphide, chloral, water and other solvents,

led to unsatisfactory results, as the melting-point of the successive products varied irregularly within limits of two or three degrees. The preparation of the hydrate from chloral and water also gave a product which did not differ from the substance on hand, so that eventually it was decided to use the commercial article without further purification. The substance, moreover, satisfied all the requirements of pure chloral hydrate.

The experiments of Ramsay and Young¹ were repeated and the apparatus used was essentially the same as that used in their earlier experiments.² The pressure was measured by a differential manometer instead of barometer and cathetometer, exhaustion being effected by a water-pump. The **H** form of the tube was found useful as duplicate experiments could be made under identical conditions. The tube was heated in a water-bath, the temperature of which was varied from 80° to 100°. The temperature of the bath had apparently no effect on the final results. The thermometer bulbs were coated with chloral hydrate by immersing in fused chloral hydrate cooled nearly to the solidification point, and the length of time after coating was noted. In one instance, a thermometer was allowed to stand in a closed test-tube for some three weeks after coating.

It was found that when the thermometers were used shortly after coating that a slight preliminary fusion took place at 50° under a pressure of 22 mm. This appearance of rounded edges soon disappeared and the coating was then in every respect identical with that on the thermometer which had stood for twenty-four hours after coating.

The temperature of the thermometer rose slowly to 72° and remained there for some time. During this time the coating on the thermometer becomes perceptibly thinner.

If now the pressure be raised to 35 mm by the admission of air, slight fusion takes place. The thermometer drops to 69°, 70°, and if the vacuum be restored quickly enough, the mass solidifies, the temperature of the mass rising again to 72°. If, however, a large amount of air be introduced into the apparatus,

¹ Phil. Trans. 177, I, 77 (1886).

² Ibid. 175, II, 471 (1884).

the substance melts instantly. In this case the thermometer drops an indefinite number of degrees according to the amount of substance remaining on the bulb.

The hydrate evaporates quickly, and the thermometer then rises and indicates a temperature nearly that of the bath. Under no circumstances could the substance be fused at 22 millimeters, so that it is safe to assume that at this pressure the sublimation point is in the neighborhood of 72° , and consequently the true melting-point of the undissociated substance must lie higher. That the temperature can be raised to this height is due either to the fact that the products of dissociation are removed so quickly that they have no time to lower the melting-point or, in case a second form be present, that one modification is removed more quickly in the vapor phase. It is more probable that the former is the case. Experimental evidence to test this view will be advanced further on in this paper.

It was thought advisable to try to reproduce these experiments, using a mass of the substance, immersing the thermometer in the crystals. To this end a number of trials were made under various conditions.

The simple apparatus consisted of a long tube provided with a side neck and jacketed by an outer tube which served as an air-bath. The inner tube contained a thermometer, the bulb of which was completely covered with crystals. This tube was connected to the water-pump and exhausted to the vapor-tension of the water, a manometer being interposed to record any change of pressure which might take place. It was found that the greater part of the hydrate sublimed off before the thermometer rose to 50° . Furthermore, the hydrate which seemed to be condensed on the side of the tube in a supercooled condition, flowed back and saturated the crystals, making it impossible to observe any preliminary melting. This was partially obviated by taking a retort of about 200 cc capacity, which was filled nearly to the angle with chloral hydrate. The neck was joined to a distilling flask, which acted as a condenser, and this, in turn, was connected with the manometer and pump. The retort was heated by a calcium chlorid bath, giving a temperature of 115° .

Numerous pressures and temperatures were tried in order to get a means by which the vapor would be removed with sufficient rapidity, and which would still admit of the substance being heated to its melting-point without too much volatilization taking place. This plan was not found to be feasible with the large amount of the substance taken. The sides of the retort were superheated to such an extent by the bath that the hydrate next the walls was completely fused before the temperature in the interior was 40° . On the other hand, if the bath were not heated high enough, sublimation took place so rapidly that a great deal of heat was extracted, more than sufficient to raise the temperature of the mass inside.

A side-necked tube, sufficiently long to contain the thermometer, was next made. Into this was introduced a paper capsule, such as is used for ether extraction. This rested on a layer of cotton wool in the bottom of the tube. The bulb of the thermometer occupied the center of the capsule surrounded by the crystals. All precautions were taken to prevent the annoying soakage effects. The tube was jacketed and heated in a water-bath to 100° . This apparatus gave equally unsatisfactory results. It is thus evident that at pressures sufficiently low to remove the vapor phase, it is impossible to heat a quantity of the hydrate uniformly throughout the mass, without volatilizing it in a comparatively short time. Whereas, if sufficient heat be supplied, either the experiment is vitiated by the reflux of super-cooled hydrate or the crystals in contact with the walls are heated to a much higher temperature than those in the center of the tube. Besides, it is more than probable that the products of the dissociation which take place are removed with difficulty from the interior of a mass, and hence, remaining there, lower the melting-point of the whole enormously. On the other hand, should one of the isomers be the more volatile, it would seem to be impossible under these conditions, to remove the vapor of the one sufficiently rapidly to leave the product of but one modification at the end of the experiment.

The conditions of the Ramsay and Young experiment are

therefore more favorable to success, as here one has a thin layer of substance closely adherent to the bulb of the thermometer, and absence of superheating through complete independence of the walls of the heating vessel, and of the crystals.

It was next of interest to know how, under carefully observed conditions, chloral hydrate behaves when heated alone in the ordinary way in capillary tubes and in mass, and if the presence of dissociation products or of modification would make itself evident.

Small sealed capillary tubes containing the substance were heated in the ordinary melting-point apparatus, no particular attention being paid to the rate of heating. The substance commences to soften at 48° , is incompletely fused at 51° , and completely melts at 54.1° . This may be said to be but one case for, as will be shown, the conditions under which the experiment is done, play a very great part in the results obtained. In another case, when a modification of the double-walled Anschütz flask was used, melting commenced at 49.2° and was complete at 50.6° . This latter is the temperature given by Ramsay and Young as the melting-point for the substances.¹ If the tube be cooled rapidly no crystallization takes place for some time, and indeed on standing at room temperature an hour may elapse before crystals appear, showing undoubtedly the tendency to supercooling possessed by the substance. A tube which had been melted and had stood over night gave a melting-point of 51.6° . Small crystals remained at this temperature, and these disappeared when the bath was raised to 52.6° .

Since the melting-point of the substance, as determined in the ordinary way, would point to no definite result, it was thought advisable to examine the substance in an open tube with the thermometer in the melt. These conditions were also favorable for observing the freezing-point, as supercooling could be avoided by the introduction of crystals of the substance at any convenient time. In each case the tube was jacketed to facilitate equal heating, and in most instances where the melting-

¹ Phil. Trans. 177, I, 77 (1886).

point was observed, the bath was kept in constant motion with a stirrer.

If one heat fresh chloral hydrate slowly in an open tube in this way, preliminary melting takes place at 47.8° , at which temperature the crystal edges become rounded. At 50.6° the substance is rapidly melting and the melt is clear at 52.7° except for some few crystals which remain in the liquid in spite of vigorous agitation and keeping the liquid at this temperature for some time. The crystals persisted while the temperature was raised to 61.5° . This phenomenon is frequently observed when one has occasion to melt the hydrate, whether it has been previously fused or not.

After complete fusion was obtained the same tube was cooled and allowed to stand for some time, and the melting-point again taken. Softening took place at 48° , and an hour's heating at this temperature did not apparently change the condition of the substance. On heating to 50° , melting was fairly well completed. On allowing the same tube to stand over night, softening took place at a higher temperature, viz. 50.5° . There was still a small amount of the substance unmelted at 54.6° , and at 57° the crystals had entirely disappeared. The latter experiment lasted 105 minutes.

There was a marked difference between the recently melted hydrate and that which had stood for some time, in that the former substance was much more completely melted at 50° than the latter. That this was not due to the presence of a second form, but solely to dissociation products which had not combined, was shown by the following experiment.

Chloral hydrate was fused in a small test-tube and cooled as quickly as possible with water. The melt was well stirred, and as soon as the mass had assumed the solid state, the tube was broken, the contents taken out and well pressed between folds of filter-paper. A certain amount of oily substance was absorbed by the paper. When the crystals were dry they were transferred to a melting-point tube, sealed in, and compared with the fresh crystals, both tubes being attached to the same thermometer.

Both the tubes behaved in an identical manner. The melting-point was 50.4° – 50.6° .¹

In the course of an investigation of polymorphous substances, Pope had examined chloral hydrate crystallographically and has stated that the crystals formed on the solidification of chloral hydrate are different in form from those of the ordinary chloral hydrate, or to those which crystallize from chloroform. I have repeated Pope's work in this direction, in which I had the assistance of Prof. Gill, to whom I should like to acknowledge the very material help he has given me. According to Pope, on cooling chloral hydrate under a microscopic cover slip, long needles appear which are uniaxial and thus differ essentially from those deposited from chloroform, which are monosymmetric, and therefore cannot possess this optical property. Moreover the uniaxial crystals in the course of some days change to monosymmetric plates identical with the unfused substance. I have repeated Pope's work in this direction and have been able to follow the change which takes place, but not to the extent which Pope has shown in his paper. Furthermore, it is quite possible that the acicular crystals which appear on standing are not in reality uniaxial, but have so small an optical angle that they appear to possess this quality except when examined with the utmost care. Or what is also not at all unlikely, the large needles consist of aggregates of monosymmetric plates which behave very similarly to a uniaxial crystal. The breaking down of these segregates does occur as Pope has shown in his photomicrographic plates. That these acicular crystals do not differ in their behavior from ordinary chloral hydrate was shown

¹ In a recent paper (Chem. News, 80, 270 (1899)) Kuhara and Chikashigé have proposed the determination of melting-points by heating the substance between microscopic cover glasses, and have found the melting-point of chloral hydrate identical with that of Meyer and Dulk (Liebig's Annalen, 171, 75 (1874)). The latter observers probably gave the point at which the last traces of crystals disappeared in the capillary tube. In the method of Kuhara and Chikashigé it is possible that the high melting-point is due to the small amount of the vapor phase allowed by the closely approximating surfaces of the glass plates. Hence, dissociation would have a relatively small effect on the melting-point, and the specimen could be heated to a high temperature without fusing the substance.

by the following experiment. Fresh crystals were melted in a small beaker immersed in a water-bath and held above the melting-point sufficiently long to permit of any change which could take place. The melt was cooled and on the appearance of crystals the liquid was removed by a small inverted funnel tube, the mouth of which was covered with cambric. As soon as the liquid was removed by exhaustion, the remaining crystals were taken out, dried with filter paper, and compared at once with the original substance. No difference between the two tubes could be observed.

The crystallographic examination shows that the form appearing on first cooling the melt consists exclusively of the acicular crystals described by Pope.

As a footnote to Pope's paper appears the suggestion made by Armstrong that the two forms may be represented by different structural formulæ, one being a hydrate of chloral

The other corresponding to a dihydric alcohol,

Were these two structurally different compounds present in the melt, one would expect that on cooling to the solidification point the solution being saturated with respect to one form only, but one of the crystals would grow. That this is not the case is shown by the behavior of the melt. On cooling the fused chloral hydrate quickly to 46° and inoculating the supercooled mass with the two forms of crystals, solidification takes place equally rapidly. No trace of the temporary disappearance of either of the two forms can be observed. This is analogous to the classic example of sulfur. When this element is melted in a U tube and the melt in each of the arms sown with crystals of rhombic and monoclinic sulphur respectively, both forms of crystals grow, showing the production at the same temperature of both forms from one modification in the melt. The two crystalline forms also behave similarly when heated in vacuo. This was shown by a repetition of the Ramsay and Young experiment.

The thermometer was coated with chloral hydrate and allowed to stand three weeks. The coating which in this instance may be assumed to have changed to the truly monosymmetric crystals behaved on heating at 22 mm exactly as did those which were allowed to stand but a few hours.

To determine the equilibrium point, sealed tubes containing fused chloral hydrate and also the fresh crystals were brought into a bath regulated carefully by means of a calcium chlorid regulator, at 46.5° liquefied chloral hydrate solidifies while the crystals remain unchanged. At 48° the crystals melted after eighteen hours' heating and the mass after resolidifying melted again at 47.5° . It is thus safe to assume that the point for stable equilibrium for solid chloral hydrate with solution and vapor is between 46.5° and 47.5° .

To sum up the results of the work described in this paper, it may be said :

I. Chloral hydrate exists in but one modification in the melt.

II. The differences in the observed melting-point are due to dissociation phenomena and not to the presence of two forms in the melt.

III. The melting-point of undissociated chloral hydrate lies above 72° .

IV. The two forms described by Pope behave similarly on heating.

V. The sublimation pressure for undissociated chloral hydrate at 72° is about 22 mm.

VI. The stable triple point for chloral hydrate and the dissociation products is about 47° .

The experiments detailed in this paper were performed in the laboratory of Professor Bancroft.

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