THE PERSISTENCE AND DEVELOPMENT OF CRYSTAL NUCLEI ABOVE THE MELTING TEMPERATURE

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Introduction

The crystallization of metastable liquids has been the object of considerable study, but has yielded singularly little systematic information. Outstanding in this field are the researches of Tammann[1] and his co-workers which have defined an important relationship between the number of nuclei formed per unit time in a given mass of liquid and the temperature of the liquid. For the purposes of the discussion to follow, the "nuclei number" of Tammann may be expressed in somewhat different terms. If we consider a very large number, N_0, of tubes each containing unit weight of metastable liquid at a given temperature, and if after a time y a number N_t of these remain uncrystallized, it is reasonable to suppose these quantities to be related by an expression of the form

$$N_t = N_0 e^{-ft}$$

where f, a constant, has the dimensions of a reciprocal time and hence may conveniently be called the crystallization frequency of the substance at the temperature of observation. The investigations of Tammann have established that f passes through a maximum with decreasing temperature, and that this maximum does not necessarily coincide with that of the linear crystal growth velocity.

It will be profitable to examine more closely the conditions under which f may be expected to be independent of time. If we consider a large volume of homogeneous metastable liquid at uniform temperature, and divide the volume into imaginary elements of unit weight, the constancy of f among these elements follows from the kinetic theory of heat, since it implies only that the probability of formation of a crystal center is the same in each element. If the imaginary boundaries are replaced by glass walls no change can occur provided that the walls are indifferent to the crystallization process, and provided that the condition of the liquid in each tube remains identical. If, however, the tubes are subjected to different conditions, as, for example, a considerable alteration of temperature, there is no reason to suppose, a priori, that the crystallization frequency will be unaffected when the initial temperature is reëstablished. This is at once apparent when it is remembered that the metastable liquid is not in equilibrium. The constancy of f will be destroyed if the liquid, in passing from one temperature to another, must undergo a molecular adjustment which is not more rapid than that necessary to form a crystal center.

[1] G. Tammann, "Aggregatzustande," Leipzig, 1922, summarized in Chapter IX.

Experimental evidence is at hand which indicates that one of the factors influencing the crystallization frequency is the treatment of the liquid previous to undercooling. Othmer[2] observed that the number of crystal centers in piperonal and several other substances diminished as the liquids were raised increasingly above their crystallization temperatures. He further reports that, with fatty acids and their esters, the nuclei number increases rapidly with time. Hinshelwood and Hartley[3] have noted, in apparent contradiction to Othmer's second result, that a far greater number of tubes containing salol and p-toluidine crystallized immediately on undercooling than was consistent with a simple explanation based on probability; they have found, in other words, that f is a function of time. Like Othmer they also observe a diminution in tendency to crystallize with increased preheating of the liquid. In support of these systematic investigations there is a quantity of vague laboratory experience. The increased supercooling of non-metals and metalloids if their melts are strongly heated seems, for example, to be generally recognized. The control of grain number and size by heat treatment of the fused metal is becoming an important factor in the manufacture of steel and alloys. Again, it is habitually found with glycerin and many of the sugars that, whereas the initial crystallization is a matter of considerable difficulty, subsequent recrystallizations occur readily enough even when the substance has been raised many degrees above its melting temperature.

A number of explanations are available for this behavior, but none to date is wholly free from objection. The hypothesis of Othmer, which is supported by Tammann,[1] postulates the existence above the melting point of what may be called a "memory" of the crystalline condition. Loose aggregates, the nature of which is not clearly defined, but which possess at least some of the anisotropic characteristics of crystals, are supposed to exist in the melt, and to be destroyed increasingly with increasing temperature. This explanation assumes that the velocity of transition between the liquid and pseudo-crystalline states is slow compared to that between the pseudo-crystalline and the crystalline, a condition which it is not impossible to imagine. Apparent partial support to such a view is given by recent evidence concerning x-ray diffraction in liquids.[4] This hypothesis cannot, however, be accepted without reserve. If aggregates of this kind exist in a liquid raised only a few degrees above its melting point, its thermodynamic properties must differ from those of a more strongly preheated liquid at the same temperature and experimental evidence for this difference is entirely lacking. Furthermore, if this hypothesis is accepted it is necessary, on the basis of experimental evidence, to suppose

[2] P. Othmer, Z. anorg. Chem., 91, 209 (1915).
[3] C. N. Hinshelwood and H. Hartley, Phil. Mag., [6] 43, 78 (1922).
[4] G. W. Stewart, Phys. Rev., 32, 558 (1928).

that the crystal state itself may be dual, one modification being metastable to another, for it will be demonstrated below that several liquids which are deactivated by preheating may be crystallized without regaining their activity, for this reason the explanation of Tammann and Othmer will be supposed, in this communication, to be of limited applicability and reserved for cases inexplicable by other hypotheses.

A second hypothesis, advanced by Herzfeld[5] to explain Othmer's results and consequently applicable also to those of Hinshelwood and Hartley, is based on adsorption. Herzfeld supposes that the primary liquid may contain impurities which are adsorbed on small crystals to such an extent that their free surface energy becomes actually negative. Since this means that less work is necessary for the crystals to maintain their lattice than to become liquid, they do not melt until their temperature has been raised considerably above the true melting point. Such an explanation seems in high degree improbable, since under these conditions solid solution could scarcely fail to take place. Again, the interfacial tensions of the substances investigated by Othmer are low, and they cannot, therefore, adsorb strongly. Furthermore, such a system should, on crystallization and remelting, undergo an identical cycle, which is not substantiated by experiment. Finally, the experiments of Tammann[6] and others[7] show that the presence of strongly adsorbed foreign materials tends to inhibit the growth of crystals. This hypothesis will receive further consideration in the experimental section.

A third explanation, of an obvious character, which does not appear to have been previously suggested, is that crystals of isomorphous impurities of melting point higher than that of the substance under observation are contained in the liquid. At a sufficiently high temperature these melt and undercool in turn. If the liquid is subsequently crystallized mixed crystals are formed which are destroyed by melting the primary substance, and the impurities are then evaporated from the crystal form in the state of an undercooled solute. This explanation appears improbable for the type of phenomenon observed by Othmer, since he found that the number of nuclei progressively diminished with increasing temperature, and not that the crystallization of the liquid abruptly ceased at a critical point. It will further be shown experimentally that the activity of the agent producing crystallization may be increased by suitable treatment above the melting point of the primary substance, a fact which it is difficult to explain by this hypothesis. The presence of isomorphous impurities will not, therefore, be advanced as a general explanation.

[5] K. F. Herzfeld, "Colloid Symposium Monograph," Vol. VII, 1930, p. 51.

[6] G. Tammann, "Kristallisieren und Schmelzen," Leipzig, 1903.

[7] A comprehensive bibliography is given in H. Freundlich "Kapillarchemie." Leipzig, 1923, p. 448.

A fourth explanation for the influence of preheating on the melt is due to Hinshelwood and Hartley, who ascribe it to decrease in the catalytic activity of colloidal dust particles derived from the air. These are considered to be surrounded by an oriented adsorbed layer, the system thus formed taking the place of a fragment of pure crystal in discharging the undercooled liquid. If large enough the system is effective immediately; if not, a series of fortunate chances is necessary to build it to the necessary size. The degree of dispersion of the active colloidal particles is supposed to change irreversibly with preheating, time, and other experimental conditions, thus accounting, *ad hoc*, for any observed behavior. In general, this explanation appears the most satisfactory of the four. Indeed, it may be considered that the explanation supported below is a revision of that of Hinshelwood and Hartley, although it retains few points of similarity. Much unsatisfactory vagueness concerning catalysis and adsorption has been removed by the accumulated knowledge of nine intervening years. For this reason a further discussion of the viewpoint of Hinshelwood and Hartley, which would add inordinately to the bulk of this communication without materially increasing its value, will not be attempted.

An hypothesis of a more specific character appears to be at present possible. The liquid may be supposed to contain minute particles of an active adsorbent, the adsorption space of which may be filled with liquid or crystalline adsorbate depending on its previous treatment. If, now, the reasonable assumption is made that the entropy change of the transition from free liquid to free crystal is not greatly different from that of adsorbed liquid to adsorbed crystal, and it is further postulated that in certain cases the heat of adsorption of the crystalline adsorbate is greater than that of the liquid, a plausible explanation for the results obtained by Othmer and by Hinshelwood and Hartley at once emerges. If the adsorption space contains the crystalline modification its heat of adsorption will, in effect, be added to the melting heat of the free crystal in opposing the destruction of the lattice by thermal agitation, and the melting temperature of the crystalline adsorbate will be above that of the pure crystal. The crystalline arrangement may, therefore, persist above the ordinary melting temperature of the solid, and grow into the liquid if the temperature is subsequently lowered. There is no reason to suppose, however, that the rate of crystal growth in the liquid adsorbate will be identical with that in the free liquid at a given temperature. It is only necessary for it to produce normal crystals more rapidly than they are produced by the spontaneous crystallization of the free undercooled liquid for the presence and growth of the crystalline adsorbate to be the decisive factor in crystallization. In cases cited below the apparent crystallization frequency is increased over a million-fold owing to this process. At a temperature somewhat above the true melting point the crystal form of the adsorbate will be destroyed, and

the germ, therefore, deactivated. After this the apparent crystallization frequency of the liquid may diminish very greatly. While no statement can be made concerning the spontaneous tendency to crystallize in the adsorption space, it is easy to imagine cases where this will not be very different from that of the pure liquid.

It is apparent that the heat of adsorption referred to above is not easily accessible to experiment, for adsorption isobars cannot be obtained. If the vapor pressure against temperature lines for liquid and crystal are drawn as in Fig. 1 only one point, D, on the liquid line AB, that representing the temperature above which the germ loses its activity, may be observed. The slope of the line, DE, which represents the vapor pressure of the most strongly held crystalline adsorbate as a function of temperature,

cannot be directly obtained. There appears, instead, the apparent paradox that from D to the true melting point B the crystalline adsorbate is identical in activity with the liquid.   That this situation presents, in fact, no serious difficulties in interpretation is due to the researches of Taylor[8] on the complexity of adsorbing surfaces, and the theoretical treatment of adsorption given by Polanyi.[9]   As a result of these it is now generally agreed that the adsorption volume is filled with material bound by widely differ-

Fig. 1.—Vapor pressure–temperature diagram for liquid, crystal, and crystalline adsorbate. AB represents the vapor pressure–temperature function of the liquid, BC that of the crystalline solid, and DE that of the most strongly bound portion of crystalline adsorbate. B and D give the melting and deactivation temperatures, respectively.

ent adsorption heats. It is quite reasonable to suppose, therefore, that, as the temperature is progressively raised above the melting point, crystalline material evaporates from the adsorption space progressively from lower to higher heats of binding, the crystalline adsorbate being replaced by liquid. When, at a sufficiently high temperature, crystal form is finally obliterated in the adsorption space, the liquid adsorbate may be supposed to differ importantly from the free liquid in crystallization frequency only because the former becomes metastable below the deactivation temperature, whereas the latter becomes metastable below the true crystallization temperature. At any point below the deactivation temperature any crystalline adsorbate present may develop, with a velocity which cannot be predicted, until it attains a vapor pressure identical with that of the free
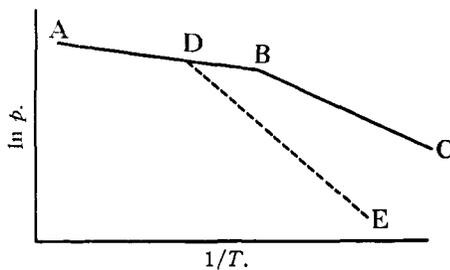
[8] H. S. Taylor, *Proc. Roy. Soc. (London)*, A108, 105 (1925).

[9] M. Polanyi and co-workers, *Z. physik. Chem.*, **132**, 321 (1928), and subsequent papers.

liquid. If the free liquid happens to be below its crystallization temperature, crystallization of the entire system, of course, results.

This point of view, if it can be experimentally substantiated, is capable of explaining in some detail the observations of Othmer and of Hinshelwood and Hartley. In both these cases the active adsorbents were introduced by accident, and were, therefore, presumably of diverse character. It is not to be expected, in view of this, that they should all be cleared of crystalline adsorbate at the same temperature. The destruction of the activity of the adsorbent by aging which is noted by Hinshelwood and Hartley indicates, perhaps, that relatively few active spots were present in each portion of liquid, and that in time these became overlaid with traces of dissolved impurities more strongly adsorbed than the crystalline adsorbate. Even the apparent contradiction, that Othmer notes increase in nuclei numbers with time, whereas Hinshelwood and Hartley report that fewer portions of undercooled liquid crystallize after a few hours than at first, is easily resolved. For Othmer's observation times were only a few minutes whereas Hinshelwood and Hartley carried on their experiments for several days. Both were observing the effect of the development of the crystalline adsorbate below its melting temperature, a process which may take several minutes to become manifest under a microscope at temperatures not far from the melting point, but which, in most cases, would be essentially complete after a few hours.

Experiments with Salol and Benzophenone

Methods and Choice of Substances.—The method of Hinshelwood and Hartley is preferred to that of Othmer because it permits sealing the material under observation in glass tubes, and, therefore, removes all possibility of subsequent contamination. It imposes, however, severe restrictions. The substances studied must, first of all, be capable of prolonged undercooling in order that the effect of adsorbents may be distinguished from the spontaneous crystallization of the liquid. Secondly, they must be stable at temperatures far above their melting points, because strong preheating is necessary to deactivate the adsorbents, and if important decomposition takes place during this process, the conditions on recooling will not be reproducible. Again, convenience dictates that the melting temperature should be higher than 23° because many degrees of supercooling are necessary to make the phenomenon clearly manifest, and prolonged maintenance of constant temperature baths below 0° is a laborious and expensive undertaking. Finally, the substances must be obtainable in large quantity and in a reasonably pure state.

Of some twenty compounds examined only two were found suitable. Most others decomposed before the adsorbent could be deactivated, or showed too high an apparent spontaneous crystallization frequency.

Salol (phenyl salicylate, melting point 42°) and benzophenone (diphenyl ketone, melting point 48°) were found satisfactory on all the counts given above, and had several additional advantages. Each of them is known to exist in several crystalline modifications, but these were readily recognizable by eye. The monoclinic modification of benzophenone, which melts at 27°, has a growth velocity[10] far less than that of the stable,[11] whereas the unstable modification of salol, which melts at 39°, has been found to grow with only one-fourth the rapidity of the stable.[10] Other modifications of benzophenone were not observed. A third modification of salol not previously known, which melts at 31°, was found to grow even less rapidly than the two others at 25°. Where doubt existed a rough measurement of the melting point at once decided which modification was present.

Since the argument under consideration may be tested by a series of critical experiments, these will be reported separately, and numbered for the sake of convenience.

Experiment 1. Spontaneous Crystallization Frequency.—Twenty sealed tubes, each containing 3 g. of U. S. P. salol, were subjected to a temperature of 130° for one hour. They were then kept for a month at 25°, in which time none had crystallized. An exactly similar experiment with benzophenone yielded an identical result.

One hundred fifty grams of salol, and a similar quantity of benzophenone were separately distilled into large tubes which had been carefully freed from dust by repeated distillations of water *in vacuo*. Both substances were distilled *in vacuo*, and as nearly as possible without ebullition. The salol distillation was accompanied by decomposition, but not in important amount. Both the tubes so prepared remained for six months at 25° without crystallization.

From this experiment it is concluded that the spontaneous crystallization frequencies of salol and of benzophenone are small.

Experiment 2. Accidental Inclusion of Adsorbents.—Twenty sealed tubes containing 3 g. each of U. S. P. salol were raised above the melting point to a determined temperature, kept there one hour, and then returned to 25° for two hours. This process was repeated, raising the preheating temperature progressively. At each temperature the contents of one or more of the tubes failed to crystallize in the allotted time. Such a tube was considered partially deactivated, but not removed from the experiment. The percentage of tubes partially deactivated plotted against the number of degrees by which the preheating temperature exceeded the melting point is given in Curve A, Fig. 2. A different sample of U. S. P. salol, which was considered to have somewhat higher purity than the first because more nearly colorless when fused, gave the result represented by Curve B, Fig. 2.

An exactly similar experiment with c. p. benzophenone yielded the result indicated by Curve A, Fig. 3. With both salol and benzophenone the contents of a tube, once partially deactivated, remained so throughout with few exceptions. These are accounted for under Experiments 5 and 7.

Experiment 2 is believed to indicate that commercially obtainable salol and benzophenone contain active adsorbents. The fact that different samples of salol showed

[10] Tammann, Ref. 6, p. 146 ff.

[11] Von Pickardt, *Z. physik. Chem.*, **42**, 17 (1902).

different deactivation temperatures is somewhat against the explanation of his experiments accepted by Othmer, and may be interpreted in favor of that of Herzfeld. Against
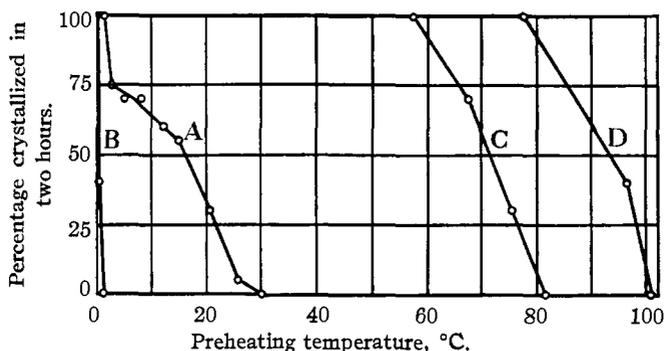

Fig. 2.—The influence of preheating on the crystallization of tubes containing undercooled salol. Curves A and B were obtained with different samples of U. S. P. salol, Curve C with salol containing powdered crystalline quartz, and Curve D with salol containing active charcoal. The "preheating temperatures" represent the number of °C. above the melting temperature to which the various samples were subjected before being supercooled. In this figure, as in Fig. 3, the lines connecting experimental points have little significance, and are included merely to clarify the diagram.

both it must be noted, however, that relatively large volumes of substance from the same sample behaved quite differently, which points toward minute heterogeneous impurities
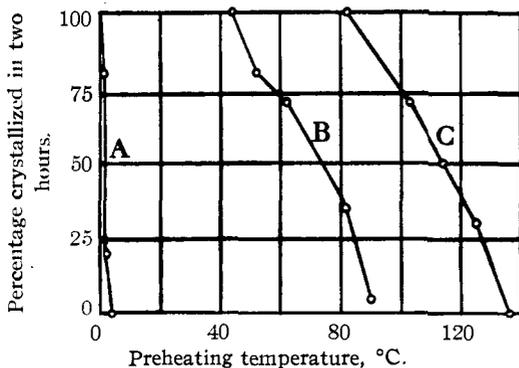

Fig. 3.—The influence of preheating on the crystallization of tubes containing undercooled benzophenone. Curve A was obtained with c. p. benzophenone, Curve B with benzophenone containing active charcoal, and Curve C with benzophenone containing powdered crystalline quartz.

Experiment 3. Rate of Crystal Growth in the Adsorption Space.—The twenty partially deactivated tubes containing salol which were obtained in Experiment 2 were kept at 25° for one month, being observed every twelve hours during this time. They crystallized at the rate, which was maintained with surprising constancy throughout, of 8% of the tubes present in ten hours. A similar set of observations with the benzophenone from Experiment 2 yielded somewhat similar results, but the percentage crystallizing in ten hours was considerably greater in the early stages of the experiment.

It may be concluded from this that a reasonably constant value for f in the equation given above may be obtained by a mechanism quite other than fluctuation phenomena in the liquid. For Experiment 1, which is in every way identical except for the extent of preheating, yielded no crystallization in a time sufficient for the

tubes wholly to crystallize in Experiment 2. Important decomposition at 130° could not have taken place for the salol crystallized with a normal velocity, and had changed less than 0.1° in melting point. Othmer's explanation cannot be accepted in view of the behavior of benzophenone, which confirms the results obtained by Hinshelwood and Hartley. It is convenient, therefore, to suppose that the crystal form had never entirely disappeared from the system, and that its gradual growth ultimately inoculated the undercooled liquids. At the normal growth velocity of crystalline salol any tube would have been filled under the conditions of the experiment in five minutes. The growth velocity is therefore, greatly retarded. We may suppose, with Herzfeld, that this is due to adsorbed impurities, or, alternatively, that the growth velocity in the adsorption space is far less than in the free liquid. The enormous time intervals involved and the differences in behavior of different samples of the same substance seem to favor the latter hypothesis. The regularity in the rate of crystallization of the tubes merely indicates that the impurities are included at random.

Experiment 4. The Effect of Various Adsorbents.—The results of Experiment 2 indicate that different substances have different powers of maintaining the crystal form of the adsorbate above the melting temperature. Three classes of these may be predicted: those for which the difference between the crystalline and liquid adsorption heats is positive, when preheating will be necessary to greatly supercool the liquid; those where this difference is negligible, which will be indifferent to the crystallization process; and those where it is negative, when the transition from crystal to liquid adsorbate will occur below the true melting temperature. The last class has no practical importance, since a crystal may be superheated only under very unusual conditions. Only the first class will be considered here.

In order to test the effectiveness of various substances in this respect, salol and benzophenone were separately ground with various possible adsorbents. Sets of three sealed tubes were prepared for each adsorbent with both salol and benzophenone, roughly 0.5 cc. of adsorbent and 3 cc. of primary substance being included in each tube. They were then raised above the melting points in progressive steps, the temperature above the melting point at which partial deactivation was first observed in a single one of the set of three containing a given adsorbent being noted in Table I as the partial deactivation temperature. Since these temperatures are neither exactly defined nor clearly reproducible they have been quoted to the nearest 10° only.

TABLE I

PARTIAL DEACTIVATION TEMPERATURES FOR VARIOUS ADSORBENTS WITH SALOL AND BENZOPHENONE

Adsorbent	Mer-cury	Ignited ferric oxide	Brass filings	Pulver-ized mica	Ground Pyrex	Roll sul-fur	Silica gel	Pow-dered quartz	Active char-coal
Salol...............	10	10	10	80	80	60	80	110	150
Benzophenone......	10	10	10	50	70	50	70	140	110

Deactivation temperatures of 10° or less may mean complete inactivity since the primary materials may contain active adsorbents as impurities. The experiments with sulfur are not satisfactory, since it causes both salol and benzophenone to undergo chemical change.

Since it was evident that active charcoal was extremely effective in preserving the crystalline modification, several brands, which were obtained through the courtesy of Professor Edward Mack of The Ohio State University, were tested for their relative activities. The least active, a Holland norit was partially deactivated with salol 40°, and with benzophenone 70°, above the melting temperature. The most active of

eighteen varieties tested bears the trade name of Nuchar, and its partial deactivation temperatures are given in Table I.

This experiment is taken to indicate that different adsorbents have different powers of retaining the adsorbate in crystalline form, and the difference is interpreted as due to differences in the adsorption heats of crystal and liquid. In the light of the extraordinary divergence of their behavior, it seems that the interpretations of Herzfeld and Othmer should be further considered only when the absence of such adsorbents is definitely proved.

It may not be at once apparent why it is possible to supercool a liquid in a glass tube after a preheating of only 10° or less when powdered glass is not deactivated without preheating some 70°. The reasonable explanation is two-fold: firstly, the active spots in the complex surface of the glass tubing have been obscured by the aging of the tube by adsorption, evaporation, slow surface reactions and the like, and secondly, when the adsorption space of the glass is filled with gas, intimate contact between crystals and the adsorbent is prevented. If the liquid is carefully deactivated by gentle preheating and adsorbent added without contact with crystalline material no activation of the adsorbent is observed until the metastable liquid is crystallized at low temperature, after which the normal course of events is established. Grinding crystals with adsorbent is, of course, the most effective means for securing activation.

A Detailed Study of Quartz and Carbon.—Since active charcoal appears the most effective of the adsorbents, and since crystal quartz is that least likely to cause chemical action or introduce impurities, a somewhat closer scrutiny of their behavior was undertaken. Using the method of sealed tubes, and supercooling at 15° for two hours or more after each preheating, Curves C and D, Fig. 2, and Curves B and C, Fig. 3, were obtained. After the deactivation process was complete, melting point determinations on representative samples of the various mixtures were made. The benzophenone–quartz system showed no change, and the benzophenone–carbon mixture had dropped only 0.3° as a result of its preheating. This change may be attributed to impurities introduced by the active charcoal. The salol–quartz system showed no decomposition by the melting point method, but the salol–carbon system, which had been subjected to 150° for fifteen minutes, showed a drop of 1.0°, too much to be due to impurities from the charcoal. Several independent experiments demonstrated that this decomposition was not due to the presence of the charcoal, but that at the temperature necessary for deactivation enough decomposition of salol always occurred to lower its melting point at least 1°.

A word should be said concerning the time of heating necessary to produce deactivation. At temperatures above 130° partial deactivation usually occurs in the time necessary to bring the melt of salol or benzophenone to the bath temperature. For example, a set of ten tubes containing charcoal and benzophenone were immersed for fifteen minutes in a bath at 110°. On cooling to 15° one of these resisted all attempts to produce crystallization at this temperature. The tubes were then kept at 110° for three days. On recooling to 15° exactly the same result was obtained. Similar persistence of the tendency to crystallize with benzophenone–quartz was observed, but the decomposition of salol at high temperatures made a repetition of this experiment with that substance futile.

It should also briefly be noted that 0.5 g. of carbon required a definitely higher temperature for deactivation than did 0.01 g. This indicates either that very active spots are rare with this adsorbent or that adsorption equilibrium has not been established over a greater part of the surface. The rather indefinite character of the deactivation temperature must be due to the same cause.

Experiment 5. Development of Crystal Form Above the Melting Temperature.—

Since crystal growth in the adsorption space is greatly retarded it is possible, as has been demonstrated by Experiment 2, for a volume of liquid to remain undercooled for many days and yet finally to crystallize owing to the presence of active adsorbents. If the velocity of the liquid-crystal transformation in the adsorption space increases with temperature and the adsorption space contains undercooled liquid adsorbate above the melting point, it should be possible to develop the crystalline adsorbate above this temperature more rapidly than at a temperature at which the free liquid is undercooled.

Experiments of this type have been carried out with salol and benzophenone, using both charcoal and quartz as adsorbents, although they are somewhat more striking with the former. In a representative experiment twenty tubes containing salol–charcoal in an activated condition were heated at 135° for thirty minutes, and undercooled to 15° for two hours. During this time eight crystallized, the others being partially deactivated. All the tubes were then kept at 100° for one hour and returned to 15°, upon which twelve tubes crystallized immediately. The eight tubes here remaining uncrystallized may be considered deactivated. The distinction between partial deactivation and deactivations thus acquires a clear-cut meaning: partial deactivation indicates that crystalline adsorbate cannot develop into the undercooled liquid within two hours at 15° and deactivation implies that the adsorption space has been cleared of crystalline adsorbate. The distinction between the two is conveniently established by development of the crystalline adsorbate some 50° above the melting temperature, and this method was consistently used to ascertain whether or not crystal form had disappeared from the system.

This experiment is a powerful support to the conception of complexity of the adsorbing surface which was found necessary in the introduction. Furthermore, by demonstrating the partial reversibility of the adsorption process, the experiment makes reasonable the assumption that, in some cases, adsorption equilibrium is attained between crystalline adsorbate and liquid above the melting temperature. Finally, the points of view of Othmer and Herzfeld cannot account for these results in a straightforward manner.

Experiment 6. The Activation Energy of Adsorption.—It has been demonstrated in Experiment 5 that the crystalline adsorbate develops more rapidly at high temperatures than at low. It is customary to interpret behavior of this kind in terms of an activation energy. In view of the success of recent work of Taylor[12] on diatomic gases, where the theory of activated adsorption was developed for the first time, it becomes of interest to inquire whether other means of demonstrating that an activation energy is required for adsorption of the crystalline modification may be devised. One has met with partial success, although it leaves much to be desired in elegance.

Ten tubes containing salol and carbon, which had been prepared by mixing the two after the salol had been deactivated in order to avoid decomposition attendant on strong preheating, were crystallized by eight hours' immersion in a solid carbon dioxide-acetone mixture. Of these, five were removed and held at the crystal–liquid transition temperature of salol for eight hours, the others being kept at low temperature during this time. All ten tubes were then plunged into a bath at 60° and melted as rapidly as possible. After an hour's immersion at 60° all of the five developed at the melting point, and only one of the five kept at low temperatures crystallized at 15°. This experiment was frequently repeated with variations, and, although sufficient activity could always be restored by treatment at the melting point, a small percentage of the tubes kept at low temperatures always showed activity. With benzophenone no conclusive results were obtained, probably because of its higher crystal growth velocity. The weakness of the method lies, of course, in the necessity for carrying the salol through its melting

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[12] H. S. Taylor, THIS JOURNAL, **53**, 578 (1931).

temperature, at which the crystalline growth velocity into the adsorption space is presumably considerable, before it can be preheated.

Experiments 5 and 6 together are considered as a strong indication that the adsorption of the crystalline modification is a process requiring an activation energy. Experiment 6 alone is the final piece of evidence to be advanced in this communication against Othmer's and Herzfeld's viewpoints since, after crystallization, the germ-forming ability of a substance is not immediately regained.

Experiment 7.   The Effect of Shaking and of Supersonic Waves.—When a system is deactivated shaking has no effect whatever, but when partially deactivated shaking may strikingly accelerate crystallization.   For example, ten sealed tubes containing benzophenone and activated quartz powder were kept for one hour at 100° and allowed to cool slowly to room temperature.   After eight hours at 25° they showed no signs of crystallization and might be examined, and even mildly agitated without crystallization.   Violent shaking sufficed, however, instantly to crystallize the liquid.   With other systems the effect of shaking was often similarly manifest; in some cases it could cut days from the duration of the undercooled condition.

An explanation for this behavior at once suggests itself in terms of the adsorption layer.   If this consists of crystal obscured by liquid adsorbate the momentary removal of the latter would permit access of the free liquid to the inner adsorption space, and hence greatly accelerate crystal growth.   If the onset of turbulence in the undercooled liquid is accompanied by violent shearing forces at the surface of the adsorbent, it is reasonable to suppose that crystalline adsorbate might thus be made momentarily accessible to the free liquid.   This explanation, while in high degree tentative, is partially confirmed by the effect of high intensity sound waves where turbulence may be secured with very little mechanical displacement.   Supersonic waves have an effect exactly parallel to that of shaking, being somewhat more effective when the adsorbent is present in traces and somewhat less when it is present in bulk, as is to be expected, but being totally without effect on deactivated systems.

Miscellaneous Experiments.—Several points which have no bearing on the main argument must be briefly mentioned to give completeness to the work.   Benzophenone–charcoal systems showed an enormously enhanced tendency to crystallize from a state of partial deactivation if rapidly cooled.   A complete picture of the effect of a sharp temperature gradient between adsorbent and free liquid on the material in the adsorption space will doubtless emerge only after more intimate knowledge of the latter becomes available.

Crystallizations at low temperature deserve a word of mention.   It is believed that this occurs wholly owing to the so-called Helmholtz process which consists of the formation by fluctuations of a crystal nucleus of sufficiently small vapor pressure for continued growth.   If the conclusion of Experiments 5 and 6, that the development of the crystalline adsorbate requires a considerable activation energy, is correct, no other cause for the crystallization of undercooled liquids at low temperatures is apparent.   Benzophenone crystallized readily when just above its glassy state, giving generally the stable rhombic modification.   Salol, when undecomposed, gave the stable modification at about −90° in about 95% of the cases observed.   When its melting point has been lowered as little as 1°, however, by ten minutes' heating at 160° in the presence of carbon, an unstable modification with a melting point of about 31° and an extremely low growth velocity at 15° was almost invariably obtained at −90°.   The transition of this modification to the stable form after inoculation was an extremely slow process, and mechanical disturbance without inoculation appeared to cause a transition to the 38.8° modification noted by Tammann, although this was not definitely established.

Occasional cases were noted in which a drop of 10° produced immediate crystalliza-

tion in one or two of a large number of tubes which had remained strongly undercooled for a long period. Thus of twenty sealed tubes containing U. S. P. salol, which had stood at 25° for three weeks after apparent deactivation at 100° for one hour, one crystallized at once when the temperature was lowered to 10° and no more crystallized after twelve hours at this temperature. If it is true that the development of the crystalline adsorbate proceeds less rapidly at low temperatures than at high, another cause must be assigned to this phenomenon. This appears from the Helmholtz expression which indicates that the radius of the smallest particle which may act as a crystallization center diminishes with diminishing temperature. If the undercooled liquid contains an active adsorbent on which a crystalline area of less than the critical radius at one temperature has developed, this area may exceed the critical radius at a somewhat lower temperature and produce immediate crystallization. The crystalline adsorbate is wholly prevented from evaporation by the adsorption heat and remains, so to speak, in a stationary state in the undercooled liquid without the ability to develop into the latter. This situation, although theoretically straightforward, occurs relatively seldom in practice, and, as might be expected, only under special conditions of pretreatment like those described above.

Experiments with Other Substances

Slowly Crystallizing Liquids.—Although the microscopic technique originating with Tammann is not capable of as rigorous interpretation as the sealed tube method, it is more economical of both time and material, and may be applied to any substance of small crystal growth velocity. The reëxamination of all the substances thus studied by Tammann and his school is indicated, but was not undertaken because it was felt that the generality of the thesis here supported would be little advanced by knowledge of a class of substances with properties so highly specialized. An investigation of substances of low molecular weight, whose heats of adsorption are far inferior to those here considered, is essential. It should be possible to develop a method more rigorous and general for this purpose than any at present at hand, and a further test of the reasoning will hence be postponed. The microscopic technique, suitably modified, was therefore applied only to three substances, two of which are important because of the work of previous investigators, and the third because its properties are quite different from any other included in this survey. Piperonal and *p*-toluidine, both of which gave promising indications by the sealed tube method, but neither of which could support without decomposition the preheating necessary to secure deactivation, gave satisfactory results. In the former charcoal produced about twenty more germs per unit weight than the untreated substance, and silica gel about five. In the latter the ratios charcoal, silica gel, and untreated substances were approximately 20:3:1. These quantities varied, of course, within wide limits depending on the quantity of adsorbent and the nature of pretreatment. Acetamide, because of its high crystallization velocity, did not permit counting the nuclei formed, but undercooled consistently to far lower temperatures if charcoal were not present. Silica gel and the pure substance showed

little difference in behavior.   In no case was a birefringent adsorption layer observed with low magnification.

Supersaturating Solutions.—It appeared of interest to inquire whether similar persistence of crystal form above the transition temperature occurred with crystalline hydrates.   To determine this a brief study of sodium acetate was undertaken, which answered this question in the affirmative. Similar indications were obtained with sodium thiosulfate, although these will be omitted to conserve space.   A slight alteration in technique was found necessary, the sealed tubes being slowly rotated in a revolving rack in the constant temperature bath in order to accelerate solution.

The solutions of sodium acetate were prepared in lots of twenty sealed tubes as before with salol and benzophenone.   After the first attempt the concentration was made consistently 12 M in order to prevent the separation of the unstable anhydrous modification.   Experiment 2 of the previous section was paralleled with two lots of material obtained from different sources.   Using the first lot 100% of the solutions crystallized when preheated 2° above the transition temperature of the trihydrate, only 35% with 3.5° above this, and only 5% with 7.0° preheating.   The solutions were kept at room temperature in the intervals between preheating, and slowness of development in the adsorption space was observed as in Experiment 3, the maximum time noted for the development of a crystallization center being nine days.   With this sample of sodium acetate it was found possible to parallel Experiment 5 by reactivating a partially deactivated adsorbent at a lower preheating temperature than that which had produced partial deactivation.   The second lot of sodium acetate was 100% partially deactivated by 1° of preheating, and, although two of the twenty solutions crystallized after sixteen hours, no further experiments were attempted.   Both samples were cleared of the trihydrate by one hour's preheating at 100°, and none of sixty tubes so treated crystallized in eighteen months at room temperature, showing that the spontaneous crystallization frequency of the trihydrate is low.[18]   On recrystallization at low temperature only one of the adsorbents was reactivated by three hours' immersion in a bath at 45°.   An attempt to find an active apolar adsorbent met, however, with virtual failure.   Active charcoal appeared capable of sustaining preheating up to 1°, and sulfur

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[18] The recent letter of W. W. Conner in THIS JOURNAL, **53**, 2806 (1931), is confirmed by the observation that, in a few of the solutions made more than 12 M, the crystalline anhydrous modification remained eighteen months in contact with supersaturated solution without producing the trihydrate.   Similar observations, over far shorter periods, are recorded above for salol and benzophenone, and have been made with sodium thiosulfate.   It is quite in accord with the point of view expressed above that the presence of crystals not isomorphous with the stable modification should be as inactive as the glass walls.   It should further be noted that growing crystals, which are known to possess great adsorptive powers, are thus proved also indifferent.

had a definitely positive effect but underwent chemical change with the acetate solution. Polar adsorbents were avoided in order to prevent phenomena akin to isomorphism.[14]

Possible Applications

An attempt has been made in the preceding sections to demonstrate the persistence and development of crystal form above the melting temperature as clearly as possible with the limited means available. It cannot be claimed that the phenomenon has more than academic interest at present except for the explanation of the behavior of metastable liquids. It seems possible, however, that a number of other phenomena may profitably be examined from this viewpoint. Some of these will be discussed briefly below, it being understood that the suggestions which follow are based on little or no experimental evidence, and are merely intended to indicate directions in which further research may be desirable.

Perhaps the most obvious application of this viewpoint is to the purification of materials. It will be seen at once that beyond a certain point recrystallization is merely the most effective method of concentrating foreign material in the substances undergoing purification. Thus, Tammann reports a four-fold increase in the number of nuclei formed per gram of betol after three recrystallizations.[1] This he attributes to greater purity of material, but it seems equally likely that it is due to concentration of active nuclei. This is especially probable since those products which tend to inhibit crystal growth are adsorbed on growing crystal faces, and are, therefore, unlikely to be removed by crystallization. In view of this the most satisfactory procedure for purification by recrystallization is seen to be the discarding of all crystal centers which form immediately. This has the added advantage of removing impurities readily adsorbed by the growing crystals. It is also seen to be advisable to digest the material for some time just below its melting or transition point.

The application of this viewpoint to devitrification is also at once apparent. Evidently a substance which it is desirable to maintain for long periods of time in a vitreous state should be heated far above its softening point. Conversely it should easily be possible to devitrify difficultly crystallizable glasses by the introduction of active germs which have been obtained from the crystalline condition but maintained thereafter above its melting point. The case of glycerin at once suggests itself: the melting point of this substance is too low to permit its maintenance in the solid condition at room temperature. If, however, a suitable activated adsorbent is sealed with liquid glycerin in a glass tube it should crystallize immediately upon cooling even although the temperature of the preparation has greatly exceeded the melting point.

[14] C. A. Sloat and A. W. C. Menzies, *J. Phys. Chem.*, **35**, 2005 (1931).

Again, it seems probable, as previously suggested, that the supercooling of non-metallic and metalloidal melts may be profoundly influenced by similar phenomena. The reasoning given during the discussion of devitrification might in some cases profitably be applied even to the development of grains in metals and alloys.

The experiments outlined above throw grave doubt on the observations of Tammann concerning the quantitative relation between the velocity of formation of crystal nuclei and temperature and appear to disqualify many of his "nuclei number" measurements, since the preheating conditions which he describes are inadequate to deactivate any adsorbing germs which might have been present. Othmer and Tammann both report influence of metals and solid powders on the "nuclei number" without, apparently, at all appreciating the significance of their results. A systematic reëxamination of the question of crystallization frequency in the absence of active adsorbents should clearly be undertaken.

Some manifestations of the so-called Law of Stages may be supposed to be due to a similar mechanism. If we suppose activated adsorbing germs in a system capable of two crystalline modifications, it seems entirely reasonable to suppose that the stable modification of the germ will undergo a transition to the unstable at a temperature somewhat above the true transition temperature. Thus, it may be demonstrated with sodium acetate and sodium thiosulfate of suitable concentration in sealed tubes that, when these are heated ten degrees above the transition point, an unstable modification soon makes its appearance, whereas, heated fifty degrees above the transition point, they remain without crystallization for long periods. Of course, this cannot be the sole important factor, for the spontaneous crystallization frequencies of the stable and unstable modifications are in many cases wholly different, as it is easy to demonstrate with sodium acetate. It is merely asserted that unless orienting germs are excluded the interpretation of the appearance of the metastable modification may be quite different from that suggested by de Coppet[15] and others.

Going somewhat further afield it is not perhaps entirely fantastic to suggest that the large groups of molecules which are indicated by certain x-ray diffraction patterns in liquids may be due to a similar cause. If this were the case there would be no difficulty in reconciling the measurements of Stewart and Morrow[16] with the more recent results of Trillat.[17] While it is highly unlikely that an alcohol of a low molecular weight two hundred degrees above its melting point should contain germs bearing the crystalline adsorbate, it is perhaps worth while to exclude the possibility by preheating and distillation in vacuo. x-Ray diffraction offers, in fact, a most promis-

[15] L. C. de Coppet, *Ann. chim. phys.*, [5] 6, 275 (1875); [8] 10, 457 (1907).

[16] G. W. Stewart and R. M. Morrow, *Phys. Rev.*, 29, 919 (1927).

[17] J. J. Trillat, *J. chim. phys.*, 27, 525 (1930).

ing means of directly detecting the existence of the crystalline state above the melting point, and preliminary experiments with molybdenum targets have already been undertaken with inconclusive results. A copper target tube for this purpose is at present under construction at the Loomis Laboratory.

Finally, there is a possibility that, by suitable experiments, the heat of melting on the adsorbent necessary to give the thermodynamic theory of adsorption from solutions[18] quantitative significance, may become accessible. If this hope proves founded it will provide the most suitable means for demonstrating the general existence of this phenomenon, and supply as well quantitative data concerning adsorption heats.

Summary

It is suggested that crystal form may persist above the melting temperature if an adsorbent is present for which the heat of binding of the crystalline adsorbate is greater than that of the liquid adsorbate. This hypothesis is seen to be successful in accounting for the behavior of undercooled liquids observed by previous investigators, and to supply a plausible explanation for further experiments. Since the liquid adsorbate is in part undercooled above the melting temperature, a mechanism is found for the enhancement of the ability of a liquid to crystallize by treatment above its crystallization temperature. It is inferred from experimental evidence that the development of the crystalline adsorbate must require a considerable activation energy.

A somewhat similar explanation has been found to apply to the behavior of two types of supersaturated solution, and the relation of the hypothesis to the Law of Stages is discussed.

Possible applications of this viewpoint to x-ray diffraction, the purification of materials, the treatment of glasses and alloys, and the thermodynamic theory of adsorption are briefly indicated.

PRINCETON, NEW JERSEY

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[18] W. Heine and M. Polanyi, Z. physik. Chem., **132,** 385 (1928).