MECHANICAL STIMULUS TO CRYSTALLIZATION IN SUPERCOOLED LIQUIDS.[1]

By S. W. Young.

Received October 21, 1910.

The phenomenon of the supercooling of liquids (which is here used to include the supersaturation of solutions) is apparently of virtually universal occurrence. It rarely, if ever, happens that a liquid cannot be cooled to some distance below its melting point without solidifying, and similarly almost any solution may be cooled to a temperature noticeably below its saturation temperature without the spontaneous appearance of crystals of the dissolved substance. In fact there is no positive evidence to show that these phenomena are not perfectly general. In the case of mixtures of two liquids, which at a definit temperature may separate into two layers, supercooling seems to be impossible. Investigations carried on in this laboratory with the assistance of Mr. Lovell Langstroth, with mixtures of several pairs of liquids, gave uniformly negative results.

Numerous attempts have been made to determin with accuracy the conditions under which crystallizations may occur in a supercooled system, and a rather voluminous literature has developed. A very complete abstract of it is to be found in various chapters of Ostwald's "Lehrbuch." The first positive result of these earlier investigations was to show that crystallization may be brought about without fail by the introduction into the supercooling system of a crystallin fragment, however small, of any solid phase in respect to which the liquid is supercooled. If the liquid is supercooled in respect to more than one solid phase, any one of these may be produced at will by introducing a fragment of the particular phase desired. This is called crystallization by "seeding" or "inoculation." Somewhat later it was likewise definitly established that a fragment of a true isomorph was equally effective in bringing about crystallization, and that pseudomorphs were in no case effective.

Thus far the subject may be considered as a closed book. But quite the contrary is the case concerning our knowledge of the conditions which determin crystallization from supercooled liquids which are not seeded or inoculated. The investigation of this phenomenon of spontaneous crystallization, or crystallization without the introduction of crystallin fragments of the solid phase, has led to extremely conflicting and indeterminate results. Most of the recent investigations in this field have been conducted upon the assumption of the existence of what has been called the "metastable limit." The concept of the metastable limit was first introduced by Ostwald, and it has since been so generally accepted that it has rarely needed any defense.

---

[1] Read in abstract before the Division of Physical and Inorganic Chemistry at the San Francisco meeting of the Society, July 16, 1910.

The significance of the idea of a metastable limit may be made clear in a few words. If a liquid be cooled ever so little below its melting point, it is to be looked upon as being in an unstable condition, capable of undergoing a change of aggregate state with the development of work or energy. The greater the amount of supercooling the greater the degree of instability. According to Ostwald, this unstable field may be divided into two parts. When the liquid is cooled below its melting point it remains through a certain range of temperature in what is called the metastable field or state. The distinguishing characteristic of this state is this: while a substance remains therein, it can never spontaneously crystallize, even under the influence of stirring and jarring. Only under the condition that a crystallin fragment of the solid phase be introduced can crystallization occur. As the liquid is more and more supercooled, however, it passes abruptly, at a definit temperature, out of this metastable state into what is called the labil or truly unstable state. In the labil field the conditions are entirely changed, and crystallization must spontaneously occur sooner or later. The time required may be very short or very long, and may in general be greatly reduced by a variety of causes, especially by agitation, and perhaps by the presence of dust particles. Precisely similar considerations apply to solutions.

Most of the investigators in this field, basing their work upon this distinction between metastable and labil, have attempted to determin, for a variety of substances and solutions, the value of the metastable limit, *i. e.*, that temperature at which a given substance passes from the metastable into the labil field. Until recently these attempts have met with but little apparent success. A single instance, that of the formation of the Liesegang rings,[1] appeared to give definit results. But even here the evidence is probably at fault, for more recent investigations seem to indicate that the formation of these rings is not at all, or at most only in part, a supersaturation phenomenon. In fact, Mr. G. D. Barnett, in this laboratory, has obtained Liesegang precipitates which were not rings at all, but spirals.

More recently the work of Miers, Hartley, Jones and others[2] in England and India has produced results that at first sight seem convincing. They sealed solutions of various salts, whose concentrations were known, into small tubes with added fragments of glass, platinum tetrahedra or other hard bodies. These tubes were then placed in a thermostat whose temperature could be very gradually lowered. As the cooling proceeded, the tubes were frequently shaken by hand, and the temperature at which crystallization occurred in each tube was noted. The results were reasonably constant for duplicates, and when plotted were found to lie fairly

[1] Morse and Pierce, *Z. physik. Chem.*, 45, 589.

[2] *J. Chem. Soc.*, **95**, 1672, and preceding papers.

well on curves overlying the normal solubility curves for the various salts, and running approximately parallel to these. These new curves are called the "supersolubility" curves for the various substances, and points upon them are considered by the authors to represent values for the metastable limit for solutions of the corresponding concentrations. When one considers that the metastable limit is defined as that temperature above which a given system cannot be brought to crystallization by mechanical shock or jar, and below which this is possible, the conclusion appears, on the face of it, to be justifiable.

de Coppet, in an extensive contribution,[1] summarizes his researches on the spontaneous crystallization of Glauber's salt and other substances. These researches have extended over thirty years, and as a result of his experience, de Coppet finds himself unable to accept the idea of the metastable limit. Without denying the virtual existence of metastable and labil distinctions, he considers the transition from the one field into the other to be a gradual one, and not the sudden one assumed by Ostwald. He interprets his results from the standpoint of the kinetic theory and the theory of probabilities, and concludes that the metastable state is to be looked upon as that state in which the probability of sufficient molecules under given kinetic conditions so arranging themselves that a crystallin aggregate may be formed, is indefinitly small in finit time. If the probability becomes very great the liquid is in a truly labil state, and between these two limits there may be a considerable range in which sporadic crystallization is likely to occur. For greater detail reference must be made to the original. In a closing paragraph de Coppet expresses his belief that mechanical agitation is unable to bring about crystallization except in the "fully labil" field, and that its principal effect is to "facilitate the development of germs already in the process of formation."

In this laboratory a very considerable amount of time has been devoted to the study of the phenomena of supercooling. Some of the results have been published, but much, and perhaps the greater portion of the work done has yielded nothing that seemed worthy of record, as the inconsistent and vagarious character of the results obtained produced more confusion than order. After having accepted for many years the hypothesis of the metastable limit, the writer was led, about three years ago, to the belief that it was probably fallacious and untenable, but on account of the apparent impossibility of obtaining consistent experimental data, was left for the time without any evidence wherewith to attack it, and it must be confessed, without very much hope of obtaining any. Finally, however, some observations upon the degree of supercooling,

---

[1] *Ann. chim. phys.*, [8] 10, 457.

noted in a series of cryoscopic determinations, suggested a clue which, when followed up, led us to the present investigations.

Experimental Part.

The preliminary cryoscopic experiments involved in the work were very numerous, and for a time the results were very conflicting. They will be very briefly cited here. The experiments were all made with distilled water, without the addition of any solute. In the first place (all these experiments were carried out in an ordinary Beckmann apparatus) it was found that the amount of supercooling permitted was considerably less with a platinum stirrer than with a glass one. The majority of the results were fairly consistent, but showed frequent and occasionally large fluctuations. A stout copper wire used as a stirrer was found to admit of even less supercooling than the platinum one. In order to determin, if possible, what factors contributed to this result, a Beckmann apparatus was arranged with a mechanical stirrer, so that the character of the stirrer and the rate of stirring could be readily varied. With this apparatus a large number of observations were made, which, while still showing considerable fluctuations, yielded interesting results. In general, the values were nearly independent of the rate of stirring over a considerable range. In this series only copper and glass stirrers were used, and these were so arranged that there was friction between the stirrer and the stem of the thermometer. The following are a few of the typical results:

TABLE I.

Glass stirrer, θ[1]........	2.4	3.0	3.5	2.4	2.4	3.2	3.2	...
Copper stirrer, θ.......	0.9	0.9	0.9	0.8	0.8	1.0	0.9	1.0
Glass stirrer again, θ...	2.9	2.5	3.0	...	...	...	...	...

The simplest explanation of these results is that the friction between the stirrer and the thermometer is a potent factor in stimulating the crystallization of water, and that the copper-glass friction pair is much more effective than glass against glass. Similar results were obtained with stirrers of brass, platinum, iron and steel. The copper was always the most efficient.

Gas Stirrers.—In order to isolate so far as possible the influence of friction between two surfaces within the liquid, the apparatus was modified as follows: (1) A glass tube was introduced through the stopper, reaching nearly to the bottom of the Beckmann tube, through which a continuous stream of gas could be maintained. This produced regular and efficient stirring, and permitted the independent observation of the effect of the friction parts; (2) a straight rod was substituted for the usual Beckmann stirrer, and so arranged that it could play through a

---

[1] θ is used throughout to represent the amount of supercooling in centigrade degrees.

ring which was suspended in the liquid, by means of a rigid attachment to the stopper. Rods and rings could be easily made of any desired materials, and a considerable variety of experiments were thus made possible. A sketch of the apparatus is shown in Fig. 1.

A is the rod whose lower end plays through the ring *B*. *C* is the tube for introduction of the gas. *D* is a thermometer reading to tenth degrees.

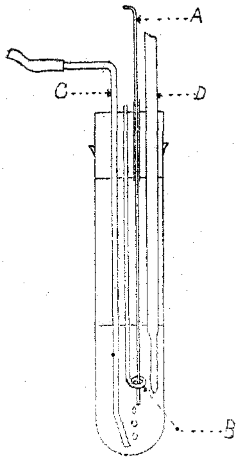

Fig. 1.

The conduct of this apparatus was first observed while using the gas stirrer alone, *i. e.*, without the introduction of the rod and ring. Hydrogen, oxygen and air were successively tried as stirrers, and rather remarkable results were obtained. The values obtained for the supercooling of water, when agitated by continuous streams of either oxygen or hydrogen, were extremely uniform, with no appreciable differences for the two gases. A large number of determinations were made, and with remarkably few exceptions all of them lay between 5.4 and 5.6 for the value of θ. Within wide limits the results were independent of the rate of flow of the gas, as well as of the form of the aperture through which the gas was admitted. With air, even when fairly well cleaned, the results were rather erratic. Hydrogen, being the easiest gas to generate, was used in the following experiments. As a safeguard it was washed by passing in through a column of wet absorbent cotton about three feet long.

Influence of the Character of the Water.—In general, as has been stated, all experiments were made upon distilled water. At this point, however, it seemed worth while to get some little idea of the way in which different specimens of water would conduct themselves toward the hydrogen stirrer. The investigation has not gone far, but has given some interesting results. A pure, clean drinking water gives values in close agreement with those for ordinary distilled water, namely, close to 5.5°. On the other hand, a sample of dirty irrigation water carrying considerable silt gave values lying closely around 4.6°, *i. e.*, nearly a whole degree less of supercooling was possible. After being carefully filtered, however, this water gave regularly values coinciding with those for distilled water. The addition of small amounts of powdered emery or pumice to distilled water reduces its θ value greatly, and this effect may be removed by filtration. Following is a series of observations upon this point. In all cases the stirring was by hydrogen alone.

TABLE II.

	θ	θ	θ		θ
Distilled water, no addition.	5.4	...	...	Distilled water, emery filtered out	5.4
Distilled water, emery added	1.8	1.9	1.9	Distilled water, pumice added.....	2.1
				Distilled water, pumice filtered out	5 5

Purification of the water by boiling, or even by redistillation, produces no noticeable effect. If, however, the water is purified by direct distillation into a tube freshly cleaned with chromic acid mixture, and especially if the tube is thoroughly steamed out before allowing the water to condense; under these conditions a very considerable increase in the supercooling is found. It is best to exclude air also, which may be done by keeping a continuous stream of hydrogen flowing through the apparatus, even during the distillation. By this means what may be called "hydrogen values" for θ have been obtained as large as 8.5°. Carefully prepared water hammers may be cooled to temperatures as low as —15° if precautions are taken to avoid mechanical shocks. The whole matter of the effect of mechanical and other impurities will be made the subject of special investigation.

Rod and Ring Friction Experiments.—A very large number of determinations were next made with the rod and ring apparatus above described. A few only of these results are shown in Table III:

TABLE III.

Nature of stimulus.	θ	θ	θ	θ	θ
Hydrogen stirrer alone..................	5.4	...	...	...	...
Copper ring-copper rod................	1.6	1.2	1.25	1.2	1.2
Copper ring-platinum rod..............	2.8	2.5	2.9	...	...
Copper ring-iron rod..................	2.7	2.85	2.6	...	...

Upon removing the metal parts, the hydrogen value returned to 5.5. The results for platinum and iron against copper are virtually the same, while those for copper against copper are much smaller. At first thought this might seem explainable by the fact that in general the friction coefficients between like bodies is greater than that between unlike ones. Certain incidental observations, however, led to the belief that factors as yet uncontrolled were concerned. Owing to the fact that there was always considerable space between the rod and the ring, considerable impacts between the two were always possible. It was thus considered wise to so modify the apparatus that it became still more purely frictional in its action. The first modification tried was the substitution of a piece of tubing for the ring. The tube was of such size that the rod would just easily pass through it, and in order that there should be no clattering between it and the rod, it was placed slightly out of alignment with the latter. Three sets of these friction parts were made, one of tool steel, one of brass and one of glass. Following (Table IV) are some of the results obtained:

TABLE IV.

	Friction parts tool steel.	Tool steel + emery.	Brass.	Glass.	Glass (rough).[1]
ϑ =	1.7	1.1	2.5	4.0	1.3
"	2.2	1.25	2.3	4.4	2.0
"	2.2	1.2	4.4	5.0	1.5
"	2.05	1.1	2.9	4.7	1.4
"	2.70	1.3	2.85	...	2.0
"	2.30	1.45	3.1	...	...
"	1.60	1.30	3.4	...	...
"	2.30	1.35	3.1	...	...
"	2.35	1.20	4.4	...	...
"	3.00	1.35	2.9	...	...

In the experiments with this apparatus the freezing always started at the point of friction, which was shown by the fact that the first evidence of freezing was the adherence of the rod to the collar. The results still show very considerable fluctuations, in fact greater ones as a rule than were shown in the rod and ring apparatus. Otherwise their main significance lies in the fact that they clearly show the greater effect of friction between rough than between smooth surfaces of a given substance (see results with glass).

Rotary Friction.—Still another type of apparatus was tried, in the hope of finding a frictional device that would yield more definit and consistent results. This was a rotary frictional contrivance, the essential features of which are shown in Fig. 2. The rod *A* of any desired material is turned to a conical tip at either end. The lower end is seated in a similarly formed conical bearing, *B*, which is likewise of any desired material. The copper end is also seated in a cone bearing carried in the under side of a lever, *C*, whose fulcrum is at o. By means of the movable weight at *E*, the load upon the bearing *B* may be altered at will. The rod is rotated at any desired speed by a belt connecting the pulley *F* with a motor shaft.

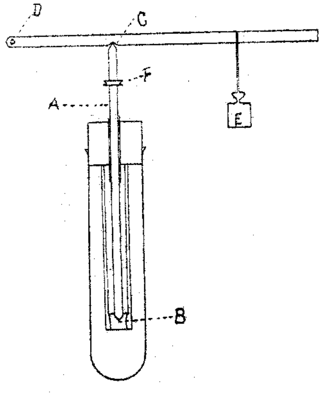

Fig. 2.

The results obtained with this apparatus were very unexpected, and for a time seemed wholly inexplicable. Without giving the voluminous data obtained, the conclusions may be summarized as follows:

(1) Both tool steel and brass friction parts give results that are nearly independent of the rate of rotation, although a slight increase in efficiency with increasing velocity is noticeable in all cases.

---

[1] Roughened with emery paper.

(2) With tool steel the result of increasing the load on the counterpoise was to decrease the values for the supercooling. This is of course what is naturally to be expected, if it is assumed that friction is the effective impulse.

(3) Brass parts, however, gave results of the opposit character; that is, as the weight upon the counterpoise was increased the value for the supercooling also increased, and this in a quite noticeable degree. A repetition of the measurements with tool-steel parts showed that the same phenomenon may occur as with brass, but in this case the apparatus must be in continuous use for a long time before the values under large load fall below those under light load. These results, conflicting as they seem, led to a train of thought which finally cleared up the whole problem.

If one considers what must be the nature of friction occurring between two solid surfaces, it seems probable that it will always consist of a series of small jumps and impacts, similar to the effect produced when one rubs the finger over a pane of glass, or around the rim of a goblet, in such a way that the glass is set in vibration. Only in mathematically smooth surfaces, probably, can such a thing as "pure friction" be imagined. The amplitude of the jumps and the magnitude of the resulting impacts will depend upon a variety of factors, among the more important of which will be the hardness of the bodies and the physical character of the surfaces. It has been noted above that friction between rough surfaces is more efficient in stimulating crystallization than that which occurs between smooth surfaces of the same material. This, in connection with the above considerations, leads to the inquiry as to whether mechanical impacts may not be the true stimulus to crystallization in all of the above experiments, and friction only efficient in so far as it is to be looked upon as a series of impacts. Such a theory readily explains the results obtained with the rotary apparatus. The brass friction parts, being soft, grind themselves a smooth seating in a comparatively short time, especially under a heavy load. The magnitude of the impacts is thus rapidly reduced, and the conduct of the apparatus is perfectly explained. With tool-steel parts the grinding of a smooth seating will be a matter of much greater time, even under a considerable load. The immediate effect of increasing the load on the counterpoise will be an increase in effective stimulus, and this may persist for a long time. Finally, however, as the seating becomes smoother the effective stimulus will fall off, and in time may become less than had been previously observed under a lighter load. This is also in accordance with the observations made.

Impact Experiments.—If these considerations are correct and crystallization is stimulated rather by impact than friction (in the ordinary sense), experimental demonstration of the fact should be comparatively easy. With this in mind an apparatus was constructed which worked on the principle of a stamp mill. Fig. 3 shows the essential features of this apparatus. The stamp consisted of the steel rod *A*, at the lower end of which was attached a collar into which the bit *B* could be cemented. This bit is interchangeable, so as to allow of the investigation of any desired substance. To the upper end of the rod was cemented the glass tube *C*, which could be loaded with any desired quantity of mercury, thus producing considerable variation in the weight of the stamp. The stamp could be raised to any desired height and allowed to drop through the guide *D*, thus producing impact between the bit and the anvil *E*. Upon the anvil was cemented a flat disc, *F*, which served as the striking surface for the bit. This disk was also interchangeable, and could be of any desired material. In operating the apparatus, an arrangement was devised whereby the stamp could be kept in continuous action at any height by means of a motor. Thus a continuous series of impacts of nearly constant value was produced within the liquid under investigation. The liquid was continually agitated by means of the hydrogen stirrer, and being surrounded by a cooling bath so arranged that the temperature fell from one-quarter to one-half degree per minute, that temperature was noted at which crystallization occurred. This was the value for the supercooling possible under the influence of the given mechanical stimulus.

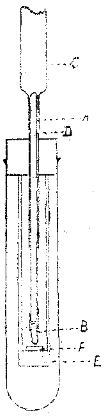

Fig. 3.

Preliminary investigations were made with a considerable variety of impact materials. With most substances the continued impacts produce such marked changes in the character of the impact surfaces that the results were somewhat inconsistent. This is true of all soft metals such as brass, and even soft steel. It is especially true of very hard substances which are also brittle. A series of measurements were made with corundum impact parts, and gave the most uncertain results of all. As a result of these preliminary experiments, tool-steel parts, mercury-hardened, were found to give thoroughly reliable results, especially after thorough smoothing and polishing with crocus. After considerable use it was found advisable to repolish. In the following series of measurements such an impact pair was used. The disk was flat, and the bit was turned into a hemispherical tip so that slight inaccuracies in the guiding of the stamp would not affect the area of the surface of impact. This apparatus, while rather crude and shaky, gave unexpectedly reliable results, which are tabulated below. Measurements were made upon water, benzene, and a concentrated solution of the hexahydrate of calcium chloride.

TABLE V.

	Distilled water.			Benzene.		
Drop..........	1 cm.	1 cm.	5 cm.	3 mm.	1 cm.	5 cm.
Weight........	40 g.	100 g.	100 g.	40 g.	140 g.	100 g.
$W \times D$.......	40	100	500	12	40	500
Values of θ....	2.9	0.8	0.1			
	2.9	0.8	0.1	0.4	0.3	0.2
	2.7	0.9	0.1	0.4	0.3	0.2
	2.9	0.8	0.1	0.4	0.3	0.2
	3.0	0.7	0.1			

Owing to the slowness of the rate of crystallization in the immediate neighborhood of the melting point, it is probable that the values for θ recorded in the last column for water are considerably too large.

The hydrogen value for benzene was found to be about 3°. Both the rate of crystallization and the latent heat of fusion for benzene being less than for water, an even greater lag is to be expected. In tubes which were supercooled but one-tenth of a degree, crystallization could be forced by "throwing" the stamp. This was accomplished by lifting the stamp by hand and forcing it down upon the anvil, just as one would throw the ramrod in loading a muzzle-loading gun. In this case, of course, no definit idea of the value of the impact can be had.

TABLE VI.—MEASUREMENTS ON FUSED $CaCl_2.6H_2O$.

Drop................	1 cm.	1 cm.	5 cm.	Forced by throwing.
Weight..............	40 g.	100 g.	100 g.	
$W \times D$.............	40	100	500	...
Values of θ..........	8.4	2.7	2.2	1.6
	7.4	2.6	2.0	1.5
	11.0	2.6	2.0	1.5
	7.0	2.9	...	...

The calcium chloride used was a commercial preparation showing a melting point of 28.9°, and consequently carried some little excess of water. It showed a hydrogen value of about 21°. The discrepancies in the values found in column 1 are probably due to two causes: (1) the apparatus itself had become very badly used up, especially as a result of so much "throwing;" (2) at the temperatures corresponding to these values, the calcium chloride is already very sensitive to external jars. In fact, by running the apparatus without the stamp, *i. e.*, allowing the lifting and dropping device to run alone, the jarring would usually start the crystallization when the supercooling was about 10°. Of course only such results are reliable as are obtained when the shock of the stamp transcends all others. Consequently the values in column 1 are doubtful.

Discussion of the Results.

In attempting to plot the results of the above measurements, the question immediately arises as to what function of the weight and drop distance is to be used. Until more data can be gathered, but little ground for choice is apparent. Whether the stimulus is directly mechanical or perhaps due to local high temperature or pressure is uncertain. Assuming, however, that it is a purely mechanical effect, it is still impossible to say whether the energy developed, *i. e.*, the "impact" value which is equal to the mass × the height, or the impulse value, *i. e.*, the mass × the square root of the height, is to be considered as a measure of the stimulus. It is perfectly possible even that neither of these functions is the true one. The fact that the apparatus used was so crude, and also that it had become at this point so shaky in its action, made it impossible to carry out the necessary precise measurements for the determination of this point. A new and much improved apparatus is in process of construction, and it is hoped that with its aid conclusive data may be obtained. In the meantime the results already obtained have been plotted in terms of the impact values, rather than the impulse values. For the general interpretation of the results the matter is not of great importance, since the general form of the impulse and impact curves is not essentially different.

In Fig. 4 are plotted the relationships between the θ values and the impact values for water, benzene and the hexahydrate of calcium chloride.

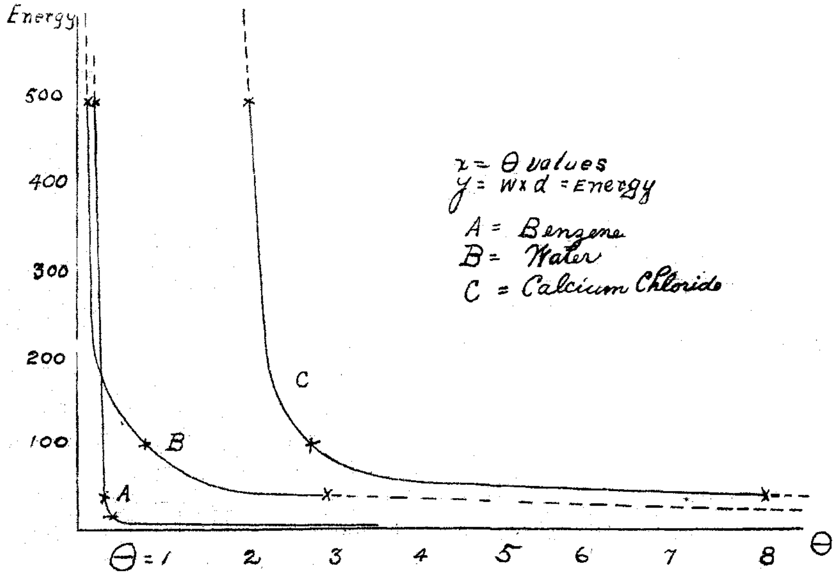

Fig. 4.

These curves are manifestly asymptotic to both axes, and possess, at least superficially, the characteristics of hyperbolas of very short focal distance. The curve for water is extrapolated along the X-axis in such a way that the impact value would be almost zero at a θ value of 16. This seems fairly justifiable in consideration of the fact that when supercooled to this extent, water becomes extremely sensitive to such slight jars as may occur ordinarily about a laboratory.

As a result of these experiments it seems to be no longer necessary or even justifiable to assume the existence of a metastable limit in the generally accepted sense, nor does it seem desirable to distinguish between a metastable and a labil field in the de Coppet sense. The whole unstable field is labil and crystallization may be brought about in any portion of it by the production of sufficient mechanical shock. In many cases the shock required may be enormous even in very considerably supercooled systems. This is undoubtedly the case with Glauber's salt. A few experiments were made with a solution of this salt, which was saturated at 25°. Glauber's salt could be forced to crystallize from such a solution at temperatures below 7°, but only with the severest shock that could be given by throwing the stamp. Thus such a solution may supercool 18° under the influence of such shocks as would allow no measurable supercooling with water.

On the other hand, an inspection of these curves shows very clearly why the idea of the metastable limit has for so long seemed plausible, and why the values for the supercooling limit frequently group themselves very closely together. The Y-arm of the curves is for a long time nearly vertical, and throughout a more or less considerable range of temperature the shock required to force crystallization is very large. Along the X-arm the reverse condition holds, and a large variation in temperature corresponds to a very small variation in impact value. These two nearly straight lines are connected by the sharp curves found in the neighborhood of the foci. Thus the transition of the system from a condition of very slight sensitiveness to shock to one of very great sensitiveness, while continuous, is nevertheless very rapid, and it is undoubtedly this short, sharp curve which has heretofore been mistaken for the metastable limit. If this sharp turn, which may perhaps as well be called the "transition" curve (although it probably has not the attributes of a true transition curve), lies at impact values corresponding to ordinary laboratory disturbances, and perhaps to the activity of dust particles, fairly agreeing values would be obtained from experiments made at rest. This is shown more or less in the conduct of benzene. If the transition curve lies at higher impulse values, such as correspond to shaking and stirring, a comparatively closely grouped set of results will be obtained by working under those conditions, which is shown in the conduct of the hexahydrate of calcium chloride. If it lies at very high values, conduct like that of glycerol and alcohol, which rarely crystallize, even when highly supercooled, is to be expected.

The results of the shaking experiments of the English chemists, which were referred to in the early part of this paper, are thus to be looked upon as approximately constant results obtained with approximately constant maximum shock. They find some substances unsuited to the determination of the metastable limit by their method, which presumably means that their method did not give sufficient impulses to enable them to reach the neighborhood of the transition curves for those substances. It is interesting to note that their values for the metastable limit for water (from solutions) lie closely about six-tenths of one degree. This temperature lies upon the transition curve for water as determined from these experiments.

If one desires any mechanical analogy to explain the phenomena under consideration, the following seems to serve the purpose fairly well. One may consider the crystallizing forces in a liquid to be roughly analogous to the magnetic forces in a field. At temperatures above the melting (or saturation) point, these directive forces are overcome by the disruptive forces, mainly probably, the kinetic energy of the molecules. At the melting point, the molecules are in such a condition that the directive and disruptive forces just balance one another. At temperatures below the melting point the directive forces are the greater, but the molecules being also under the influence of resistive forces such as viscosity, are like the iron filings in a weak field, unable to arrange themselves into the stable form until assisted by a mechanical jar.

Interesting complications occur when the supercooled liquid is in a position to yield more than one solid phase. Ostwald has suggested, as covering such cases, the rule which bears his name, and which states that when two or more solid phases may separate from a liquid, it is always the least stable one that appears first. While often giving correct conclusions, the rule is subject to frequent violation. From the above results it would seem reasonable to assume that each of the two or more possible phases would have its own impact curve, and that any phase might be produced at will, according to the impact given. This has been accomplished in the case of Glauber's salt and the heptahydrate of sodium sulfate.

A solution of Glauber's salt was prepared, which was saturated at 25°. Such a solution would also be saturated with heptahydrate at 7.5°. Below 7.5° the solution is thus in a position to yield two solid phases. With the hydrogen stirrer it yields heptahydrate invariably at about 2°. By means of increasing shocks with the stamp apparatus, heptahydrate may be brought down at temperatures as high as 6°. In this connection it is to be noted that Hartley's value for the metastable limit of the heptahydrate in such a solution is —4°.[1] At temperatures

---

[1] *J. Chem. Soc.*, **94**, 825.

below 7° Glauber's salt may be brought down in preference if the shocks are sufficiently great, but this is a matter of much difficulty and required the severest possible throwing of the stamp. Thus at temperatures below 6 or 7° moderate shocks will force the crystallization of heptahydrate, while more severe ones will bring down Glauber's salt. Since the solution is saturated as to heptahydrate only at temperatures below 7.5°, it follows that the impact curve for this particular solution with respect to heptahydrate must become asymptotic to the Y-axis at this temperature. Similarly the impact curve for Glauber's salt in the same solution becomes asymptotic to the Y-axis at 25°. These facts, in connection with the lower impact values for heptahydrate below 6 or 7°, show that the two impact curves in question must cross one another at a temperature in the neighborhood of 6 or 7°. At temperatures below this point Glauber's salt will require the greater impact, while at temperatures above this same point, the heptahydrate will require the greater impact. If these considerations are correct, it would seem that the separation of any one of all the possible solid phases from a supercooled liquid is a matter which is determined by the course of its impact curve with respect to those of all other possible phases. In general, by cooling a liquid at rest, that phase will first appear whose impact value first reaches a very small magnitude. The curves in Fig. 5 show this relationship. It is to be added that these curves are of only a qualitative character. Further, it is not necessary that such pairs of impact curves should intersect.

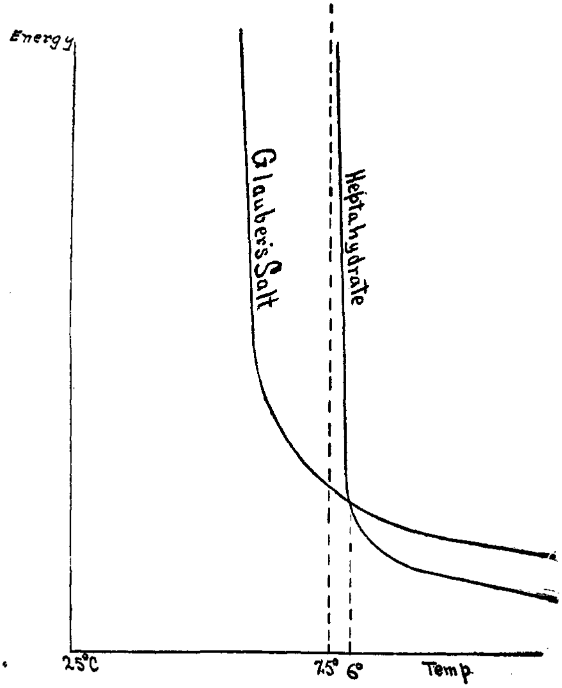

Fig. 5.

The above considerations apply only when other influences which may cause crystallization are excluded, or at least are present only in such degree that the efficiency of the mechanical impact used is greater. That other influences do exist will not be denied by any one who has worked in this field. Oftentimes with some substances, what seem to be wholly fortuitous cases of crystallization, will occur in liquids at rest, under such conditions that a very large mechanical shock would be required to accomplish the same result. As to the nature of these influences but little can be said at the present time. Investigations are under way which it is hoped may throw some light on the subject. Also the researches upon the mechanical stimulus are being extended.

STANFORD UNIVERSITY, CAL.

BISMUTH OCHERS FROM SAN DIEGO CO., CALIFORNIA.

BY WALDEMAR T. SCHALLER.

Received November 28, 1910.

Introduction.—The bismuth ochers which are herein described were found at several of the mines yielding lithium minerals in San Diego Co., California. Native bismuth occurs sparingly, as a primary component, in several of the pegmatite bodies which have produced gem tourmalin, lepidolite, etc. From this metallic mineral, a number of secondary alteration products have formed and it is the purpose of this paper to briefly describe these. The presence of these bismuth ochers, which have been called bismite, has been noted by Kunz[1] and also by the writer.[2] A recent paper by Rogers[3] notes the occurrence of bismite in distinct crystals, agreeing in form and angle with the artificial Bi_2O_3. The correctness of the determination of these crystals as bismite (Bi_2O_3) was not verified by chemical data and, in the light of the facts set forth in this paper, it seems not at all sure that the material is the oxide of bismuth (Bi_2O_3). These ocherous oxidation products are found coating the quartz and other minerals of the pegmatite, as gray, yellow, or green pulverulent masses, usually in very limited quantities. Examination under the microscope showed them all to be amorphous, and not transparent. Nothing indicated, however, that they were not homogeneous.

Yellow Bismuth Ocher, Stewart Mine.—The yellow powder is the most abundant and nearly a gram of it was obtained for analysis from specimens found in the Stewart Mine, at Pala. About a quarter of it was sacrificed for qualitative tests which showed the presence of an insoluble residue (mostly quartz and feldspar), and, in the solution, of abundant bismuth and vanadium with very small quantities of silica, alumina and lime. A small amount of water was given off when the ocher was heated in a closed tube. No carbon dioxide was given off on dissolving the

---

[1] G. F. Kunz, "Native Bismuth and Bismite from Pala, California," *Am. J. Sci.*, [4] 16, 398 (1903).

[2] W. T. Schaller, "The Tourmaline Localities of Southern California," *Science*, 19, 266 (1904).

[3] A. F. Rogers, "Minerals from the Pegmatite Veins of Rincon, California," *School of Mines Quart.*, 31, 208 (1910).