

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

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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.

less than 5 mols of water of crystallization. It was the purpose of the experiments to be described in this paper to determine the composition of these different forms, as well as their solubility at different temperatures. The solubility determinations above all are of prime importance to the complete understanding of the phenomena of supercooling discussed in the previous paper, because from a knowledge of these data it is possible to determine at what temperatures a given form is stable or metastable with regard to another, since the metastable form must always have the greater solubility. The temperature at which the solubilities of two forms become the same is the transition point for those two forms, at which they become equally stable, and may exist indefinitely long in contact with one another.

Although the work has not been entirely completed, that which has been done has such direct bearing on the results of the work described in the previous paper that it seems well worth while to publish it at this time.

(I) DETERMINATIONS OF COMPOSITION.

The determination of the composition of any of the metastable forms of sodium thiosulphate offers very considerable difficulties. Under ordinary conditions all other forms are metastable in respect to the α , that is, the commercial salt, and upon the slightest inoculation with this, any one of them is readily and rapidly converted into the α . How, then, to remove any one of the metastable forms from the solution out of which it had crystallized, and to dry it so that any reliable determinations of its composition could be made was a very considerable problem. A number of methods were tried, including centrifuging under such conditions that the salt was protected as well as possible from inoculation. But the results were of no value, being irregular and not approximating to any rational formula. In all cases there was ample evidence that the samples had become converted to the α , undoubtedly mixed in some cases with some lower hydrate or with the anhydride.

Finally the attempt was made to dry the salts at temperatures above the melting-point of the α , *i. e.*, at above 49° . The temperature chosen for the drying was 55° , at which temperature it was naturally impossible for any α to form. Of course, this did not preclude the possibility of some other transformation

taking place. No difficulty was experienced from such sources with the *b*, but with the *a* only approximate results could be obtained, as will be shown.

Composition of β.—No determination of the composition of this was made. Its formation by complete solidification of the fused *a* and its conduct as a chemical individual are sufficient to show it to be a pentahydrate. And furthermore, Parmentier and Amat,¹ who obtained the substance from solutions, analyzed it and concluded that such was the case.

Composition of γ.—There is every reason to believe that the *γ*-form is also a pentahydrate,² although no analysis has as yet been obtained. Being stable only at temperatures in the neighborhood of 0° and below, special devices must be resorted to in working with it. We hope to get direct evidence as to its composition in the future.

Composition of α.—Samples of *a* were obtained by filling a large test-tube two-thirds full of molten *a* and then drawing off the top and sealing it. The whole was then immersed in water near the boiling-point for about fifteen minutes. After several days the large crystals of *a* appeared and after further standing acquired their maximum size. They were accumulated near the bottom of the tube, and adhered rather firmly to the wall so that, on inverting, the crystals remained above the mother-liquor, and could thus be thoroughly drained. The tube was then opened in the inverted position, the tip being kept under water, by which the heavier mother-liquor was replaced by pure water. A bath at 55° was held in readiness and the tube removed from the water, held sufficiently long for most of the water to run out, then brought to the upright position and immersed to the neck in the 55°-bath. This accomplished, all danger of inoculation by *a* is past. A glass tube connected with the suction was introduced into the tube to facilitate drying, which was carried on until the crystals began to show signs of efflorescence at the edges. Samples were then removed, weighed, and titrated with standard iodine solution. From these data was calculated the number of molecules of water to one of thiosulphate. The values found were: I, 1.213; II, 1.132; III, 1.191; IV, 1.110—corresponding fairly closely to the formula $\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$. It seems likely that

¹ *Ber. d. chem. Ges.* 17 (3), 198.

² See previous paper, p. 1390.

partial transformation to *b* may have occurred during the treatment, and it is doubtful if better results can be obtained without great expenditure of time.

Composition of b.—The composition of *b* was determined the same way as that of *a*, except that it was not necessary to seal the tube, a good rubber stopper being in this case sufficient. This was because of the relatively short time that it was necessary to wait for the deposition of the crystals, which, with the *b*, was sufficiently complete in half an hour. In order to obtain the *b* crystals the fusion of the *a* was never carried above 55° , as it had been shown in the previous work that such fusions were most favorable for the production of *b*. Otherwise the drying and analysis were carried out as above. Two determinations gave the number of molecules of water to one of thiosulphate as follows: I, 2.003; II, 2.006. The substance is thus a dihydrate, having the formula $\text{Na}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$.

Composition of c.—No determinations have as yet been made.

Composition of d.—Only a single determination of the composition of *d* is at hand, and that was made in a rather crude manner. When it was first noticed that there was such a substance formed by the partial fusion of β , a portion was hastily taken, thrown on clean filter-paper, rapidly pressed out, a sample taken and titrated. The result obtained was 4.18 molecules water to 1 of thiosulphate, which would seem to indicate that the substance was a tetrahydrate. If the *d* is a tetrahydrate, then the trihydrate formula would be the only one left for the *c*, unless this should contain a fractional number of molecules of water, or be dimorphic with some of the other forms. Our information is too incomplete to enable us to draw any definite conclusions, as yet, and these uncertain compounds will be further investigated.

(2) DETERMINATIONS OF SOLUBILITY.

The determinations of the solubility of the sodium thiosulphate in its various forms were made in the usual manner, by placing suitable amounts of water and commercial thiosulphate in tubes of about one-half inch internal diameter, sealing in the flame, giving such treatment as to produce the desired form, and then rotating in the thermostat at the desired temperature until saturation was attained, sampling and analyzing. Preliminary determinations showed that saturation was very quickly reached, *i. e.*,

after about fifteen minutes or so. In the actual determinations, however, no measurements were made on tubes that had not been rotated for at least an hour. Preliminary determinations were also made with both supersaturated and undersaturated solutions, but as both gave identical results in a very short time it was not in general the practice to make determinations in both ways.

When everything was ready for the determination the tube was removed from the rotating device and placed in a holder fastened in the thermostat tank, so that the top of the tube projected somewhat above the water. A cut was then made and the top broken off. The samples were taken in a small weighed pipette, weighed and titrated with standard iodine. In order to avoid taking up small crystals with the solution, a piece of small rubber tubing, about one inch long, was attached to the tip of the pipette and a wad of cotton wool packed fairly tightly into it. This served as a filter.

Solubility of the α .—This was naturally the easiest of all the forms to work with, being the most stable. All that was necessary was the filling and rotating of the tubes, the sampling and analysis. The results are given in Table I. In the last column are given the

TABLE I.—SOLUBILITY OF α -SODIUM THIOSULPHATE.
(Commercial pentahydrate.)

Tempera- ture.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 solution.	Average.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 H_2O .	Mulder's results.
10°	37.38			
10°	37.37	37.38	59.69
10°	37.38			
20°	41.20			
20°	41.17	41.20	70.07	69.00
20°	41.23			
25°	43.17			
25°	43.06	43.15	75.90	75.00
25°	43.21			
30°	45.19			
30°	45.24	45.19	82.45	82.00
30°	45.13			
35°	47.70			
35°	47.71	47.71	91.24	89.00
35°	47.71			
40°	50.84			
40°	50.79	50.83	103.37	98.00
40°	50.85			
45°	55.32			
45°	55.35	55.33	123.87	109.00

results of Mulder,¹ which show fair agreement with ours, except at higher temperatures. As the original of Mulder's paper is not accessible to us, we do not know just what his method may have been, but probably it was the usual method of those times in which flasks containing the substances were shaken occasionally at the desired temperatures, and then portions poured off through filters held at, nearly as possible, the same temperature.² If this were the case, it would readily account for his low results, particularly at high temperatures.

Solubility of β .—In order to obtain tubes containing β and solution we always started with a and water. These were sealed up in the tubes, and heated to 100° and then cooled to force the crystallization of β . In doing this two difficulties were encountered. In the first place the tubes all showed a marked tendency toward the formation of γ instead of β . This seems characteristic of tubes containing an excess of water. In the majority of cases the γ -tubes went over into β on long standing, although some were very persistent in the γ -form. The second difficulty arose from the very great temperature coefficients of the solubility, and from the fact that the β crystallized out in very fine needles. This made it very difficult to judge of the amount of water which should be added in order that a given tube might be worked with at a given temperature. A very small quantity of the β -crystals is sufficient to make a stiff broth of the whole solution, so small an amount, in fact, that by raising the temperature 2° the solubility will have increased to an extent sufficient to carry the broth over into a clear solution. Of course, samples can be taken only from tubes that, at a given temperature, lie between these two conditions, so that the difficulty of obtaining a tube that can be used at a given temperature becomes considerable.

A further difficulty is met with in taking the sample (and this is true of all other forms than the a) in that the solution, being supersaturated in respect to a , is likely to become inoculated with that salt and thus render the tube worthless. The difficulty was, to a great extent, avoided by keeping the pipettes in an air-bath at 60° for some time before using, and working with great rapidity after a tube was opened. Transformation to a after the pipette is once filled is, of course, of no importance. Results with β are given in Table II.

¹ Scheik. Verh., 1864, p. 84.

² See Kremers: Pogg. Ann., 94, 271.

TABLE II.—SOLUBILITY OF β -SODIUM THIOSULPHATE.
(Pentahydrate.)

Temperature.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 solution.	Average.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 H_2O .
20°	49.34		
20°	49.39	49.38	97.55
20°	49.40		
25°	52.11		
25°	52.26	52.15	108.98
25°	52.09		
28°	54.49		
28°	54.48	54.48	119.69
29.5°	55.85	55.85	126.50
30°	56.58		
30°	56.68		
30°	56.62	56.57	130.26
30°	56.57		
30°	56.53		
30°	56.53		

Solubility of a.—The tubes for this purpose were prepared by sealing up the commercial salt without water, heating for a few minutes in boiling water and allowing to stand a few days until the *a* appeared. With such tubes, determinations could be made up to 30° only, since at that temperature the saturated solution of the *a* has the composition of a pentahydrate. The results obtainable were, however, sufficient for present purposes. The data are given in Table III.

TABLE III.—SOLUBILITY OF α -SODIUM THIOSULPHATE.
(Monohydrate.)

Temperature.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 solution.	Average.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 H_2O .
20°	62.03		
20°	62.20	62.11	163.92
20°	62.10		
25°	62.76		
25°	62.71	62.73	168.32
30°	63.54		
30°	63.53	63.53	174.20

Solubility of b.—The tubes for these determinations were obtained by fusing the *a* in tubes, without water, and allowing the temperature to rise no higher than 55°. In this way the *a* was entirely destroyed and the residual crystals of *b* caused rapid crystallization as the tubes cooled. The results are given in Table IV.

TABLE IV.—SOLUBILITY OF *b*-SODIUM THIOSULPHATE.
(Dihydrate.)

Temperature.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 solution.	Average.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 H_2O .
20°	55.15		
20°	55.16	55.15	122.68
25°	55.97		
25°	56.05	56.03	127.43
25°	56.06		
30°	57.17		
30°	57.11	57.13	133.27
30°	57.11		
35°	58.18		
35°	58.11	58.13	138.84
35°	58.10		
40°	59.16		
40°	59.19	59.17	144.92
50°	62.23		
50°	62.32	62.28	165.11
50°	62.30		

Solubility of d.—The solubility curve of this substance was obtained by simply carrying tubes containing β to temperatures above its transition point into saturated solution and *d*. The results are given in Table V. It was found impossible to carry out any determinations below the transition point, as supercooling of *d* in respect to β does not seem to occur.

TABLE V.—SOLUBILITY OF *d*-SODIUM THIOSULPHATE.
(Probably tetrahydrate.)

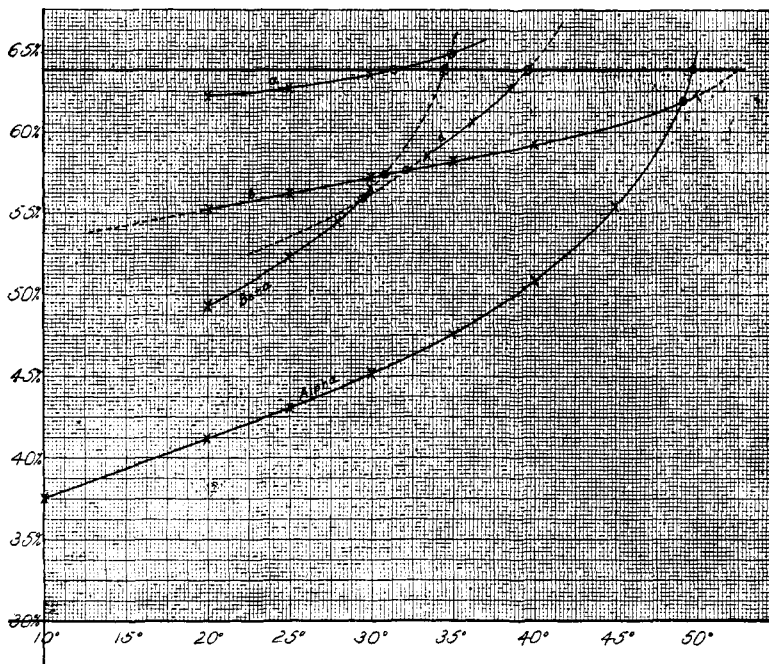
Temperature.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 solution.	Average.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 H_2O .
33.5°	58.55		
33.5°	58.64	58.59	141.48
36.2°	60.51		
36.2°	60.54	60.51	153.23
36.2°	60.49		
38.6°	62.84		
38.6°	62.71	62.80	168.82
38.6°	62.85		

Solubility of γ and c.—No data have been obtained as yet.

(3) THE SOLUBILITY CURVES.

In the accompanying set of curves the solubility data, above given, are plotted. The \times marks actual determinations, or rather

the average of these, while transition points and points of complete solution in pentahydrate fusions are marked with circles. The dotted lines are extrapolated. The horizontal line just below 64 per cent. is the line of composition of pentahydrate. As all of our determinations were made with samples containing at least as much water as the pentahydrate, this line forms the limit of all of these determinations. Determinations at still higher concen-



trations of the lower hydrates are under way. The point at which the solubility curve for any pentahydrate cuts this line will evidently be the true melting-point of the pentahydrate. The curves show that the true melting-point of neither the *a* nor the *β* can be reached without passing transition points, *i. e.*, without passing through a superheated state. Neither of these melting-points seems to be practically attainable. The two transition points into lower hydrates are readily seen from the diagram.

An interesting relationship is noticed in connection with the curves for the *b* and the *d*. A transition point is shown at about

31.7° between these two hydrates in contact with saturated solution in such a way that d is stable at lower and b at higher temperatures. The range for the stable existence of the d is thus limited to the range of temperature lying between 30° and 31.7° , but d was observed and its solubility measured at temperatures as high as 38.6° . Thus between 31.7° and 38.6° the d exists in a superheated state. As is well known, this is a very rare phenomenon. It is possible that, since the three transition points at 30° , 30.5° and 31.7° lie so close together, we have been deceived as to their exact location, but this seems hardly probable.

The chief value of the curves at present is that they define very exactly the fields of supersaturation and supercooling for the forms already studied. To interpret the curves briefly, we see that at temperatures below 31.5° (on a curve) a fused pentahydrate is supersaturated or supercooled in respect to all forms considered in this paper. Above 31.5° supersaturation in regard to a ceases. At 34.5° supercooling in regard to β ceases, while above 39.5° , 49.5° and 53° supercooling or supersaturation as to d , a and b , respectively, ceases. The detailed interpretation need not be given here, as any one interested can make it for himself.

We shall extend the investigation to all the remaining forms, including the anhydride.

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A STUDY OF REVERSIBLE OXIDATION AND REDUCTION REACTIONS IN SOLUTIONS.

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INFLUENCE OF THE CONCENTRATIONS OF THE COMPONENTS UPON THE EQUILIBRIUM IN ACIDIFIED SOLUTIONS OF IODINE, POTASSIUM FERROCYANIDE, POTASSIUM FERRICYANIDE AND POTASSIUM IODIDE.

THE investigation here described was undertaken for the purpose of studying a reversible oxidation reaction in solution. The reaction used was selected on the basis of the following considerations:

- (1) The action should be simple.