Vol. XXVI. [November, 1904.] No. 11.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

A STUDY OF THE SUPERCOOLED FUSIONS AND SOLUTIONS OF SODIUM THIOSULPHATE.

By S. W. Young and J. P. Mitchell.

Received July 25, 1904.

The general phenomena of supercooling and supersaturation, as well as of metastability in general, have been so thoroughly described and discussed in Ostwald's "Lehrbuch der Allgemeinen Chemie"[1] that it is wholly unnecessary to go into any general treatment here. Since the appearance of the last volume of the Lehrbuch, two papers having an important bearing on the subject have appeared.[2] The relationship of the results of previous investigation to our results will be taken up in a later portion of this paper. The investigations described in the following pages were carried out with the hope of throwing light on some of the many conditions that influence the separation of sodium thiosulphate from its metastable solutions and fusions. In the course of the work the fact was developed that sodium thiosulphate was capable of existing in a far greater number of forms than had hitherto been known. In order to assist in the ready comprehension of the main features of the investigation it will be well to first describe these forms, and to give a general idea of the methods by means of which they may be obtained.

---

[1] Vol. II, Part I, p. 516; Vol. II, Part II, pp. 347, 705, 773.

[2] Jaffé: *Ztschr. phys. Chem.*, **43**, 565; Morse and Pierce: *Proc. Am. Acad.*, **38**, 625.

THE FORMS OF SODIUM THIOSULPHATE.

Ordinary commercial thiosulphate of sodium is a pentahydrate, and is always formed in the process of crystallization at room temperature in open vessels. This substance we will call the α-form. In addition to this there are two other forms of the pentahydrate, which we have called the β- and the γ-form. The β-form has been described by Parmentier and Amat,[1] while the γ-form is hitherto undescribed.

The β-form is most readily obtained by sealing the α-form in a glass tube, heating for a few minutes at from 80° to 100° in a water-bath, and then cooling strongly. The fusion usually solidifies into the β-form with considerable promptness, at temperatures between 10° above and 20° below zero. It exists in the form of long needles and is readily distinguished from the α. It is readily convertible into the α by opening the tube, and dropping in a small crystal of the latter. The transformation then progresses through the tube bodily and offers a very pretty illustration for lecture purposes. Parmentier and Amat obtained the substance from supersaturated solutions instead of from fusions. They give analytical evidence that its composition is that of a pentahydrate

As to the conditions which are most favorable for the formation of the γ-form we are not as yet in a position to say much. This form was discovered quite accidentally, forming occasionally in tubes that did not readily yield β on cooling to low temperatures. There are indications also that the presence of a small excess of water in the tube inclines to the formation of the γ. In appearance the γ is quite different from either the α or β. It forms a very compact and opaque appearing mass, while both the other forms are more or less translucent. It undergoes complete transformation into solution and a lower hydrate at temperatures a few degrees above zero, while the β begins to liquefy at a little above 30° and the α at about 49°. We have no analytical evidence as yet that the γ is really a pentahydrate, but the fact that it is formed by the complete solidification of the fused α shows that it is not a hydrate with less than 5 mols of water to 1 of thiosulphate. It cannot be a cryohydratic mixture, because it is stable at temperatures somewhat above zero. Its conduct on fusion is not such as to lead to the belief that it is a mixture of a hydrate with more than

---

[1] *Ber. d. chem. Ges.*, **17** (3), 198; *Compt. Rend.*, **98**, 735.

5 mols of water, with one with less than five. The evidence then points rather strongly to its being a third modification of the pentahydrate, and until further evidence is obtained we shall consider it as such.

Parmentier and Amat give the melting-points of the α- and β-forms as 32° and 49° respectively. It required but little observation to show us that neither form showed a true melting-point. On the other hand, both go over in the neighborhood of the temperatures mentioned in saturated solutions and lower hydrates. In the case of the α this is very easy to see, as the crystals of the corresponding lower hydrate are of markedly different form from those of the α. In the case of the β the difference in the appearance of the crystals is very slight, but as the salt shows the phenomenon of incipient fusion at near 30°, and as the temperature must be raised some 8° or 9° above this in order for the fusion to become complete, there was little doubt as to the nature of the transition. The solubility data in the following paper give added confirmation of the fact that in neither case is there true fusion, but that both the α- and β-forms go over into lower hydrates and saturated solution on being heated to incipient liquefaction.

The conduct of the γ-form is wholly analogous. When it is warmed to a few degrees above zero, it begins to liquefy, and only after the temperature has been raised to some degrees above the point of incipient fusion does the solution become clear of residual crystals. The appearance of the residual crystals from the γ is quite different from that of either of the other lower hydrates mentioned.

A fourth lower hydrate is obtained when α is fused and allowed to stand at room temperature for a day or two. This lower hydrate forms in very large transparent crystals, often only one in a tube and rarely more than two or three. It is very soluble, as it is formed only in very small quantity.

In addition to the three forms of the pentahydrate there are then four different lower hydrates of sodium thiosulphate. For convenience and brevity we have named these as follows: The one which forms at room temperatures from clear fusions (the last one mentioned above) is called the *a*-form, that formed by partial fusion of the α is called the *b*-form, that formed by the partial fusion of the β is called the *d*-form, and that formed by the partial fusion of the γ is called the *c*-form. Data as to the composition of these lower hydrates, in so far as they have been obtained, are given in the following paper.

THE SUPERCOOLING PHENOMENA.

The α or commercial sodium thiosulphate is well known as a substance which shows the phenomenon of supercooling or supersaturation in the liquid state. In the following work we used altogether fusions and not solutions. In such a case as this, however, a fusion may be looked upon as merely a solution whose composition is that of the solid salt. The phenomenon of supercooling is readily observed. The α-form, for example, remains solid on warming until the temperature of 49° is reached. If a portion of the salt be warmed until complete fusion has resulted, for which purpose it is necessary to heat to about 60°, and then allowed to cool, re-solidification does not occur at 49°, nor at any temperature until about +10° has been reached, and in many cases not until —20° or lower has been reached, provided the entrance to the fused mass of particles of the solid α is not permitted, and leaving out of account the formation of *a* or *b* for the present. The easiest and surest way of avoiding contamination with α is by sealing the tube before fusion. Thus the substance is kept in a liquid state through a long range of temperatures at which the solid is distinctly the more stable form.

When such a supercooled mass is brought to solidification by lowering the temperature sufficiently it is *never* the α-form which is produced, but usually the β, and sometimes, though comparatively rarely, the γ. In the course of this work we have made observations on some hundreds of tubes, and in no single case has the spontaneous formation of the α been observed. α has been found very rarely in some of the tubes, but in all such cases careful search showed the presence of a crack or of a hole in the tube through which the inoculation could have taken place. As has been stated, in the vast majority of cases the β-form was the one to appear, while occasionally the γ was observed. The temperatures at which solidification occurred were widely distributed, as also the length of time required for the starting of the solidification. Without going into details, the following summary will show what has been observed in a general way as to the supercooling and supersaturation of the fusions and solutions of all of the seven different forms of the salt with which we have worked.

(1) The α-form shows supercooling most markedly, and in no case has it been possible to produce this form in a sealed tube, either from its fusion or from any of the other forms. The metastable limit in respect to this form seems to lie at a very low temperature.

(2) Fusions supercooled as to β (at all temperatures below 30° a fusion of the α is also supercooled as to β) are very readily obtainable, but may almost invariably be forced to the spontaneous formation of the solid β by cooling to sufficiently low temperatures for a sufficiently long time.

(3) Such fusions of α or of β as are very resistant to the formation of β frequently yield γ. The γ, when once produced, shows a very marked tendency to go over spontaneously into β, if kept for any considerable length of time.

(4) All fusions of α or β (or γ) are supersaturated as to the *a*-form at temperatures below about 32°, and *a* practically always appears in such tubes when the appearance of β or of γ has not been already forced, provided the tubes have not been heated for too long a time and at too high a temperature (see later).

(5) If α is fused to a liquid free from crystals, that is, if it is heated to temperatures somewhat above 55° until all crystals of the *b* form have passed into solution, but not much higher, the fusion frequently, and as a matter of fact, commonly yields the *b* spontaneously on cooling, thus being apparently labile. This may possibly be due to there being left minute indiscernible crystals of the *b* in the fusion. Actual supercooling as to the *b*-form does occur, however, in all tubes that have been heated to 60° or higher, and such fusions do not immediately deposit the *b*-form. Sometimes tubes that have not been heated too high deposit *b* after a few hours or days. This is without doubt a case of genuine supercooling, as in the case of tubes that have been inoculated with *b*, the growth is immediate and rapid, the whole apparent deposition being complete in about five minutes.

(6) By reference to the solubility curves in the following paper it will be seen that the system consisting of *b* and saturated solution is supercooled as to α at temperatures below 49° and as to *d* at temperatures below 32°, while at temperatures below about 31° it is supercooled as to β. Neither the transformation into α nor into *d* has been observed, which means that the solution with the

b crystals may be very strongly supercooled as to both of these forms. On strong cooling, the transformation to β is not uncommon.

(7) In marked contrast to the above phenomena is the conduct of the *d*-form. This, in contact with the saturated solution, as produced by the warming of the β to about 35° or so, seems rarely, if ever, to become supercooled as to the β. So soon as the temperature falls below its transition point into β the transition occurs. This was shown very clearly in the attempts to follow the solubility of the *d* at temperatures below 30°.

(8) On the other hand, the transition of the *d* into the *b*, with rising temperature, which, according to the solubility curves, should take place at about 32°, has never been observed. This is manifestly a very clear case of the superheating of a solid, a phenomenon which is very rare.

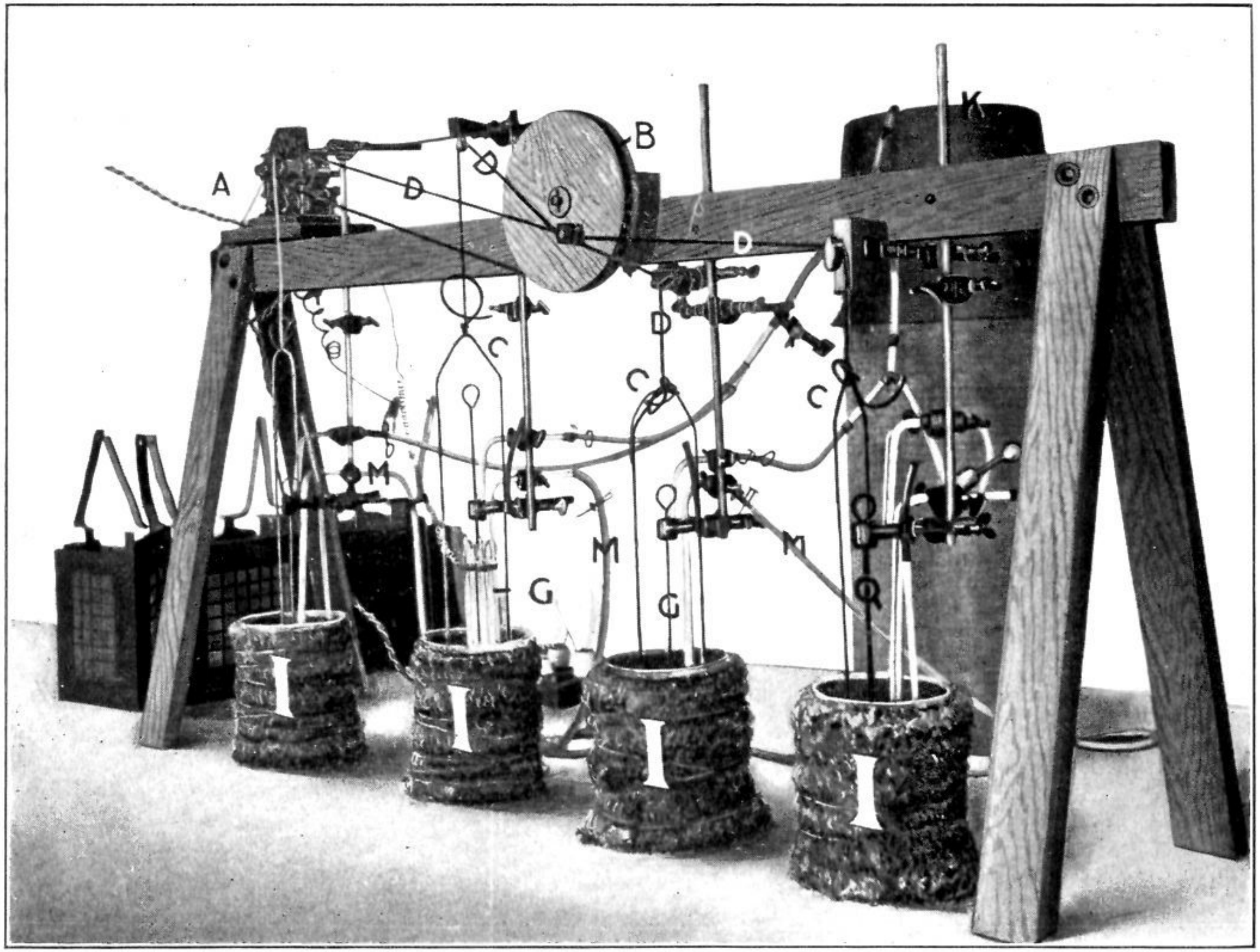
(9) The conduct of the γ and *c*-forms has as yet been only superficially examined.

The bulk of the work described in the present paper was carried out in order to find, if possible, some regularities in the conditions under which the β forms from supercooled fusions, although incidentally some observations were made on some of the other forms, which give more important results than those made on the β. We have, in the main, limited ourselves to a study of the influence of the variation of the following conditions:

(*a*) The previous formation of β in the same tube.
(*b*) The rate at which the tubes were cooled.
(*c*) The temperature to which the tubes had been heated.
(*d*) The length of time which the tubes had been heated.

THE APPARATUS.

All observations were made upon samples of the substances contained in sealed glass tubes of about 6 mm. internal diameter, and 18 to 20 cm. long. As it was necessary to have always at hand a number of baths whose temperatures could be regulated to within something less than a degree, the device shown in the accompanying figure was built. The baths were made of battery jars wrapped with felt. For temperatures above zero the regulation was accomplished by merely adding cold or warm water, as necessary. This, with occasional attention, was sufficient. For the lower temperatures salt solutions of different concentrations in contact with ice were used. With the aid of the automatic


K
B
A
D
D
D
D
D
C
C
C
C
M
M
M
G
G
Q
I
I
I
I

stirring arrangement little difficulty was experienced in holding the temperature sufficiently constant for hours. The details of the apparatus may readily be worked out from the figure and its accompanying key.

THE METHOD OF OBSERVATION.

All of the tubes were numbered and a careful record was kept of the treatment that each had received. In the following tables the procedure for each series of tubes is, in general, sufficiently indicated to make any specific description unnecessary. The appearance of a letter α, β, γ, *a*, *b*, etc., in any column indicates that under the conditions specified in the table that particular form appeared. In cases where time data were taken they are indicated at the caption of the table, or in some other way.

The following abbreviations are used in the tables:

A star (*) indicates that the tube was still clear, *i. e.,* free from crystals under the conditions corresponding to the position in the table.

A dash (—) indicates a continuation of the condition specified in the next space above the one where the dash occurs.

A dagger (†) indicates that the tube was broken. This occurred frequently upon the formation of γ, and also with tubes that had been heated for a long time.

TABLE I. SERIES II.

Time of heating, ten minutes. Allowed to stand five minutes at room temperature.[1] Figures give the temperature at which β formed. The cooling was so regulated that the range from +10° to —20° was compassed during an afternoon. A corresponding set of tubes heated to 60°, and not reported here, gave *b* with a single exception, on cooling from the first fusion (of α).

	Tubes heated to 80° C.								
Tube.	9	10	11	12	13	14	15	16	Average.
First fusion, Jan. 22..	—17	—17	—14	—8	—12	—8	—12	—12	—12
Second fusion, Feb. 2	— 9	—15	— 9	—9	—10	—1	— 5	†	— 8
Third fusion, Feb. 4..	— 9	—10	—14	—4	— 8	—6	γ —18	—	— 8
Fourth fusion, Feb. 5	—17	— 8	—16	0	†	—6	†	—	— 9

	Tubes heated to 100°.								
Tube.	17	18	19	20	21	22	23	24	Average.
First fusion, Jan. 22 ..	—14	—19	—19	—14	†	—12	—19	—14	—15
Second fusion, Feb. 2.	—16	†	— 1	—15	—	†	—14	— 1	— 9
Third fusion, Feb. 4 ..	γ —16	—	— 1	—14	—	—	— 5	0	— 5
Fourth fusion, Feb. 5 .	†	—	—18	+ 1	—	—	—15	— 8	—10

---

[1] This was done in almost all cases, in order to be certain that small crystals of some form were not left which would start immediate crystallization, in which case the tube could not, of course, be considered as supercooled.

TABLE II. SERIES III.

Time of heating, ten minutes. Stood five minutes at room temperature. Tubes held for one hour at each of the temperatures indicated in column 1.

	Heated to 60° C.							
Tube.	33	34	35	36	37	38	39	40
+10°	*	*	*	*	*	*	*	*
+ 5°	*	*	*	*	*	*	*	*
0°	*	*	*	*	*	*	*	*
— 5°	*	*	*	*	*	*	β	*
—10°	*	β	β	*	β	β	—	β
—15°	β	—	—	β	—	—	—	—
—20°	—	—	—	—	—	—	—	—

	Heated to 65° C.							
Tube.	41	42	43	44	45	46	47	48
+10°	*	*	*	*	*	*	*	*
+ 5°	*	*	*	*	*	*	β	*
0°	*	*	*	*	*	*	—	*
— 5°	*	*	*	*	*	*	—	*
—10°	*	*	*	*	*	*	—	β
—15°	*	*	†	*	β	β	—	—
—20°	β	β	—	γ	—	—	—	—

	Heated to 70° C.							
Tube.	49	50	51	52	53	54	55	56
+10°	*	*	*	*	β	*	*	*
+ 5°	*	*	*	*	—	*	*	*
0°	*	*	*	*	—	*	*	*
— 5°	*	*	*	*	—	*	*	*
—10°	*	*	*	β	—	*	*	*
—15°	β	β	β	—	—	*	β	β
—20°	—	—	—	—	—	β	—	—

	Heated to 80° C.							
Tube.	57	58	59	60	61	62	63	64
+10°	*	*	*	*	*	*	*	*
+ 5°	*	*	*	*	*	*	*	*
0°	*	*	*	*	*	*	*	*
— 5°	*	*	*	*	*	*	*	*
—10°	β	*	β	*	β	*	*	*
—15°	—	β	—	β	—	β	*	*
—20°	—	—	—	—	—	—	β	γ

	Heated to 100° C.							
Tube.	65	66	67	68	69	70	71	72
+10°	*	*	*	β	*	*	*	β
+ 5°	*	*	*	—	*	β	*	—
0°	*	*	*	—	*	—	*	—
— 5°	*	*	*	—	*	—	*	—
—10°	*	β	β	—	*	—	*	—
—15°	β	—	—	—	β	—	β	—
—20°	—	—	—	—	—	—	—	—

TABLE III. SERIES IV.

Time of heating, sixteen hours. Stood five minutes at room temperature. Tubes held for one-half hour at each of the temperatures indicated in the first column. In this series complete observations were carried on at 10°, 5°, 0°, and −5°, but as no tube showed any crystallization at any of these temperatures, the data for these temperatures is put into one row in the table. This is also the case in Table IV.

	Heated to 60° C.							
Tube.	9	10	11	12	13	14	15	16
+10° to −5°	*	*	*	*	*	*	*	*
−10°	*	*	*	*	*	*	*	*
−15°	γ	*	β	β	β	β	*	*
−20°	—	*	—	—	—	—	*	*

	Heated to 70° C.							
Tube.	17	18	19	20	21	22	23	24
+10° to −5°	*	*	*	*	*	*	*	*
−10°	*	*	*	*	*	*	*	β
−15°	*	β	β	β	*	*	*	—
−20°	*	—	—	—	γ	γ	β	—

	Heated to 80° C.							
Tube.	25	26	27	28	29	30	31	32
+10° to −5°	*	*	*	*	*	*	*	*
−10°	*	*	*	*	*	*	*	*
−15°	*	*	β	*	*	*	*	*
−20°	β	*	—	γ	β	*	γ	*

	Heated to 100° C.							
Tube.	33	34	35	36	37	38	39	40
+10° to −5°	*	*	*	*	*	*	*	*
−10°	*	*	*	*	*	*	*	*
−15°	*	*	*	β	β	*	*	β
−20°	†	†	*	—	—	*	*	—

TABLE IV. SERIES IV.

Time of heating, three and one-half days. Stood at room temperature for five minutes. Tubes held for one-half hour at each of the temperatures indicated in the first column.

	Heated to 60° C.								Heated to 70° C.								Heated to 80° C.								Heated to 100° C.							
Tube.	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76
+10° to −5°	†	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	†	*	*	*	*	*	*	†	†	†	*
−10°	—	*	*	*	*	*	*	*	β	β	*	*	*	*	*	β	*	*	*	*	*	—	*	*	†	*	*	*	—	—	—	†
−15°	—	*	β	—	β	β	β	β	—	—	*	*	β	*	*	—	β	*	β	*	*	—	*	*	—	*	*	*	—	—	—	—
−20°	—	β	—	β	—	—	—	—	—	—	*	β	—	*	β	—	—	β	—	β	β	—	β	*	—	*	β	β	—	—	—	—

TABLE V.

Time of heating, ten minutes. Tubes then allowed to stand at room temperature. Tubes heated under these conditions to 50° and 55°, gave *b* immediately, most of them showing residual crystals of *b* on removal from the bath. They are therefore omitted from the table.

	Heated to 50° C. Series II.				Heated to 65° C. Series III.				Heated to 70° C. Series III.				Heated to 80° C. Series II.				Heated to 100° C. Series II.			
Tube.	39	40	41	42	9	10	11	12	13	14	15	16	43	44	45	46	47	48	49	50
Feb. 12	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
		b		b																
Feb. 13	*	—	*	—	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Feb. 15	b	—	*	—	b	b	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Feb. 17	—	—	*	—	—	—	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Feb. 18	—	—	*	—	—	—	a	a	*	a	a	*	*	*	*	*	*	*	*	*
Feb. 19	—	—	*	—	—	—	—	—	*	—	—	a	*	*	*	*	*	*	*	*
Feb. 20	—	—	*	—	—	—	—	—	a	—	—	—	a	a	a	*	*	*	*	*
Feb. 22	—	—	*	—	—	—	—	—	—	—	—	—	—	—	—	a	*	*	*	*
Mch. 21	—	—	a	—	—	—	—	—	—	—	—	—	—	—	—	—	a	*	a	a
Apr. 4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	a	—	—

TABLE VI. SERIES III.

Time of heating, sixteen hours. Tubes then allowed to stand at room temperatures.

	Heated to 60° C.				Heated to 70° C.				Heated to 80° C.				Heated to 100° C.			
Tube.	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96
Mch. 1	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Mch. 14	*	*	*	*	*	*a*	*	*	*	*	*	*	*	*	†	*
Mch. 21	*a*	*	*a*	*	*	—	*	*	†	*	*	*	*	*	—	*
July 4..	—	*	—	*a*	*	—	*	*	—	*	*a*	*	*	*	—	*
July 19.	—	*	—	—	*	—	*	*	—	*	—	*	*	*	—	*

DISCUSSION OF THE RESULTS.

Although the investigation was primarily upon the conditions for the appearance of the β-form, much more decisive results have been obtained from the study of some of the others. But as the bulk of the data refers to the β, it will perhaps be as well to discuss it first.

(*a*) The influence of the previous formation of β in the same tube upon the ease with which it would appear a second time was quite extensively studied. The results obtained were not of sufficient certainty to warrant any very definite conclusions, and the large mass of data obtained is not given. There seemed to be a fairly constant tendency for the appearance of the β to occur the second time at a somewhat higher temperature than at first. Since the first appearance of the β was always from a fusion of the α, and the second from a fusion of the β, it would seem that the previous formation of the β might have had some influence. Table I gives the results of one series of experiments along this line. It will be seen that while the average temperatures of fusions after the first are somewhat lower than those for the first, nevertheless there is considerable variation among the individual results. The observations were made under most unfavorable conditions, and before we had any experience. They will be repeated in order to avoid certain sources of trouble which our experience has shown to exist.

(*b*) The rate at which the tubes were cooled was also quite extensively investigated, the results for the most part being negative in so far as any influence on the temperature of formation of the β is concerned. One thing was noticed, and that was that tubes which had been heated to 60° or 65° only, and which would be expected to yield the *b*-form in from one to three or four days at room temperature, would yield β instead, if they were rapidly cooled. The formation of β was never observed above 10°, and all fusions which, if cooled, would have given β (or possibly γ) gave *a* when held at room temperature for a sufficiently long time, unless owing to the low temperature of heating, *b* appeared, or unless owing to high heating, *a* was barred from forming (see later). In the latter case nothing appeared. The rate of cooling may, therefore, determine which form shall appear, but so far as we have yet seen it has no marked influence on the temperature at which a form appears.

(*c*) The temperature to which the tubes have been heated also has relatively little influence on the temperature at which the β appears, although, as will be seen later, of very great influence in the cases of some of the other forms. Tables II, III and IV give the results of three series of observations of this sort. In every case it will be seen that it makes but little difference whether the tubes had been heated to 60°, 70°, 80° or 100°; the appearance of the β is scattered over a considerable range of temperature, and is quite irregular. The work of Jaffé[1] has shown conclusively that the length of time that a supersaturated solution is held at a given temperature is of great influence upon its crystallization; that is, in the present case there were doubtless many tubes which did not solidify until 20° below zero was reached, which would have solidified at higher temperatures if they had been held at them for a sufficiently long time. All that we have attempted is to maintain practically constant conditions of cooling.

(*d*) The influence of the length of time that the tubes were heated is also shown in the same tables, II, III and IV. In Table II the tubes were heated for ten minutes, in Table III for sixteen hours and in Table IV for three and one-half days. In Tables III and IV the procedure on cooling was practically the same as in Table II, but as no cases of solidification occurred in these series at temperatures above —10° the results of the cooling from +10° to —5° are condensed into one row in the tables. The results are readily seen. In the case of the ten-minute heating there were a considerable number of scattered solidifications at relatively high temperatures and some of them occurred as high as at 10°. In the cases of longer heating no solidification occurred above —10°. The effect of long heating is thus to considerably

---

[1] *Loc. cit.*

restrict the range of temperature within which solidification occurs. Table III is noticeable for the large number of appearances of γ. We have no notion why this should have been. There is no noticeable difference in the results in Tables II and III which would indicate either that the influence of heating was complete at the end of sixteen hours or else that the jump from sixteen hours to three and one-half days was not sufficient to cause any further appreciable difference.

To summarize, the results obtained from the study of the solidification of the β are, for the most part, negative, although a very distinct influence is noticed as a result of long heating, in that sporadic solidifications at relatively high temperatures are excluded.

THE CRYSTALLIZATION OF THE *a*- AND *b*-FORMS.

Considerable data on these forms was obtained incidentally to the study of the β. In addition a few series of observations were carried out directly on these forms. In this case the observations are limited to the temperature and time of heating and these forms have shown themselves much more sensitive to these influences than did the β.

Temperature of Heating.—Tables V and VI give the results of two series of experiments to determine the influence of the temperature of heating on appearance of the *a*- and *b*-forms. In Table V the tubes were heated at the temperatures given for ten minutes, and then allowed to stand at room temperature. It will be noticed that two of the tubes heated to 60° formed *b* on the same day, a third three days later, while the fourth formed *a* something more than a month later. This formation of *a* is exceptional, as we have worked with many tubes heated to 60° and they almost invariably give *b* on the first day or within a few days after, provided they have been heated for only a short time. Of the tubes heated to 65° two formed *b* on the fourth day and two did not form *b* at all, but *a* appeared at the end of six days. All of the tubes that were heated to still higher temperatures refused to give *b*, but sooner or later gave *a*. The length of time required for the appearance of *a* increases very rapidly with the temperature. In Table VI, where the period of heating was longer, no *b* was formed in any of the tubes, and the *a* shows an increasing disinclination to form after higher heating.

Time of Heating.—The same tables show the influence of this condition: In Table V the heating was for ten minutes, and in Table VI for sixteen hours. The formation of *b* is prevented altogether by the longer heating. Also the first *a* to form was after two weeks, instead of less than one in the short heating, while even after four months every tube that had been heated to 100° for sixteen hours remained perfectly clear, save one that cracked as a result of the prolonged heating. An inspection of the table will show very clearly that in spite of the fact that a single tube which had been heated to 70° formed *a* earlier than did any that had been heated to 60°, there is, on the whole, a distinctly increasing disinclination to form the *a* with increasing temperature of heating.

This is about all of the facts that we have obtained that permit of being put into coherent form at present. We shall next briefly discuss a working hypothesis that has suggested itself and then attempt to show how it accounts for the above facts, as well as for a considerable number of interesting isolated observations that we have made.

HISTORICAL.

Starting upon considerations based upon the continuous form of the theoretical curve for the transition of liquids into vapors, and the existence of theoretical metastable limits in this particular case, Ostwald has developed a very reasonable theory for cases of supercooling and supersaturation as well (see above citations in the Lehrbuch). Up to the present time, however, no success has attended the many attempts to experimentally determine this metastable limit for any case excepting one, where the supersaturation is produced by means of chemical reaction in gelatine. In fact, it is generally recognized that there are a great many disturbing influences, *i. e.*, influences which cause the given transition to occur before the metastable limit has been reached, and the bulk of the work has resulted in discovering and defining some of these influences. In the case of the condensation of supercooled water vapor an electric charge is known as a potent factor in causing the reaction in a body of vapor. In the case of supercooled liquids and supersaturated solutions, sudden jarring will frequently start the transition, and dust particles have been more or less commonly supposed to have this power. The bulk of the

---

[1] Morse and Pierce : *Proc. Am. Acad.*, **38**, 625.

research, however, tends to show that dust is inoperative, unless it contains solid particles of the substance that is to crystallize.

Both before and after the suggestion of the metastable limit there are found many hypotheses to explain the spontaneous crystallization of supercooled and supersaturated systems. Thus Lehmann[1] suggests that when a solid is fused there remains a thin layer of the substance next the walls of the vessel, which is of molecular dimensions, and unfused. There is required a considerably higher temperature than that of the melting-point in order to eliminate this. As to the many objections to this hypothesis nothing need be said here (*cf.* Schaum and Schönbeck[2]). DeCoppet[3] suggests a molecular-kinetic explanation of the spontaneous crystallization of supercooled solutions, in that he considers that as the molecules have to unite to form the crystalline aggregate which can start the crystallization, it is largely a matter of uncertainty under just what conditions the crystallization will start, as the molecules must first come into a favorable configuration in order to form the aggregate.

Jaffé worked mainly upon supersaturated solutions of potassium nitrate, and came to the very interesting conclusion that the limit to which the solution can be supercooled is greatly extended by repeated filtration of the solution. Thus the most concentrated solution that could be maintained in the supersaturated state at 20° for any length of time was 51 per cent., unless the solution was first repeatedly filtered. When this was done it was found possible to keep 57 per cent. solutions for about the same length of time. Jaffé explains his results as follows: There are contained in the solution nuclei (Keime) which are capable of starting crystallization sooner or later, and these are of such dimensions that they may be, at least in part, filtered off by passing the solution through cotton wool. As to the source and nature of these nuclei Jaffé says but little.

Schaum and Schönbeck[4] point out the difference in conduct of fusions of benzophenone, when they are made under different conditions. We shall recur to this interesting work later.

THE NUCLEAR HYPOTHESIS.

The hypothesis which we offer in explanation of the results of our own work, and of many of the phenomena observed by others,

---

[1] Drude's *Annalen*, **2**, 659 (1900).

[2] *Ibid.*, **8**, 652 (1902).

[3] *Ann. chim. phys.* (5), **6**, 275 (1875).

[4] *Loc. cit.*

we shall call the nuclear hypothesis. We start with Jaffé's notion of nuclei, but assign to the existence of these a definite cause, and to their origin, a definite source. We consider them to be residues left upon the breaking-down of the crystalline structure of the solid itself, upon fusion or solution.

Crystals are usually looked upon as aggregates of smaller aggregates, and the smallest fragment of a crystal is still a crystalline aggregate. It seems reasonable to consider, in the light of the work of Ostwald and others, that one of these crystalline aggregates would be capable of starting immediate crystallization in any supercooled fusion or solution of itself. Crystalline aggregates cannot, therefore, be present in any supercooled liquid, which means that a substance once thoroughly fused or dissolved must be free from them.

Although the phenomena of supercooling demand that all crystalline aggregates shall have disappeared when complete fusion or solution has occurred, it does not necessarily follow that they shall all have become transformed into the homogeneous liquid. It is imaginable that, although the breaking-down of the gross crystalline structure is a discontinuous process, taking place at a definite temperature, there are nevertheless left in the liquid either fragments of crystalline aggregates, amorphous particles of the substance, or particles in the colloidal state, or perhaps some other heterogeneous conditions. We assume, in absence of any good reason to the contrary, that the residues are fragments of the crystalline aggregates, and are to be looked upon as solid particles. This assumption is wholly tentative, but has certain advantages from the standpoint of clearness of presentation.

Concerning the dimensions of these nuclei, all that can be said is that from Jaffé's work they seem to be of such a size that they are, at least in part, entangled in cotton wool fibers, although it may be that only such of them as are already entangled in dust particles are capable of being filtered out. Although in themselves incapable of starting crystallization, not being fully possessed of the crystalline structure, they may, under certain conditions, unite to form crystalline aggregates, and thereby cause the crystallization to start.

Owing to the general disintegrating action of heat the above described nuclei would be more or less rapidly destroyed by more or less prolonged heating at higher temperatures. Thus, on the basis of the nuclear hypothesis, there are two possible methods of removing nuclei, at least in part, namely, filtration and heating. Also the addition of a foreign substance might bring about such destruction. There are many recorded cases of marked increase in the possibility of supercooling upon the addition of small quantities of foreign substances, *e. g.*, alcohol to benzophenone. Some nuclei may naturally be more sensitive to the action of high temperatures than others, whence, in order to bring about the same degree of "sterilization," longer heating, or heating to higher temperatures may be required in some cases than in others.

The possibility of two or more nuclei uniting to form a crystalline aggregate increases with falling temperature, and would be more or less a matter of chance unless the concentration of the nuclei were relatively large. This may account, to some extent, for the irregular results usually obtained. We give at present no theoretical grounds for the assumption that the aggregates are more prone to unite at lower temperatures than at high. The phenomenon might be explained as due to action between a single nucleus and the homogeneous liquid, and not between two or more nuclei.

The possibility of starting crystallization will also depend upon the concentration of the nuclei in the solution. Thus concentrated solutions will be more liable to spontaneous crystallization, not only because they are more supersaturated, but also because of the greater concentration of the nuclei.

If it is assumed that there are definite forces which tend to bring the nuclei together into aggregates, it is clear that this orientation may be assisted by shaking and jarring, just as, for example, iron filings are assisted in taking on figured positions in the magnetic field by the same influences. This offers a possible explanation of the common phenomenon of spontaneous crystallization resulting from these causes, and does not interfere with the notion that these same influences may cause local transgressions of the metastable limit.

One more assumption is necessary to make the nuclear hypothesis cover all the facts which we wish to bring under it, namely, that as different substances give different nuclei just so different polymorphic forms of the same substance and different hydrates of the same substance may give different nuclei, and these different nuclei may be capable of existing alongside of one another. It by no means follows that the nature of the nuclei in a fusion of a given polymorphic form may be predicted from the nature of the form. For example, the α-thiosulphate does not seem to give any nuclei that are capable of regenerating the same form because, so far as our experience goes, α is never regenerated except as a result of inoculation with a bit of itself. On the other hand, β seems to give chiefly nuclei that regenerate itself.

It may be mentioned that it is possible to explain the phenomena in question on the assumption that all the nuclei from a given substance are the same, and that different concentrations of them and different temperatures are more favorable for the production of the various possible aggregates. The data at hand are not sufficient to enable us to see any advantage in that point of view. and for the present we assume that the nuclei are different, as this assumption has many advantages in clearness and concreteness.

The nuclear hypothesis, as above stated, may seem, in some respects, rather crude, but it is offered simply as a working hypothesis, subject to change or rejection at any time. The hypothesis has thus far been very useful, and it was only by its use that we were able to introduce anything like order into the classification of our experimental results. We shall now give, in some detail, the application of the hypothesis to the explanation of some of the phenomena that we have observed, as well as of some of the observations of Schaum and Jaffé.

(*a*) From fused α-sodum thiosulphate, so far as our observations go, any one of four forms may separate, according to the conditions of fusion and the subsequent treatment. These forms are the β and γ (pentahydrates), and the *a* (monohydrate) and *b* (dihydrate). Never thus far have any of the other forms been observed to form from fused α. In the terms of the nuclear hypothesis we should say that the fused α might contain the nuclei corresponding to these four forms, and either no others or else others in such a small concentration that their influence is never apparent. As to the γ there is as yet no evidence on which to base any assertion. The nuclei of the β-form do not become effective in any case observed until the temperature is dropped to about +10°, and they seem to be not much affected by very considerable heating. However, on heating for sixteen hours or more all cases of solidification above —10° seem to be eliminated (Tables

II, III and IV). The nuclei of *b* are, on the other hand, very sensitive to heating. Tubes become practically completely "sterilized" against *b* by heating for ten minutes to 70° and for sixteen hours at 60° (Tables V and VI). The *a* nuclei conduct themselves similarly, although not so sensitive as the *b* sort. Practically complete sterilization occurs after heating for sixteen hours at 100° (Tables V and VI).

(*b*) Fusions of different polymorphic forms and of different hydrates conduct themselves differently. Strictly speaking, what we have called a fusion of *α* is in reality a solution formed from *b*, because the *α* becomes transformed into *b* at some temperature below that at which a clear solution is produced. In the same way a so-called fusion of *β* is a solution prepared from *d*. Now the two solutions prepared in these different ways conduct themselves in a wholly different manner as regards their supercooling. While that from *a* (or *b*) yields, according to conditions, *a* or *b* at room temperatures and *β* at low temperatures (sometimes *γ*) the conduct of the fusion from *β* conducts itself as follows, the results being based on the conduct of twenty-one tubes of *β*, heated to 43°; a single tube gave *β* immediately, undoubtedly on account of incomplete fusion. A second gave, after seven hours, a crystal of a very slow growing substance, from its conduct undoubtedly a lower hydrate, but neither *a*, *b* nor *d*. It is as yet a matter of uncertainty as to what the substance is. It may be a form still different from those described, or possibly it may be the form which we have called *c*, with which we are not as yet sufficiently familiar to recognize it under all conditions. All other tubes remained perfectly clear for over four days. At this time nine of them were taken and cooled at intervals of 5°, and for fifteen minutes at each temperature. Of these nine tubes three gave *β* at 0°, five gave *β* at —5° and the other one gave *β* almost instantly at —15°. The remaining ten tubes were kept, as before, at room temperature, and observed from time to time, with the following results: One week after the time of fusion six of the tubes showed crystals of *a*, while the remaining four are still clear at the time of writing—two weeks after fusion.

Thus fusions of *β* conduct themselves differently from those of *α* in the following respects:

(1) They never yield *b*.

(2) They may yield a substance (possibly c) which has never been observed to form from fusions of α.

(3) They show very considerably less inclination to yield α than do fusions of α heated for the same length of time (compare Table V), even though the latter have been heated to temperatures from 20° to 40° higher.

(4) They form β much more readily than do fusions of α. This was also shown, although less markedly, in the results given in Table I, the reason probably being that in that series the fusion of the β was carried on at much higher temperatures than in the present one.

(c) Schaum and Schönbeck found similar conditions to exist in regard to benzophenone. This substance exists in two forms, the stable and the metastable. Either form may result from supercooled fusions, according to conditions. When the metastable form was once obtained it conducted itself very differently in different cases, sometimes going over into the stable form almost immediately after solidification, sometimes going over into the stable form within an hour, and sometimes requiring much longer time. It was apparently the rule, however, that if a sample did not go over into the stable form within an hour it remained permanently in the metastable form. The authors, therefore, divide the different samples of the metastable benzophenone which they obtained into three classes: (1) Those going over within fifteen minutes are called *unstable;* (2) those going over in less than an hour, but requiring more than fifteen minutes, are called *stable;* (3) those requiring more than an hour, and which do not, in general, go over at all, are called *very stable.* In the following table is given a brief summary of the results. Under T is the temperature of heating; under θ is the time of heating; under N is the total number of tubes that were under observation in each series; under A the percentage of the tubes that remained liquid after cooling to room temperature, *i. e.,* that showed supercooling at all; under B the percentage of the supercooled tubes that solidified into the stable modification on cooling in ether-carbon dioxide mixture; under C, D and E are the percentages of the supercooled tubes that, under the same treatment, solidified respectively into the unstable. stable and very stable modifications of the metastable form.

θ. Minutes.	T. °C.	N.	A. Per cent.	B. Per ct.	C. Per cent.	D. Per ct.	E. Per ct.
15	50–52	260	17	88.6	11.4	0	0
180	50–52	139	54	89.3	10.7	0	0
15	100	112	99	64.9	22.5	7.2	5.4

These phenomena allow of a satisfactory and fairly simple explanation in terms of the nuclear hypothesis. The temperature of heating in the first two series is only 2° to 4° above the melting-point of the ordinary benzophenone, and, therefore, no considerable sterilization occurs even with relatively long heating. Thus after three hours' heating at this temperature only about one-half of the tubes remain in the supercooled state at room temperature, while with only fifteen minutes' heating less than one-fifth remain supercooled. On the other hand, heating for fifteen minutes at 100° sterilizes practically all of the tubes against solidification at room temperatures. The similarity in conduct here with that observed as to the appearance of the *b*-form of sodium thiosulphate in tubes heated to various temperatures and for various times is very striking. We obtained many results with the *b*-form which are not included in the tables. The substance of these results was that heating even for a considerable length of time at temperatures only 2° to 5° above the temperature of clear fusion yielded tubes which almost invariably gave *b* at room temperatures, and usually in a comparatively short time.

Schaum's results further show that of those tubes which persisted in the supercooled state at room temperatures, the large portion crystallized in the stable form on cooling to —79°, *i. e.*, in ether-carbon dioxide solution, but that while about 90 per cent. of the 50° to 52° fusions showed this conduct it was shown by only about 65 per cent. of the 100° fusions. This requires no further explanation than that given for the solidification at room temperatures.

Those supercooled tubes which did not solidify into the stable modification gave the metastable form, and this was shown by about 10 per cent. of the 50° to 52° tubes and 35 per cent. of the 100° tubes. Thus the fused ordinary benzophenone is a liquid containing two sorts of nuclei, one capable of causing solidification under certain circumstances of the stable form, and the other sort capable of bringing about solidification in the metastable form. In just fused benzophenone the stable nuclei so preponderate in influence that the bulk of the samples solidify immediately into the stable form, but on heating for a longer time or at a higher temperature, increasing numbers of samples are restrained from solidifying at room temperature. The metastable nuclei, *i. e.*, those capable of combining to form the aggregates necessary for the solidification in the metastable form, seem to become efficient only at lower temperatures, and the relative numbers of the two sorts of nuclei, or rather perhaps the relative activity of efficiency of them, will determine into which of the two forms the sample will solidify. Thus the 50° to 52° tubes, in which the stable nuclei still largely preponderate, give the metastable form only in 10 per cent. of the cases, while the 100° tubes give this form in 35 per cent. of the cases. On the basis of the nuclear hypothesis one would readily be able to predict that had the heating to 100° been carried on for a much longer time, or had even higher temperatures been resorted to, complete or nearly complete sterilization against the stable form might have been attained.

Also the appearance of metastable solidifications of differing degrees of persistence is readily explained. If in a tube containing both stable and metastable nuclei a group of the metastable nuclei come into conditions favorable for starting the solidification, and do start it, it is also more than likely that a group of the stable nuclei will also have reached a similar condition and there may be started a stable solidification even before the metastable one is complete. If there happens to be a group in favorable condition, *i. e.*, just ready to start the stable solidification, even after the metastable solidification was complete, it might persist and subsequently start the transformation of the metastable form into the stable. If there were no group of stable nuclei in approximately favorable conditions, the chances for this transformation setting in would be very small after the tube had solidified into the metastable form. Thus metastable tubes of different degrees of stability are easily imaginable. We have observed all of the above phenomena in the case of the β- and γ-forms of sodium thiosulphate. The γ forms relatively rarely, and when it does form is very likely to be assimilated by a growth of β, which may start either before or after the complete solidification into the γ-form.

(*d*) Jaffé found that the effect of repeatedly allowing his supersaturated solutions to crystallize out and then heating to redissolve was to considerably increase the degree of supercooling possible. In the light of what has been said it seems probable that this phenomenon is due solely to the heating to which the solution was subjected, and not to the fact of repeated solution and crystallization. At any rate, this is a point which future investigation can readily decide. It is to be said, however, that Schaum noticed the same thing as a result of repeated fusion and solidification, a fact which does not fit into our theory so readily. The distinction between the two cases is as follows: If 50 grams of potassium nitrate are dissolved by warming with 50 grams of water, the solution will contain all of the nuclei corresponding to the 50 grams of potassium nitrate. On crystallization, only a part of the salt will leave the solution, and on re-solution only a small number of nuclei will be re-introduced, and these, as well as those remaining in the solution will be influenced by the heating to bring about re-solution, and a gradually increasing degree of sterilization will result, up to a certain limit. In the case of a liquid that completely solidifies, this is no longer the case. One would expect the same number of nuclei as a result of each fusion, provided the fusion occurred each time under the same circumstances. Even here an explanation is not impossible, but rather forced. The phenomena discussed in the next paragraph, however, do furnish a fairly reasonable explanation.

(*c*) It has been repeatedly observed that when a supercooled liquid crystallizes the crystallization frequently starts from not more than two or three points, and very commonly from only one. These points are frequently on the wall of the tube and in many cases fixed so that crystallization always starts from the same point. Such points are called critical spots and the belief is common that they are due to some peculiarity of the glass itself. We have repeatedly observed, however, that these spots are not necessarily either fixed or located on the wall of the tube. For example, we found one tube in which β had formed, which, if carefully fused at not over 45°, invariably solidified at 5°, and always from a single point. By turning this tube, while the β was in the fused state, and allowing the fluid to flow from end to end of the tube and then cooling, the critical spot would have usually moved to another portion of the tube, sometimes at the wall and sometimes in the midst of the liquid. Schaum found these critical spots of very common occurrence, and also found that they could be, to a great extent, eliminated by heating. In a general way, and looked at from the point of view of the nuclear hypothesis, any point at which solidification starts would be a critical point. Thus when a sufficiently great number of nuclei come into favorable positions a critical point will be spontaneously formed. Furthermore, it is possible that, since the nuclei are solid particles (may be filtered out), they might easily become entangled occasionally with dust particles, and that an enclosed dust particle might, when the solid was melted, entangle a sufficient number of nuclei to create a spot from which solidification could most readily take place. Such a critical spot once attached to the wall of the tube would be inclined to stay there. The nuclei contained in such a place would also be susceptible to sterilization. Any dust particles that were adhering to the walls before the fusion would also be inclined to stay there, so that there is ample explanation of the fact that the critical points occur very frequently at the walls of the tube. Such critical spots might become gradually disentangled by repeated fusion, and this may explain Schaum's results with benzophenone, mentioned in the last paragraph.

Jaffé noticed a great tendency for solidification to start from points near the bottom of his tubes. We have also noticed this. In about 70 per cent. of the tubes examined, in which β had crystallized, the starting-point was well below the middle of the liquid column. Possibly this percentage would have been larger, if all tubes had been allowed to stand longer in an upright position before forcing solidification. Jaffé very reasonably explains this as due to the settling out of the nuclei.

(*f*) Tammann[1] has investigated the phenomenon of supercooling from a somewhat different standpoint. He determined the number of points at which crystallization started at different temperatures and found a maximum at pretty definite temperatures, which lie within that temperature interval in which the velocity of crystallization increases. Any discussion at this time of the relationship of his work to ours would be premature, and will be left until our data are more complete. We do not, at present, see anything in his results that conflicts with our conclusions.

There are many interesting questions that come up in regard to the possibility of producing supersaturated solutions as a result

---

[1] *Ztschr. phys. Chem.*, **22**, 306.

of chemical action, and the real function of the gelatine in the production of supersaturation in the case of the Liesegang rings,[1] but the data is too insufficient to permit of intelligent discussion at this time.

The Ostwald Rule and the Metastable Limit.—Ostwald has suggested that it seems to be a fairly general rule that when a supercooled or supersaturated system is forced into transition it is not the stable but the metastable form which separates out.[2] He also gives theoretical grounds for the rule. Wald,[3] in a paper discussing this rule, concludes that it is not thoroughly well founded and predicts that it will be found that the necessary conditions will be discovered, by whose regulation the different forms may be obtained at will. Our results show that at least a start has been made in that direction.

Although we do not intend to enter on any considerable discussion of this point here, a few words may not be out of place. The existence of a metastable limit, in the first place, presupposes in the case of supercooled liquids, a perfectly homogeneous phase. In other words, any crystallization or solidification that is due to nuclei of any sort, cannot be said to be due to a transgression of the metastable limit in the strict sense of the word. Ostwald himself[4] points out that when once the metastable limit is transgressed the whole body of the liquid *en masse* would be affected at once, although he likewise points out that it is easy to imagine that the metastable limit might be reached locally, as a result of local disturbances—as of pressure. But the main point at present is that in the case of the nuclei we are dealing with a disturbing factor, and no true metastable limit can be reached until their influence is eliminated. It seems probable that under ordinary circumstances it may become possible to control the particular form in which a substance may solidify, and the Ostwald rule need not necessarily apply. In case the conditions for the reaching of the true metastable limit were attainable the rule might possibly hold, although Wald does not think so. The above considerations do not apply to the possible case that a perfectly homogeneous liquid spontaneously forms nuclei; but the nuclei which we assume to produce spontaneous crystallization are apparently not produced in this way.

---

[1] See Morse and Pierce: *Loc. cit.*

[2] *Ztschr. phys. Chem.*, **22**, 306.

[3] *Ibid.*, **24**, 503.

[4] See Lehrbuch

SUMMARY.

The more important results of this investigation may be summarized as follows:

(1) Seven different forms of sodium thiosulphate are described, of which three are pentahydrates and four hydrates with less than 5 molecules of water of crystallization. The general conditions for the production of the various forms are given.

(2) Considerable progress has been made in determining under what conditions some of these forms may be obtained from supercooled solutions and fusions.

(3) In determining these conditions the whole previous history of the sample is of importance, mainly in three respects: (*a*) The form of the salt from which the solution or fusion is prepared; (*b*) the time of heating; (*c*) the temperature of heating.

(4) A fairly satisfactory hypothesis has been devised to account for the phenomena observed, as well as for many observations of Jaffé and particularly of Schaum. The hypothesis also suggests many lines of investigation. It is the intention to carry out a systematic study of these phenomena in this laboratory in order to determine to what extent the hypothesis is useful.

NOTE.—Some days after the above was written I received the copy of the *Zeitschrift für physikalische Chemie*[1] containing Füchtbauer's paper on the "Spontaneous Solidification of Supercooled Liquids." From a rather hasty reading I find nothing in the experimental part which seems necessarily to conflict with the conclusions of the above paper, while the theoretical treatment seems not to cover many of the phenomena that were observed with sodium thiosulphate.—*S. W. Young.*

STANFORD UNIVERSITY, CAL.,
July 19, 1904.

ON THE COMPOSITION AND SOLUBILITY OF THE HYDRATES OF SODIUM THIOSULPHATE.

BY S. W. YOUNG AND W. E. BURKE.

Received July 25, 1904.

AS HAS been shown in the previous paper, sodium thiosulphate is capable of existing in a variety of different forms, some of them being polymorphic pentahydrates and others hydrates with

---

[1] 48, 549.