[CONTRIBUTION FROM THE NONMETALLIC MINERALS EXPERIMENT STATION, U. S. BUREAU OF MINES, RUTGERS UNIVERSITY]

Solubility Equilibria of Sodium Sulfate at Temperatures of 150 to 350°. I. Effect of Sodium Hydroxide and Sodium Chloride[1]

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As a result of the attention directed in recent years toward the use of sodium sulfate in the prevention of "embrittlement" of boiler steel, the solubility of this substance in complex solutions at temperatures in the range of steam-boiler operation has become a matter of great interest. To obtain this solubility information a coöperative investigation under the sponsorship of the Joint Research Committee for Boiler Feed-Water Studies[2] was begun at this station in March, 1933. The present paper is the first of a series which will outline the effect of the most common soluble constituents of boiler waters upon the solubility equilibria of sodium sulfate in the temperature range 150 to 350°, corresponding to a pressure range for pure water of approximately 3 to 160 atmospheres gage (50 to 2400 pounds per square inch gage).

The data obtained during this investigation are of practical interest not only in connection with the embrittlement problem, but also in the recovery of sodium compounds from natural or artificial brines.

Equipment for High-Temperature Solubility Studies

All of the solubility determinations were made in special nickel bombs which were rotated end over end in an air thermostat to attain equilibrium. The bombs, shown in Fig. 1, were essentially of the type developed and used by Waldeck, Lynn and Hill.[3] One improvement, however, was found necessary. While it was possible to obtain satisfactory service from a rubber composition gasket at temperatures as high as 250°, rapid failure due to carbonization occurred at 300° and above. A metal-to-metal seal formed by a stainless steel conical surface running on a copper seat cut at a slightly greater angle proved satisfactory for the severe duty at 300 and 350°.

The air thermostat, shown in Fig. 2, was designed to maintain the solubility bombs at any desired temperature between 100 and 350°. It consisted of a rectangular steel box, 60 cm. (2 ft.) square and 120 cm. (4 ft.) long, lined with 7.5 cm. (3 in.) of heat-insulating material, and heated by four 1000-watt strip heaters. A fan and baffle plates were so placed in the thermostat that the air temperature throughout was uniform within 0.5°. The current to the heaters was controlled by a recording and controlling potentiometer, and the indicated temperature was checked by means of a Leeds & Northrup Type K potentiometer at least once during each solubility run.

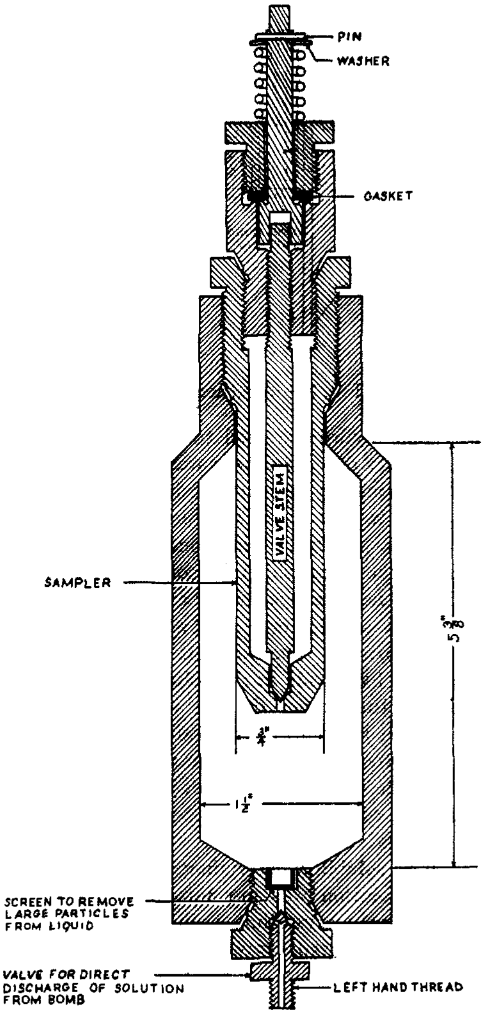

Fig. 1.—Bomb used for solubility studies.

A study was also made of the maximum possible difference between the bomb temperature and the recorded temperature by inserting thermocouples in the end bombs and measuring their temperatures at various thermostat temperatures. It is estimated that the actual temperature within a bomb during any solubility determination did not deviate by more than ±2° from the temperature setting of the thermostat.

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[2] Sponsored by The American Boiler Manufacturers' Association, The American Railway Engineering Association, The American Society of Mechanical Engineers, The American Society for Testing Materials and The American Water Works Association.

[3] (a) W. F. Waldeck, G. Lynn and A. E. Hill, THIS JOURNAL, **54**, 928–936 (1932); (b) **56**, 43–47 (1934).

A flat bar with seven holes drilled in it supported the bombs in the thermostat. This bar, which extended through the center of the box, was revolved at about 4 r. p. m. to ensure intimate mixing of solid and solution. Small holes in the top of the thermostat permitted the insertion of a wrench to open the sampling valve on each solubility bomb without opening the thermostat. After the solution sample had been taken a wrench was inserted through similar holes in the bottom of the thermostat, and the solution remaining in each bomb was discharged directly to the atmosphere through a blow-off valve. A dry sample of solid which had not been exposed to change of temperature while in contact with the liquid could thus be obtained.

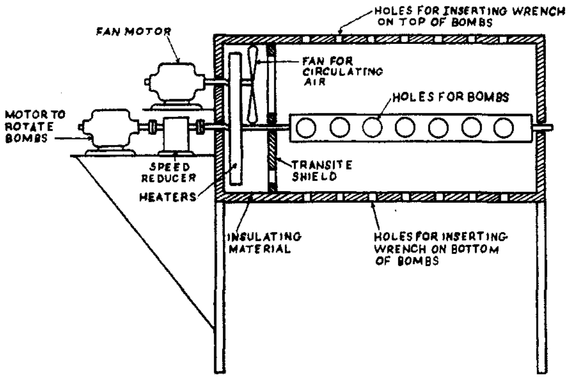

Fig. 2.—Air thermostat.

The sodium hydroxide used to make up the solutions for the solubility determinations was stored as a saturated solution at room temperature, and the amount for each determination was measured volumetrically into the bomb as rapidly as possible. The concentration of sodium carbonate in the saturated stock solution was determined at the end of the investigation by evolution of the carbon dioxide from a small sample and absorption in standard barium hydroxide.[4] The amount present was 0.17% of the sodium hydroxide in the solution which, as will be shown in another paper dealing with the solubility of sodium sulfate in solutions of sodium carbonate, is insufficient to produce a measurable solubility effect. The sodium chloride used also was added to the bombs from a stock solution containing about 35 g. of sodium chloride per 100 g. of water.

In making a solubility determination the desired amount of water or solution was put into each bomb, and an excess of coarsely crystalline anhydrous sodium sulfate (Baker C. P. analyzed) was added. The bombs were placed in the thermostat and rotated at the desired temperature for twelve to forty-eight hours. Comparison tests demonstrated that equilibrium always was reached in twelve hours or less. Before sampling, the bomb was allowed to stand upright for at least thirty minutes to settle out the suspended solid.

To make sure that the thirty-minute settling period was sufficient to free the solution from suspended particles, one of the samplers was equipped with a filter which consisted of a number of layers of nickel screen. This bomb and another bomb not equipped with a filter were charged with identical mixtures of solution and solid, rotated in the thermostat until they reached equilibrium, and allowed to settle for thirty minutes; then both bombs were sampled. The comparative results, shown in Table I, indicate that insufficient suspended matter was present to produce a measurable effect on the results. Good agreement is also shown between the values for the filtered samples and values obtained from the plots for all the solubility data.

TABLE I

EFFECT OF FILTERING ON COMPOSITION OF SOLUTION SAMPLE

Layers of 80-mesh screen	Temp., °C.	*Composition of sample,* g./100 g. H_2O NaOH	NaCl	Na_2SO_4	Value as determined from solubility curves[a] g. Na_2SO_4 100 g. H_2O
2	200	31.3	..	17.3	17.6
Not filtered	200	31.3	..	17.3	17.6
3	250	26.9	..	28.5	28.5
Not filtered	250	27.2	..	28.8	28.5
5	250	24.2	24.4	20.0	19.8
Not filtered	250	24.4	24.3	19.8	19.8
10	250	27.3	..	29.1	28.5

[a] Values from plot of data shown in subsequent tables.

The weight of sample was determined within 0.01 g. by weighing the complete sampler assembly before and after each determination. After the sampler had been weighed its contents were washed into a beaker with hot water and then diluted to 250 cc. Aliquots of this volume were taken for each analysis.

The sodium sulfate present in the solution was determined by precipitating the sulfate as barium sulfate, filtering and washing on a filter paper, igniting at 900°, and weighing. The hydroxide was determined by titration with 0.1 or 0.4 *N* sulfuric acid to the methyl red end-point. Chloride was determined by titration with 0.1 *N* silver nitrate using potassium chromate as indicator. The total solid present was determined by converting the hydroxide to sulfate, evaporating the sample to dryness, igniting it at 350°, and weighing. If the total solid by direct weighing did not agree within 1% with the total solid as calculated from the individual analyses the determination was repeated.

Solubility Measurements.—This paper presents new data in the systems Na_2SO_4–H_2O, NaCl–H_2O, Na_2SO_4–NaOH–H_2O, Na_2SO_4–NaCl–H_2O and Na_2SO_4–NaOH–NaCl–H_2O. The concentrations of sodium hydroxide and sodium chloride in the three- and four-component systems were limited to not more than approximately 35 g. per 100 g. of water. Determinations were made at temperature intervals of 50° from 150 to 350°, and a method of predicting solubilities at intermediate temperatures was developed and tested.

Sodium Sulfate–Water.—Data previously available have been combined with the results of

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[4] E. P. Partridge and W. C. Schroeder, *Ind. Eng. Chem., Anal. Ed.*, **4**, 271–283 (1932).

the present investigation given in Table II to define the curves shown in Fig. 3 for the solubility of sodium sulfate in water at 0 to 350°. As in a number of other cases, the high-temperature measurements of Tilden and Shenstone[5] seem to be much more accurate than those of Étard.[6] The data of Wuite[7] obtained indirectly agree substantially with the directly determined values of Tilden and Shenstone and those found in the present investigation below the inversion point at approximately 241°; above this point Wuite's values fall first below and then above the curve defined by direct measurement. This curve indicates that the solubility decreases continuously from 241 to 350° and probably approaches zero or a very small value asymptotically as the temperature approaches the critical point, which for pure water is 374°.

TABLE II

SOLUBILITY OF SODIUM SULFATE IN WATER AT 140 TO 350°

Temp., °C.	Soly., g. Na_2SO_4/100 g. H_2O	Temp., °C.	Soly., g. Na_2SO_4/100 g. H_2O
140	41.8	230	45.5[b]
140	42.0	240	45.9[c]
150	42.1	241	45.7
156	42.6	241	45.5
160	42.5	250	43.0
160	42.0	251	44.7
170	42.7	251	44.5
170	43.1	260	42.1
180	43.3	260	41.6
180	43.9	260	41.4
180	43.0	270	40.8
180	43.3	270	38.9
190	44.5	279	35.1
190	43.9	279	35.8
190	44.1	281	34.3
190	44.2	288	31.7
204	43.0[a]	299	24.0
210	44.8	301	25.5
210	45.0	301	22.5
219	45.0	310	18.4
219	44.9	320	13.0
221	45.6	330	7.3
221	45.2	340	4.2
230	46.3[b]	349	2.4
		350	2.4

[a] Value low. [b] At 300° for 7 hrs.; 230° for 9 hrs. [c] At 300° for 7.5 hrs.; 240° for 7.5 hrs.

Determination of Solid Phases.—Throughout the investigation the residual solid phases from the solubility bombs have been subjected to examination by the powder immersion method using a petrographic microscope. In the systems described in the present paper no solid phases other than sodium chloride and the various forms of anhydrous sodium sulfate were encountered, but the identification of the latter was complicated by the rapid inversion of the higher-temperature forms into Na_2SO_4 V, thenardite, during cooling in the presence of water vapor. Some evidence, however, was obtained concerning the stable intervals of the different forms.

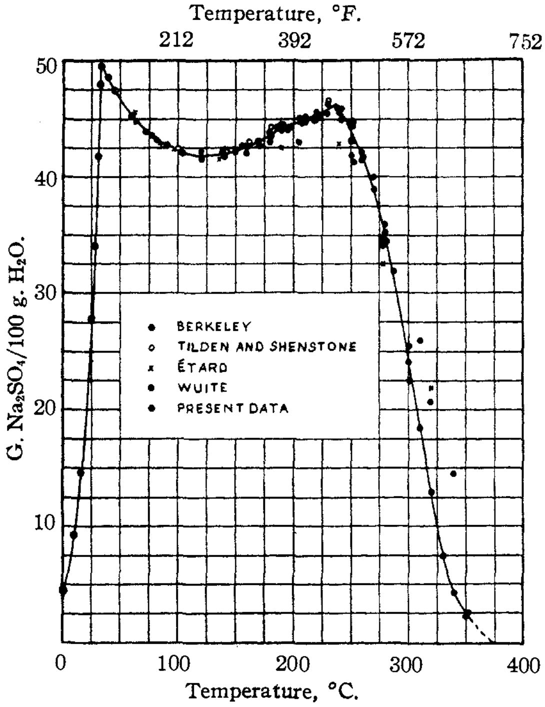

Fig. 3.—Solubility of sodium sulfate in water from 0 to 350°.

Samples from determinations made at temperatures below 185° always showed homogeneous crystals of Na_2SO_4 V, which gave no indication whatever of having been produced by inversion from another form. Samples originating at temperatures above 185° also consisted largely of Na_2SO_4 V, but here this form occurred as a mosaic of smaller unoriented crystals within a larger crystal outline, indicating inversion during cooling. A small amount of Na_2SO_4 III occasionally could be identified in these samples. Infrequently, crystals of Na_2SO_4 III were observed; these had been transformed only partially to Na_2SO_4 V, the inversion having been arrested before completion. As Kracek[8] has reported,

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(5) (a) W. T. Tilden and W. T. Shenstone, *Proc. Roy. Soc.* (London), **35**, 345–346 (1883); (b) *Trans. Roy. Soc.* (London), **A175**, 23–36 (1884).

(6) Étard, *Ann. chim.*, [7] **2**, 503–574 (1894), p. 548.

(7) J. P. Wuite, *Z. physik. Chem.*, **86**, 349–382 (1914).

(8) F. G. Kracek, *J. Phys. Chem.*, **33**, 1281–1303 (1929), p. 1298.

Na_2SO_4 III has a very low birefringence, and all indices lie between 1.480 and 1.485.

Na_2SO_4 I was never observed. Samples originating in the temperature range above 241°, where this modification is the stable phase,[9] were, however, usually characterized by elongated crystals with a definite hexagonal prismatic outline. These crystals consistently showed a number of heavy transverse cracks, formed probably by change in volume of the solid during inversion. Crystals having an apparently hexagonal or pseudohexagonal outline were also observed in samples originating between 185 and 241° in which Na_2SO_4 III should be the stable phase.[9] These crystals were usually shorter than those originating in the temperature range of Na_2SO_4 I and were relatively free of fracture. Possibly the elongated crystals with hexagonal outline represent the high-temperature modification, Na_2SO_4 I, and the shorter, apparently hexagonal crystals observed in the Na_2SO_4 III range were actually orthorhombic crystals in which the axes *a* and *b* were nearly equant.

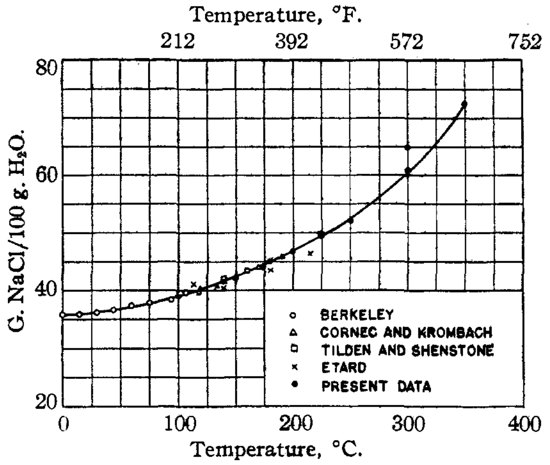

Fig. 4.—Solubility of sodium chloride in water from 0 to 350°.

Although the crystal habits of the higher-temperature forms were indicated in the samples from above 185° the crystal form actually present during examination under the petrographic microscope was, as noted above, predominantly Na_2SO_4 V. The mosaic appearance indicated that inversion had taken place from a number of different centers within the original crystal of the higher-temperature form.

The observations made under the petrographic microscope may best be correlated with the solubility determinations and with the careful investigations of Kracek and his co-workers[8,9,10,11] by assuming that in the system Na_2SO_4–H_2O the stable intervals of the solid phases may be expressed by the following relation

$$Na_2SO_4{\cdot}10H_2O \overset{32.4°}{\rightleftharpoons} Na_2SO_4\ V \overset{185°}{\rightleftharpoons} Na_2SO_4\ III \overset{241°}{\rightleftharpoons} Na_2SO_4 I$$

Kracek and Gibson[9] originally attributed the inversion at 185° to the change between Na_2SO_4 III and Na_2SO_4 IV, but subsequently Kracek and Ksanda[11] suggested that Na_2SO_4 IV, like Na_2SO_4 III, might be unstable at ordinary pressures and that actually Na_2SO_4 III might be in equilibrium with Na_2SO_4 V at this temperature. All of the evidence from the current investigation supports this suggestion.

Sodium Chloride–Water.—Since sodium chloride shows almost the same solubility as sodium sulfate over the range of 100 to 215°,[12] it might appear as a solid phase during the extreme evaporation of a boiler water high in chlorides. The solubility curve of this substance therefore was extended to 350° as an incidental part of the investigation. Table III presents the results, which have been combined with previously available values[5b,13,14,15] in Fig. 4.

Table III

Solubility of NaCl in Water at 150 to 350°

Temp., °C.	Soly., g. NaCl/100 g. H_2O	Temp., °C.	Soly., g. NaCl/100 g. H_2O
150	42.0	250	52.0
173	43.6	300	64.9[a]
200	46.2	300	60.9
225	49.7	350	72.4

[a] Value high.

Sodium Sulfate–Sodium Hydroxide–Water.—The solubility of sodium sulfate in solutions of sodium hydroxide at five different temperatures is shown in Table IV and Fig. 5. The effect of the sodium hydroxide is to cause a decrease in the solubility of sodium sulfate at 150, 200 and 250°. At 300°, however, the addition of sodium hydroxide increases the amount of sodium sulfate dissolved, and at 350° this effect has become very pronounced, a small increase in the concentration

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(9) F. G. Kracek and R. E. Gibson, *J. Phys. Chem.*, **34**, 188–206 (1930).

(10) F. C. Kracek and R. E. Gibson, *ibid.*, **33**, 1304–1308 (1929).

(11) F. C. Kracek and C. J. Ksanda, *ibid.*, **34**, 1741–1744 (1930).

(12) "Int. Crit. Tables," Vol. IV, p. 235.

(13) Earl of Berkeley, *Trans. Roy. Soc.* (London), **A203**, 189 (1904); *Proc. Roy. Soc.* (London), **73**, 435–436 (1904).

(14) E. Cornec and H. Krombach, *Compt. rend.*, **194**, 714–716 (1932); *Ann. chim.*, [10] **18**, 5–31 (1932).

(15) Étard, *Ann. chim.*, [7] **2**, 503–574 (1894), p. 532.

of sodium hydroxide causing a large increase in the solubility of sodium sulfate.

TABLE IV

SOLUBILITY OF SODIUM SULFATE IN SOLUTIONS OF SODIUM HYDROXIDE AT 150, 200, 250, 300 AND 350°

Solution composition, g./100 g. H_2O		Solution composition, g./100 g. H_2O		Solution composition, g./100 g. H_2O	
NaOH	Na_2SO_4	NaOH	Na_2SO_4	NaOH	Na_2SO_4
150°		200°		250°	
3.0	36.8	5.8	34.6	3.0	40.5
6.9	29.3	12.3	29.2[a]	6.7	36.6
12.6	22.8	18.5	23.5	13.4	32.8
17.0	17.8	18.8	23.6[a]	20.7	30.0[a]
16.9	18.0	22.8	21.4[a]	26.0	28.1
24.7	12.7	25.6	19.7	26.9	28.5
38.6	7.9	31.3	17.3	27.2	28.8
46.1	6.8	31.3	17.3	27.3	29.1
		32.2	17.4	27.7	28.3
		32.8	17.7	34.9	28.0

300°		350°	
0.8	25.0[a]	1.6	4.1
.9	24.8	3.2	6.4
1.6	25.5[a]	4.9	11.2
3.1	26.6	5.7	14.5[a]
3.2	26.6[a]	9.7	24.5[a]
6.5	29.9	11.3	29.2
7.4	30.6[a]	16.4	41.8
7.4	38.1[a,b]	18.3	44.8
15.1	36.0[b]	20.0	45.3[a,c]
15.7	36.2	20.0	44.4[c]
23.2	39.5[a]	28.2	58.7
23.6	38.3	31.0	62.6
23.5	38.0	42.9	69.4
32.8	40.2		
37.5	41.5		

[a] Calculated from initial concentrations. [b] Value high. [c] Value low.

The values given by Prikhodko[16] for this system over the range of 50 to 140° seem low in sodium sulfate when compared with the curve for 150° in the present paper.

In Fig. 5 and some of the subsequent figures certain points marked "calculated from initial concentration" represent experiments in which more or less water vapor was lost from the sampler owing to leakage during or subsequent to sampling. Leakage almost always was indicated by the appearance of solid salt around the valve-stem wrench or threads of the sampler. Since the initial concentration of sodium hydroxide or sodium chloride in the solution placed in the bomb at the start was known accurately, it was possible to calculate the probable true composition of the solution in the bomb at the time of sampling. The corrected values obtained in this way fall well in line with the values obtained by direct analysis when no leakage occurred.

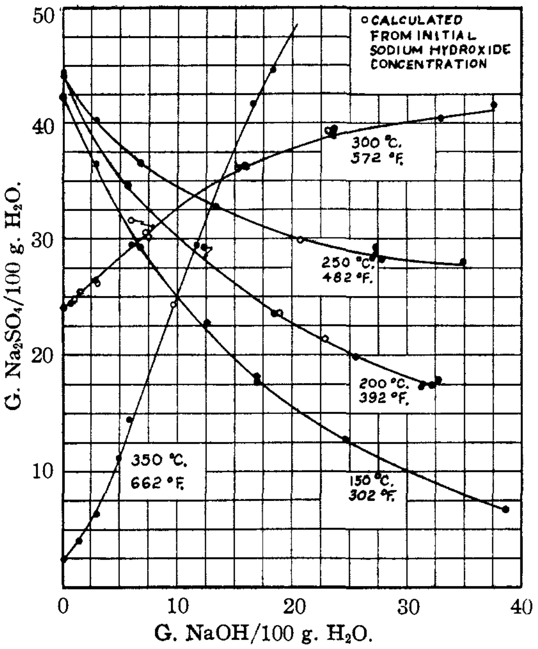

Fig. 5.—Solubility of sodium sulfate in solutions of sodium hydroxide at 150, 200, 250, 300 and 350°.

TABLE V

SOLUBILITY OF SODIUM SULFATE IN SOLUTIONS OF SODIUM CHLORIDE AT 150, 200, 250, 300 AND 350°

Solution composition, g./100 g. H_2O	
NaCl	Na_2SO_4
150°	
4.8	33.6
9.7	26.6
20.0	16.3
26.1	12.2
32.2	10.3
40.8	7.2
200°	
5.0	36.0
9.8	28.4
15.5	23.2
21.2	18.0
22.0	18.8
32.6	12.7
250°	
5.3	34.1[a]
8.1	30.0[a]
11.0	28.1
16.7	21.8[a]
22.7	18.1[a]
5.0	34.0[b]
15.1	22.9
30.7	16.5

Solution composition, g./100 g. H_2O	
NaCl	Na_2SO_4
300°	
3.1	20.5
6.0	19.3[a]
6.1	20.0
6.6	20.0[a]
12.2	17.2[a]
13.5	17.6[a]
19.5	17.5
20.9	16.9[a]
26.3	17.6
32.6	16.8[a]
33.5	17.7
350°	
1.4	3.1
3.7	3.9
3.9	5.2
7.8	6.0[a]
8.1	6.4
10.1	7.2
13.1	9.3
16.1	10.9[b]
24.8	18.1[a,b]
24.7	14.8
34.5	19.2
35.2	20.1

[a] Calculated from initial concentration. [b] Value high.

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(16) Prikhodko, *J. Applied. Chem.* (U. S. S. R.), **5**, 31–33 (1932).

Sodium Sulfate–Sodium Chloride–Water.—The marked effect of sodium chloride upon the solubility of sodium sulfate is shown in Fig. 6, the data for which are given in Table V. It is apparent from the curves that a change in temperature from 150 to 250° produces only a relatively slight change in the solubility relations. The new data and those of Chrétien[17] at temperatures up to 100° are mutually consistent.

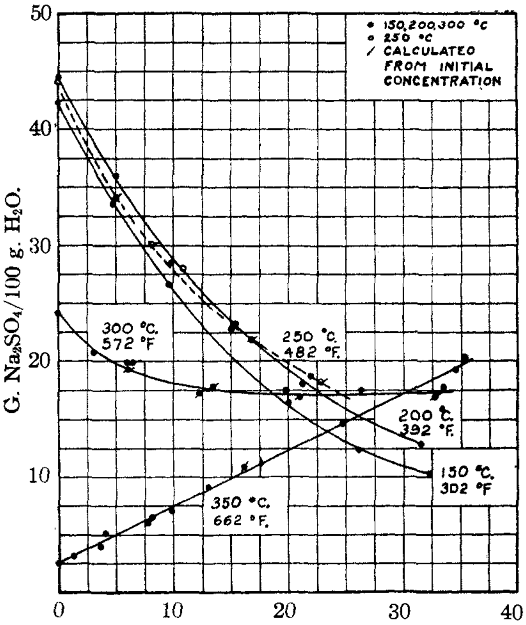

Fig. 6.—Solubility of sodium sulfate in solutions of sodium chloride at 150, 200, 250, 300 and 350°.

At 150° sodium chloride on the weight basis has almost exactly the same effect as sodium hydroxide in decreasing the solubility of sodium sulfate. With progressive increase in temperature, however, the sodium chloride becomes relatively more effective than the sodium hydroxide. Although at 350° the addition of sodium chloride causes an actual increase in solubility, this change is small compared to that produced by sodium hydroxide.

Examination of Figs. 5 and 6 immediately raises the question as to why the effect of sodium hydroxide and of sodium chloride upon the solubility of sodium sulfate should be reversed with increase in temperature, in the first case between 250 and 300° and in the second between 300 and 350°. Careful examination under the petrographic microscope has revealed no differences between the solid phases from determinations at these three temperatures either in water alone or in the presence of the added substances. Na_2SO_4 I probably was present in all cases under the conditions of the solubility determination. Assuming that it was, the observed effect must be ascribed to changes in the properties of the liquid phase. In this connection it is significant that the ionization constant of water increases more than 5000-fold from 0 to 218° but that at 306° it shows a lower value, according to the conductance measurements of Noyes and his co-workers.[18] The fact that the ionization constants of substances in aqueous solution generally exhibit maxima when plotted against temperature has been emphasized by Harned and Embree.[19] The observed change in effect of the added sodium salts in the present work possibly may be due to a marked decrease in ionization over the upper part of the temperature range.

Sodium Sulfate–Sodium Hydroxide–Sodium Chloride–Water.—The data for the solubility of sodium sulfate in solutions containing both sodium hydroxide and sodium chloride are given in Table VI at temperatures of 150, 200, 250, 300 and 350°. The independent effects of the two added substances may be deduced from a plot of these data. At each of the two lower temperatures an increase in the concentration of either sodium hydroxide or sodium chloride, over the range investigated, renders the sodium sulfate less soluble. At 250° the data show that at a high concentration of sodium chloride the solubility actually may be increased slightly by increase in the concentration of sodium hydroxide. At 300° increase in the sodium hydroxide concentration causes an increase in solubility in all the solutions. This effect would be expected from the curve for the solubility of sodium sulfate in solutions of sodium hydroxide at 300° shown in Fig. 5. Increase in the concentration of sodium chloride causes a slight decrease in the solubility of sodium sulfate.

At 350° sodium hydroxide causes a large increase in the solubility of sodium sulfate in all the solutions. Sodium chloride causes a slight increase in the solubility for concentrations of sodium hydroxide up to about 12 g. per 100 g. of water, but at sufficiently high sodium hydroxide concentrations this effect is reversed and the sodium chloride causes a slight decrease in the solubility.

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(17) A. Chrétien, *Ann. chim.*, [10], **12**, 9–155 (1929).

(18) A. A. Noyes, *Carnegie Inst. Wash.*, Pub. 63, p. 346 (1907).

(19) H. S. Harned and N. D. Embree, This Journal, **56**, 1050–1053 (1934).

TABLE VI

SOLUBILITY OF SODIUM SULFATE IN SOLUTIONS OF SODIUM HYDROXIDE AND SODIUM CHLORIDE AT 150, 200, 250, 300 AND 350°

Solution composition, g./100 g. H_2O NaOH	NaCl	Na_2SO_4
	150°	
3.0	4.9	29.4
3.0	10.0	24.0[a]
3.0	10.0	22.9[a]
3.1	15.2	17.6
3.0	20.6	13.8[a]
6.0	5.0	25.3
6.2	11.1	19.7
6.1	15.3	15.4
6.1	21.8	12.0
6.1	26.6	9.5[a]
6.1	33.1	7.6
12.2	5.0	18.5
12.1	10.3	14.7
12.2	15.8	11.6
12.2	21.6	9.4
12.3	26.7	7.8
24.8	5.3	10.7
24.5	10.5	8.6
24.9	16.3	7.5
24.6	25.2	6.1[a]
	200°	
3.1	2.5	35.3
3.2	5.0	32.6
3.1	10.2	25.9
3.1	16.8	20.0[a]
3.1	26.8	14.4
6.1	2.5	31.4
6.0	4.9	28.6
6.1	5.0	28.6
6.0	10.1	23.3
6.0	10.1	23.2
6.0	15.3	18.9[a]
6.2	16.7	17.8
6.1	22.2	15.2[a]
6.2	27.6	13.3
12.0	2.6	26.3
11.8	5.0	23.3
12.0	12.1	17.4
12.0	16.0	16.8
12.3	27.9	12.6
25.0	2.8	18.9
25.4	5.5	17.8
24.9	10.9	15.2
25.3	16.8	13.9
25.8	26.7	12.2
	250°	
3.0	0.0	40.5
3.2	2.8	36.1
3.0	5.3	31.4[a]
3.1	10.9	25.5[a]
3.1	16.9	22.0
2.9	25.9	17.7
6.1	2.8	33.2
5.9	5.4	32.3
6.0	11.0	24.6
6.0	16.9	21.0[a]
5.9	25.9	17.8
12.3	2.9	31.4
12.1	5.7	28.3[a]
12.1	11.5	24.5
12.2	17.5	21.8
12.1	27.0	18.7
23.9	3.0	19.5[b]
24.3	7.0	25.7
25.2	12.1	23.8
24.6	24.3	19.8
24.4	24.2	20.0
24.3	24.3	19.8
	300°	
5.3	3.3	26.2[a]
5.2	6.7	24.7[a]
5.2	13.5	21.5[a]
5.2	21.2	20.6[a]
5.3	30.2	20.9
12.6	3.6	32.4[a]
12.6	7.2	29.8
12.6	14.1	27.5[a]
12.2	30.6	24.9
24.5	3.5	35.3[a]
24.5	7.2	33.7[a]
24.5	17.2	32.0[a]
24.5	21.8	29.9
24.5	26.9	30.2
	350°	
5.0	4.0	13.0
4.6	7.6	14.7
4.9	16.4	18.8[a]
4.8	17.7	20.1
4.9	24.4	22.5
4.9	25.2	22.6[a]
11.8	1.2	30.6[a]
12.0	3.6	31.2
11.8	4.2	30.9
11.7	5.9	30.4
12.0	17.5	32.1[a]
11.6	21.2	32.3
11.5	28.8	33.2
25.1	1.4	54.2
24.4	3.1	53.1
24.4	3.1	53.0[a]
24.4	3.5	52.0[a]
24.5	6.2	50.9
24.4	6.9	51.5[a]
24.2	12.5	48.4
24.9	13.6	48.3
24.4	19.0	47.5[a]
23.8	21.0	47.3
23.9	22.8	46.2

[a] Calculated from initial concentrations. [b] Value low.

Interpolation at Intermediate Temperatures.—Solubility values at temperatures lying between the isotherms may be estimated roughly by direct interpolation. A more precise method is illustrated in Figs. 7 and 8 where curves for the solubility of sodium sulfate in constant concentrations of sodium hydroxide and of sodium chloride are drawn as a function of temperature. In locating these curves advantage has been taken of the fact that the inversion temperatures between the different forms of anhydrous sodium sulfate must be substantially independent of solution composition. While variation in the pressure of the

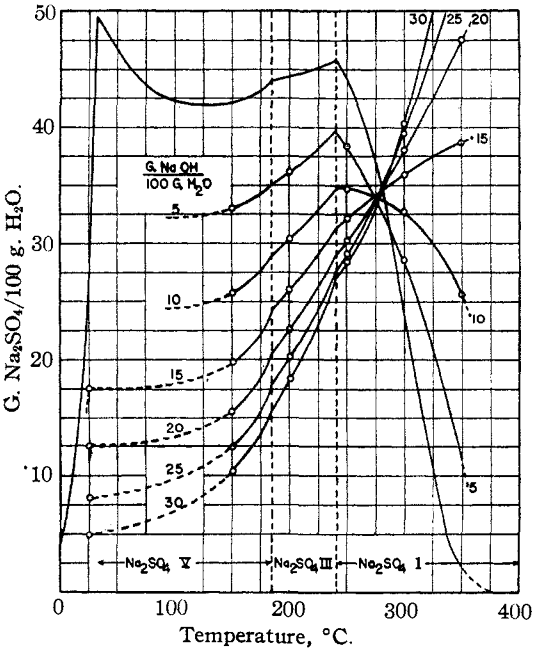

Fig. 7.—Curves for interpolation of solubility values in sodium hydroxide solutions at intermediate temperatures: points at 25° from J. D'Ans and O. Schreiner, *Z. anorg. Chem.*, 67, 437–441 (1910).

TABLE VII

COMPARISON OF MEASURED SOLUBILITY VALUES AT 275° WITH THOSE PREDICTED FROM FIGURES 13 AND 14

Solution composition, g./100 g. H_2O NaOH	NaCl	Determined Na_2SO_4	Predicted Na_2SO_4	Error, %
5.0	..	32.8	33.9	+3.3[a]
10.0	..	33.9	34.0	+0.3
..	5.2	28.1	28.0	−0.4
..	10.2	22.6	23.3	+3.1

[a] Calculated from initial concentration.

system as a result of variation in composition of the solution phase theoretically will displace these inversion points, the actual effect in the present case must be small.

The accuracy of interpolation from Figs. 7 and 8 was checked by four direct determinations at 275° with the satisfactory results shown in Table VII.

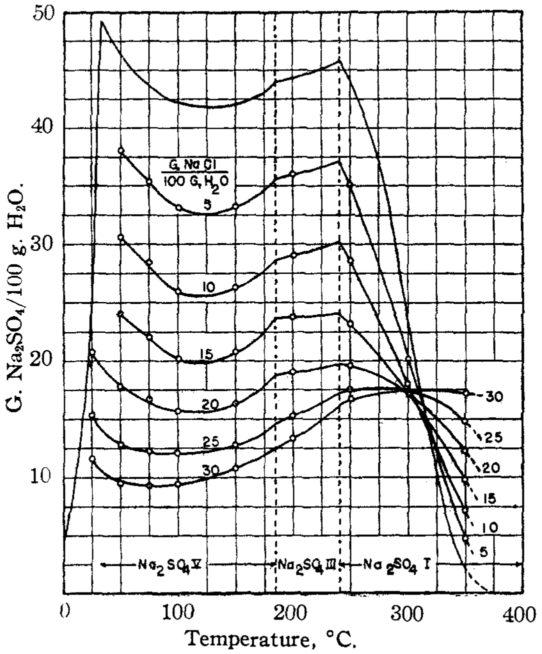

Fig. 8.—Curves for interpolation of solubility values in sodium chloride solutions at intermediate temperatures: points at 25, 50, 75 and 100° from A. Chrétien, *Ann. chim.*, [10] **12**, 9–155 (1929).

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Summary

1. A curve has been presented showing the solubility of sodium sulfate in water from 0 to 350°. The solid phases which are in equilibrium with the solution in the various temperature ranges have been indicated.

2. The solubility data for sodium chloride in water have been extended to 350°.

3. The effect of sodium hydroxide, in concentrations up to 35 g. per 100 g. of water, on the solubility of sodium sulfate at temperatures of 150, 200, 250, 300 and 350°, has been determined. At the three lower temperatures the sodium hydroxide decreases the solubility; at the higher temperatures it increases the solubility, this increase being great at 350°.

4. The effect of sodium chloride, in concentrations up to 35 g. per 100 g. of water, on the solubility of sodium sulfate at temperatures of 150 to 350° has been determined. From 150 to 300°, inclusive, sodium chloride decreases the solubility; at 350° it causes a slight increase in solubility.

5. The solubility of sodium sulfate in solutions consisting of mixtures of sodium hydroxide and sodium chloride has been determined. In general, each salt exerts its effect quite independently of the presence of the other salt.

6. A method has been presented for predicting solubilities at intermediate temperatures from data obtained at 50° temperature intervals.

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