

The test tubes containing the melted material were cooled in air at room temperature and were stirred with the thermometer until the first crystals appeared. It is stated that "with the use of such small amounts of material and this method of measurement, there is possibly an error of 2° as a maximum."

For the melting point of sodium nitrate the following values have been obtained: Person (1849), 310.5°; Braum (1875), 342°; Carnelley (1876-78), 319°, 316°, 330° ± 2; Guthrie, 305°; Maumené (1883), 298°; Carveth (1898), 308°. We found 315.1°.

For potassium nitrate, the following are the melting points obtained by others: Person, 339°; Schaffgotsch (1857), 338.3°; Braum, 342°; Carnelley, 353° ± 1, 332° ± 5, 339° ± 2; Guthrie, 320°; Maumené, 327°; Carveth, 337°. We found 346.3°.

For the freezing point curve for binary mixtures of potassium and sodium nitrates, the four curves shown in Fig. 3 embody the results obtained by Schaffgotsch,¹ Maumené, Carveth and ourselves. Percentage by weight is represented on the axis of abscissas. The usual large discrepancies between the results of different observers are here again in evidence.

For the freezing point of the mixture represented by $[\text{NaNO}_3, \text{Ca}(\text{NO}_3)_2]$, Maumené obtained 235°. Interpolation on the appropriate curve would lead us to 261°.

KENT LABORATORY, THE UNIVERSITY OF CHICAGO.

THE MECHANICAL STIMULUS TO CRYSTALLIZATION. II.

BY S. W. YOUNG AND R. J. CROSS.

Received June 5, 1911.

In a previous paper² by one of us it has been pointed out that mechanical impacts produced within supercooled liquids and solutions are capable of stimulating these to crystallization, and that further, the sensitiveness of the supercooled system increases with the degree of supercooling, and that to stimulate crystallization in very slightly supercooled systems requires very large mechanical stimulus. It was also pointed out that there seems to be no justification for dividing the supercooled field into metastable and labil fields as the whole supercooled field appears to be labil in such a sense that crystallization may be forced at any point within it by sufficient mechanical stimulus.

It has long been held that foreign particles, such as dust and the like, exert under some circumstances an influence upon the production of crystals in supercooled liquids. No very definite ideas concerning the influence of such particles have been advanced up to the present time,

¹ *Pogg. Ann.*, **102**, 293 (1857).

² *THIS JOURNAL*, **33**, 148.

so that on account of the vague and speculative character of the many references to be found in the literature, it seems hardly necessary to cite them here.

The following investigation was taken up for the purpose of throwing some light upon the question. Two points of view are possible:

1. That the effect of foreign particles is entirely a kinetic one, and that the stimulus which they offer to crystallization is of an entirely mechanical character, and depends upon the production of a mechanical disturbance when two such particles come into impact with one another, or perhaps when one of them comes into impact with the walls of the containing vessel.

2. That the effect of the foreign particles is at least in part of some other nature, not at present definable.

In the investigation to be described the arbitrary assumption was made that the effect of the particles is purely kinetic. Upon the basis of this assumption certain quite definite predictions could be made as to the conduct of supercooled liquids carrying known numbers of particles of known size, and moving at a known rate. It must, however, be stated at the outset that so many factors enter into the determination of the rate of motion of a particle within a liquid when the latter is in a state of agitation (as being stirred by a stream of gas) that such predictions cannot possibly be of more than a roughly qualitative character.

The more important points upon which such predictions may be made are the following:

1. *The Effect of the Mass of the Particles.*—If the effect of the particles is purely kinetic, the disturbance which would be produced by impact between two particles of the same size would be proportional to their masses. Thus at a given velocity of agitation, and other factors remaining constant, a liquid charged with particles of large mass should permit of less supercooling than the same liquid charged with particles of small mass.

2. *The Effect of the Number of Particles.*—If but relatively few particles are present in a liquid, the chances of an impact between any two of them occurring within a given interval of time will be relatively small. As the number of particles in a given volume increases, the probability of such an impact occurring in a given interval of time will increase, and as a matter of fact in proportion to the square of the number of particles. Thus in a liquid carrying a small number of particles, and being cooled at a given rate, and at the same time being kept in a constant state of agitation, erratic values for the amount of supercooling observed are to be expected. This will be due to the fact that in one case the impact which causes the crystallization may not occur until after a considerably greater lapse of time than in another case, and as the liquid is

being continually cooled the observed temperature of crystallization will be considerably lower.

Since when the number of particles increases, the probability of the impact occurring within a given time increases very rapidly, it is to be expected that the results for the supercooling observed will become more nearly constant and at the same time show a somewhat lower average. When the number has increased to such an extent that the impacts succeed one another in very rapid succession, the result should be an approximately constant value for the supercooling, and one which is independent of the number of particles within considerable limits.

When the number of particles become very great the mechanical character of the liquid will become considerably altered, especially when agitated by a gas stream. Under these conditions the liquid will take on more or less of the character of a mud; the successive bubbles of gas will lift greater amounts of the liquid and these will drop back with considerable force into the bulk of the liquid. With liquids in this state it is to be expected that considerably greater impact values may occur than those due to the mere meeting of the individual particles, and consequently less supercooling is to be expected.

3. *The Effect of the Character of the Liquid.*—It is readily seen that certain physical properties of the liquid, especially its viscosity, will play an important part in determining the velocity with which two particles meet within the liquid under the stimulus of a given agitation. This fact, together with the more or less fortuitous character of the agitation produced by a stream of gas, makes it impossible to reach any exact quantitative idea of the impact values produced under the conditions of such experiments. It may be predicted, however, that small particles, owing to the relatively greater surface which they expose, will be more retarded in their motions than will large ones. Hence it is to be expected that in order to reach the constant maximum effect (barring the mud effect), there will be required a considerably greater number of small particles than of large ones.

It may also be foreseen that any influence which increases the viscosity of the liquid will decrease the impact values for all particles, and will affect small to a greater extent than large ones. Thus the addition of a substance such as gelatin to water, which materially increases its viscosity without largely affecting its other physical properties, should to some extent protect the water against the crystallization stimulus of foreign particles, and this effect should be greater for small particles than for large ones.

Experimental Part.

Several forms of apparatus were used in the preliminary experiments. In principle these were all the same. They consisted of a Beckmann

freezing tube with a two-hole stopper. Through one hole was introduced a thermometer and through the other a tube leading nearly to the bottom, which served to admit the hydrogen gas used to stir the liquid. The particles whose effect was to be investigated were dropped into the liquid. The whole was surrounded by an ammonia cooling bath which produced a rate of cooling of about one-half degree a minute.

A number of preliminary experiments were devoted to studying the effect of the rate of flow of the gas and the form and nature of the aperture through which the gas was admitted. The effect was found to be independent of the material of which the aperture was made, the value for the supercooling being the same for apertures of glass, aluminium and brass. The effect of the rate of flow of the gas was negligible when pure water was used, at least within considerable limits. When foreign particles were present a distinct effect was found, in such a sense that a low rate of flow favored greater supercooling. Increasing the amount of gas and constriction of the aperture both produced the same effect; namely, less supercooling was possible. In order to avoid these effects the same gas tube with a constant flow of gas was used in the following experiments.

A few further preliminary experiments were then made by adding portions of a number of solid powders to the water and observing the temperature of freezing. The distilled water used showed an approximately constant degree of supercooling; namely, -5.7° . The addition of powdered gamboge to this produced an effect so slight as to be practically negligible. Addition of starch gave occasional values as high as -3.0° , and varying from that to the normal value of the water. The results were very erratic, and owing to certain difficulties in its use, the observations were carried no further. Crocus was next tried, and found to give results in the neighborhood of -4° . These were also somewhat erratic, and it was found after a few freezings that the crocus had largely flocculated. Furthermore it showed a marked tendency to adhere to the walls of the tube, whence it was not considered a satisfactory substance to work with. Emery gave much more satisfactory results, but was not altogether free from flocculation and was consequently discarded.

Finally a satisfactory substance was found in the commercial powdered quartz such as is used as a flux in assaying laboratories. This consists of particles of a great variety of sizes, and was found to be nearly free from flocculation, even among the particles of very small sizes. The remainder of the investigation was carried out entirely with this substance, which was first separated into particles of various sizes by methods to be described in the following. The freezing apparatus was also somewhat modified.

1. *The Method of Separation.*—A first rough separation was made by the method of settling. A considerable quantity of the powdered quartz was stirred up with a large volume of water, and the portions remaining unsettled after respectively one, two and five minutes were decanted off. The portions obtained by such settlement were then brought successively into a flotation apparatus and subjected to further separation. This apparatus consisted of a glass tube of four centimeters diameter and thirty-five centimeters long. The lower end of this tube was drawn down and a small tube soldered on through which a stream of distilled water could be introduced. The upper end was provided with a two-hole rubber stopper, through one hole of which was introduced a thistle tube. Through the other hole was passed a short glass tube which served as the overflow. The separation was carried out as follows: A stream of distilled water was passed through the tube at a constant rate, which rate could be determined by measuring the amount of water passing through in a given time. The partially separated quartz powder mixed with water was then introduced a little at a time and the apparatus allowed to run until no more particles were carried over. By now somewhat increasing the rate of flow of the water, other particles of a somewhat larger size were carried over. If the two rates of flow were not very different, the particles which passed over were of quite uniform size.

By this method four portions of the quartz powder were obtained whose sizes were comparatively uniform in each sample but which differed very considerably in different samples, the intermediate sizes being discarded. These portions will hereafter be characterized as Nos. 1, 2, 3 and 4. No. 1 consisted of such particles as refused to float over when the rate of flow of the water was forty centimeters a minute, but did float over at a water rate of forty-eight centimeters a minute. No. 2 was obtained between rates of flow of 7.7 and 10 centimeters. On account of the great length of time required to obtain appreciable quantities of the finer particles by this method, a somewhat different procedure was used for Nos. 3 and 4. No. 4 was obtained by allowing the separator to run at a rate of 0.4 centimeter a minute. There was thus obtained a sample consisting of particles that would just pass over at that rate, together with particles of all smaller sizes. The sample was freed from smaller particles by repeated settling until under the measuring microscope the particles showed a nearly uniform size. No. 3 was similarly obtained from samples which passed over with the separator running at a rate of 1.2 centimeters a minute.

2. *Determination of the Number of Particles in a Given Volume.*—The four samples thus obtained were brought into known volumes of distilled water, and a count of the number of particles in a cubic centimeter of each was made. For samples 2, 3 and 4 the method used was the

usual blood count method under the microscope with a Zeiss blood count cell. On account of the settling of the particles it was difficult to obtain a uniform field. This difficulty was obviated by suspending the particles for the purpose of counting in a potassium mercuric iodide solution of the same density as the quartz. In this manner satisfactory results were obtained. In the case of No. 1 the particles were somewhat too large to be accommodated in the blood count cell. They were therefore counted by allowing one cc. of the suspension to flow uniformly from a pipette in drops upon a glass plate. The number of particles in every fifth drop was counted, and the average result was multiplied by the whole number of drops in the one cc. A count of No. 2 was also made by this method, the result checking well with the results for the same sample by the blood count method.

3. *The Diameter of the Particles.*—The diameter of the particles was roughly determined with a measuring microscope. Since the particles were mostly of jagged and irregular shapes these measurements have no very great significance. The results are as follows:

No. 1, 0.10–0.12 mm.; No. 2, 0.03–0.05 mm.; No. 3, 0.012–0.016 mm.; No. 4, 0.008–0.012 mm.

4. *The Mass of the Particles.*—The average mass of the particles in each sample was determined by pipetting off one cc. of each, placing on a weighed watch-glass and allowing the water to evaporate. Dividing the total weight of the particles by the already known number, the average weight of each particle in milligrams was obtained. The results are as follows:

No. 1, 0.002 mg.; No. 2, 0.0005 mg.; No. 3, 0.00002 mg.; No. 4, 0.000007 mg.

Having obtained the above data, each sample was either diluted or concentrated until the number of particles in one cc. of each was some convenient whole number. When finally ready for use, No. 1 contained 40,000, No. 2 80,000, No. 3 2,000,000, and No. 4 14,000,000 particles in one cc.

5. *The Apparatus.*—The apparatus used in all the following experiments is shown in the figure. It consists of a freezing tube, *A*, with a capacity of 50 cc. To the bottom of this was soldered a tube, *B*, through which hydrogen from a generator could be admitted at any desired rate, and which served to stir the contents of the tube. The freezing tube was also provided with a two-hole stopper, *C*, carrying a thermometer, *D*, and a gas outlet tube, *E*. Surrounding the freezing tube was a liquid ammonia jacket, *F*, which served to cool the contents of the tube at an approximately constant rate. A gas regulator served to maintain the flow of the hydrogen at a nearly constant rate throughout the whole series of experiments. The rate chosen was from 350 to 390 cc. a minute, this rate being found necessary in order to avoid settling out of the coarser particles during an experiment.

6. *The Method of Experiment.*—For use in these experiments a considerable quantity of redistilled water was prepared in order to have a uniform material for all the measurements. This was found advisable, as the ordinary supply of distilled water showed some variations from day to day, in its supercooling value. In carrying out a series of experiments the method was as follows:

The freezing tube was filled with the pure water to the 50 cc. mark, the flow of gas started, and several observations of the temperature at which freezing started were made. These results showed but little variation throughout the whole series of experiments, lying in general between -5.6° and -6.2° . Next a quantity of one of the above described suspensions was introduced, sufficient to produce the desired number of particles in one cc. After settling for a few moments the added water was pipetted off, the volume being again brought back to the original 50 cc.

A series of four observations (sometimes many more) was made upon the temperature at which freezing started in this suspension. Thereafter further numbers of particles were added, and corresponding observations made. In so far as it was possible, observations were made with all four sizes of particles in equal concentrations, in order to obtain results that would be directly comparable. The range in the numbers of particles per cc. was from such small values that but little effect was produced, to such large ones that the experiments could not be carried further on account of the mud-like character of the suspensions. Upon filtering these suspensions the supercooling value returned to that of the original water.

The results of these experiments are summarized in the accompanying table. The number of particles in one cc. of the suspension used is indicated at the top of each column. At the left of each horizontal column is indicated the sample of the quartz powder used. The results given are the values for Θ , that is, the amount of supercooling observed, expressed

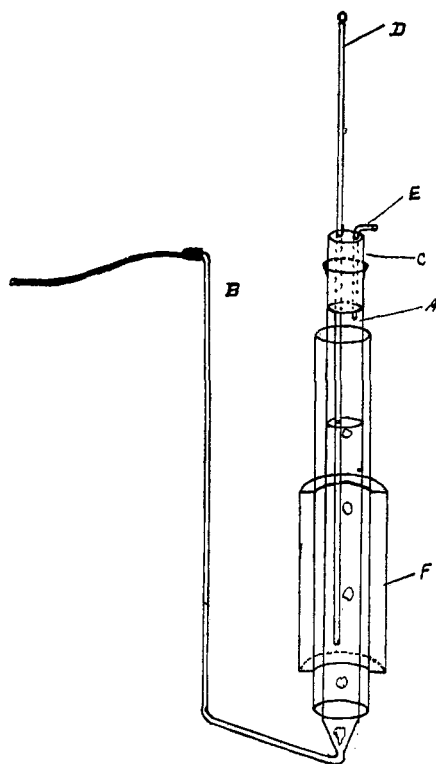


TABLE I.

	14,000,000.	4,480,000.	2,000,000.	500,000.	240,000.	80,00	40,000.	20,000.	15,000
No. 1.....	1.3	1.6	1.3
"	1.3	1.4	1.5
"	1.1	1.5	1.3
"	1.3	1.5	1.5
"	(1.2)	(1.5)	(1.4)
No. 2.....	2.0	2.7	3.2	2.6
"	2.2	2.1	3.3	2.7
"	2.1	1.8	2.6	3.2
"	2.2	2.0	2.9	3.5
"	(2.1)	(2.2)	(2.9)	(3.0)
No. 3.....	...	3.1	2.8	1.6	4.8	4.2	4.4	6.5	...
"	...	2.8	3.1	3.6	3.3	4.0	5.5	5.5	...
"	...	2.7	3.8	2.9	3.6	5.4	4.0	4.5	...
"	...	2.3	3.2	4.4	3.4	4.9	6.2	4.1	...
"	...	(2.7)	(3.2)	(3.0)	(3.8)	(4.6)	(5.0)	(5.2)	...
No. 4.....	2.7	...	3.9	3.0	4.5	3.4	6.3
"	3.3	...	4.5	4.7	5.3	6.4	6.0
"	3.2	...	3.5	3.6	5.5	6.3	3.4
"	2.8	...	4.0	5.7	5.2	5.7	5.4
"	(3.0)	...	(4.0)	(4.2)	(5.1)	(5.4)	(5.3)
	10,000.	5,000.	2,000.	1,000.	500.	100.	50.	25.	10.
No. 1.....	1.5	1.7	2.2	2.1	2.2	2.9	3.1	4.9	5.5
"	1.5	1.2	1.2	1.8	2.8	2.8	4.1	4.9	4.4
"	1.4	1.5	1.8	2.1	2.5	3.0	3.1	3.3	4.8
"	1.6	1.7	1.8	2.0	2.3	2.6	2.3	3.0	6.0
"	(1.5)	(1.5)	(1.7)	(2.0)	(2.4)	(2.8)	(3.2)	(4.0)	(5.2)
No. 2.....	3.9	4.4	4.6	3.7	5.7	4.6
"	4.1	3.6	4.3	5.1	5.5	5.0
"	3.4	4.5	4.7	5.7	5.3	5.0
"	3.2	4.2	4.2	5.6	3.5	5.3
"	(3.6) ¹	(4.2)	(4.5)	(5.0)	(5.0)	(5.0)
No. 3.....	5.6
"	5.2
"	3.8
"	6.8
"	(5.3)
No. 4.....
"
"
"
"

¹ Other series of determinations give 3.2 as the more probable average for this concentration.

in positive centigrade degrees. The numbers enclosed in brackets are averages. In many cases far greater numbers of observations than the four given were made. In such cases the first four results obtained have been given, with one or two exceptions, to be noted later.

Discussion of the Results.

At the beginning of this paper the assumption was made that the effect of foreign particles in stimulating crystallization in supercooled liquids was a purely kinetic one, that is, that crystallization was caused by impacts between the foreign particles. From what is already known concerning the effects of impacts between larger bodies, and on the basis of the theory of probabilities, certain predictions were made as to the phenomena which should occur when definite numbers of particles of various masses were moving through a supercooled liquid at definite rates. It will now be shown that the results recorded in the above table satisfactorily confirm these predictions.

1. *The Effect of the Mass of the Particles.*—By reference to the table it will be seen that observations were made upon all the different sizes of quartz powder at a concentration (meaning number of particles) of 40,000 per cc. These results show a distinct decrease in the average amount of supercooling as the mass of the particles increases, which is entirely in accord with the prediction. Without exception, the results in the vertical columns confirm this. The fact that the results do not show a direct proportion or other simple relationship to the mass of the particles is due to several causes. Firstly, there is as yet no established quantitative relationship between impact value and crystallization stimulus. It is known that the stimulus increases with the energy of the impact, but the quantitative law which regulates these factors is not known. Secondly, the particles used were not of perfectly uniform size and were of very irregular shapes. Thirdly, the effect of the viscosity of the liquid in restricting the freedom of motion of the particles is far greater with small than with large ones. This fact may be readily predicted from the usual theory of viscosity, and ample confirmation of it will be given later.

2. *The Effect of the Number of Particles.*—By reference to the horizontal columns of the table, especially those for the two coarser samples of quartz powder (Nos. 1 and 2), it will be seen that all the predictions that were made concerning the effect of the number of particles are confirmed. At low concentrations the results are very erratic, and the average amount of supercooling is large. As the concentrations of the particles increase the average supercooling becomes less, and at the same time the results become far more uniform. When a certain concentration is reached (about 2,000 per cc. for the No. 1 powder), further increase over a considerable range (up to 20,000 for the No. 1 powder) does not further affect the results. At a concentration of 40,000 per cc. the results are

somewhat lower. At this concentration the liquid began to show a distinct mud-like character, and it was found impossible to work at higher concentrations, since with the rate of stirring chosen, settling out of the particles could not be avoided.

With the No. 2 powder the same general phenomena are to be observed. The fact that the results do not become constant until a much higher concentration is reached is to be expected, because on account of the greater effect of viscosity in restricting the motions of the small particles through the liquid the probability of the occurrence of an impact in a given time will be less. It is however quite certain that the average of 3.6° obtained at a concentration of 10,000 per cc. with the No. 2 powder does not represent a true average. It will be observed that the first two results in this series are abnormally high. As has been stated, the results in the table are the first four obtained. As a matter of fact, ten observations were made at this point. Taking the average of these, the result is 3.2, which, if the latter result be accepted, gives a more striking confirmation of the prediction.

In experiments of this sort, where the factor of probability enters in so largely, it is of course to be expected that occasional, more or less persistent successions of abnormal results, either high or low, would be obtained, corresponding to succession of red or black in the turning of cards. In these present experiments, such successions are most likely to occur when the concentrations of the particles are small. In confirmation the following data are offered: With the No. 2 powder, at a concentration of 500 per cc., the first four results obtained give an average of 5.0 as shown in the table. Two other series of observations were made with the same sample under the same conditions. The first of these additional series contains twenty-five results, and the second six. The results are as follows:

Series 1.—6.4, 4.8, 4.4, 3.5, 3.2, 4.2, 4.8, 3.3, 3.2, 3.4, 3.2, 5.4, 5.1, 4.4, 4.0, 4.1, 4.2, 5.7, 4.0, 3.8, 3.5, 4.9, 3.2, 5.3, 5.3; average, 4.4.

Series 2.—6.3, 3.8, 4.3, 4.6, 5.1, 4.8; average, 4.8.

The average of the first four results of series 1 is 4.8, in close agreement with the result given in the table. Then begins a long and persistent series of low results, only occasionally interspersed with normal values. Series 2 was made with the same apparatus and the same sample, the only difference between the two series being that several hours had elapsed between the taking of the observations. Series 2 gives results in strict accord with the normal. Thus the large number of low results obtained in series 1 are to be looked upon as due to chance. Similar abnormalities were occasionally noted in the other series, but they were not common. With the single exception of the case above cited, the averages

obtained from long series of readings, would, if they had been used in the table, have confirmed the predictions even more strikingly than those given. In order to avoid any possible influence from the personal equation, however, the original intention of giving only the first four results obtained was followed.

With respect to the results with the two finer powders, it will be noted that they show the same general character as those obtained with the coarser ones, except that the range in concentration throughout which the effect is independent of the concentration is less well defined. This is probably to be explained as follows; on account of the great effect of viscosity on the smaller particles, very considerable concentrations will be required before this constant range will be reached. Thus the great number of particles present may lend to the liquid a considerable mud-like character before this constant range becomes well defined.

Thus it is seen that the experiments so far described confirm in all respects the predictions made at the outset concerning the effect of the size and number of particles upon the conduct of water in regard to its supercooling. The whole effect of the foreign particles is entirely explainable upon the assumption that their activity in stimulating crystallization is due to the occurrence of impacts between them, and that this activity is a direct function of the energy value of the impacts.

Further predictions were made concerning the effect which variations in the viscosity of the liquid would produce, provided such variations could be brought about without materially affecting the other physical properties of the liquid. A few simple experiments were carried out for the purpose of determining the validity of these predictions.

3. *The Effect of Variations in the Viscosity of the Liquid.*—These experiments were carried out as follows: First, the supercooling value was determined for a sample carrying a known number of quartz particles of a known size; a small known quantity of gelatin solution of known concentration was then added, which served to materially increase the viscosity of the liquid; finally its supercooling value was determined. The following table summarizes the results of a number of experiments of this character. In column 1 is indicated the sample of quartz powder used. In column 2 is given the number of particles of quartz per cc. Column 3 gives the concentration of the gelatin in the liquid. Column 4 contains the supercooling values for the water with the indicated number of quartz particles, but without the gelatin. In column 5 are given the supercooling values for the samples after the addition of the gelatin. All the supercooling values given are averages of a considerable number of determinations:

TABLE II.

Powder used.	Particles per cc.	Conc. of gelatin per cc.	Supercooling values.	
			Without gel.	With gel.
No. 1.....	1,500	0.10	1.8	2.4
No. 2.....	100	0.20	4.8	6.1
No. 3.....	40,000	0.05	4.5	5.6
No. 4.....	280,000	0.05	4.4	6.9
None.....	...	0.05	5.7	7.2

These results show very clearly the protective influence of the gelatin. The protection increases as the particles used decrease in size, in spite of the fact that the smaller particles are used in far greater concentrations, while at the same time the concentration of the gelatin is less. The protection in the case of the No. 2 powder is slightly greater than that within the No. 3, which is, however, to be ascribed to the fact that four times the concentration of gelatin was used.

The results obtained with water to which no particles were added show a smaller specific protection than that found for the No. 4 quartz powder. This is partly due to the fact that the distilled water is comparatively free from particles, whence less protection is possible, and partly to the fact that at such low temperatures the sensitiveness of the water to crystallization stimulus is very great. Thus a specific protection of one degree at these low temperatures is of much greater significance than the same protection at higher ones. It is to be noted that the protected value for water without particles is the lowest obtained.

Thus the predictions made at the outset seem to be confirmed without exception. These predictions were made upon the assumption that the crystallization stimulus is a purely kinetic phenomenon, and this assumption seems to be reasonably justified by the results of the preceding investigation. It is not, however, to be concluded that impact is the only form of mechanical stimulus possible. For example, it might be the case that a particle in rapid rotary motion would serve as a more effective stimulus in some cases than an impact of the same energy value. At the present time there is no evidence from which conclusions upon this point may be drawn. It is also possible that stimuli not mechanical in character may be discovered, although none seem to be known at present. Several attempts to induce crystallization under the influence of electrons have been made in this laboratory, but without success.

It may be not without interest to attempt to apply the above principle to the explanation of the conduct of supercooled liquids at rest with respect to their spontaneous crystallization. As is generally known such conduct is highly erratic. Under apparently identical conditions, identically prepared samples give the most diverse results. Of a number of samples some may crystallize in a few minutes, and others only after hours or even weeks. In the light of the foregoing investigation, such

results seem readily explainable. Most such investigations have been carried out with liquids not freed from foreign particles, and the fortuitous manner of their crystallization is readily explained. It has been repeatedly observed that the effect of long continued heating of a liquid is to increase its average supercooling value. This is explainable as due in the main to the disintegration and perhaps solution of some of the particles existing in the liquid.

Jaffé¹ has shown that the supercooling value may be much increased by filtration, which is, of course, to be looked upon as due to the removal of small particles. He has also noticed that in a liquid which remained at rest for a considerable time, crystallization was most likely to start from the bottom of the tube. This is, of course, due to the slow accumulation of particles at the bottom of the tube by settling.

It has been frequently observed that greater supercooling is possible in a small body of liquid than in a large one. Two factors probably contribute to produce this result: First, in a small body less convection currents, and consequently less agitation among suspended particles will occur; secondly, under otherwise like conditions the probability of the occurrence of an impact will be less in a small volume than in a large one, especially in the case of liquids in which particles are very sparsely distributed; this latter factor may be of great importance.

Tammann² has shown that the number of crystallin nuclei which appear in a supercooled liquid increases with the supercooling, reaches a maximum value at a temperature corresponding approximately to the temperature of the maximum crystallization velocity, and thereafter falls off. A little thought will show that the same factors which cause the maximum in the crystallization rate should also cause a maximum in the number of crystals which can start within the liquid. Assume a liquid charged with a considerable number of particles. As this becomes more and more supercooled, its sensitiveness to mechanical crystallization stimulus increases, and the number of effective impacts in a given time will increase. When the viscosity increases materially, it will tend to restrain the motions of the particles, and the probable number of effective impacts in a given time will decrease.

One other point only remains to be considered. The query naturally occurs as to what would be the conduct of a particle-free liquid at rest, and cooled in such a way that convection currents and other mechanical disturbances are avoided. Would crystallization ever occur in such a system? The answer must be that it is perfectly possible that such crystallization might occur. The mere instantaneous appearance within the liquid of a molecule possessed of a kinetic energy considerably above

¹ *Z. physik. Chem.*, 43, 565.

² *Ibid.*, 25, 441.

the average might produce sufficient disturbance to start crystallization when the liquid had reached an extremely sensitive condition. If, however, before reaching so sensitive a state, the viscosity of the liquid had reached a great value, the likelihood of such an occurrence would be correspondingly small. Tammann's investigations¹ showed that many liquids could be cooled to amorphous solids without great difficulty. The method is merely that of cooling very quickly, and its effectiveness depends upon the avoidance of the necessary mechanical stimuli to crystallization by not allowing them time to occur.

STANFORD UNIVERSITY, CAL.

RADIOACTIVITY.²

BY ANDRE DEBIERNE.³

Received July 1, 1911.

Radioactivity comprises to-day a very large number of facts and theories of which it would not be possible to give a complete survey in a brief address. Nevertheless, I shall make an effort to bring out all the chief points of interest of the new science, the birth of which may be considered without exaggeration as the most important scientific event of the past few years.

Not only has this new science revealed the existence of extremely curious substances and brought a rich harvest of new natural phenomena, but it has led us to the attack of a problem which seemed absolutely chimerical only a few years ago—the problem of the transmutation of atoms or of the chemical elements; for it is now demonstrated that the phenomena of radioactivity are concomitants of the disintegration of atoms. Radioactivity may now be defined as the science of atomic transformations; it is not impossible that in time radioactivity may become the art of changing chemical elements into one another. The facts known at present leave no doubt as to the reality of atomic disintegrations; if as yet these transformations are entirely beyond our control, possibly some day we may learn how to bring them about and to control them.

The fundamental phenomenon, which was discovered by Henri Becquerel and has served as the point of departure for the development of radioactivity, is as follows: Certain substances emit spontaneously a peculiar radiation whose properties are analogous to those of the rays obtained in a Crookes tube. The new rays render gases conductors of electricity, act on a photographic plate, and produce fluorescence in certain substances. This spontaneous emission of rays was first observed in the case of uranium and its compounds, later also in the case of thorium compounds. Then were discovered new substances possessing the same property in a very high degree. All these substances are said to be *radioactive*. They constitute a new source of energy.

An apparently essential characteristic of the phenomenon of radio-

¹ *Loc. cit.*

² A summary presented at the Second Decennial Celebration of Clark University, Worcester, Mass., September 17, 1909.

³ Translated from the French by M. A. Rosanoff.