

equivalent of silver. There is also a memoir by Reuterdahl¹ on electrochemical equivalents and atomic weights.

Makower² has attempted to determine, from their rates of diffusion, the molecular weights of the radium and thorium emanations. For the radium emanation he finds the values 85.5, 97, and 99, assuming the substance to be monatomic. The thorium emanation is but slightly different. Makower suggests that the emanation may fill the vacant place in the periodic table between molybdenum and ruthenium. The atomic weight of radium itself has been discussed by Jones,³ who, from a critical examination of all the evidence, is inclined to favor the higher of the two rival values, namely, $Ra = 258$.

On the calculation of atomic weights, there is an interesting paper by J. Meyer.⁴ An important suggestion by Luther⁵ is to refer combining weights, through the aid of Faraday's law, to the C. G. S. system of units. In this way the question of standards might be settled, and a rational table devised.

FURTHER STUDIES ON THE HYDRATES OF SODIUM THIOSULPHATE.

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INTRODUCTION.

IN A previous paper⁶ we gave an account of some investigations upon the solubility and composition of some of the hydrates of sodium thiosulphate. Since that time we have completed the study of the hydrates there mentioned, and also have discovered and investigated a number of new hydrates. This paper contains the results of this work, as well as a considerable number of observations upon the supercooling, superheating, and transitions of the various substances.

THE VARIOUS HYDRATES, THEIR PREPARATION AND COMPOSITION.

Following is a list of the hydrates of sodium thiosulphate, together with descriptions of the methods of their preparation,

¹ Trans. Amer. Electrochem. Soc. 7, 187.

² Phil. Mag. [9] 9, 56.

³ Am. Ch. J. 34, 467.

⁴ Z. anorg. Chem. 43, 242.

⁵ Z. Elektrochem. 11, 273.

⁶ This Journal, 26, 1413.

and later, experimental data regarding their composition. The classification and nomenclature used in this paper are based upon a definite system. This system cannot well be explained until after the experimental data have been considered. One point must however be made clear, namely, when, for example, a tetrahydrate is spoken of as "secondary" tetrahydrate, it does not follow that a primary, or any other tetrahydrate is known. The adjective is used simply to indicate certain affiliations of the hydrate, which will be explained later.

(1) Primary pentahydrate, formerly called α -pentahydrate. This is the ordinary commercial salt and is stable at all temperatures below 48.2° . It forms spontaneously from any of the other forms when they are cooled to about -35° , for in working with these other forms we had occasion to immerse sealed tubes containing them in liquid ammonia, and found that this treatment caused the formation of the primary pentahydrate in every case. So long as the tubes remained in the liquid ammonia no change could be observed, but as soon as they were taken out and warmed up, the primary pentahydrate would start and grow rapidly through the mass of crystals and solution contained in the tubes. The explanation of this is that the crystals start at the lower temperature, but grow extremely slowly. The rate of growth increases rapidly with the temperature and soon becomes very great. All the forms gave the same result, and a very brief immersion in the liquid ammonia was sufficient to start them over. The primary pentahydrate crystals belong to the monoclinic system.¹ We have not determined the crystalline structure of any of the other hydrates on account of the impossibility of handling them except in sealed tubes.

(2) Primary dihydrate (α -dihydrate), originally called *b*.² This is the stable form between 48° and 65° , and may be readily obtained by fusing the commercial salt and holding the fusion at a temperature of from 50 – 55° until crystallization starts. The crystals are coarse needles resembling those of the primary pentahydrate.

(3) Secondary pentahydrate, formerly called β -pentahydrate. For preparation see Young and Mitchell.³ This form exists in

¹ Dammer: Handb. anorg. Chem. II, 2, 163.

² Young and Mitchell: This Journal, 26, 1391.

³ Loc. cit.

long fine needles which, upon standing, undergo a peculiar slow transformation. The opaque mass of fine crystals gradually becomes clearer and in some cases perfectly transparent, to the eye resembling a very clear jelly. Its other properties remain unchanged. If partially melted and allowed to solidify, it comes down in fine needles, as at first.

(4) Secondary tetrahydrate, originally called *d*. Formed from secondary pentahydrate on heating to above 30° , the crystals resembling those of the pentahydrate very closely.

(5) Secondary monohydrate (α -monohydrate), formerly called *a*. Besides forming spontaneously in supercooled fusions of the pentahydrates,¹ it forms in solutions of anhydride at temperatures below 50° , and in solutions of the secondary tetrahydrate above about 41° . It grows very slowly even from concentrated solutions, the crystals being either long coarse needles, or small seemingly rectangular prisms, the habit depending on the conditions under which the crystallization occurs.

(6) Tertiary (acts also as quaternary) hexahydrate. This form was originally misnamed γ -pentahydrate and the method of its preparation is given under that name.² Prepared, as it usually was when first discovered, from fused pentahydrate, it came down as a white opaque mass. This mass is, of course, not pure hexahydrate but presumably a mixture of hexahydrate and anhydride. If prepared from a solution containing sufficient water, very hard transparent crystals are obtained.

(7) Tertiary sesquihydrate. This hydrate was discovered in a rather peculiar manner. In attempting to investigate the conduct of the mixture of hexahydrate and anhydride, formerly called γ -pentahydrate, in the neighborhood of the melting-point of the hexahydrate, some tubes containing this mixture were rotated in the thermostat, the temperature being raised only one-tenth of a degree at a time, and held at each temperature for two hours, it was noticed that at about 14.2° the mixture seemed to soften up a little. As it did not melt to more than a very slight degree with the gradual rise in temperature, some of the tubes were taken out and examined. The crystals found in the tubes were very fine needles, resembling those of the four-thirds-hydrate, but somewhat finer. Their rate of growth was much

¹ Young and Mitchell: Loc. cit.

² Ibid.

greater than that of the four-thirds-hydrate crystals, and they seemed to fill the mother-liquor even more completely.

(8) Tertiary monohydrate (β -monohydrate). This hydrate is formed from the tertiary sesquihydrate by transition at a little below 50° . The crystals resemble those of the secondary monohydrate.

(9) Quaternary four-thirds-hydrate ($3\text{Na}_2\text{S}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$) originally called *c*.¹ Besides forming from the hexahydrate on heating to about 15° , it sometimes forms spontaneously in supercooled solutions of anhydride. The crystals appear as fine needles, and if the solution is at all concentrated it becomes filled with them, and appears to be almost completely solidified, when in reality the crystals form but a small proportion of the total mass.

(10) Quintary dihydrate (β -dihydrate). This hydrate is formed from the four-thirds-hydrate by transition at temperatures slightly above 0° . Little is known about this transition, which was discovered in the following manner: Some tubes of the four-thirds-hydrate having been allowed to stand in ice-water for several days, it was found when they were taken out, that several had gone over into this new form. It crystallizes in very thin radiating plates, and is readily recognized when it first comes down. On standing, however, the plates thicken up and lose their distinctive character.

(11) Quintary monohydrate (γ -monohydrate). This hydrate is formed by heating the quintary dihydrate to temperatures above 35° . The crystals resemble those of the other monohydrates.

(12) Quintary hemihydrate. This is formed by heating the quintary monohydrate to temperatures above 50° . The crystals also resemble those of the monohydrates.

(13) Anhydride. The anhydride is very easily prepared as it is the stable form above 70° . The crystals appear to be rectangular prisms.

The composition of the different hydrates was determined in various ways, as was most convenient in the particular case. Following are the data concerning the composition, the hydrates being listed in the same order as above. For the determinations of the composition of the starred hydrates, see Young and Burke.²

¹ Young and Mitchell: Loc. cit.

² This Journal, 26, 1413.

(1) Primary pentahydrate, long known in the literature as a pentahydrate.

(2) Primary dihydrate.*

(3) Secondary pentahydrate.*

(4) Secondary tetrahydrate.* In addition to the direct determination of the composition of this hydrate, the fact that the solubility curve (see chart) meets the line of tetrahydrate composition at a right angle shows this substance to be a tetrahydrate.

(5) Secondary monohydrate.*

(6) Tertiary hexahydrate. The composition of this hydrate was determined in the following manner: A solution containing 59.4 per cent. of anhydride was prepared; tubes containing this solution were inoculated with crystals of the hexahydrate and when about one-half of the solution had crystallized, the composition of the remaining liquid was determined, and found to be the same as at the beginning. The crystals therefore had the same composition as the solution, whence the formula, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$.

(7) Tertiary sesquihydrate. The composition of this hydrate, and of all the succeeding ones, was determined in the following manner: Crystals of the desired modification were prepared in small glass tubes, about 7 mm. internal diameter and 10 cm. long, (Fig. 1, *a*); the major portion of the mother-liquor was removed from these tubes by placing the tips under water, and forcing in air through a fine glass tube. The constricted tip of the tube was then washed out with wet cotton, and heated in the flame until only a very small opening was left. This was necessary in order that the fine crystals should not be thrown out in the subsequent treatment. In order to guard against inoculation from floating particles, the brass cap *b* was placed over the open tip, being joined air-tight by means of the rubber band *c*. During the time that the caps and bands were not in use, they were kept under water, in order that they might not collect solid particles which would cause inoculation.

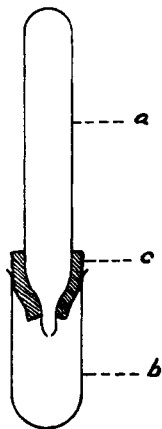


Fig. 1.

The tubes thus prepared were then placed in the holders of a

centrifugal machine and rotated for fifteen minutes. The machine gave 2500 revolutions per minute, and an effective radius of 6 inches. After centrifuging, the tubes were removed, weighed samples taken, and titrated with standard iodine solution.

To determine approximately the error introduced by the adhering mother-liquor, analyses were first made upon a known form, namely, the primary dihydrate. Following are the results obtained:

	Per cent. $\text{Na}_2\text{S}_2\text{O}_3$.		Per cent. of solution retained by crystals.
	Theoretical.	Found.	
(1)	81.43	77.76	13.90
(2)	81.43	78.50	11.10
(3)	81.43	77.91	13.30
			Average, 12.80

The large amount of solution retained by the crystals is due to the fact that small crystals were used, and to the very high viscosity of the solutions. In order to obtain comparative results, small crystals were always used, for while with some forms large crystals may be obtained, this is almost impossible with others. In making corrections it was assumed that the percentage of mother-liquor retained was always the same. The composition of the liquor was known in each case from solubility data.

Following are the results for the sesquihydrate: In this case as in all the following ones there is given under A the percentage of $\text{Na}_2\text{S}_2\text{O}_3$ found; under B this value as corrected from the data on primary dihydrate; under C the theoretical value corresponding to the given formula:

A.	B.	C.
81.60	84.90
82.37	85.70	85.41
82.21	85.60

(8) Tertiary monohydrate.

A.	B.	C.
86.48	89.40	89.80
86.32	89.30

(9) Quaternary four-thirds-hydrate.

A.	B.	C.
83.77	87.10
83.33	86.70	86.82
83.64	86.90

(10) Quintary dihydrate.

A.	B.	C.
80.11	82.80
80.24	82.90	81.43
80.26	82.90

These determinations are seen to be abnormally high in case of the quintary dihydrate. This may be due to either one of two reasons: (1) The substance may be a hydrate of the composition $5\text{Na}_2\text{S}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$, containing 82.99 per cent. of anhydride; (2) it may be that on account of the form of the crystals, less solution was retained than in the other cases. This hydrate crystallizes in large thin plates, which would be expected to retain less mother-liquor than the finer, needle-like crystals of the other hydrates. On the whole we are inclined to think that the substance is a dihydrate.

(11) Quintary monohydrate.

A.	B.	C.
85.41	88.70	89.80
86.24	89.50

(12) Quintary hemihydrate.

A.	B.	C.
91.22	94.80	94.62
91.49	95.10

(13) Anhydride.

A.	B.	C.
96.03	100.20	100.00
97.79	102.10

Thus there are at present known thirteen crystalline forms of sodium thiosulphate, namely, one anhydride, one hemihydrate, three monohydrates, one four-thirds-hydrate, one sesquihydrate, two dihydrates, one tetrahydrate, two pentahydrates and one hexahydrate.

SOLUBILITY DETERMINATIONS.

Following are determinations of the solubility of the various hydrates mentioned in the previous paper¹ at temperatures not investigated at that time, also solubility determinations for the newer hydrates above mentioned. This work completes the data as to the solubility of all the known forms throughout their various ranges of existence, in so far as these ranges are included between the temperatures of 0° and 80° . Determinations were made at 5° intervals for all forms, except that in some cases

¹ Loc. cit.

determinations were made at smaller intervals, this being occasionally necessary in order to follow the course of the solubility curves more accurately.

(1) *The Method*.—In all essentials the method used was the one described in the previous paper. Several modifications of the details have, however, been introduced, and these will be described here.

(a) *The Thermostats*.—It was of course necessary to have thermostats which not only allowed of accurate and simple regulation, but which could also be readily changed from one temperature to another, over a wide range. For this purpose two well insulated copper tanks were prepared, and fitted with the usual gearing. The ordinary toluene regulator arranged for electrical contact was used. A supply of water from an external source was the thermal agent employed, hot water being used for the higher, and cold water for the lower temperatures. For higher temperatures the regulation was accomplished as follows: The regulator being set for the desired temperature, hot water from a tank was allowed to flow in through a thin rubber tube; this raises the temperature of the water in the thermostat until the mercury in the regulator makes contact with the adjustable platinum point, closing the circuit through two accumulators in parallel and an electromagnet; the armature of this electromagnet, on being pulled down, closes a stronger current through a second, more powerful electromagnet, so arranged that its armature in closing pinches the soft rubber tube, thereby shutting off the supply of hot water. As the temperature in the thermostat spontaneously falls, the contacts are again opened, and hot water is again admitted. For lower temperatures ice-water is used, and the contacts so arranged that when the circuit is closed in the first magnet, it is broken in the second. With this device it was a simple matter to work at any temperature between 0° and 95° , excepting that at 0° it was necessary to put crushed ice in the tanks. With two tanks of this sort, fairly rapid work was possible. The following details in the manipulation are of importance: (1) The circuit operating the first electromagnet should be of the lowest possible voltage to avoid excessive sparking at the contact in the regulator, which soils the mercury. A drop of water placed on the surface of the mercury, obviates to a great extent the bad effects of sparking; (2) the hot or cold water

should be introduced into the tank as close as possible to the bulb of the regulator, for thus the regulator will feel the temperature change too quickly rather than too slowly, which is favorable to accurate regulation; (3) the accuracy of regulation is increased by avoiding too great a difference of temperature between the water in the tank and the supply water. With this apparatus under favorable conditions, the fluctuations in temperature were so small as to be scarcely observable with a Beckmann thermometer.

(b) *Preparation of the Tubes.*—Originally the tubes were prepared by placing in them suitable amounts of water and thiosulphate, sealing them off and subjecting them to such round-about treatment as would yield the desired form. With some of the forms this was very laborious, and the following method was devised: The requisite thiosulphate and water were put into the tube and the open end closed with a wad of wet cotton; the tubes were then heated in a water-bath until complete solution and sterilization were accomplished: they were then cooled, and crystals of the desired form introduced on the end of a wet glass rod, and finally the tip was sealed off. It was found that the cotton wad was ample protection against inoculation so long as it remained wet.

(c) *The Standard of the Iodine Solution.*—This was determined daily by the anhydrous sodium thiosulphate method.¹ Occasionally a check was made by running a solubility determination of the primary pentahydrate at some temperature at which the solubility had been previously accurately determined.

(d) *The Pipette.*—The pipette used is shown at a Fig. 2. It is easily made from an ordinary 1 or 2 cc. pipette, and possesses many advantages over the forms usually employed for such work. The sample is sucked up wholly into the bulb, and the weighing made by suspending the pipette in a horizontal position by means of the wire b. At lower temperatures, where the introduction of the hot, sterilized pipette might introduce con-

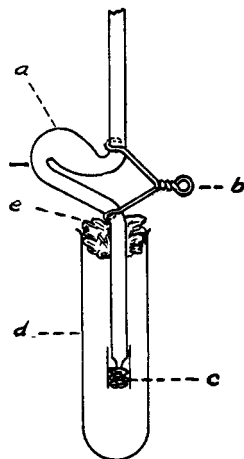


Fig. 2.

¹ Young: This Journal, 26, 1028.

siderable errors, the tip of the pipette with its attached cotton-wool filter, *c*, was placed in a small test-tube, *d*, whose neck was packed with cotton-wool, *e*. After sterilization in an air-bath, it was removed and allowed to cool with the test-tube still attached. Kept in this condition it would remain sterile until needed.

(2) *Solubility Data*.—In the following determinations of solubility, two-tenths per cent. was taken as the maximum allowable variation between parallels. However in relatively few cases is the error much greater than one-tenth, and when required, as in cases where it was necessary to distinguish points on two very close-lying curves, it was found possible by taking special precautions, to reduce this error to considerably less than one-tenth.

TABLE I.—SOLUBILITY OF PRIMARY PENTAHYDRATE.

Temperature.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of solution.	Average.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of H_2O .
0°.....	33.35, 33.44	33.40	50.15
5°.....	35.34, 35.32	35.33	54.64
10°.....	37.36	37.37 ¹	59.66
15°.....	39.09, 39.13	39.11	64.22

¹ For additional data at 10°, as well as data from 20° to 45°, see previous paper: Loc. cit. Melting-point is at 48.45°. Transition-point into primary dihydrate is at 48.17°.

TABLE II.—SOLUBILITY OF PRIMARY DIHYDRATE.

Temperature.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of solution.	Average.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of H_2O .
0°.....	52.68, 52.76, 52.76	52.73	111.60
5°.....	53.40, 53.46, 53.48	53.45	114.90
10°.....	53.95, 53.88, 53.98	53.94	117.10
15°.....	54.62, 54.62	54.62	120.40
35°.....	58.16, 58.18, 58.21, 58.10, 58.11	58.15	139.00
40°.....	59.33, 59.32, 59.48	59.38	146.20
45°.....	60.71, 60.75	60.73	154.70
55°.....	63.83, 63.87	63.85	176.60
60°.....	65.66, 65.70	65.68	191.30
65°.....	68.03, 67.98, 68.10	68.04	212.90

For data at 20°, 25° and 30° see previous paper. Data at 35° taken in part from previous paper. New data at 40° C. substituted for that in the previous paper. Transition point into anhydride at 66.5°.

TABLE III.—SOLUBILITY OF SECONDARY PENTAHYDRATE.

Temperature.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of solution.	Average.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of H_2O .
0°.....	41.87, 42.06	41.96	72.30
5°.....	43.54, 43.59	43.56	77.17
10°.....	45.25, 45.25	45.25	82.65
15°.....	47.12, 47.27	47.19	89.36

For data from 20° to 30° see previous paper. Transition point into secondary tetrahydrate is at 30.22° C.

TABLE IV.—SOLUBILITY OF SECONDARY TETRAHYDRATE.

(See Table V in previous paper.) Transition point into secondary monohydrate at 40.65° . Melting-point at 41.65° .

TABLE V.—SOLUBILITY OF SECONDARY MONOHYDRATE.

Temperature.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of solution.	Average.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of H_2O .
0°	60.43, 60.46, 60.53	60.47	153.00
5°	60.75, 60.75, 60.73	60.74	154.70
10°	61.03, 61.06	61.04	156.70
15°	61.56, 61.51, 61.65	61.57	160.20
20°	62.03, 62.20, 62.10	62.11	163.90
25°	62.76, 62.71	62.73	168.30
30°	63.54, 63.53, 63.53, 63.63	63.56	174.40
35°	64.27, 64.30, 64.39	64.32	180.20
40°	65.16, 65.25, 65.25	65.22	187.60
45°	66.04, 66.07, 65.95	66.02	194.30
50°	66.79, 66.86	66.82	201.40
55°	67.86, 67.94	67.90	211.50

Data at 20° , 25° and 30° taken in part from previous paper. Transition point into anhydride at 56.5° .

TABLE VI.—SOLUBILITY OF TERTIARY (AND QUATERNARY) HEXAHYDRATE.

Temperature.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of solution.	Average.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of H_2O .
0°	46.12, 46.17	46.14	85.67
5°	48.41, 48.48	48.44	93.95
10°	51.63, 51.70	51.66	106.80
13°	54.92, 54.92, 54.98, 55.03	54.96	122.00

Melting-point at 14.35° . Transition point into the quaternary four-thirds-hydrate at 14.3° , and into tertiary sesquihydrate at 14.25°C .

TABLE VII.—SOLUBILITY OF TERTIARY SESQUIHYDRATE.

Temperature.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of solution.	Average.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of H_2O .
0°	57.40, 57.45	57.42	134.80
5°	57.80, 57.89	57.84	137.20
10°	58.26, 58.31	58.28	139.70
15°	58.79, 58.82	58.80	142.70
20°	59.27, 59.30	59.28	145.60
25°	60.17, 60.19	60.18	151.10
30°	60.77, 60.80	60.78	155.00
35°	61.53, 61.62	61.57	160.20
40°	62.53, 62.67	62.60	167.40
45°	63.97, 63.97, 63.98	63.97	177.50
47.5°	64.65, 64.71	64.68	183.10

Transition point into tertiary monohydrate at 48.5° .

TABLE VIII.—SOLUBILITY OF TERTIARY MONOHYDRATE.

Temperature.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of solution.	Average.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of H_2O .
47.5°	64.74, 64.83	64.78	183.90
50°	65.25, 65.28, 65.34, 65.35	65.30	188.20
52.5°	65.86, 65.92	65.89	193.20
55°	66.42, 66.46, 66.48	66.45	198.10
60°	68.05, 68.10	68.07	213.10

Transition point into anhydride at 61°.

TABLE IX.—SOLUBILITY OF THE QUATERNARY FOUR-THIRDS-HYDRATE.

Temperature.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of solution.	Average.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of H_2O .
0°	57.63, 57.64	57.63	136.00
5°	58.05, 58.11	58.08	138.60
10°	58.45, 58.45, 58.56	58.49	140.90
15°	58.98, 58.95, 59.00, 59.07	59.00	143.90
20°	59.54, 59.61	59.57	147.30
25°	60.30, 60.40	60.35	152.20
30°	60.98, 60.99, 61.06, 61.09	61.03	156.60
35°	61.90, 61.93, 61.95, 61.97	61.94	162.80
40°	62.91, 62.96, 62.98	62.95	169.90
45°	64.18, 64.26	64.22	179.50
50°	65.48, 65.42	65.45	189.50
55°	67.07, 67.08	67.07	203.70

Transition into anhydride at 58°.

TABLE X.—SOLUBILITY OF QUINTARY DIHYDRATE.

Temperature.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 in solution.	Average.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of H_2O .
0°	57.61, 57.65	57.63	136.00
5°	58.20, 58.26	58.23	139.40
10°	59.02, 59.09	59.05	144.20
15°	60.01, 60.03	60.02	150.10
20°	61.02, 61.02	61.02	156.50
25°	62.27, 62.33	62.30	165.30
30°	63.54, 63.54, 63.56, 63.62	63.56	174.40
35°	65.27, 65.28	65.27	188.00

Transition point into quintary monohydrate at 27.5°.

TABLE XI.—SOLUBILITY OF QUINTARY MONOHYDRATE.

Temperature.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of solution.	Average.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of H_2O .
30°	63.30, 63.33, 63.39	63.34	172.80
35°	64.04, 64.10	64.07	178.40
40°	64.71, 64.76, 64.78	64.75	183.70
45°	65.55, 65.61	65.58	190.50
50°	66.53, 66.64, 66.56	66.58	199.20
55°	67.59	67.59	208.50

Transition point to quintary hemihydrate at 43°.

TABLE XII.—SOLUBILITY OF QUINTARY HEMIHYDRATE.

Temperature.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of solution.	Average.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of H_2O .
25°.....	64.21, 64.22	64.21	179.40
35°.....	64.59, 64.62	64.60	182.50
40°.....	64.95, 64.97, 65.04	64.99	185.60
45°.....	65.58, 65.61, 65.63	65.61	190.80
50°.....	65.94, 66.01, 66.07, 66.07	66.02	194.30
55°.....	66.55, 66.55, 66.61	66.57	199.10
60°.....	67.32, 67.48	67.40	206.70
65°.....	68.22, 68.26	68.24	214.90
70°.....	69.04, 69.08	69.06	223.20

Transition point into anhydride at 70°.

TABLE XIII.—SOLUBILITY OF ANHYDRIDE.

Temperature.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 in solution.	Average.	Parts $\text{Na}_2\text{S}_2\text{O}_3$ in 100 of H_2O .
40°.....	67.38, 67.42	67.40	206.70
45°.....	67.57, 67.63	67.60	208.60
50°.....	67.75, 67.78	67.76	210.20
55°.....	68.14, 68.16	68.15	214.00
60°.....	68.45, 68.52	68.48	217.30
65°.....	68.77, 68.84	68.80	220.50
70°.....	69.04, 69.05, 69.07	69.05	223.10
75°.....	69.29, 69.42	69.35	226.30
80°.....	69.85, 69.87	69.86	231.80

DIRECT DETERMINATIONS OF TRANSITION POINTS.

In addition to locating transition points by the intersections of the various solubility curves, a number of these were also directly determined. This was necessary in cases where these points could not be readily located by means of the solubility curves, as for example is the case with melting-points, with very close-lying transition points, and with forms which refuse either to superheat or supercool.

(1) *The Method.*—Most of these determinations were made in the apparatus shown in Fig. 3. This consists of a containing vessel *a*. For this a 40×170 mm. test-tube was used.

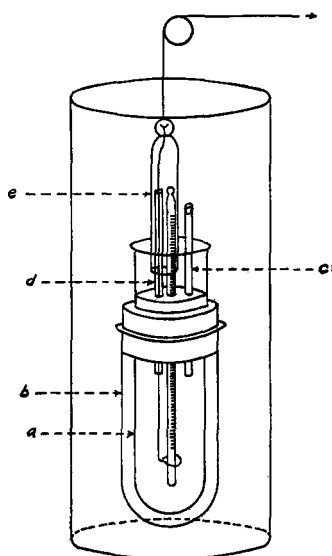


Fig. 3.

The lower part of this containing vessel was enclosed by the glass jacket *b*, into which it was fastened by means of a ring cut from A stout rubber stopper. The object of this outer air jacket was to prevent too rapid interchange of heat between the containing vessel and the surroundings. A rubber stopper was then chosen which closely fitted the bore of the containing vessel. Three holes were bored in this stopper, one of which carried the thermometer, a second carrying the short glass tube *c*. Into the third hole is introduced the glass tube *d*, through which plays the shank of the stout wire stirrer. In order that the apparatus might be operated without danger of inoculation from floating particles, the stirrer opening was protected by a water-seal. This consists simply of the glass tube *e*, into the top of which the end of the stirrer wire was sealed by means of sulphur. The glass tube *d* prevented any inflow of water through the stirrer opening. With the aid of this device a determination could be made with the apparatus completely submerged in an outer bath as shown in the figure.

The determinations were carried out in the following manner: A solution of the desired strength was placed in the containing vessel, the thermometer and stirrer placed in position, and the whole sterilized by submerging in a water-bath at a temperature of from 80° to 100°, the air jacket being removed to facilitate this operation. The apparatus was then allowed to cool, and the solution inoculated through the tube *c* with the hydrate whose transition it was desired to observe. During the crystallization the stirrer was kept in operation in order that the finest possible crystals should be obtained. The air jacket was then replaced, the apparatus immersed in the constant temperature bath and mechanical stirring begun. According to the direction of the transition, the bath was kept at about 1° above or below the expected transition temperature. When the thermometer in the apparatus showed about the same temperature as the one in the bath, the mixture was inoculated with the form into which transition was to occur, the stirring was continued and temperature readings were taken at regular intervals extending over a considerable range of time.

The thermometers used were two high-grade instruments, graduated into twentieth degrees. They were compared with normal thermometers calibrated by the Reichsanstalt, and their

readings found to coincide very closely. We believe that the following determinations are probably correct to within one-twentieth degree.

(2) *The Determinations.* (a) *The Transition Secondary Pentahydrate \rightleftharpoons Secondary Tetrahydrate.*—From the indications of the solubility curves this point was expected at slightly above 30° . The first determinations were made from below, *i. e.*, upon the transition of tetrahydrate into pentahydrate. The bath was held at 29° , thus supercooling the tetrahydrate by about 1° . Upon inoculation with pentahydrate the temperature rose very rapidly to 30.20° , and remained constant at that point for thirty minutes.

In order to determine this same transition point while the reverse reaction was going on, *i. e.*, while the pentahydrate was going over into tetrahydrate, the same apparatus still at 30.20° was used, the temperature of the bath being simply raised to 31.5° . The temperature of the mixture in *a* then rose slowly to 30.25° , and remained constant for forty-five minutes. The most probable value for this transition temperature is the average of these two readings, namely 30.22° .

(b) *The Transition Primary Dihydrate \rightleftharpoons Secondary Tetrahydrate.*—From the solubility determinations this transition point was to be expected at about 31.5° . The bath was therefore held at 30° . The apparatus containing primary dihydrate and solution was placed in the bath and its temperature allowed to fall to 30.25° , *i. e.*, to a temperature just above that of the secondary pentahydrate-secondary tetrahydrate transition point, and inoculated with secondary pentahydrate. Since at this temperature the pentahydrate goes over into the tetrahydrate, this was equivalent to inoculation with the tetrahydrate itself, and much more convenient. Upon inoculation the temperature remained constant for about five minutes, and then very slowly rose to 31.45° , at which point it remained constant for one hour. A second determination made under the same conditions gave identical results. A third determination made with the bath at 31° gave as the transition point 31.48° .

As in the case of the previous transition, this transition point was also determined with the bath above the transition temperature. For this purpose the bath was held at 32° . Under these conditions the temperature rose from 31.48° (the tem-

perature reached with the bath below the transition temperature), to 31.55° , and remained constant for thirty minutes. The most probable value for this transition point is therefore 31.50° .

Since the tetrahydrate readily superheats past its transition point into primary dihydrate, another method for the determination of this transition point is possible. This consists in the inoculation of the superheated tetrahydrate with crystals of the dihydrate. Several attempts were made to determine the point by this method. On account of the long, fibrous character of the tetrahydrate crystals it is impossible to stir a solution in which more than a small percentage of them is present. Thus, in carrying out these determinations the amount of transformable substance was very limited, and consequently the heat value per gram of mixture was very small. Add to this the fact that the reaction is very slow, and it is readily seen that the method is not a good one for obtaining accurate results. In all these determinations the bath was kept at 32° . In the first few attempts small quantities of primary dihydrate were used for inoculation. Under these conditions almost no temperature change was observed. When, however, about 5 cc. of a thick broth of the dihydrate crystals was added, a very gradual fall in temperature was noted. Two determinations gave respectively as the minimum temperatures, 31.70° , and 31.65° . These results, while interesting on account of the method in which they were obtained, were not considered of sufficient accuracy to be utilized in fixing the probable value of the transition point.

(c) *The Transition Secondary Pentahydrate \rightleftharpoons Primary Dihydrate.*—It was at first thought that this point could not be experimentally realized, as it was not supposed that the secondary pentahydrate could be superheated past its transition point into tetrahydrate. However, in one of the attempts to determine the primary dihydrate-secondary tetrahydrate point by inoculating the primary dihydrate with secondary pentahydrate as above described, it was noticed that the temperature rose, but soon became stationary at a point considerably below the one expected. The bath was at 31° , and the mixture before inoculation was at 29.75° . Upon inoculation the temperature rose rapidly to 30.52° , where it remained constant for twenty minutes. In another determination the bath was at 30° , and the mixture at 29° . Upon inoculation the temperature rose rapidly to 30.40° ,

where it remained stationary for twenty-six minutes, after which it again rose slowly to 31.45° , thus giving an additional determination of the primary dihydrate-secondary tetrahydrate point. From these results it would seem largely a matter of chance whether upon inoculating primary dihydrate with secondary pentahydrate, the mixture proceeds directly to the higher point, or whether it stops either temporarily or permanently at the lower point. These results show the transition point between secondary pentahydrate and primary dihydrate to be at 30.46° .

(d) *The Melting-point of Primary Pentahydrate.*—To determine this point a quantity of the pure primary pentahydrate was placed in the transition point apparatus, melted and sterilized, cooled to 35° , placed in a bath held at 47° , and then quickly* inoculated with primary pentahydrate crystals. The temperature rose very rapidly from 35° to 48.45° , where it remained constant for several minutes. That this temperature is the true melting-point of the primary pentahydrate, and not the temperature of its transition into primary dihydrate, is shown in the following paragraph.

(e) *The Transition Primary Pentahydrate \rightarrow Primary Dihydrate.*—In the above experiment, after the temperature had remained constant for several minutes at 48.45° , it suddenly fell to 48.18° , where it again remained constant. After some time the temperature of the bath was raised 48.50° . This had no noticeable influence upon the temperature of the mixture, which remained constant at 48.18° for one hour. That this latter temperature was that of the transition primary pentahydrate-primary dihydrate can not be doubted. Still further evidence is, however, found in the results of the following experiment.

In this experiment a broth of the dihydrate crystals was brought to 42° , immersed in a bath held at 47° , and inoculated with the pentahydrate. The temperature rose rapidly to 48.17° , where it remained constant as long as observed. Thus the temperature of this transition is fixed at 48.17° .

(f) *The Melting-point of Secondary Tetrahydrate.*—A solution of the composition of the tetrahydrate was prepared from weighed quantities of pentahydrate and anhydride, sterilized, brought to 33° , placed in a bath at 39° , and inoculated with secondary pentahydrate (see under b). The temperature rose with extreme rapidity to 41.65° , where it remained constant for a few minutes.

On attempting to repeat this determination, difficulty was invariably experienced, owing to the fact that during sterilization a crust of anhydride would form in the upper part of the apparatus. This was avoided by the following modification of the method: The materials in the requisite proportions, together with some mercury, were placed in a 100 cc. wide-mouthed bottle. The bottle was tightly stoppered and rotated in a thermostat at 80° . This rotation prevented the formation of the anhydride crust. The bottle was then taken out, cooled to 35° , after which the stopper was removed, the contents inoculated with secondary pentahydrate and a second sterile stopper, carrying the thermometer, quickly introduced. In order to avoid excessive radiation, the bottle was wrapped in a dry cloth. It was then violently shaken by hand, the mercury assisting the agitation, whereupon the temperature rose to 41.60° .

From a consideration of the results obtained by these two methods, the most probable value for this transition point is believed to be 41.65° .

(g) *The Transition Secondary Tetrahydrate \rightleftharpoons Secondary Monohydrate.*—In both of the above determinations, after the temperature had remained for some time at the melting-point of the tetrahydrate, it fell, in the first case to 40.65° , in the second to 40.60° , at which points it remained constant for some time. Previous experience had shown that when the tetrahydrate undergoes transition with rising temperature, it is always the secondary monohydrate into which it is transformed. This, coupled with the evidence of the solubility curves, shows beyond doubt that the transition point there measured was that of the tetrahydrate into the secondary monohydrate. The most probable value for this point is 40.65° .

(h) *The Melting-point of Tertiary (and Quaternary) Hexahydrate.*—This was determined by the second of the methods used with the tetrahydrate. Two determinations were made, the solution of the hexahydrate composition being cooled in each case to 10° . Upon inoculation the temperature rose in the one case to 14.35° , and in the other to 14.37° . As the room temperature was somewhat above that of the melting-point, it is considered that 14.35° is the most probable value.

TABLE XIV.

[illegible]

TABULAR AND GRAPHIC COMPILATION OF RESULTS.

The averages of all solubility determinations given above and in the previous paper, together with the temperatures of such transitions as spontaneously occur, are compiled in Table XIV. The symbol $>$ before a temperature indicates a transition with rising temperature, and the symbol $<$ a transition with falling temperature.

These results are also graphically plotted in Chart 1. The solid lines represent averages of actual determinations not more than 5° apart. The lines - - - - - are extrapolated. The lines — — — — — are lines of composition of certain of the hydrates. The curves as plotted follow the actual determinations within two tenths per cent. in all cases, and in the great majority of cases much more closely. Through a small error in draughting, the melting-point of the hexahydrate is placed about three-tenths of a degree too high. On the same chart the trio of transition points lying near 31° is also plotted on a much enlarged scale.

DISCUSSION OF THE RESULTS.

(1) *Supercooling*.—This phenomenon is of such common occurrence that only a few points of special interest will be taken up here. All of the hydrates of sodium thiosulphate supercool to a greater or less extent, at least when in contact with the saturated solution, this being the only condition under which we have worked with them. The range of temperature through which supercooling is possible varies greatly with the different hydrates, as does also the time for which they may remain supercooled. Thus, sealed tubes containing primary dihydrate have been kept at room temperature for nearly two years, and in no case has the primary pentahydrate appeared in them. Occasionally, however, the secondary pentahydrate has appeared in such tubes. On the other hand the tetrahydrate supercools to so slight a degree that no solubility determinations were possible at temperatures below its transition point into secondary pentahydrate. That slight supercooling does occur for a short time, is shown under *a*, p. 329.

On the whole our experience seems to indicate that possibly all supercooled systems are transitory, and that all such may, after the lapse of sufficient time (often very great), go over into the more stable systems.

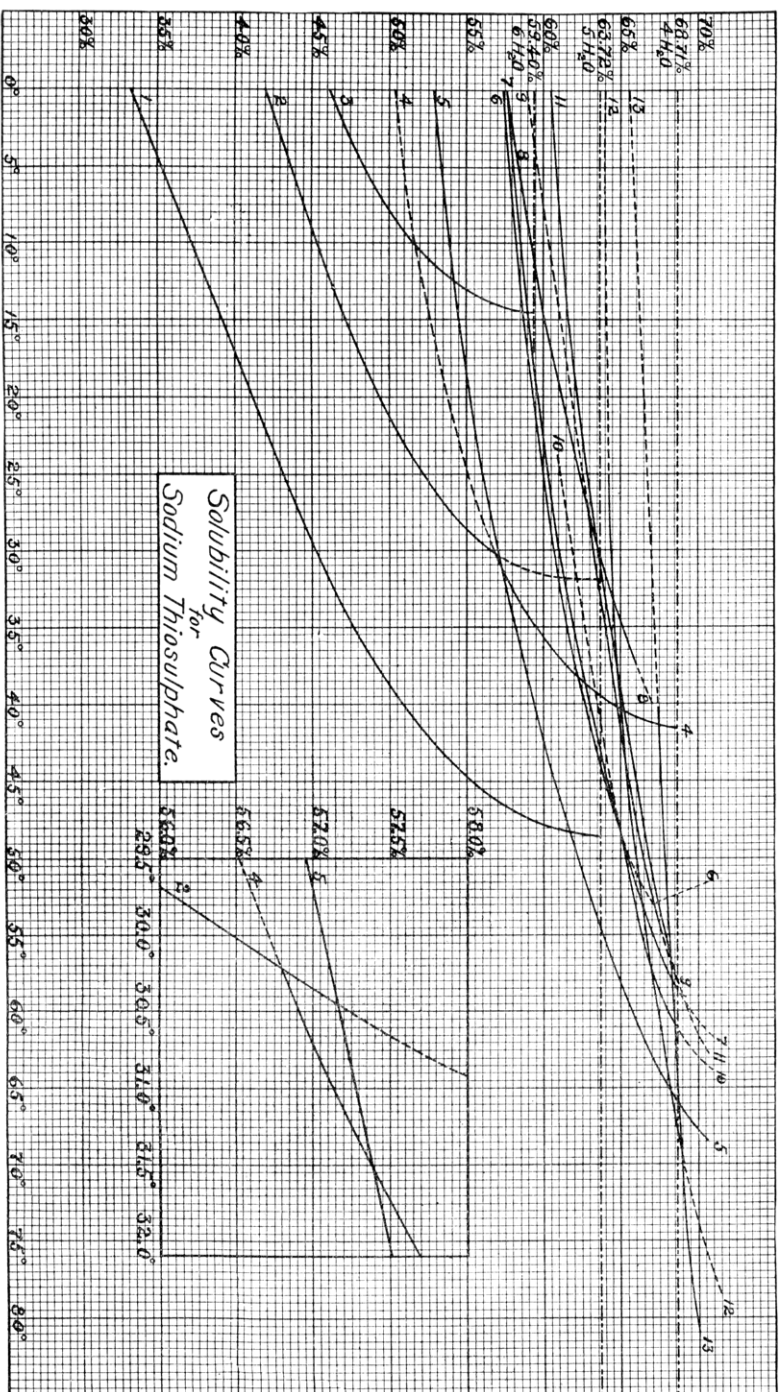


CHART I.—The curves are numbered at the lower ends, and, where necessary, also at the upper ends. The compounds corresponding to this numbering are shown in the following tabulation: 1, Primary pentahydrate; 2, Secondary pentahydrate; 3, Tertiary (quaternary) hexahydrate; 4, Secondary tetrahydrate; 5, Secondary trihydrate; 6, Quinary dihydrate; 7, Quinary monohydrate; 8, Tertiary; 9, Quinary monohydrate; 10, Tertiary; 11, Quinary monohydrate; 12, Tertiary; 13, Quinary monohydrate.

(2) *Superheating*.—In the previous paper it was pointed out that the tetrahydrate offers a marked case of the supposedly very rare phenomenon of superheating. With the completion of the work on the hydrates of sodium thiosulphate, this phenomenon has been found to be of such common occurrence as to almost lead to the belief that it may be universal. A striking illustration of the frequency with which this phenomenon occurs may be seen from Chart 1, where it will be found that the solubility curves of seven different hydrates cross that of the hemihydrate in such a way that transitions into this latter would be expected. These transitions do not actually occur, with the single exception of that of the quintary monohydrate, and even this one does not occur until the temperature has been raised to fully 10° above the transition point.

In this connection the conduct of the secondary pentahydrate is of interest. For a long time this hydrate was not supposed to show superheating at all, but the determination of the temperature of its transition into primary dihydrate (see *c*, p. 330) shows that slight superheating does occur.

From considerable evidence which will be given later, it seems probable that the superheated state, like the supercooled, is, strictly speaking, transitory.

(3) *Origin of the New Phase in Transitions*.—A matter of very considerable interest in this field of work is the question as to whether, in the transition of one solid phase in contact with saturated solution into a second solid phase, the second solid phase appears as a product of the direct transformation of the first solid phase, or whether it may not have its origin directly in the homogeneous liquid. That the second solid phase is in many cases formed by the direct transformation of the first solid phase, cannot perhaps be reasonably doubted. However, evidence is at hand which proves conclusively that in some cases the second solid phase may have its origin solely in the homogeneous liquid phase. For example, clear crystals of primary pentahydrate on heating to 50° melt to a perfectly clear liquid, which condition persists for some minutes. Sooner or later, however, the liquid becomes turbid, owing to the appearance of crystals of the primary dihydrate. The same conduct is shown by the hexahydrate. In both of these cases the hydrates allowed themselves to be heated directly to their melting-points

and fused, without undergoing expected transitions, and the only possible source of the second solid phase was manifestly the homogeneous liquid. This conduct may at first seem surprising, but will, on second thought, be found wholly analogous to that of supercooled liquids from which, under certain conditions, a solid phase separates.

In the following discussion, this possibility in regard to the formation of the second solid phase in transitions with rising temperature, will be found of great utility, many curious phenomena finding therein a simple explanation. So commonly is this the case, that it almost seems as though the formation of the second solid phase directly from the first were the exception rather than the rule.

(4) *Classification and Nomenclature of the Hydrates.*—During the course of the investigation each hydrate was given a provisional name upon its discovery. This name indicated the composition of the hydrate, and in case of polymorphic forms being found, these were distinguished by Greek-letter prefixes, as for example, the α -, β -, and γ -monohydrates. This provisional nomenclature is adhered to in Chart 2, which shows the grouping since adopted. This grouping is based solely on the mutual transitions of the various hydrates. These transitions occur in such a way that the members of one group undergo transition into members of the same group and not into members of another group. For example take Group 2. The β -pentahydrate undergoes transition at 30.22° into the tetrahydrate. This undergoes no further transition until 40.65° is reached, when it goes into the α -monohydrate, which in turn at 56.5° goes into the anhydride. From Chart 1 it will be seen that this conduct involves superheating past five points on the part of the tetrahydrate, at any one of which points transition might ordinarily be expected. Similar conduct is shown by the hydrates constituting each of the other groups.

It will be noticed that with rising temperature, all of the groups yield anhydride, which therefore is a common member of all groups. The hexahydrate is also seen to occur in both the third and fourth groups. This is on account of the fact that this hydrate may undergo two spontaneous transitions, according to the temperature at which it is held (see 7, p. 317 and 9, p. 318). Beyond this none of the groups contain common members.

Perhaps these relationships may be more readily understood with the aid of a graphic representation. If we imagine each group existing in a plane of its own, the solubility curve of the anhydride being a line of intersection common to all of the five planes, we obtain the diagram shown in Fig. 4.

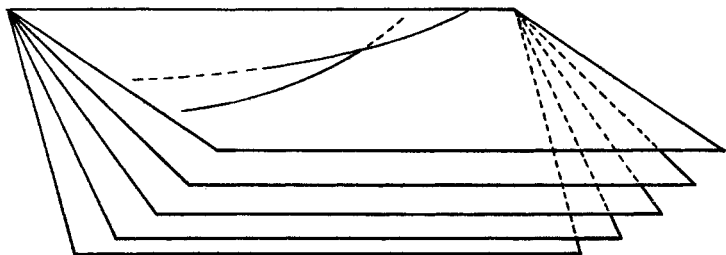
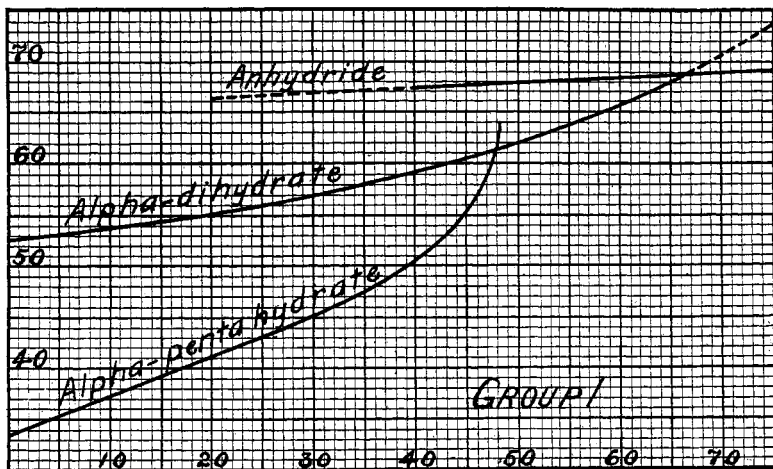


Fig. 4.

If we now imagine the solubility curves drawn in these planes, the curves for each group occupying a separate plane as indicated in the upper plane, we shall then have a fairly accurate representation of the conditions as they exist, the separation of the planes indicating the absence, under ordinary conditions, of direct transition between groups. Of course the hexahydrate curve will appear in two planes.

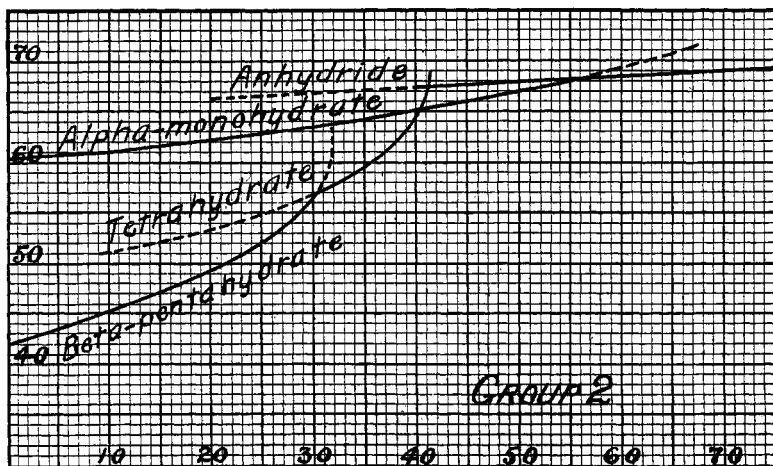
The nomenclature which has been adopted for these hydrates is based upon the above system of grouping. Those hydrates belonging to Group 1 are called primary hydrates, those belonging to Group 2 are called secondary, and those belonging to the third, fourth and fifth groups are called tertiary, quaternary and quintary, respectively. This system of nomenclature is adhered to in Chart 1. In the phraseology of the phase rule, a system including all the possible modifications of sodium thiosulphate and water would be spoken of as a "hylotropic system." The groups into which the system has been divided may therefore be called "hylotropic subsystems."

(5) *Characteristics of the Various Groups.* (a) *Group 1.*—This group having been so frequently used in the preceding paragraphs for the sake of illustration, little remains to be said. The primary pentahydrate undergoes transition into the primary dihydrate, but may be superheated past this transition temperature to that of the melting-point. Sooner or later the dihydrate appears in fusions kept near the melting-point. The



reverse transition of the supercooled dihydrate takes place only with great difficulty. With rising temperature the dihydrate goes into the anhydride.

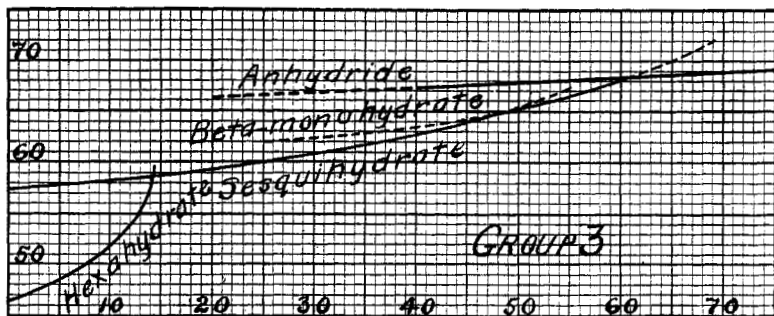
(b) *Group 2.*—The pentahydrate superheats only very slightly, going over with the greatest ease into the tetrahydrate. It is also impossible to supercool the tetrahydrate to any considerable



extent, since the reverse transition to pentahydrate occurs very readily. The transition of the tetrahydrate into the monohydrate takes place with greater difficulty, it being possible to

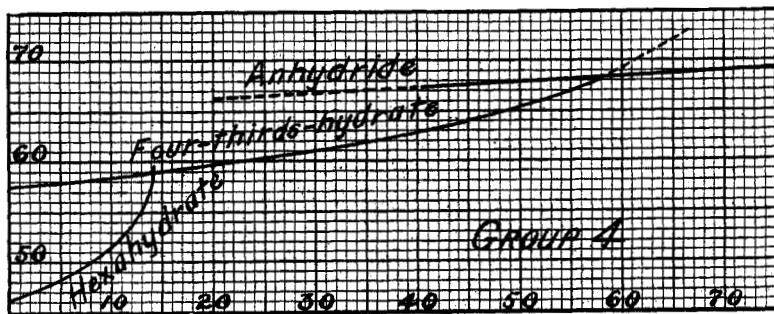
superheat the tetrahydrate to its melting-point for some minutes. The monohydrate supercools readily, only occasionally undergoing transition after months of standing at room temperature, and then not into the tetrahydrate, which is unstable at these temperatures, but into the pentahydrate (secondary). At higher temperatures the monohydrate goes into the anhydride.

(c) *Group 3*.—The hexahydrate acting as a tertiary hydrate may be superheated even to fusion without the appearance of the sesquihydrate. The converse supercooling is also very marked. The sesquihydrate appears when the hexahydrate is held for a



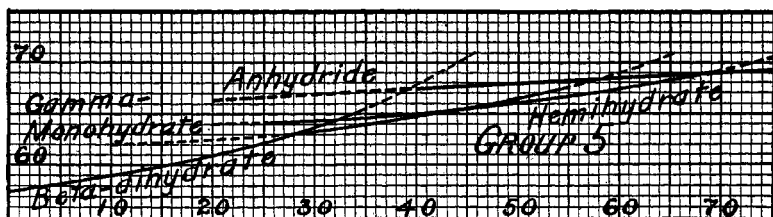
long time at temperatures but slightly above the corresponding transition point. The sesquihydrate goes over into the monohydrate at 48.50° , neither superheating nor supercooling occurring to any considerable extent. At higher temperatures the monohydrate goes over into anhydride.

(d) *Group 4*.—The quaternary group of hydrates conducts itself very similarly to the tertiary. The hexahydrate superheats to fusion, but if the fusion is held for some time at tem-



peratures a degree or two above the melting-point, the four-thirds-hydrate appears, especially if anhydride is present. At a higher temperature the four-thirds-hydrate goes over into anhydride.

(e) *Group 5*.—The quintary group is in some respects the most interesting of all. In the first place the dihydrate superheats not only past the monohydrate, but also past the hemihydrate. When the limit of superheating is reached, the transition takes place, not into the hemihydrate, as might be expected, but directly into the monohydrate, that is, into that form with respect to which it is most superheated. The monohydrate super-



cools but slightly with respect to the dihydrate. On the other hand, the monohydrate readily superheats some 10° above the transition point into hemihydrate, where a limit to its persistence in the superheated state is found, and it goes over into the hemihydrate. The hemihydrate readily supercools with respect to the monohydrate, and also with respect to the superheated dihydrate. At 70° the hemihydrate goes over into the anhydride.

(6) *Inter-group Connection*.—From what has already been said, the possibilities for inter-group connection should be reasonably clear. These possibilities may, however, be briefly summarized here. In the first place, the anhydride, being a member common to all groups, might naturally be looked to as a source of other members of each group, merely by reverse transition. It has been found experimentally that the anhydride, on cooling to below 40° , sooner or later invariably yields the secondary monohydrate. However, while making the solubility determinations of the anhydride between 45° and 55° , values which lay upon the curve of the four-thirds-hydrate were frequently obtained, thus showing transition into the quaternary group. It is not unreasonable to assume that, under the proper conditions, transitions of the anhydride into members of the other groups might occur.

The hexahydrate, as has been repeatedly indicated, serves to connect the tertiary and quaternary groups. The transition of the quaternary four-thirds-hydrate into the quintary dihydrate, which is complete at 0° within four or five days, gives connection between these groups. In general supercooled hydrates not infrequently undergo transition into members of other groups. Thus both the four-thirds-hydrate and the primary dihydrate, upon long standing at room temperature, have been observed to yield secondary pentahydrate. Analogously, superheated hydrates, particularly if held at temperatures below that of their usual group transition points, may yield hydrates belonging to other groups. Thus tubes containing quintary dihydrate, and in which this form had persisted for some weeks, occasionally went over into the four-thirds-hydrate. The opportunities for such transitions are very numerous. For example, solutions in which hexahydrate crystals are present, if held at a temperature just below that of the transition into the sesquihydrate, might yield primary dihydrate after sufficient time. Several such possibilities exist in the case of the tetrahydrate.

Besides the above methods of passing from one group to another, there is also the possibility of obtaining members of different groups from solutions which contain no crystalline hydrate whatever. Thus solutions of about pentahydrate composition on cooling to between 10° and 20° below zero, sometimes yield secondary pentahydrate, and sometimes hexahydrate, while on cooling to about 35° below zero they yield primary pentahydrate.

(7) *Analogies between Supercooling and Superheating.*—A careful consideration of the experimental evidence given in this paper, together with the intimate familiarity with these phenomena which we have gained through working for a considerable period of time in this field, have led us, in so far as generalizations may be drawn from work upon a single hylotropic system, to the following conclusions concerning the phenomena of supercooling and superheating.

(a) *That Supercooling and Superheating are Probably of Invariable Occurrence when a System Passes through a Transition Point.*—(Melting-points are to be considered as excluded from this discussion.) On Chart 1 there are to be found 29 intersections of solubility curves, each one of which locates a transition

point. Solubility determinations show that marked supercooling occurs in respect to 24 of these points. Other evidence shows that slight supercooling occurs in respect to 3 others. Concerning the remaining 2, no positive evidence is at hand.

Solubility and melting-point determinations also prove conclusively that superheating occurs in respect to 22 of the 29 points. Five of the remaining points are those at which transition into the anhydride occurs. In regard to these and one of the other points, there is evidence of slight superheating. In the three cases in which either supercooling or superheating has not been definitely found, there is no evidence whatever to show that these phenomena do not occur.

(b) *That the Two Phenomena are Subject to Essentially the Same Laws.*—The transformation of a supercooled system into a more stable one has been found by several investigators to be determined mainly by two factors: First, the degree of supercooling, by which is meant the extent to which the system is cooled below its transition point; in heterogeneous systems, such as those with which we have to deal here, the concentration factor may be eliminated, as the concentration is wholly determined by the temperature. Second, the time during which the system is held at a given temperature. Thus the phases of a more stable system, if they do not appear in a metastable system at a given temperature after a short time, may appear after a longer time. The transformations of superheated systems into more stable ones are controlled by the same conditions. For example, the quintary dihydrate, whose transition point into the quintary monohydrate lies at about 27.5° , remains in the superheated state for a long time at 30° , and at 35° remains in this condition long enough for accurate determinations of its solubility to be made, although at this latter temperature transition not infrequently occurs within an hour. At 40° the transition begins so soon that no solubility determinations could be obtained. In so far as they have been investigated, other cases show the same conduct.

Almost the only distinction between the two phenomena lies in the fact that the degree of supercooling possible, as well as the time during which a system may be held in the supercooled state, are usually greater than the corresponding possibilities in the case of superheating. However, reference to Chart 1

shows several cases for which this is not true, as for example, the transition between the monohydrate and the dihydrate of Group 5. The fact that, at least with all substances having positive temperature coefficients of solubility, superheating involves an increase in the total concentration, while supercooling involves a decrease in this value, may possibly explain why supercooling so often takes place to a greater degree than does superheating.

(8) *Application of the Nuclear Hypothesis.*—In a previous paper¹ an hypothesis was suggested to explain certain phenomena in regard to supercooling. Since experience had clearly shown that solutions and fusions obtained from the different hydrates of sodium thiosulphate conducted themselves in very different ways upon supercooling, the assumption was made that these solutions and fusions contained nuclei whose nature depended upon that of the hydrate used in their preparation. It was assumed that the character of the hydrate which would appear in a given supercooled solution or fusion, depended upon the character of the nuclei contained in it. For details, reference must be made to the original. This hypothesis has been of great assistance in the present further researches, and an explanation of the above results will now be given from this point of view.

(a) *Superheating.*—In the same way that this hypothesis has already been applied to supercooling, it may also be applied to superheating. Thus when a hydrate is superheated past a transition point, the expected transition will occur if the requisite nuclei are present in the solution, after sufficient time has elapsed for the nuclei to form the necessary crystalline aggregate. This, of course, presupposes that the second solid phase has its origin in the solution, which is known to be true in all cases where evidence has been obtained. The time required for the nuclei to form a crystalline aggregate may be very different in different cases, which accounts for the fact that different forms show very different degrees of superheating.

(b) If it be assumed that the nuclei are formed as a result of slow reaction of some sort in the solution, the fact that this reaction would undoubtedly be accelerated by increase of temperature would account for the fact that less superheating than supercooling is possible, other things being equal.

¹ Young and Mitchell: Loc. cit.

(c) *The Nuclear Explanation of Grouping.*—The fact upon which the division of the hydrates into groups rests, is that a given hydrate can superheat past points at which, from consideration of the energy relationships, transition could occur, but that each such hydrate selects a certain specific other hydrate into which it becomes transformed. A group then consists of such hydrates as are regularly formed from a given initial hydrate by transitions with rising temperature. If the principle that the new solid phase has its origin in the liquid phase is accepted, there seems to be no simple explanation of this conduct on the basis of the usual conception that the solutions formed from different solid phases of the same system are identical. On the other hand, the nuclear hypothesis offers a very simple explanation. If a given hydrate in contact with saturated solution be superheated past a number of transition points, that particular transition will occur for which the nuclear condition of the solution is most favorable. If this particular transition be excluded, as, for example, by holding the temperature below that of the corresponding transition point, that one of the remaining possible transitions, for which the nuclear condition of the solution is most favorable, will occur. In case the nuclear condition of the solution is relatively unfavorable for the occurrence of any of the possible transitions, a very long time may elapse before any transition whatever will be realized. From this it will be seen that, if the requisite conditions be maintained for a sufficient length of time, any possible transition might be realized. From these considerations, which are based upon direct experimental evidence, the belief that both the supercooled and the superheated states are always transitory, would seem to find reasonable justification, it being borne in mind that a transitory state may persist for a long time.

From this point of view, the grouping of the hydrates, as given above, is seen to represent nothing more nor less than the conduct of the hydrates with rising temperature, under the usual laboratory conditions, where a considerable range of temperature is compassed in a relatively short time. If conditions were such that a very much more gradual rise in temperature was used, an entirely different grouping would probably be found. With falling temperature the grouping is usually the same as with rising temperature, although exceptions to this occur.

(d) *The Ostwald Rule.*—The rule suggested by Ostwald, that when a supercooled system undergoes transition, it is always into the next lying, that is, the most metastable of all the possible systems, is so frequently violated by the hydrates of sodium thiosulphate that, at least in this system, it cannot be considered as even approximately representing the facts. The same is true for superheated systems. For example, quintary dihydrate, superheated to 40° , undergoes direct transition into the quintary monohydrate, thereby passing two forms metastable to the monohydrate, either of which, when once produced, persists at this temperature, and even at temperatures much below this, for a long time. Other similar cases may be found by reference to Chart 1. The explanation of this by the nuclear hypothesis is self-evident.

SUMMARY.

The results of the foregoing investigation may be summarized as follows:

(1) Thirteen crystalline modifications of sodium thiosulphate are described, namely, one hexahydrate, two pentahydrates, one tetrahydrate, two dihydrates, one sesquihydrate, one four-thirds-hydrate, three monohydrates, one hemihydrate, and one anhydride.

(2) Data proving the composition of these hydrates are given.

(3) The solubility of the various forms has been determined at intervals of 5° or less over the range of temperature extending from zero to 80° .

(4) All of the transition points of the system have been determined from the intersections of the solubility curves, and a considerable number have been also directly measured.

(5) Numerous observations concerning the supercooling and superheating of the different forms are recorded. Evidence is cited which tends to show that, in so far as this hylotropic system is concerned, superheating is as common as supercooling, in fact that both probably occur in the neighborhood of every transition point, excluding melting-points. Evidence is also given which seems to indicate that both phenomena are probably transitory.

(6) It has been found possible to divide the hydrates of this system into groups, on the basis of their conduct in undergoing

transition with rising temperature. In this connection many cases are cited which conflict with the Ostwald rule.

(7) The nuclear hypothesis has been shown to afford a simple explanation of the phenomena described.

STANFORD UNIVERSITY, CAL., December 1905.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

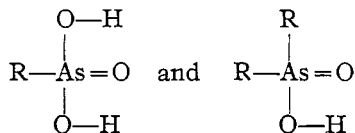
ARSONIC AND ARSINIC ACIDS.

BY WILLIAM M. DEHN AND S. J. McGRATH.

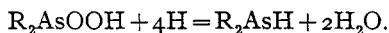
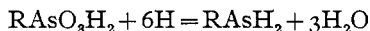
Received January 2, 1906.

ARSONIC acids may be considered as derived from arsenic acid, $\text{AsO}(\text{OH})_3$, by replacing one of the hydroxyl groups by a univalent hydrocarbon or substituted hydrocarbon radicle; thus the arsonic acids have the general formula $\text{R}-\text{AsO}(\text{OH})_2$. Arsinic acids may be considered dialkyl or dialkyl substitution-products of arsenic acid and have the general formula $\text{RR}'\text{AsOOH}$, wherein R and R' are any two univalent hydrocarbon radicles. All of the arsinic acids hitherto prepared have the two radicles identical, except phenyl-*p*-toluylcacodylic acid.¹ The arsinic acids are, of course, homologues of cacodylic acid and are therefore frequently termed cacodylic acids—for instance phenylarsinic acid is also known as phenylcacodylic acid.

The structural formulas usually assigned to the arsonic and arsinic acids are:



The best proof of the direct union² of the radicles with arsenic is seen in their reduction to the corresponding arsines,³ which unquestionably contain the radicles in direct union with arsenic:



The possibility here of molecular rearrangement is precluded

¹ Ann. 321, 157.

² Ibid. 107, 269.

³ Ber. 27, 1378; Am. Ch. J. 33, 104.