[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN.]

# THE EFFECT OF DISSOLVED SUBSTANCES ON THE VELOCITY OF CRYSTALLIZATION OF WATER.

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The measurement of the speed of crystallization of undercooled water has been described in a previous communication.[1] The linear velocity of crystallization (hereafter designated as V. C.) was measured to —9°. It was shown that the internal diameter of the tube and the thickness of its walls are important factors in the rate of growth of the crystals.

Inasmuch as no investigation has been made on the influence of foreign substances on the V. C. of water, it was considered of interest and importance to determine the effect of various types of dissolved substances on the rate with which ice crystals are formed.

## Historical.

The general subject of the effect of foreign substances on the V. C. of undercooled liquids has already been the field of numerous investigations. One of the best known researches on this subject was carried out by von Pickardt,[2] who dissolved various organic compounds in fused benzophenone and determined their influence on the V. C. of this substance. He came to the following conclusions:

1. That all dissolved substances lower the V. C.
2. The decrease in the V. C. is proportional to the square root of the concentration of the dissolved substance.
3. In equimolecular concentrations of different substances the lowering of the V. C. is the same.

The conclusions of this investigation are questioned by Padoa and Galeati,[3] and also by Dreyer.[4] The former increased the number of dissolved substances used and found that out of thirty-two cases investigated, three agreed with von Pickardt's rule, twelve were in fairly good agreement, seven approximated it, and ten showed no relation whatever. The investigations of Dreyer with undercooled formanilide showed similar disagreements between the V. C., and the molecular weight of the solutes used. Dreyer found that when ethyl or methyl alcohol was used each actually *increased* the V. C. of the formanilide. The influence of the solute upon the V. C. of undercooled liquids, therefore, is specific.

Tammann[5] has carried out experiments showing the relation between the temperature and the V. C. of various undercooled liquids. The

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[1] *J. Phys. Chem.*, 18, 722 (1914).

[2] *Z. physik. Chem.*, 42, 17 (1902).

[3] *Gazz. chim. ital.*, 35, I, 181 (1904).

[4] *Z. physik. Chem.*, 48, 467 (1904).

[5] "Kristallisieren und Schmelzen," 1907, p. 131.

speed of crystallization at first increases with increased undercooling (Zone A); it then generally remains constant for several degrees (Zone B) and finally decreases (Zone C). For benzophenone Zone A extends from 48°, the melting point of this substance, to 25°. The maximum V. C., Zone B, takes place from 25° to about —20°. It is obvious that in this region the V. C. is independent of the temperature. Below —20° the V. C. decreases with the fall in temperature. The experiments of von Pickardt and of Padoa and Galeati were carried out in in the zone of the maximum V. C.

The V. C. from supersaturated solutions has been the subject of exhaustive investigations by Marc,[1] who completely eliminated the velocity of diffusion in his experiments, and measured the true speed of crystallization from aqueous solutions. The V. C. was decreased by the presence of many dissolved substances, dyes, for examples, being particularly operative in this respect. Marc came to the conclusion that the inhibition of the crystallization is an adsorption effect, being due in this particular case to adsorption of the dye on the surface of the crystal. The adsorption is supposed to affect the V. C. as follows: The substance that is being separated from the supersaturated solution is adsorbed at the surface of the crystal, consequently at that point there is a greater supersaturation than in the other parts of the solution. The concentration of this adsorbed layer determines the V. C. If other substances capable of being adsorbed are present in the solution, the concentration of the crystallizing substance in the surface layer is thereby decreased, and consequently the V. C. is retarded.

Freundlich[2] believes that the V. C. of undercooled liquids can also be explained by adsorption phenomena. A study of the experiments of von Pickardt and Padoa and Galeati led him to the following conclusions:

1. The decrease of the maximum V. C. of undercooled liquids by foreign substances, present in not too great concentration, may be expressed by the equation

$$G_0 - G = kc^{1/n}.$$

In this equation $G_0$ = V. C. of pure fusion; G = V. C. of impure fusion; $c$ = concentration of the dissolved substance; $k$ and $1/n$ are constants, the value of $1/n$ lying between 0.2 and 0.7.

2. The equation may be explained by the assumption that the dissolved substance is adsorbed on the surface of the crystal and this results in decreasing the V. C. in proportion to the amount adsorbed.

The formula used by Freundlich is the well-known adsorption formula, and is the same as that used by von Pickardt. The latter assumed the

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[1] *Z. physik. Chem.*, 61, 385 (1908); **67**, 470 (1909); **68**, 104 (1909); **73**, 685 (1910); **75**, 710 (1910).

[2] *Ibid.*, **75**, 245 (1910).

value of $^1/n$ to be 0.5, but this assumption is not borne out by experiment. Its value is variable, depending on the specific nature of the substance in the fusion. Freundlich states that, while the V. C. depends upon adsorption of the dissolved impurity, there are doubtless other factors that influence it in a large degree.

## Experimental.

**Method.**—The method used in these experiments was to introduce into a constant low temperature bath,[1] an L-shaped tube that contained the solution to be undercooled. The dimensions of the tubes were practically the same as those used in the determination of the V. C. of undercooled water, the outside diameter being about 12 mm., and the bore about 7 mm. After the tube had arrived at the temperature of its surroundings, which took 3–4 minutes, it was inoculated, and the time necessary for the crystal growth to progress a distance of one meter in the tube was measured by a stop watch.

In preparing the solutions the purest chemicals obtainable were employed. In several cases these were recrystallized, but this was found to be unnecessary, as the error caused by any trace of impurity in these substances was found to be well within the error of the experiments. In the preparation of the solutions, conductivity water was used. Whenever possible, the solutions were boiled to remove any dissolved gases. The surface of the liquid was then covered with a half-inch layer of paraffin oil, and the tube kept in ice water until ready to be placed in the low temperature bath.

TABLE I.

Showing the agreement of duplicate measurements of the velocity of crystallization of typical undercooled aqueous solutions. Temperature —9.1°.

| Solution. | Tube. | Time in seconds per meter. | | |
|---|---|---|---|---|
| Cane sugar | 10 | 69.9 | 69.9 | 71 |
| Cane sugar | 12 | 71 | 68.0 | 70 |
| Cane sugar | 6 | 75.4 | 75.1 | 75.2 |
| Urea | 10 | 20.0 | 20.5 | 20.3 |
| Urea | 12 | 18.4 | 19.1 | 18.3 |
| Succinic acid | 10 | 31.4 | 33.5 | .. |
| Succinic acid | 1 | 36.8 | 37.0 | 35.4 |
| Cupric chloride | 10 | 40 | 40.0 | .. |
| Cupric chloride | 14 | .. | 39.5 | .. |
| Dextrose | 14 | 87.8 | 86.4 | .. |
| Dextrose | 1 | 78.4 | 77.0 | .. |
| Mannose | 14 | 85 | 83.4 | .. |
| Mannose | 4 | 86.5 | 85.2 | .. |
| Sodium sulfate | 14 | 29.6 | 29.3 | 29.0 |
| Sodium hydroxide | 14 | 22.6 | 21.8 | .. |
| Sodium hydroxide | 12 | .. | 22.4 | .. |

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[1] *J. Phys. Chem.*, **18**, 717 (1914).

The velocity of crystallization was determined several times with the same tubes. After one determination had been made the ice was melted by placing the tube in a bath heated to about 60° and allowing it to remain there for ten or fifteen minutes. By heating the tube to this temperature there seems to be less of a tendency for the solution to crystallize spontaneously. As will be shown later, however, the occurrence of spontaneous crystallization seems to depend largely on the nature of the substance in solution.

TABLE II.

The linear velocity of crystallization of 0.1 *M* undercooled aqueous solutions. Temperature —9.1°.

| Compound. | Formula. | Mol. wt. of anhydrous substance. | No. atoms in mol. of anhydrous substance. | Time per meter. Seconds. | Velocity cm. per min. |
|---|---|---|---|---|---|
| Pure water | $H_2O$ | 18.0 | .. | 16.3 | 368 |
| Lithium chloride[1] | $LiCl$ | 42.5 | 2 | 35.3 | 170 |
| Potassium iodide | $KI$ | 166.0 | 2 | 26.1 | 230 |
| Sodium chloride | $NaCl$ | 58.5 | 2 | 24.3 | 247 |
| Hydrochloric acid[2] | $HCl$ | 36.5 | 2 | 24.0 | 250 |
| Cupric chloride | $CuCl_2$ | 134.6 | 3 | 40.0 | 150 |
| Mercuric chloride | $HgCl_2$ | 271.6 | 3 | 27.7 | 217 |
| Calcium chloride | $CaCl_2$ | 111.7 | 3 | 38.6 | 155 |
| Sodium hydroxide | $NaOH$ | 40.0 | 3 | 21.9 | 274 |
| Ferric chloride | $FeCl_3$ | 162.5 | 4 | 84.8 | 70.8 |
| Hydrogen peroxide | $H_2O_2$ | 34.0 | 4 | 24.1 | 248 |
| Potassium chlorate | $KClO_3$ | 122.6 | 5 | 26.2 | 229 |
| Mercuric cyanide | $Hg(CN)_2$ | 252.0 | 5 | 23.4 | 256 |
| Silver nitrate | $AgNO_3$ | 169.8 | 5 | 22.5 | 267 |
| Sodium carbonate | $Na_2CO_3$ | 106.0 | 6 | 33.3 | 180 |
| Sulfuric acid[1] | $H_2SO_4$ | 98.0 | 7 | 28.7 | 209 |
| Potassium sulfate | $K_2SO_4$ | 174.0 | 7 | 23.4 | 256 |
| Sodium sulfate | $Na_2SO_4$ | 142.0 | 7 | 29.2 | 205 |
| Urea | $CO(NH_2)_2$ | 60.0 | 8 | 19.1 | 314 |
| Ethyl alcohol | $C_2H_5OH$ | 46.0 | 9 | 34.0 | 177 |
| Potassium dichromate | $K_2Cr_2O_7$ | 294.2 | 11 | 31.1 | 194 |
| Succinic acid[2] | $C_4H_6O_4$ | 118.0 | 14 | 35.3 | 170 |
| Glycerol[1] | $C_3H_8O_3$ | 92.0 | 14 | 33.6 | 176 |
| Tartaric acid | $C_4H_6O_6$ | 150.0 | 16 | 43.4 | 138 |
| Mannose[3] | $C_6H_{12}O_6$ | 180.0 | 24 | 83.6 | 71.8 |
| Dextrose[3] | $C_6H_{12}O_6$ | 180.0 | 24 | 82.3 | 72.9 |
| Fructose | $C_6H_{12}O_6$ | 180.0 | 24 | 86.5 | 78.4 |
| Antipyrine | $C_{11}H_{12}N_2O$ | 188.0 | 26 | 53.7 | 112 |
| Cane sugar[1] | $C_{12}H_{22}O_{11}$ | 342.0 | 45 | 152.0 | 39.5 |
| Lactose[3] | $C_{12}H_{22}O_{11}$ | 342.0 | 45 | 178.8 | 33.6 |
| Raffinose | $C_{18}H_{32}O_6$ | 344.0 | 56 | 215.5 | 27.8 |

[1] Shows great tendency to crystallize spontaneously.

[2] Little tendency to crystallize spontaneously.

[3] Appearance of crystals different from those separating from undercooled water.

**The Velocity of Crystallization of 0.1 *M* and 0.02 *M* Solutions.**—In the first series of experiments 0.1 *M* solutions of typical salts, alkalies, acids, and a number of organic compounds were used. The substances used and the results obtained are given in Table II. A number of other compounds were used, among which were copper nitrate, magnesium sulfate, castile soap, gelatin, gum arabic, and egg albumin, but no results were obtained because the solutions always crystallized spontaneously. The results contained in Table II are the average of three or more determinations.

Table I gives results obtained from repeated measurements with solutions using the same tube. The agreement of different tubes containing the same solution is also given.

Because of spontaneous crystallization many of the results in Table II were obtained only after repeated trials. Cane sugar shows this tendency to a marked degree. Hydrochloric acid solutions on the other hand proved to be very stable and were kept at —9°, in one case, for half an hour. With a few exceptions the appearance of the crystals formed was the same with the solution as with pure water.

A series of experiments was carried out in which the substances used have a very high molecular weight. Inasmuch as many of the compounds are not sufficiently soluble to permit the preparation of 0.1 *M* solutions, the concentration used was 0.02 *M*. The results of these experiments are incorporated in Table III.

TABLE III.

The linear velocity of crystallization of 0.02 *M* undercooled aqueous solutions. Temperature —9.1°.

| Compound. | Formula. | Mol. wt. of anhyd. subs. | No. atoms in mol. of anhyd. subs. | Time per meter in seconds. | Velocity. |
|---|---|---|---|---|---|
| Hydrochloric acid....... | $HCl$ | 36.5 | 2 | 15.8 | 380 |
| Succinic acid............ | $C_4H_6O_4$ | 118.0 | 14 | 19.7 | 305 |
| Tannic acid............. | $C_{14}H_{10}O_9$ | 322.0 | 33 | 18.3 | 327 |
| Cocaine hydrochloride... | $C_{17}H_{21}NO_4.HCl$ | 339.5 | 45 | 28.0 | 214 |
| Lactose................ | $C_{12}H_{22}O_{11}$ | 342.0 | 45 | 26.3 | 228 |
| Quinine hydrochloride... | $C_{20}H_{24}N_2O_2.2HCl$ | 397.0 | 52 | 31.5 | 190 |
| Quinirie bisulfate........ | $(C_{20}H_{24}N_2O_2).H_2SO_4$ | 422.0 | 55 | 33.5 | 180 |
| Raffinose............... | $C_{18}H_{32}O_6$ | 344.0 | 56 | 29.0 | 207 |
| Brucine sulfate.......... | $(C_{23}H_{26}N_2O_4)_2.H_2SO_4$ | 886.0 | 115 | 53.0 | 118 |

The experiments of von Pickardt, Dreyer and Freundlich, to which reference has been made, were carried out in the zone of maximum V. C. This could not be done in the experiments described in this paper, for spontaneous crystallization made it impossible to determine the rate of crystallization in Zone B, which should be about twenty degrees below the freezing point. The lowest temperature obtainable was about 9° below the melting point of ice. Measurements carried out in this zone cannot, therefore, be considered as the true velocity of crystallization. They are of value, however, in showing the relative effects of equimolecular solutions of different types of compounds. Since the V. C. in the temperature zone in which these measurements were made increases with the degree of undercooling, the lowering of the freezing point by the addition of the solute would have an appreciable influence upon the retardation of the V. C. For it is plain that a 0.1 *M* solution at —9° is not undercooled as much as the pure solvent at this temperature, a normal solution of hydrochloric acid, for example, would be undercooled but 5°.[1] This would result in a great difference in the V. C. of the acid and pure water. To eliminate the effects of different amounts of undercooling equimolecular solutions were used in these experiments. A 0.1 *M* solution of a strongly dissociated substance, such as hydrochloric acid, however, has a lower freezing point than a 0.1 *M* solution of a nondissociated substance like cane sugar. At —9° these two solutions are not equally undercooled. An examination of Fig. 1, and Table VI, which give the

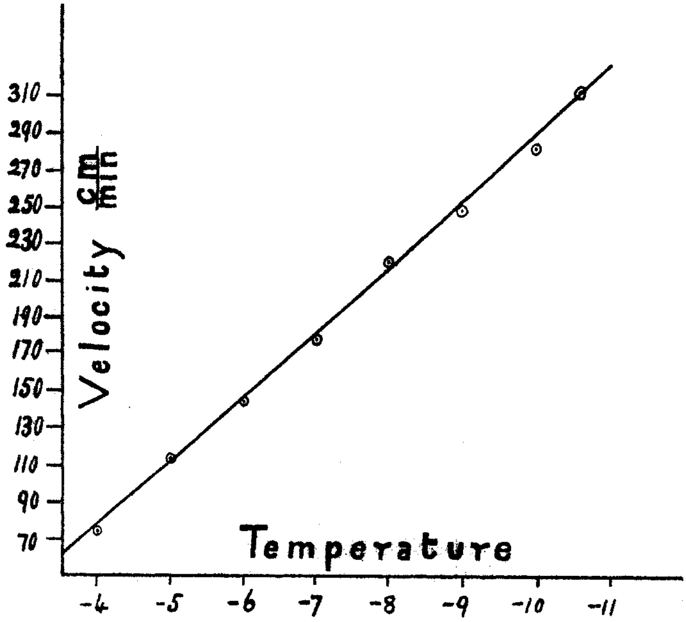

Fig. 1.

changes in velocity in 0.1 *M* solutions of hydrochloric acid for changes of temperature, shows that at —9° the velocity of crystallization is 246, while at —10° it is about 280 cm. per minute. The error caused by this difference in the amount of undercooling would, therefore, be negligible.

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[1] Richards and Jackson, *Z. physik. Chem.*, **56**, 362 (1906).

**Discussion of Results.**—The results obtained with 0.1 *M* solutions as given in Table II show that there is no relation between the molecular weight of a compound and its retardation of the V. C. of the water. Mercuric chloride with a molecular weight of 271.6 has about the same retarding effect as sulfuric acid (mol. wt. 98). Ferric chloride and potassium iodide have approximately the same molecular weights,,yet the velocity of crystallization with the former is 70.7; with the iodide it is 230 cm. per minute. A similar difference is seen in the case of potassium sulfate and glucose. The most striking relation, however, is that which exists between the number of atoms in the compound and the velocity of crystallization of the solution. The results in Table II are arranged with reference to the increase of numbers of atoms in the molecule. An examination of the compounds with more than eight atoms in the molecule shows that the number of atoms is one of the factors that determines the retarding effect of that compound on the V. C. The relation is only an approximate one, to be sure, but that such a relation does exist is evident in the case of compounds with more than eight atoms to the molecule. In the case of simpler inorganic compounds there are many exceptions. Lithium chloride and ethyl alcohol, for example, have the same V. C., although the former has two atoms, the latter nine. For compounds below ethyl alcohol the increase of the inhibiting effect with the increase in number of atoms in the compound, is fairly regular. The fact that ethyl alcohol was found by Dreyer to accelerate the V. C. of formanilide, while here it retards the formation of crystals, is worthy of note.

The results given in Table III show the effect of 0.02 *M* solutions at —9°. The same relation between the increase in the number of atoms in the molecule and the retarding of the V. C. can also be seen from these experiments.

The explanation of the inhibitive action of these compounds cannot be due primarily to adsorption, as claimed by Freundlich in the retardation of the crystallization of benzophenone by impurities.

Freundlich points out that compounds that have a large number of atoms retard the crystallization of benzophenone to a marked degree. Isobidesyl, $C_{20}H_{22}O_2$, and lepiden, $C_{28}H_{20}O$, showed a very great retarding effect not only with benzophenone but also with diphenylamine and α-naphthylamine. This is considered by Freundlich to be due to the fact that these compounds are very strongly adsorbed. He makes the following statement:

> "Allerdings sind die Abweichungen bei der Beeinflussung der Kristallisationgeschwindigkeit durch gelöste Stoffe schon häufig und gross genug. Es entspricht durchaus dem, was sonst von der Adsorption bekannt ist, dass gerade die hochmolekularen Stoffe, wie Lepiden und Isobidesyl, die Kristallisationsgeschwindigkeit besonders stark herabsetzen, also stark adsorbiert werden."

That the greater adsorption of the high molecular compounds cannot in the present investigation be the explanation of the retarding effect is shown in Table II by the V. C. of the undercooled solutions, containing the sugars. These substances retard the V. C. but they are not greatly adsorbed.

> "Die Halogene gehören zu den stark adsorbierbaren, Rohrzucker (und voraussichtlich alle stark hydroxylhaltigen Stoffe) zu den Schwach adsorbierbaren Stoffe."[1]

Succinic acid, moreover, has a greater V. C. (170) than tartaric (138.3) which has two hydroxyl groups in the molecule. The alkaloids, however, have a marked retarding effect on the V. C. and they are also known to be strongly adsorbed. They are the only strong retarders that show this relation.

While there is no regularity in the behavior of the compounds with less than eight atoms to the molecule, from the knowledge of adsorption that we possess it is evident that in this case also the phenomenon of adsorption plays a negligible role. Concerning the extent to which certain inorganic salts are adsorbed Freundlich[2] makes the following statement:

> "Nach unveröffentlichten Versuchen von Morawitz, adsorbiert Blutkohle die anorganischen Salze der Alkali und Erdalkalimetalle so wenig, dass es besonderer analytischer Hilfsmittel bedürfen würde um unzweideutig Sinn und Grösse der adsorbierten Menge festzustellen. Dagegen werden die Salze der Schwermetalle ($CuSO_4$, $AgNO_3$, $HgCl_2$) ganz merkbar positiv adsorbiert."

When the V. C. of salts of alkalies and alkaline earths are compared with the V. C. of salts of the heavy metals it is seen that adsorption plays an insignificant role.

(1) V. C. of $CaCl_2$....... 155; NaCl, 247.
(2) V. C. of $CuCl_2$....... 150; $HgCl_2$, 218; $AgNO_3$, 267.

In the light of the foregoing statement by Freundlich the salts under (2) are adsorbed much more than those under (1) and as a consequence should retard the V. C. much more. A comparison of calcium chloride with the chlorides of copper and mercury, and of sodium chloride with silver nitrate shows that this is not the case.

While the decrease in the velocity of crystallization of water cannot be explained by the assumption that the dissolved substances are adsorbed in different amounts at the crystal surfaces, on the other hand the data which have been obtained in these experiments do not permit any explanation of this phenomenon. The similarity between the velocity of formation of crystals and some of the well-known reactions in chemical kinetics, however, is very suggestive.

O. Lehmann[3] has pointed out that an undercooled liquid is by no means a collection of similar molecules, but is composed of different molecular

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[1] Freundlich, "Kapillarchemie," 1909, p. 160.

[2] "Kapillarchemie," 1909, p. 166.

[3] "Molekularphysik," 1888, I, p. 683 (Erstarren und Schmelzen).

aggregates in a state of equilibrium. Only one type of these molecular aggregates, $M_c$, is capable of crystallizing, and this is in equilibrium with the other molecules in the fusion $M_f$. The state of equilibrium would then be expressed by the equation

$$M_c \rightleftarrows M_f.$$

That water in the neighborhood of its freezing point consists of such molecular aggregates is a generally accepted fact. Sutherland[1] believes liquid water to be a mixture of dihydrol $(H_2O)_2$, and trihydrol $(H_2O)_3$, the latter compound at 0° being present to the extent of 37.5%. The formation of ice crystals may consequently be considered as an increase in the more complex molecular aggregates and may be represented by an equation similar to the following:

$$3(H_2O)_2 \rightleftarrows 2(H_2O)_3$$

That the presence of foreign substances should influence the rate at which the above change takes place is a reasonable assumption.

Smith[2] and his co-workers have shown that at the melting point of monoclinic sulfur a similar case of equilibrium exists. The liquid contains two molecular aggregates, $S_\mu$, $(S_6)$ and the monoclinic sulfur $S_\lambda$, $(S_8)$. The rate at which equilibrium between these two forms is attained is accelerated by certain reagents; by others it is retarded. Ammonia acts as an accelerator, sulfur dioxide as a retarder.

That the effect of the dissolved substances on the speed of the reaction between di- and trihydrol should be specific, is not surprising; it is, in fact, to be expected. Just why all these compounds retard the V. C., instead of accelerating the reaction, is a fact that is difficult to explain. It is of interest in this connection to point out that among the simpler compounds, those that show an unusual retarding effect belong for the greater part to one type, *viz.*, those that either crystallize with water of crystallization or are very deliquescent. There are one or two exceptions to be sure, but lithium chloride, copper chloride, calcium chloride, sodium carbonate and especially ferric chloride show an inhibiting action that is abnormal. The attraction that these substances have for water may have a relation to the unusual retarding effect[3] that they have upon the rate at which the molecules undergo rearrangement. The reason why the molecules with a large number of atoms show such an unusual retarding effect is difficult to explain. Certain it is this cannot be due to the fact that they are adsorbed to a greater extent than the simpler compounds.

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[1] *Phil. Mag.*, [16] **50**, 460 (1900).

[2] THIS JOURNAL, **27**, 797 (1905); **29**, 499 (1907).

[3] An article by Jones and one of his co-workers, published in a recent number of THIS JOURNAL, **38**, 105 (1916), is of interest in this connection. These investigators showed that "Salts with water of crystallization increase the velocity of the saponifica-

**Change of Crystal Habit.**—It has long been known that the speed of crystallization is often retarded by substances that change the crystal habit. A possible explanation of the inhibiting effect of various solutes may lie in the fact that these substances change the kind of ice crystals, and consequently the speed at which they are separated from the solution. Mention has already been made of the fact that the crystals liberated from solution of hydrochloric acid and certain of the sugar solutions were different in appearance from the crystals formed with pure water, although with most of the solutions used, the appearance of the crystals was the same as those obtained with water. Hartmann[1] found that four kinds of crystals were separated from undercooled solutions of the following compounds: cane sugar; $MnSO_4$; $HC_2H_3O_2$; $NaOH$; $C_3H_5(OH)_3$; $HCl$; $FeCl_3$. These crystals were formed, however, in strongly undercooled solutions which contained from 8 to 25% of the solute. In solutions of greater dilution ordinary ice crystals were always obtained no matter how much the solution was undercooled. These crystals are described by Hartmann as follows:

*a.* A mixture of right-angled and six-sided crystal skeletons. The six-sided plates are very similar to the ordinary snow stars with six rays. In the right-angled plates the individual crystal needles cut each other at an angle of 60°.

*b.* Opaque spherulites, in which no radial structure could be observed because of the opacity.

*c.* Opaque, spherical structure, built of opaque plates.

*d.* Ice "feathers."

A series of experiments were carried out by Hartmann in which undercooled water was inoculated with ice crystals of form *a*, and the linear V. C. for the formation of crystals of this form determined. The results obtained were within the error of experiment the same as those obtained for the V. C. of ordinary ice crystals (form *d*). These experiments show, that even if the crystals that separated from the undercooled aqueous solutions are different from those formed in pure undercooled water, the V. C. is the same, consequently the retardation is not to be explained by the change in the form of the crystals.

**Retarding Effect of Certain Colloids and Dissolved Gases.**—Mention

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tion of an ester to a greater extent than salts with no water of crystallization." It is believed that the great effect of these salts is due to the fact that they are hydrated in solution. The assumption that the inorganic salts with water of crystallization form hydrates in solution would explain the abnormal behavior of $FeCl_3$, $CuCl_2$, $CaCl_2$, etc., in this investigation. The formation of a hydrate would mean the existence of a molecular aggregate with a larger number of atoms. Since the retarding effect increases with the number of atoms in the molecule, the slowing down of the V. C. would be greater than would be expected from the formula of the anhydrous substance.

[1] *Z. anorg. Chem.*, **88**, 128 (1914).

has already been made of the fact that it was impossible to determine the V. C. of gelatin and sodium oleate solutions at —9° because of spontaneous crystallization. The behavior of solutions containing these two substances was, however, much different from that of the majority of solutions that crystallize spontaneously. In the case of water or magnesium sulfate the crystals suddenly appear at one point in the tube and grow until the tube is filled. With the gelatin and the soap solution from five to seven nuclei develop at different parts of the tube at the same instant. Whether these substances have the power of increasing the number of crystallizing centers or merely develop latent centers, is a question that can be answered only by further experiment.[1] Experiments were also carried out with gelatin at —7.1°, at which temperature the tendency to crystallize spontaneously was not observed. The results obtained are given in Table IV. The retardation is doubtless due in part to such factors as the increase in the viscosity, also the change in thermal conductivity.

TABLE IV.

The velocity of crystallization of undercooled gelatin solutions. Temperature —7.1°.

| Concentration. | Time per meter. Seconds. | Velocity cm. per minute. |
|---|---|---|
| Water | 32.2 | 186 |
| 15.00 g. per liter | 94.7 | 63.3 |
| 7.50 g. per liter | 48.6 | 123 |
| 3.75 g. per liter | 43.2 | 139 |

The retardations of the V. C. by several other substances are given in Table V. Concentrated solutions of the dyes could not be used because the depth of color made it impossible to follow the progress of the crystallizing surface. The concentration of the dyes used was so low that little can be learned concerning their effects. In general, they stabilize the undercooled solution greatly, spontaneous crystallization occurring much less frequently than with the substances in Table II. Of particular

TABLE V.

The influence of miscellaneous substances on the velocity of crystallization of water. Temperature —9.1°.

| Compound. | Concentration. | Time per meter in seconds. | Velocity cm. per minute. |
|---|---|---|---|
| Wasser blau | 1 g. in 5 l. | 13.6 | 441 |
| Safranin | 1 g. in 0.5 l. | 16.8 | 357 |
| Malachite green | 1 g. in 2.0 l. | 17.4 | 345 |
| Säure violet | 1 g. in 2.5 l. | 15.1 | 397 |
| Methylene blue | 1 g. in 5.0 l. | 19.7 | 304 |
| Rosaniline | Satd. soln. at room temp. | 18.0 | 333 |
| Carbon dioxide | Satd. soln. | 17.2 | 348 |
| Oxygen | Satd. soln. | 18.6 | 323 |
| Ferric hydroxide colloidal soln. | Concentrated | 34.1 | 176 |

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[1] "Kristallisieren und Schmelzen," p. 148.

interest is the fact that the solutions containing dissolved carbon dioxide and oxygen could be readily undercooled and were fairly stable towards spontaneous crystallization. This seems to disprove the often repeated statement that gas-free water is absolutely necessary to successful undercooling.

Further experiments were carried out in which there was measured (1) the V. C. of 0.1 *M* hydrochloric acid solutions from —4° to —10°, (2) the V. C. of undercooled solutions of hydrochloric acid of different concentrations. The results are given in Tables VI and VII and are shown graphically in Figs. 1 and 2. Table VIII (Fig. 3), gives the results obtained with solutions of brucine sulfate of various concentrations at —9.1°.

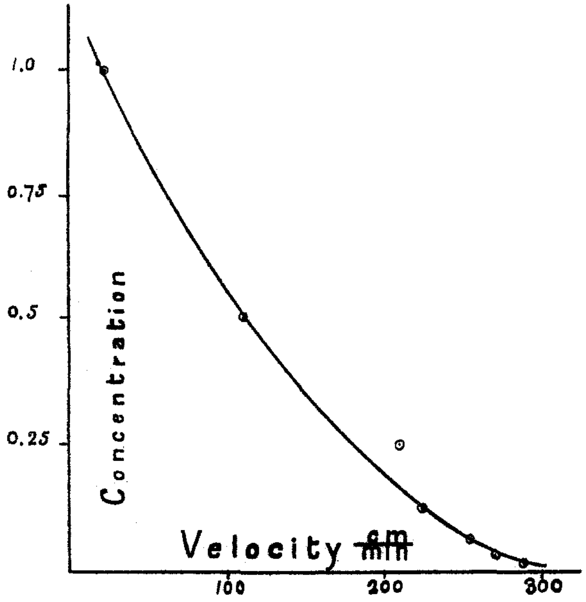

Fig. 2.

TABLE VI.

The velocity of crystallization of undercooled aqueous solutions of 0.1 *M* hydrochloric acid at various temperatures.

| Temperature | —4.1° | —5.1° | —6.1° | —7.1° | —8.1° | —9.1° | —10.1° | —10.7° |
|---|---|---|---|---|---|---|---|---|
| Velocity cm. per minute | 75.0 | 113.0 | 144.0 | 178.0 | 223.0 | 249.0 | 280.0 | 309.0 |

TABLE VII.

The velocity of crystallization of undercooled aqueous solutions of hydrochloric acid of various concentrations. Temperature —9.1°.

| Concentration gram mols per liter | 1.0 | 0.5 | 0.25 | 0.125 | 0.0625 | 0.03125 | 0.01563 |
|---|---|---|---|---|---|---|---|
| Velocity cm. per min. | 21.3 | 109.0 | 211.0 | 226.0 | 258.0 | 271.0 | 291.0 |

TABLE VIII.

The velocity of crystallization of undercooled aqueous solutions of brucine sulfate of various concentrations. Temperature —9.1°.

| Concentration gram mols per liter | 0.02 | 0.01 | 0.005 | 0.0025 | 0.00125 | 0.000625 |
|---|---|---|---|---|---|---|
| Velocity cm. per minute | 114.0 | 154.0 | 236.0 | 309.0 | 365.0 | 365.0 |

In this series of experiments it was found that although brucine sulfate when present to the extent of 0.00125 and 0.000625 gram mol per liter had no effect on the V. C. of the solvent; it did have a remarkable effect in preventing spontaneous crystallization, for solutions of this concentration can be easily undercooled and are much more stable than pure water.

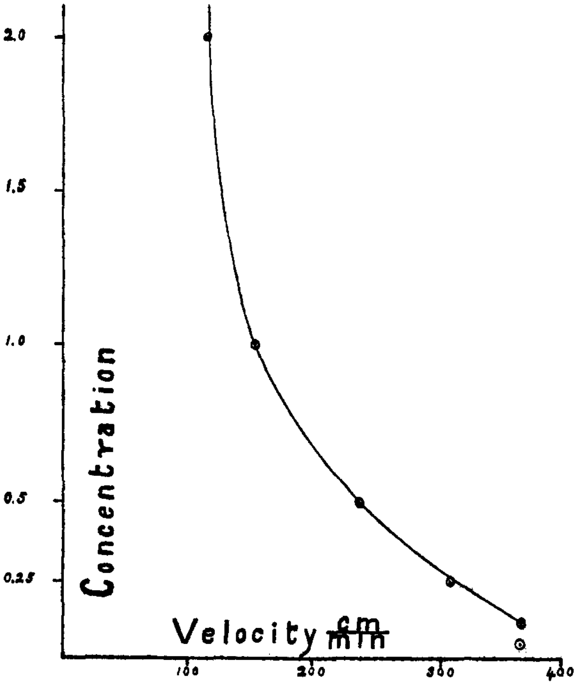

Fig. 3.

## Summary.

The results of this investigation may be briefly summarized as follows:

1. The velocity of crystallization of ice from aqueous solutions of 45 substances has been determined at —9.1°. The dissolved substances all retard the velocity of crystallization. In no case has an acceleration been observed.

2. Solutions of equimolecular concentrations show different retarding effects. The retardation is not, therefore, a colligative property.

3. For substances with more than 8 atoms in the molecule there is a rough relation between the number of atoms in the molecule and the inhibition of the velocity of crystallization; the greater the number of atoms, the lower the rate. For compounds with less than 8 atoms, the power of retardation seems to be a specific property.

4. That these effects cannot be explained by Marc's adsorption theory of the inhibition of crystallization is evidenced by the fact that the sugars, which are not greatly adsorbed, are very active in retarding the rate of crystallization. Certain inorganic salts also show no relation between the extent to which they are adsorbed, and their retardation of the formation of ice crystals.

5. Substances in the colloidal state such as gelatin, ferric hydroxide and certain dyes retard the velocity of crystallization.

6. The stability of the undercooled solutions towards spontaneous crystallization varies with the solute. 0.1 *M* solutions of hydrochloric acid are exceptionally stable.

Dilute solutions of certain dyes are also unusually stable. Solutions of brucine sulfate with a concentration less than 0.00125 gram mol per liter do not affect the velocity of crystallization. These solutions, however, are much more stable toward spontaneous crystallization than pure water at the same temperature.

MADISON, WISCONSIN.

# DIFFERENTIAL IODIMETRY.

## I—DETERMINATION OF PERIODATES, IODATES, BROMATES AND CHLORATES IN THE PRESENCE OE EACH OTHER.*

BY O. L. BARNEBEY.

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Considerable work has been done by various investigators[1-25] who have studied the rates of reaction between oxidizing agents of the type of the oxidized halogen compounds and potassium iodide. The larger portion of the previous work has been from a physico-chemical viewpoint, performed in an endeavor to establish the order of these reactions. This study has for its purpose the investigation of such reactions to ascertain the conditions under which they are applicable to analytical chemistry.

When potassium iodide is added to oxidizing agents in acid solution, free iodine is liberated more or less completely, the quantity of oxidizing agent transposed depending upon the concentrations of the substances involved, the temperature, and to a certain extent the pressure. The greater the concentration of iodide the more rapid the reaction. The greater the dissociation of the acid as well as the larger the amount of acid involved the faster the liberation of iodine occurs. This principle has been utilized for the purpose of determining the strength of acids[26-36], a mixture of iodide and iodate having been utilized for the purpose.

The utilization of such reactions for direct quantitative purposes has been studied to a comparatively limited extent. Certain reactions, like those between cupric salts, ferric salts, permanganate, dichromate, and the halogenates and an iodide, have been shown to be quantitative for the individual reactions, and they form the basis of laboratory determinations in common use. Moser[44] converted iron into a complex by the use of pyrophosphoric acid and titrated copper in the presence of iron. Edgar[45] reduced chromic and vanadic acids with hydrobromic acid, distilling into potassium iodide, then reduced the vanadium and iron with hydriodic acid, again distilling. In each case the iodine was titrated with thiosulfate. An arsenite method was used for the determination of chromic acid. By combining the schemes, chromic acid, vanadic acid and ferric iron were determined. However, no systematic study has

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* Presented at the Seattle meeting of the American Chemical Society, August 30th to September 4th.