

ACETALDOXIME

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The experiments of Dunstan and Dymond¹ upon the freezing-point of acetaldoxime brought out so many unexpected phenomena that it seemed worth while to repeat their observations, supplementing them wherever necessary. The writer's results corroborate those of Dunstan and Dymond in every detail. The oxime was prepared by mixing equivalent quantities of aldehyde ammonia and hydroxylamine hydrochloride, extracting with ether, drying with calcium chloride, distilling off the ether and purifying the residue by fractional distillation. The fraction boiling at 114.5° is a liquid which remains unchanged at ordinary temperatures but solidifies partially when cooled in ice. When the crystals are dried thoroughly, preferably on a filter plate which is kept cold, they show a melting-point of 47° if heated fairly rapidly. If one keep the tube containing the liquid at this temperature for a short time, say a minute, and then take it out into the air it will be noticed that, although the contents solidify, they do not present the same crystalline appearance as before. Some liquid is present with the crystals, although it may be only to a very slight extent. When the melting-point is taken again, it is found to be lower than the original one and by no means so sharply defined. On repeating the operations of melting and freezing, one arrives finally at a point where the liquid in the capillary melting tube does not solidify at ordinary temperatures but does when cooled to 13° . A set of measurements taken from my note book will illustrate this; the acetaldoxime was in a sealed capillary tube to prevent possible absorption of moisture.

¹ Crystals thoroughly dried in capillary tube showed M. Pt.

¹ Jour. Chem. Soc. **61**, 471 (1892); **65**, 206 (1894).

47°. Crystallized on being taken out into air, immediately after melting. Heated for five minutes at 55°. Solidified in the air (19°). Remelted at 42°. Again solidified in the air. Melting-point now becomes uncertain, starting at 36° and melting completely at 41.5°. Resolidified in air. Upper part begins to fuse at 31°, all melted at 40°. Other consecutive fusion points are 28°, 26°, 22°, 18.7° and finally, on allowing to stand several days in the sealed capillary, it remains liquid at ordinary temperature.¹

Such peculiar behavior suggests the idea that probably the acetaldoxime was contaminated by some other substance or that a depolymerization had taken place. This question has, however, been settled by Dunstan and Dymond. They studied the crystals and the liquid with care and found that the two had the same boiling-points and gave practically the same depressions of the freezing-point in benzene and in acetic acid. No difference could be detected analytically. Moreover, by freezing the oil, draining off the liquid and freezing again, it was found possible to convert practically all the liquid into the solid modification. These results alone would show the insufficiency of Franchimont's² objection that the non-crystallization of the oxime is due to impurities. The work of Bourgeois and Dambmann² is also important in its bearing on this point. By changing the oxime into an imidosulfonic acid, they obtained it ultimately in a state of undoubted purity. They then state that their observations on acetaldoxime and on propionaldoxime are in accord with those obtained by Dunstan and Dymond.

From the experiments of the writer it was apparent that the duration in time of heating and the temperature at which this was done exercised an influence on the freezing-point. Accordingly the crystals were melted and distilled quickly at the normal boiling-point (114.5°); the liquid froze at 13° instead of at 47°. With many—probably most—other oximes a similar result is obtained, the distillate beginning to freeze at one temper-

¹ *Recueil Trav. Pays-Bas*, 10, 236 (1892).

² *Ber. chem. Ges. Berlin*, 26, 2856 (1893).

ature while the crystals melt at a much higher temperature—the melting-point of the original crystals.

It was noticed that when the acetaldoxime froze at 13° , it did not act like a pure substance. It did not solidify at constant temperature. There was always considerable liquid left which, when drained off rapidly, began to freeze only at temperatures below 13° provided the measurements were made the same day. Repeating the process of freezing and draining off the mother-liquor four times gave a liquid which began to solidify at 8° . When the crystals obtained from this liquid had been thoroughly and carefully dried, they showed a melting-point of 47° . If, however, the liquid is distilled after each draining, it is found to boil at 114.5° and to crystallize, on cooling, at 13° . If the liquid with a freezing-point of 8° be allowed to remain for several weeks at ordinary temperatures, the freezing-point will rise to the original value of 13° . No theoretical significance attaches to the lowest freezing-point obtained since it was only the smallness of the amount of material at command which prevented lower values from being obtained.¹ It is evident that it is not impurities which cause such variations of the freezing-point. The material is always pure acetaldoxime and the freezing-point depends on the previous history of the compound.

In this displacement of the freezing-point, acetaldoxime does not stand alone. Dunstan and Dymond observed similar phenomena with propionaldoxime. This substance melts at -21.5° . After distillation, the liquid begins to freeze at -11.5° while, by further cooling, it is possible to obtain a liquid which does not begin to solidify at -21° . They make no mention of a gradual rise of freezing-point and assume that they had a solution of the solid in the liquid oxime at this lowest temperature.

Although the rate of change of the freezing-point of acetaldoxime is a function of the temperature to which the substance is heated, the final equilibrium is independent of the temperature. It has already been noticed that heating to 114.5° causes the freezing-point to drop from 47° to 13° . If the crystals are kept

¹ In other experiments the freezing-point has been forced below 0° .

long enough at 20° they will liquefy and if the liquid is allowed to stand for ten days or so and then cooled, the freezing-point will be found to be 13° . In other words, the equilibrium is not displaced by the temperature. Dunstan and Dymond assumed that it was; but that was because they paid little or no attention to states of stable equilibrium.

The explanation of these apparently abnormal results is a very simple one. We have merely to assume an equilibrium in solution between two modifications of acetaldoxime with the further proviso that equilibrium is reached fairly slowly at ordinary temperatures. We can then predict all the phenomena that have been observed. The general theory of such cases has been outlined by Professor Bancroft¹ so that it will only be necessary to make a very brief reference to it here. If we designate the crystals melting at 47° as the α modification and the unknown form as the β modification, the experimental data will be represented by the diagram, Fig. 1. The line AXH represents the

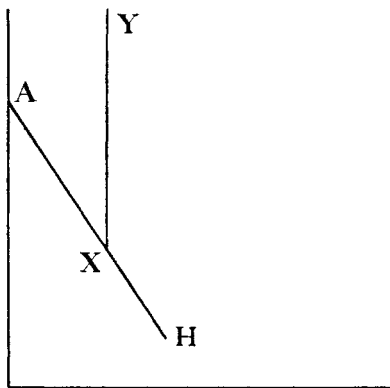


Fig. 1.

compositions of the solutions which can coexist temporarily, with the α crystals. The line YX represents the relative concentrations of the two modifications in the solution phase when the system is in equilibrium. This line runs parallel to the axis of ordinates because it has been shown that the equilibrium

¹ Jour. Phys. Chem. 2, 143, (1898).

is not displaced by change of temperature. This involves the additional conclusion that the heat of transformation of one modification into the other is zero. The absolute position of the line YX cannot be given because there is, as yet, no analytical method for determining quantitatively the relative amounts of the two modifications. The constant boiling-point shown by all solutions quite independently of the initial temperature of freezing, is to be interpreted as due to the fact that equilibrium is reached with great rapidity at 114.5° . This conclusion is confirmed by the fact that all solutions that have been heated above 100° begin to freeze at 13° regardless of the length of heating at the higher temperature.

In the diagram, the point A denotes the melting-point, 47° , of the crystals while X is the stable triple point with a temperature of 13° . It was not possible to pass down the curve AXH to the point at which the β modification separates as solid phase because the solution at 13° contains so little of the second form that there is practically no liquid left after the system has been cooled a little below zero degrees. Some semi-quantitative measurements on the relative masses of solid and liquid after different rates of cooling will illustrate this. The ordinary method of drawing off liquid from crystals is not really of sufficient accuracy for such an experiment; but some results have been obtained which will give a general idea of the phenomena. In the first three experiments a weighed amount of the oxime was put into a Brühl filtering apparatus, partially frozen, and kept at a stated temperature for some time; then drained and the liquid and solid weighed separately.

1. Liquid frozen and kept at 9° for 24 hours.
Solid 3.8 g; liquid 6.0 g.
2. Liquid frozen and kept at 0° for 1 hour: then kept at 9° for 24 hours.
Solid 4.5 g; liquid 3.3 g.
3. Liquid frozen and kept at 0° for 2.5 hours.
Solid 8.3 g; liquid 2.6 g.
4. Kept liquid in ice-box six weeks; no liquid could be drained off by means of an ordinary pressure pump.

All the experiments which have been made by Dunstan and Dymond or by the writer show that above 13° the solution is the stable form and below it the crystals which melt at 47° . Franchimont¹ reports that he obtained the α modification by crystallizing from ether at ordinary temperature. This seemed sufficiently surprising to warrant repeating the measurements. The results are exactly as he says and yet his statement is misleading, not to say inaccurate. If acetaldoxime be dissolved in ether and the solution allowed to evaporate spontaneously in a watch-glass, a crystalline residue is obtained. If one places a thermometer in the solution, one finds that the spontaneous evaporation has cooled the liquid below 13° and it is therefore not surprising that crystals are formed. If the solution evaporates at the constant temperature of 18° the acetaldoxime remains as a liquid and no crystals are formed.

Measurements were made to ascertain whether any change of vapor pressure could be detected as the solid liquefied. Two methods were used, the direct measurement by the Ramsay and Young method,² and the differential method of Andreae.³ By direct measurement no difference could be detected. The corresponding temperatures and pressures are given in Table I, the pressures being in millimeters of mercury.

TABLE I

| Temp. | Press. | Temp. | Press. |
|-----------------|--------|-------------------|--------|
| 20 ² | 8 | 30.2 ² | 14 |
| 23 | 9 | 32.7 | 16 |
| 25.4 | 10.3 | 35 | 18 |
| 27 | 11.5 | 38 | 21.2 |
| 28 | 12.2 | 41 | 25 |

The differential method gave more positive results. When one arm of the apparatus held the solid and the other liquid, it was observed that after 24 hours at $18-20^{\circ}$ the solid had become liquid and had lost one milligram in weight which corresponded

¹ Recueil Trav. Pays-Bas, 10, 236 (1892).

² Phil. Trans. 175, 37 (1884).

³ Zeit. phys. Chem. 7, 241 (1891).

exactly to the gain in weight of the other arm. In a second experiment the differential apparatus was kept in the ice-box for some time. Being undisturbed, the liquid remained supersaturated for some days. After ten days the weighings were taken and it was found that the solid had increased in weight very slightly, about 0.7 milligram, while the liquid had lost in weight. From this one may conclude that the vapor pressure of the liquid is lower than that of the solid above 13° and higher than it below this temperature. Since the difference between the vapor pressures is very small at any temperature, it is to be expected that the rate of change will be very slow. The writer has observed, after keeping a test-tube containing acetaldoxime at 0° for six weeks, that there were still traces of liquid upon the crystals.

It must be kept in mind that the theory requires that the total vapor pressure of the solution be less than that of the solid above 13° and greater than it below that temperature only in case there is but one modification in the vapor. It has already been shown that two modifications of acetaldoxime are present in the liquid phase and there is evidence in favor of the view that two modifications exist in the vapor phase as well.

When distilling under diminished pressure, the products of the distillation depend on the nature of the substance in the distilling flask. When starting with a liquid freezing at 13° , the distillate freezes at 13° . On subliming the solid under diminished pressure, it was noticed that in the arm of the condenser, which was at 20° , there was formed a solid. This became liquid in the course of time, as did also the solid in the distilling flask. It seems probable that the distillate has the same composition as the substance in the distilling flask. In other words, the same change takes place in the vapor as in the liquid and the same equilibrium is reached in the two cases. The difference between the vapor in equilibrium with the solid at say 20° and that in equilibrium with the liquid at the same temperature, may be one of partial pressures and not one of total pressures. On the other hand, it must be remembered that the argument from the nature of the distillate is not conclusive with regard to the vapor. The

distillation of arsenic and of benzophenone are cases in point. The formation of an instable form by distillation is not accepted as a proof of the existence of two kinds of vapors any more than the precipitation of yellow mercuric iodide by water proves the existence of two modifications of mercuric iodide in a methyl alcohol solution. While admitting the force of this argument, there are reasons for believing that it does not apply in the case of acetaldoxime. The fact that the nature of the distillate varies continuously with the nature of the distilling substance, would seem to exclude the possibility of serious disturbing effects due to a spontaneous appearance of a metastable phase. It must also be admitted that the existence of two liquid modifications in equilibrium makes the existence of two modifications in the vapor very probable.

Some experiments were made to determine whether the equilibrium between the two modifications in the solutions was displaced by acetone. Acetaldoxime is an especially good case for such an experiment because the line YX is parallel to the axis of coordinates. If acetone be added to the liquid freezing at 13° and the freezing-point be determined at once and again after some time has elapsed, the second freezing-point will coincide with the first or it will not. If the two readings are the same, no displacement has occurred. If the second reading is higher than the first, the acetone has caused the formation of more of the α modification at the expense of the β form. If the second reading is lower than the first, the reverse reaction has taken place. Unfortunately the amount of pure acetaldoxime available for this experiment was only about ten grams, and it was not found possible to determine the freezing-points with sufficient accuracy to warrant any conclusion being drawn. An excess of acetone was then added and the solution cooled in a mixture of solid carbonic acid and ether. Even at the lowest temperature, about -80° , the crystals which separated were the α modification. From this the conclusion may be drawn that acetone does not displace the equilibrium markedly to the side of the β modification.

It is well known that sunlight changes soluble into insoluble sulfur under certain conditions, and a flask containing acet-

aldoxime was placed in the sunlight every day for some time in hopes that the contents of the flask might solidify. No effect could be detected.

The results of this paper may be summarized as follows:

1. All the freezing-point phenomena can be accounted for on the assumption of an equilibrium between two modifications in the liquid phase.
2. The relative amounts of these two modifications is *not* a function of the temperature.
3. It is probable that two modifications exist in the vapor.
4. The liquefaction of the crystals is not accompanied by a measurable change of vapor pressure.
5. The temperature of the stable triple point is 13° .
6. Sunlight does not produce any visible effect.
7. The β modification does not crystallize from acetone solution even at about -80° .

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