THE EQUILIBRIA OF STEREOISOMERS, I

BY WILDER D. BANCROFT

Duhem¹ has recently published a series of papers in which he has developed a theory of 'permanent changes' and has also shown the way in which this theory can be applied to explain the behavior of supercooled sulfur. There are many facts in organic chemistry which become more intelligible when considered from this same point of view. It will be better, for the purpose in hand, to substitute the graphical for the analytical method. Since the phenomena are all qualitative, no quantitative test of the theory is possible and the graphical method has the advantage of enabling one to take in the whole field at a glance. What we have then to consider is the form of the diagram for a system in which there are two modifications in equilibrium in the liquid phase. Suppose we have the two constituents α and β . If we introduce the limiting condition $\alpha \rightleftharpoons \beta$, we are dealing with a one-component system. If we take into account the element of time there are then three possibilities. Equilibrium is reached practically instantaneously. No approach to equilibrium can be detected except under special conditions. Equilibrium is reached in a measurable length of time. In the first case the system will behave in all respects like any other one-component system. The second case presupposes a state of false equilibrium and will be discussed in a subsequent paper. In the third case the system will appear to contain two components provided we act rapidly enough and one component provided we act slowly. The concentration-temperature diagram

¹ Zeit. phys. Chem. **22**, 545 ; **23**, 193, 497 (1897).

for such a system is given in Fig. 1. If the two constituents are the only solid phases which can occur and if two liquid phases are impossible, the diagram would consist solely of the boundary curves AD and BD provided neither constituent could change at all into the other. The curve AD shows the coexisting concentrations and temperatures for the α modification in equilibrium as solid phase with solution and vapor. The curve BD gives the corresponding values when the β modification is solid phase. Since the two constituents can change one into the other

Fig. 1.

other, these two curves can be realized experimentally only by working with a certain degree of speed. The line YX gives the relative concentrations of the two modifications at different temperatures after equilibrium is reached. This line cuts AD at X. At this temperature, therefore, the α modification can exist in stable equilibrium with liquid and vapor. This line represents, for liquid and vapor, what Duhem calls the "natural state."

From the diagram we can make the following predictions. If we take the α modification and heat it quickly we shall find that it melts more or less sharply at the temperature denoted by A. On cooling the melt it will be found not to begin to solidify until a lower temperature is reached. What this temperature will be, depends in general on the temperature to which the

liquid is raised and the length of time during which it is kept at that temperature. The cause for this change of freezing-point is the conversion of some of the α modification into the β modification, this latter lowering the freezing-point of the former just as any other substance would. If the α modification be just melted and cooled at once, the concentration will have changed but little, the freezing-point will have been lowered not more than a fraction of a degree in some cases and the system, solid, solution and vapor, will be represented by a point on AD lying very near A. By longer heating or by heating to a higher temperature and thus increasing the reaction velocity, the percentage of the β modification will be increased and the freezing-point lowered correspondingly. We will suppose next that we cool the system suddenly when the relative concentrations in the liquid phase are those represented by the point X. The α modification will separate at the temperature corresponding to X and the mass will solidify without change of temperature provided the further cooling be done with sufficient slowness. If the system be cooled rather rapidly and if the reaction velocity is low, the α modification will crystallize faster than the β modification can change back and the solution will become more concentrated with respect to the β modification. The freezing-point will fall and the system will pass along XD. One of two things is possible. Either the solution will solidify completely before the point D is reached, owing to the complete conversion of the β into the α modification or the β modification will appear as solid phase at the point D. If we do not cool the solution so much; but stop, for instance, at a temperature represented by the point Z, we shall find that the freezing-point of this solution rises with time owing to the β modification changing back into the α modification, diluting the solution. This rise of freezing-point will cease when the temperature of the point X is reached, the "natural" freezing-point of the system. If we fuse the α modification and keep the liquid at some temperature until equilibrium is reached, we shall then have the composition of the solution represented by the point at which that particular isotherm cuts the line YX. If we cool the system very slowly, there will be

a gradual displacement of the equilibrium, the system will pass through the states represented by the line YX and the α modification will begin to crystallize at the temperature of the point X. If we have kept the system at the temperature of the point Y until equilibrium is reached and then cooled suddenly, the solid phase will not appear until the temperature of the point Z is reached. On standing, the freezing-point will rise more or less slowly to the temperature of the point X. If the line XY slants to the right, as in the diagram, raising the temperature to which the system is heated will lower the apparent freezing-point or temperature at which the solid phase first appears. If the line XY slants to the left, raising the temperature to which the system is heated raises the apparent freezing-point while this point will be independent of the temperature if the line XY is vertical.¹ It is assumed explicitly in each of these three cases that the system is kept heated at constant temperature until equilibrium is reached and that the cooling is sudden.

In order to obtain some of these changes it is not necessary to fuse the α modification. At any temperature above that of the point X the final state of stable equilibrium is represented by a point on the line XY. If the α modification be kept long enough at any temperature between that of the point X and that of the point Y, it will liquefy spontaneously. If we start with the pure β modification, melt it at the temperature of the point B and cool it suddenly, we shall find a lowering of the freezing-point due to the formation of some of the α modification. By prolonging the time during which the liquid is heated and then cooling suddenly, the system can be made to pass along the curve BD, the freezing-point falling continually. A little longer heating will cause the apparent freezing-point to rise, the system passing from D to X. At temperatures between those of the points D and B the β modification will liquefy spontaneously. If the temperature is below that of the point X, the liquid will solidify gradually to crystals of the α modification. If the tem-

¹ If soluble sulfur be taken as the α modification and insoluble sulfur as the β modification, the line XY will slant first to the right and then to the left, the change of direction coming at about 170° .

perature is above that of the point X, liquid and vapor is stable state and no crystals will be formed. At temperatures below that of the point D the β modification will change into the α modification without liquefaction.

The α modification is therefore the stable one. The temperature of the point X would be the freezing-point and the melting-point of the crystals provided the equilibrium were reached instantaneously. In such a case it would be impossible to realize any of the curves ADB except the point X. In the case that we are actually considering, in which a measurable time is necessary before equilibrium is reached, the crystals which separate as the system passes along the curve AD will melt at the temperature of the point A if heated rapidly while the crystals which separate as the system along the curve BD will melt at the temperature of the point B if heated rapidly. If we define the triple point as the temperature at which solid, liquid and vapor are in stable equilibrium, we have in our hypothetical α modification a case in which a solid can be heated above the triple point. It is to be noticed that no assumption has been made as to the relative temperatures of the points A and B. If the temperature of the point B is higher than that of A we shall have a case in which the more stable modification is the one with the lower apparent melting-point. Ostwald¹ has recently called attention to the fact that, of two solid modifications, the higher melting one will be the more stable if only one liquid modification is formed. This conclusion ceases to hold if the assumption, made explicitly by Ostwald, is not applicable.

In the discussion, it has been shown what is to be expected when two liquid modifications are possible. It is possible, of course, to reverse the reasoning and specify what phenomena will suffice to enable us to predict the existence of two liquid modifications. If a solid substance melts at one temperature and freezes at another, this is proof positive of the existence of two liquid modifications provided no decomposition takes place. This test is applicable to all cases. There is another test which is

¹ Zeit. phys. Chem. **22**, 313 (1897).

absolute as far as it goes. If the more fusible of two solid modifications be the more stable, we are justified in deducing the existence of two liquid modifications. The difficulty with this is that the converse is not necessarily true. If the less fusible of two solid modifications be the more stable, it does not follow that only one liquid modification is possible.

In the preceding pages I have pointed out some of the conclusions which may be drawn when one applies to the general case the principles laid down by Duhem in his paper on the behavior of sulfur. It now remains to be seen how far these results can be verified experimentally. The first case that we will take up is that of stilbene dichlorid, $\text{C}_6\text{H}_5\cdot\text{CHCl}\cdot\text{CHCl}\cdot\text{C}_6\text{H}_5$, studied by Zincke.¹ The α modification melts at $192\text{--}193^\circ$ and can be sublimed between watch-glasses without decomposition. If heated above the melting-point, the freezing-point falls and can be dropped to $160\text{--}165^\circ$, but no lower. This is in exact accordance with the theory. The temperature of $192\text{--}193^\circ$ is that of the point A, while the point X would then be denoted by $160\text{--}165^\circ$. From the experiments of Zincke, it is impossible to determine whether this range of five degrees at the point X is due to differences in the temperature of heating and a large displacement of the equilibrium with the temperature or whether Zincke was actually realizing part of the curve XD owing to the slow rate of change of one modification into the other. This however is immaterial as far as the general theory is concerned and is of interest merely when considering this particular case. The β modification melts at about 93° . When heated for a short time above its melting-point, there seems to be no change until the initial temperature of heating is about 160° . Then the freezing-point rises rapidly and soon reaches $160\text{--}165^\circ$, beyond which it cannot be forced. Here we have only partial confirmation of the theory. Our hypothesis requires that the freezing-point should first fall and then rise, remaining constant at the temperature $160\text{--}165^\circ$. Only the latter requirement, of the rise of freezing-point, was realized by Zincke. Fortunately this gap has been

¹ Liebig's Annalen, 198, 115 (1879).

filled in by Lehmann.¹ He found that if the α modification were just melted and cooled at once, the freezing-point was lowered some five degrees. On heating for a longer time, the freezing-point rose again. Lehmann assumes the existence of a third modification in this case; but, under the circumstances, this is not probable. The explanation of Zincke's experiments would seem to be not that the substance remained unchanged on heating above the melting-point, but that he failed to cool the melt until after the freezing-point had begun to rise again and that the crystals which first separated in the neighborhood of 94° were really the other modification. It was only when he heated the substance to a higher temperature that the reaction velocity increased sufficiently to enable him to detect a noticeable rise of temperature. This explanation is made reasonably certain by the experiments of Lehmann, just referred to; but it is, of course, desirable that the experiments should be repeated by somebody. The fact that the α modification can be sublimed between watch-glasses seems to be a proof that two modifications exist in the vapor as well as in the liquid phase. This has been shown to be true in other cases.

Each of the two stilbene dichlorids has been isolated as solid phase and the one with the higher melting-point has been found to be the more stable. With acetaldoxime, $\text{CH}_3\text{CH}:\text{NOH}$, the higher melting modification is the more stable; but the other or β modification has not yet been obtained as a solid. Acetaldoxime has been studied rather carefully by Dunstan and Dymond.² I quote from their second paper, p. 209: "The pure acetaldoxime boils at 114.5° (corr). and, when supercooled in ice after having been recently distilled, it almost entirely solidifies to a mass of long, stout, acicular crystals, which, if pressed quite free from adhering liquid, melt at 46.5° (corr.); the entire mass melts several degrees lower. . . . When these crystals are melted, and the liquid is kept at the melting-point for a short time, it does not solidify until it has been cooled several degrees below the temperature at which the crystals melted, even if a

¹ Molekularphysik, I, 206.

² Jour. Chem. Soc. 61, 470 (1892); 65, 206 (1894).

crystal of the original substance is introduced into it. The longer the liquid is heated in this way, the greater is the reduction of the freezing-point, but the maximum reduction it has been found possible to effect is to 13° , that is, 33.5° below the melting-point of the original substance. The fall to this point occurs slowly when the temperature is near that of melting, but if the original liquid is heated at 100° , the change is rapidly brought about and freezing cannot be effected above 13° , by "touching off" with a crystal. No chemical decomposition accompanies the change; the liquid freezing at 13° distils constantly at 114.5° , and furnishes, on combustion, the same data as the original crystals. The liquid thus produced does not, however, consist entirely of a new modification of acetaldoxime; it behaves as a solution of the solid oxime in a liquid modification. The liquid does not completely solidify, and the crystals which separate from it at 13° consist of the original modification; when pressed quite free from adhering liquid, they melt at 46.5° . The residual liquid, when further cooled, yields more of these crystals, and by repeating the process, the whole of the liquid may be obtained as the crystalline modification. At all temperatures an equilibrium seems to be established between the two modifications; the lower the temperature, the more of the crystalline form is produced and vice-versa.¹ Although it is possible to separate the solid modification in a pure state, no method we have tried has been successful in leading to the isolation of the pure liquid."

This quotation shows that the theory is applicable to this particular instance. Referring back to the diagram Fig. 1, the point A denotes the melting-point of the crystals 46.5° ; the melt is found to begin to solidify at temperatures varying between 46.5° and 13° , the point X of the diagram, depending on the length of heating and the highest temperature reached. The liquid does not solidify entirely at the temperature of X and the

¹ This conclusion, though a very natural one, is not really justified by any of the facts discovered by Dunstan and Dymond. Subsequent work in my laboratory by Mr. Carveth has shown that the equilibrium is practically independent of the temperature.

authors have realized a small portion of the curve XD. They have not noticed that solutions which had been cooled, say to 0° , would freeze some days later at a higher temperature; but they do record that the whole of the liquid mass can be converted into crystal in time. Here the lowering of the freezing-point of the crystals takes place so slowly at 46.5° that no precautions are necessary to determine the melting-point of the crystals. We shall see later that this is not always the case. Freezing-point determinations in benzene and in acetic acid showed that the crystals and the liquid had the same molecular weight. It was also noticed that the solid acetaldoxime will liquefy spontaneously on standing at ordinary temperatures. Propionaldoxime behaves like acetaldoxime.¹ The α modification melts at 21.5° ; the temperature at which solid, liquid and vapor are in equilibrium is -11.5° ; the crystals liquefy spontaneously at 0° ; the β modification has never been obtained in the pure state.

With benzaldoxime, $C_6H_5CH:NOH$, we have the higher melting form the less stable. Our knowledge of this substance is due in large part to Beckmann² and to Luxmoore.³ The α modification melts at 34° and the β modification at 130° . The stable triple point has not been determined; but the crystals obtained are the α modification. Since the temperature of the stable triple point is lower than room temperature, both of the modifications should liquefy spontaneously. This is the case experimentally, though Beckmann states that if the β modification be obtained absolutely pure, it may be kept for a very long time at ordinary temperatures without liquefying.

The peculiarity of forming two mutually convertible isomers is characteristic of most of the oximes, and it is very often the lower melting form which is the more stable. As yet another example, we may take the *p*-anisaldoxime.⁴ The α modification

¹ Dunstan and Dymond. Jour. Chem. Soc. **65**, 221 (1894).

² Ber. chem. Ges. Berlin, **20**, 2766 (1887); **22**, 429 (1889); **23**, 1680 (1890).

³ Jour. Chem. Soc. **69**, 177 (1896).

⁴ Beckmann. Ber. chem. Ges. Berlin, **25**, 1680 (1890); Goldschmidt. Ibid. **23**, 2163 (1890).

melts at $61-62^{\circ}$ and is the more stable. The β modification melts at 133° and changes over slowly if kept at its melting-point. It would be easy to fill pages with accounts of other oximes each furnishing further proof of the applicability of Duham's theory; but it will be more profitable not to confine ourselves to one class of compounds.

Phenylisonitromethane, $C_6H_5CH_2NO_2$, melts at 84° if heated rapidly.¹ On standing it changes spontaneously into an oil. In a benzene solution it was found that the iso-compound at first gave values for the reacting weight much higher than the normal. On standing, the freezing-point fell slowly till the normal depression was reached. From this the authors conclude that the reacting weight of the iso-compound is double that of the other compound. This is rather unusual. In the vast majority of cases the reacting weights of the two modifications have proved identical. In this particular case the result is still more surprising because the normal compound does not conduct while the iso-modification is an acid about as strong as acetic acid. Of course, it is possible that the explanation of the anomaly is due to this very fact since organic acids give abnormally high values in benzene solution. Bromphenylnitromethane melts at 60° and is stable. The iso-compound melts at $89-90^{\circ}$ and changes spontaneously into the lower melting form.

The so-called α dimethyl ketol or ketoxybutane,²

is an oil which crystallizes after long standing. The crystals are known as the β modification and melt at $127-128^{\circ}$. If the β modification be kept heated for a while and then cooled, the original oil is obtained which, in the course of time, solidifies as before. If the freshly cooled oil be stirred vigorously with something rough, such as a piece of zinc, crystals are formed which melt at $96-98^{\circ}$ and are known as the γ modification. These γ crystals liquefy spontaneously to an oil which finally solidifies to the β crystals. All three forms give a liquid

¹ Hantzsch and Schultze. Ber. chem. Ges. Berlin, **29**, 699, 2251 (1897).

² v. Pechmann and Dahl. Ber. chem. Ges. Berlin, **23**, 2425 (1890).

boiling at about 140–142°. It is obvious that the α modification is merely a mixture of the β and γ modifications. The β modification is the stable one and the stable triple point (X in Fig. 1) lies between the ordinary temperature and 127°. With the γ modification we have a striking instance of the case which was illustrated rather unsatisfactorily by the β modification of stilbene chlorid, namely of a spontaneous lowering of the freezing-point followed by a spontaneous rise. With the β stilbene chlorid, the lowering was only some four or five degrees. With the γ dimethyl ketol it is at least a hundred degrees. The crystals liquefy spontaneously and then the liquid solidifies to the other kind of crystals. We must also have a marked change of the equilibrium with the temperature. If this were not the case, the freezing-point of the β modification could be lowered by heating only to about the neighborhood of the stable triple point while, as a matter of fact, the equilibrium is displaced to such an extent that the γ crystals are the first to appear. If, in Fig. 1, the line XY had been slanted still more so that the projection of Y, the point Z, had fallen on the curve BD we should have the state of things which has been found by v. Pechmann and Dahl. We may draw yet another interesting conclusion from these experiments. It is no uncommon thing to read that 'an oil was obtained which gradually crystallized after standing three or four weeks in a vacuum desiccator'. It would advance the science very much if, under these circumstances, people would distinguish between the two sets of conditions which may have existed. It is possible that, in any given case, the oil did not crystallize because no crystals were present to start the reaction. Under these circumstances one must wait until what seems like chance starts the crystallization. This is the state of the freshly cooled dimethyl ketol and the γ crystals. The solution is super-cooled with respect to them and yet the crystals do not form readily. This is the state of things which is tacitly assumed to exist in almost all cases where one obtains oils which crystallize later. The second possibility is that two liquid modifications occur and that the oil cannot crystallize at once. Since the reaction velocity may be very low, it might well be weeks be-

fore the oil was in a state of superfusion. This can be realized also with the freshly cooled dimethyl ketol. In the course of time crystals of the β modification do separate; but it would be no use to add one of these crystals at the beginning because it would dissolve, the relative concentration, at that time, being such that the solution is supercooled with respect to the γ crystals and not with respect to those of the β modification. It would be a very simple matter for an organic chemist to decide between these two alternatives. All he has to do, after his oil has solidified, is to take out three or four crystals, heat the rest of the mass, cool it quickly and, as soon as it is cold, throw in one of the crystals. If the crystal dissolves he has two liquid modifications. If the crystal grows he can draw no conclusion. If his crystal disappears, all he has to do is to wait a suitable length of time and then add another crystal.

Returning from this digression we will next consider the experiments of Grünhagen¹ on the behavior of diorthotoluidin methylene, $(\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2)_2\text{CH}_2$. An oil is obtained that, on standing, changes slowly into the β modification which melts at 135° . The reverse change was not noticed, presumably because it was not looked for. Diparatoluidin methylene separates also as an oil which solidifies slowly to the β modification melting at 156° . In all probability these two instances differ from that of the dimethyl ketol chiefly in that the α compounds have not yet been obtained as solids. It should be noticed, however, that the evidence is indirect and not conclusive.

A more interesting case is that of formylphenylacetic ester,² $\text{HCO}\cdot\text{CH}\cdot\text{C}_6\text{H}_5\cdot\text{CO}_2\text{C}_2\text{H}_5$. The solid modification melts at $69-70^\circ$. At ordinary temperatures the solid liquefies spontaneously, while at lower temperatures (no figures given) the liquid changes back into crystals. This is precisely analogous to the behavior of acetaldoxime.

Krückeberg³ has found that α benzazocyanacetic ester,

¹ Liebig's Annalen, **256**, 285 (1890).

² W. Wislicenus. Ber. chem. Ges. Berlin, **20**, 2930 (1887); **28**, 767 (1895).

³ Jour. prakt. Chem. (2) **46**, 579 (1892); **47**, 591 (1793); **49**, 321 (1894). Cf. Haller. Comptes rendus, **106**, 1171 (1884).

$C_6H_5N_2HC.CN.CO_2C_2H_5$, melting at 125° , changes into the β modification, melting at 82° , by continued heating to 130° . The two modifications have practically the same solubility in alcohol, while in benzene the β modification is about twelve times as soluble as the other. A third isomer melting at $106-108^\circ$ is merely a mixture of the other two. Two modifications of *o*-tolueneazocyanacetic ester are known. The α crystals melt at 85° and change readily into the β crystals melting at 133° . Here the form with the higher melting-point is the more stable. On the other hand the α crystals of *p*-tolueneazocyanacetic ester melt at $116-118^\circ$, while the more stable β crystals melt at $74-75^\circ$. With *m*-xyleneazocyanacetic ester and pseudocymeneazocyanacetic ester the α modifications melt at $74-75^\circ$ and 100° respectively, while the more stable β modifications melt, one at 166° , and the other at 136° .

It has been shown by v. Baeyer and Villiger¹ that the *cis*-lactonic acid of the oxydimethyltricarballic acid,

melts at 207° , and that after fifteen hours heating at 150° nine-tenths of it is converted into the *trans*-modification melting at $211-212^\circ$. On heating, the latter goes back to a certain extent into the former. Kjellin² found that diazoniumacetacetic ester, $C_6H_5N_2.HC.COCH_3.CO_2C_2H_5$, melts at $80-84^\circ$ if heated rapidly and that the freezing-point drops to below 50° . He did not succeed in obtaining the second isomer as a solid phase. The less stable form of *o*-chloridiazoniumacetacetic ester melts at 83° , the more stable form at $62-63^\circ$, while the temperature of the stable triple point seems to be about 59° . It is of interest to note that the more stable modification is about four times as soluble in ligroin as the other. Only one solid isomer of *s*-tribromdiazoniumacetacetic ester has been isolated, but its melting-point is $121-123^\circ$, while the freezing-point may drop as low as $95-107^\circ$.

¹ Ber. chem. Ges. Berlin, **30**, 1958 (1897).

² Ber. chem. Ges. Berlin, **30**, 1965 (1897).

Raikow¹ describes two forms of α -methyl cinnamic acid, $C_6H_5 \cdot CH : CCH_3 \cdot COOH$, the more stable melting at 82° , the other at 74° . Claisen² reports that dibenzoyl acetone,

$80-81^\circ$, crystallizes from hot alcohol as the isomer which melts at $109-112^\circ$ on rapid heating and at $107-110^\circ$ when heated more slowly. The reverse change can be brought about by heating with carbon tetrachlorid. Here we are dealing with the effect of the solvent and we are handicapped by having very little information in regard to the behavior of the pure substances. For this reason it is possible merely to call attention to this as a case well worthy of careful study.

According to Walther³ β -diazoamidobenzene, $C_6H_5N_2NHC_6H_5$, melts at 81° and, on heating, changes into the α modification which melts at $98-100^\circ$. Kipping⁴ says of benzylidenhydrindone, $C_6H_4 : (CH_2)(CO)C : CHC_6H_5$: "The crystals obtained from a solution of benzylidenhydrindone in a mixture of chloroform and light petroleum melt sharply at $109-110^\circ$; if, however, after the substance has solidified, it is reheated, it melts at about 90° , but not always completely, the remainder melting at $109-110^\circ$. In some cases the portions which have been melted once, begin to liquefy at 90° and then, although the temperature is rising, gradually become completely solid, melting for the second time at $109-110^\circ$; it is also a curious fact that the presence of the liquid formed by the crystals melting at 90° does not lower the melting-point of the modification which liquefies at $109-110^\circ$; on keeping the crystals of lower melting-point at ordinary temperatures, they are transformed into the more stable modification." This is not entirely clear, but the case would seem to be analogous to that of dimethyl ketol. On heating the stable or 110° modification above its melting-point the equilibrium is displaced so much that, on cooling, some of the other modification

¹ Ber. chem. Ges. Berlin, **20**, 3396 (1887).

² Liebig's Annalen, **277**, 184 (1893).

³ Jour. prakt. Chem. (2) **55**, 548 (1897).

⁴ Jour. Chem. Soc. **65**, 499 (1894).

separates. I am inclined to consider 90° as the eutectic point of the two modifications, corresponding to the point D in Fig. 1. The temperature of the stable triple point evidently is about $109-110^\circ$ and coincides very closely with the melting-point of the stable compound, unless, as is possible, the stable modification could be made to melt higher by more rapid heating. The less stable modification, according to this hypothesis, would melt at some temperature above 90° , and it is a pity that it was not obtained pure. Kipping recognized that a second modification was formed. This is not always the case. I find a statement¹ that the methyl ester of mucophenoxybromoxime,

melts at $168-170^\circ$ when heated very rapidly and at $150-165^\circ$ when heated slowly. Mucophenoxybromoxime anhydrid melts at $124-126^\circ$ or 121° , depending on the rate of heating. The corresponding figures for phenoxybrommaleinimid are $148-150^\circ$ and $144-145^\circ$; for the methyl ester of mucophenoxychloroxime they are $162-166^\circ$ and $156-160^\circ$. Since no mention is made of any decomposition, it seems certain that each of these substances exists in at least two modifications. Unfortunately this was not perceived by the authors and they did not investigate the phenomena.

Sudborough² has noticed some very curious facts which he has not studied with care. Chlorstilbene, $\text{C}_6\text{H}_5\cdot\text{CCl}:\text{CCl}\cdot\text{C}_6\text{H}_5$, occurs usually as an oil. On heating, this oil solidifies, forming crystals which melt at 54° . A similar change occurs with methyl chlorstilbene, $\text{C}_6\text{H}_5\cdot\text{CCH}_3:\text{CCl}\cdot\text{C}_6\text{H}_5$, the crystals melting at $117-118^\circ$. Since no mention is made of a reverse reaction, these experiments will have to be repeated.

The most valuable single experimental paper on two liquid modifications with which I am familiar is one by J. Wislicenus.³ He is the only man who seems to have any real appreciation of the importance of determining experimentally the conditions necessary for the change of one isomer into another. In the

¹ Hill and Widtsoe. *Am. Chem. Jour.* **19**, 631 (1897).

² *Ber. chem. Ges. Berlin*, **25**, 2237 (1892).

³ *Dekanatsschrift*, Leipzig, (1890).

paper just referred to, there is much material to which Duhem's theory applies. When maleic acid, $\text{CO}_2\text{H}.\text{CH}:\text{CH}.\text{CO}_2\text{H}$, is heated just above its melting-point, it changes slowly into fumaric acid, the more stable modification. The reverse change is not realizable experimentally because the temperature of the stable triple point lies above 200° (apparently about 225°) and, at this temperature, maleic acid cannot exist. Fumaric acid changes therefore into the decomposition products of maleic acid, namely maleic anhydrid and water.¹ Not having the theory to guide him, Wislicenus did not notice that the freezing-point of the fused maleic acid dropped at first and began to rise only when the fumaric acid begun to crystallize. There can be no doubt that this takes place. The tolanedibromid, $\text{C}_6\text{H}_5.\text{CBr}:\text{CBr}.\text{C}_6\text{H}_5$, melting at 205° , is the more stable form, the one melting at 68.5° the less stable. A liquid mass is obtained if either modification be kept long enough at 180° ; a solid mass is obtained if either modification be kept long enough at 160° . The temperature of the stable triple point cannot be far from 170° . At each temperature at which liquid is possible, a definite equilibrium is reached.² This was easily shown experimentally, because the lower melting form is about one hundred and twelve times as soluble in alcohol as the other. Tolanedichlorid occurs in two forms, one melting at 143° , the other at 63° . On heating, each changes partly into the other. Experiments are also given to show the rate at which each of the α -chlorcrotonic acids, $\text{CH}_3.\text{CH}:\text{CCl}.\text{COOH}$, changes into the other, also for the two β -chlorcrotonic acids, $\text{CH}_3.\text{CCl}:\text{CH}.\text{COOH}$.

These instances are sufficient to show the varied nature of substances to which Duhem's theory is applicable and the way in which it is to be applied when we are considering the pure substances only. In the second paper I shall take up the question of stability when another component is added, which may or may not form compounds with the two modifications.

Cornell University

¹ If fumaric acid is sublimed at temperatures below that of the stable triple point, it passes over unchanged. Cf. Tanatar. Liebig's Annalen, **273**, 32 (1892).

² This must be the case because we have one component and two phases.