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Solubility Equilibria of Sodium Sulfate at Temperatures from 150 to 350°. II. Effect of Sodium Hydroxide and Sodium Carbonate[1]

BY W. C. SCHROEDER,[2] A. A. BERK[3] AND ALTON GABRIEL[4]

This paper is the second of a series presenting the results of an investigation carried out in coöperation with the Joint Research Committee for Boiler Feed-Water Studies dealing with the solubility of sodium sulfate in various solutions in the temperature range from 150 to 350°. The bombs and the thermostat used in the investigation have been described in the first paper.[5]

The system sodium sulfate–sodium carbonate–water and the solid phases present in this system will be considered first, followed by a discussion of the effect of sodium hydroxide on the system.

Sodium Sulfate–Sodium Carbonate–Water from 150 to 350°

Data on the solubility of sodium sulfate have been discussed in the first paper in this series,[5] while Waldeck, Lynn and Hill[6] have established the solubility of sodium carbonate up to 350° and have critically compared their results with those of previous investigators. Agreement between all the data is not exact but is satisfactory. The solubility values above 150° have been checked at four temperatures during the present work as shown in Table I, and satisfactory agreement is evident at all temperatures except 350°. It is believed that the value of zero given by Waldeck, Lynn and Hill resulted from undue allowance for expansion of the solution with temperature. If the solution did not expand as much as anticipated, their sampler may not have been completely submerged in solution during the entire sampling period, and consequently steam may have entered instead of solution. It has been found that the presence of dissolved solid has a marked effect in reducing the expansion of water as the critical temperature is approached, and this would result in a lower solution level in the bomb than was expected.

TABLE I

COMPARISON OF PRIOR DATA FOR THE SOLUBILITY OF SODIUM CARBONATE AT TEMPERATURES ABOVE 150° WITH VALUES SECURED IN THE PRESENT INVESTIGATION

Temp., °C.	Soly., g. Na_2CO_3/100 g. H_2O Waldeck, Lynn, and Hill[a]	Present work
150	37.6	37.5
150	37.6	37.4
252	20.0	20.0
300	9.2	9.4
350	0.0	1.97
350	.0	2.02
350	.0	2.01

[a] Values interpolated from plot of data.

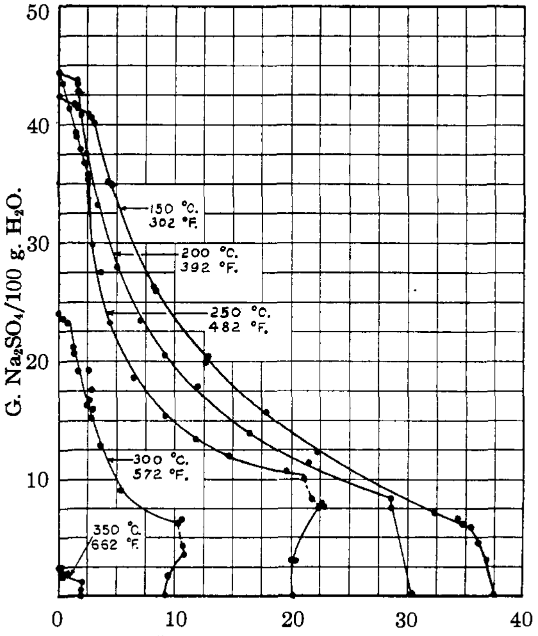

Fig. 1.—Sodium sulfate–sodium carbonate–water at 150, 200, 250, 300 and 350°.

The solubility curves for the system sodium sulfate–sodium carbonate–water are shown in Fig. 1, and the data are given in Table II at intervals of 50° from 150 to 350°. For all temperatures from 150 to 300°, inclusive, the initial branch of the curve appears to represent equilibrium with sodium sulfate or at least a solid

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(2) Research chemical engineer, Joint Research Committee on Boiler Feed-Water Studies, attached to Nonmetallic Minerals Experiment Station, U. S. Bureau of Mines, Rutgers University, New Brunswick, N. J.

(3) Junior analytical chemist, U. S. Bureau of Mines, Rutgers University, New Brunswick, N. J.

(4) Associate chemist-petrographer, U. S. Bureau of Mines, Rutgers University, New Brunswick, N. J.

(5) W. C. Schroeder, A. Gabriel and E. P. Partridge, THIS JOURNAL, **57**, 1539–1546 (1935).

(6) W. F. Waldeck, G. Lynn and A. E. Hill, *ibid.*, **54**, 928 (1932).

solution high in sodium sulfate, and the addition of sodium carbonate tends to reduce the solubility. The second branch of each curve represents equilibrium with a compound containing sodium sulfate and sodium carbonate. Increase in the concentration of either constituent in solution reduces the concentration of the other constituent.

TABLE II

SOLUBILITY DATA FOR THE SYSTEM SODIUM SULFATE–SODIUM CARBONATE–WATER AT 150. 200. 250. 300 AND 350°

G./100 g. H_2O	
Na_2CO_3	Na_2SO_4
150°	
1.5	41.3
1.5	41.4
2.6	40.8
2.8	40.6
3.1	40.0
4.2	35.3
4.3	35.0
8.2	26.3
8.2	26.6
12.7	19.9
12.9	20.3
17.8	15.6
22.2	12.3
32.3	7.2
34.2	6.7
34.7	6.2
35.5	5.9
36.2	4.7
37.0	3.0
200°	
1.5	43.9
1.6	43.8
1.7	42.9
1.9	41.4
2.4	38.1
3.7	33.1
5.1	27.9
7.1	23.4
9.3	20.5
12.2	18.0
16.4	13.9
21.7	11.4
28.7	8.4
28.7	7.5
250°	
0.5	43.4
.9	41.4
1.5	38.8
1.6	38.8
1.9	37.9
2.3	37.4
2.3	36.2
2.5	35.8
2.6	35.3
3.1	29.8
3.7	27.6
4.4	23.4
6.5	18.5
9.1	15.3
11.7	13.2
14.6	11.9
19.6	10.8
21.1	10.0
21.8	8.2
22.7	7.9
22.6	7.7
23.1	7.6
20.0	3.0
20.2	3.0[a]
20.4	3.0[a]
300°	
0.5	23.6
.7	23.4
1.2	21.1
1.4	20.6
1.7	19.1
2.6	19.2
2.6	16.3
2.6	17.2
2.7	16.5
3.0	17.6
3.0	16.3
3.0	15.1
3.6	12.7
5.4	9.0
10.7	6.7
10.4	6.4
10.7	4.0
11.0	3.4
9.4	1.7
350°	
0.2	2.5
.2	2.5
.4	1.6
.8	1.9
2.1	1.2
2.0	0.4

[a] Values calculated from initial concentrations.

At 150 and 200°, the final branch of the curve is in equilibrium with sodium carbonate. At 250 and 300°, another solid phase may intervene between the compound of sodium sulfate and sodium carbonate and the sodium carbonate alone.

At 350°, it is probable that the actual shape of the curve and the solid phases present are about the same as at 300°, but due to the low solubilities involved, the exact position of the complete curve was not determined, and the curve has been drawn to agree with the data obtained.

The data presented concern the system sodium sulfate–sodium carbonate–water at temperatures of 150° and higher. Some data also are available for this system at lower temperatures.[7,8]

Identification of Solid Phases

An attempt was made to determine the composition of the solid phases in equilibrium with the various branches of the curves shown in Fig. 1. The ratio of the salts remaining in the bombs after each run was calculated, and the solids were also examined by means of the petrographic microscope. The two methods, as will be seen, were in essential agreement and made it possible to establish the composition of each solid phase.

Chemical Composition.—The composition of the solid remaining in each bomb was secured by subtracting the amount of sodium carbonate and sodium sulfate that had gone into solution from the amount initially charged into the bomb. This method of calculating the composition was checked by chemical analysis of the samples for the curve at 150° in Fig. 1, the results agreeing within 2% of the sodium sulfate present. It is probable that the calculation is somewhat more accurate than the analysis of the solid samples as it is not influenced by the presence of mother liquor.

In Fig. 2, the mole fraction of sodium sulfate in the solid phase is plotted against the mole fraction of sodium sulfate or sodium carbonate of the total dissolved salts in the liquid phase. At 150 and 200°, the first points at the upper left indicate that the solid phase is sodium sulfate alone. The vertical branch represents equilibrium with two solid phases, and must correspond to an invariant point on the solubility curves. The solid phases present on this branch are believed to be sodium

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(7) N. S. Kurnakov and S. Z. Makarov, *Ann. inst. anal. phys. chim.* (Leningrad), **4**, No. 2, 307–63 (1930).

(8) J. E. Teeple, "The Industrial Development of Searles Lake Brines," A. C. S. Monograph, **49**, 182 pp., p. 65.

sulfate and a compound saturated with sodium sulfate. These phases have also been identified by petrographic examination. The horizontal branch indicates a compound containing dissolved sodium sulfate, passing through the pure compound, to the compound containing dissolved sodium carbonate. The final vertical branch again corresponds to an invariant point and the two solid phases are sodium carbonate and a compound saturated with sodium carbonate. The final solid phase is sodium carbonate alone. The figure indicates the composition of the compound to be $Na_2CO_3 \cdot 2Na_2SO_4$.

If these curves in Fig. 2 are compared with the solubility curves for the two lower temperatures in Fig. 1, we find the three branches that have been noted—the short sodium sulfate branch, the long branch involving solid solutions of the compound with the individual constituents, and, finally, the sodium carbonate branch.

At 250 and 300°, the curves for the composition of the solid phase are somewhat different. The sodium sulfate branch is very short, if it exists at all. The branch curving downward from the upper left-hand corner must correspond to a solid solution of sodium carbonate in sodium sulfate. Following this, there is some indication of a short vertical branch marking the transition to the region in which the compound capable of forming solid solutions exists. Between the latter and the horizontal branch at the lower right-hand corner of Fig. 2 representing sodium carbonate, there is no definite evidence of another phase, but the solubility curves in Fig. 1 indicate that one may exist over a narrow range. This may be another compound of sodium carbonate and sodium sulfate or a solid solution.

In the solubility curves in Fig. 1 for 250 and 300°, equilibrium with four solid phases is indicated—the first branch in equilibrium with the solid solution of sodium carbonate in sodium sulfate; a second branch in equilibrium with the compound containing dissolved sodium sulfate or sodium carbonate; a possible third branch in equilibrium with another compound or sodium sulfate in solution in sodium carbonate; and the fourth branch in equilibrium with sodium carbonate alone.

Microscopic Examination.—Throughout the investigation, the residual solid phases from the solubility bombs have been subjected to examination by means of a petrographic microscope. At the temperatures studied, but three fundamental solid phases were observed—(a) sodium sulfate, which at the higher temperatures shows evidence of taking up sodium carbonate in solid solution; (b) a compound, $Na_2CO_3 \cdot 2Na_2SO_4$, which forms solid solutions with both sodium sulfate and sodium carbonate; and (c) sodium carbonate.

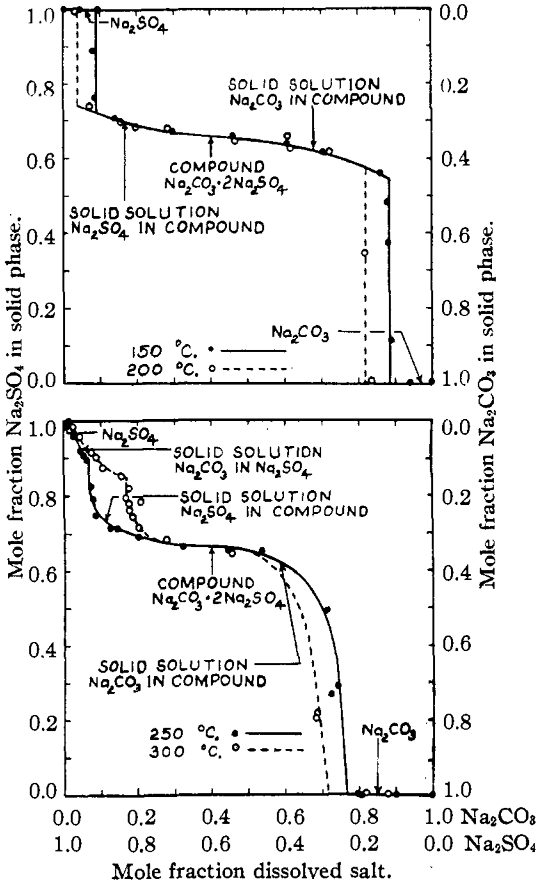

Fig. 2.—Composition of the solid phases in the sodium sulfate–sodium carbonate–water system at 150, 200, 250 and 300°.

At 150°, the solid phase consists of Na_2SO_4 V (thenardite), until the mole fraction of sodium carbonate in the dissolved salts reaches approximately 0.1. Further addition of sodium carbonate results in compound formation. At 200°, Na_2SO_4 III (modified on cooling to Na_2SO_4 V) is the solid phase to a concentration of 0.05 mole of sodium carbonate in the liquid phase. At 250°, and more strikingly at 300°, sodium sulfate possesses the property of combining in solid solution a limited amount of sodium carbonate. At the higher temperature this solid solution is the stable phase over the range up to a mole fraction of sodium carbonate in the dissolved salts of about 0.15, but may run metastable to about 0.21 in the field in which the compound described below is the stable phase. Incidentally, the tendency for the constituents to form solid solutions increases with temperature; Na_2CO_3–Na_2SO_4 melts, having been found miscible in the experimentally explored range of compositions from 0 to 0.75 mole fraction of Na_2CO_3, suggesting that the constituents form solid solutions in all proportions.

Further studies of the solid phases from the solubility bombs show that at 150° in the essentially horizontal portion of the phase diagram in Fig. 2, embracing the solids containing from about 0.75 to 0.50 mole fraction of sodium sulfate, there is obtained a homogeneous solid phase that does not resemble optically either sodium sulfate or sodium carbonate. This phase persists throughout the entire temperature range. At 250 and 300°, this branch of the curve narrows to that portion showing about 0.67 mole Na_2SO_4, which conforms to a compound with the composition $Na_2CO_3 \cdot 2Na_2SO_4$. The optical and crystallographic properties of this salt, to which the name "burkeite" has been given, are described by Foshag.[9] Rogers[10] had previously described a salt submitted to him as $Na_2CO_3 \cdot 2Na_2SO_4$, but a comparison of the optical properties of the compound, as given by Rogers and Foshag shows that they could not have had the same salt. In the present investigation, when $Na_2CO_3 \cdot 2Na_2SO_4$ was prepared, in the solubility bombs by charging with the required amount of solids to give exactly this compound, determinations of the optical properties gave values that closely checked those obtained by Foshag.

The orthorhombic crystals of the salt $Na_2CO_3 \cdot 2Na_2SO_4$ commonly show a rather wide pinacoid face (100), beveled on the side by the prism (110). The crystal shows dome (011) terminations making an angle of about 105°, sometimes truncated by the *c* pinacoid. Crystals lying on the face (100) are most commonly observed microsopically. This view shows a medium birefringence and parallel extinction, with the slower component vibrating crosswise of the crystal.

The narrow face of the side pinacoid described by Foshag is not usually developed, so that crystals lying normal to *c* (rarely observed) show the outline of a somewhat flattened hexagon. This view displays low birefringence, parallel extinction, and yields a symmetrical interference figure of the acute bisectrix type. The plane of the optic axes lies in the direction of the slower component, which vibrates parallel to the longest diagonal.

Burkeite is biaxial, negative, with medium small 2V (34°, Foshag): $r > v$ distinct; $X = B_{x_a} = c$; $Z = b$; $Y = a$; negative elongation; optic axial plane parallel to 100; refractive indices $\alpha = 1.451$ (±.003), $\beta = 1.489$ (±.003), $\gamma = 1.491$ (±.003). Foshag gives $\alpha = 1.450$ $\beta = 1.490$, $\gamma = 1.492$.

Comparison of the solid phase curves in Fig. 2 at 150 and 200° reveals a sufficient curvature in the horizontal portion to vary the composition of the solids from a possible compound $Na_2CO_3 \cdot 3Na_2SO_4$ to $Na_2CO_3 \cdot 2Na_2SO_4$ and finally to $Na_2CO_3 \cdot Na_2SO_4$, as the concentration of sodium carbonate increases. Indeed, investigators from time to time have reported "compounds" with various ratios of the two constituents.[11] However, in the present work, as samples were examined in the direction of increased content of sodium carbonate, no new solid phases were found. A single crystalline form was found to exist over the entire range, with a spread of refractive indices varying as a nearly linear function of composition from $\alpha = 1.465$, $\beta = 1.486$, $\gamma = 1.488$ at the end high in sodium sulfate to at least $\alpha = 1.445$, $\beta = 1.495$, $\gamma = 1.497$ with increasing sodium carbonate. Since the horizontal portion of each curve in Fig. 2 narrows with increased temperature to the vicinity of the salt with the composition $Na_2CO_3 \cdot 2Na_2SO_4$, it seems desirable to recognize this compound as having the property of forming solid solutions with either sodium carbonate or sodium sulfate.

Examination with the petrographic microscope did not show definitely any solid phase corresponding to sodium carbonate containing dissolved sodium sulfate, or to the second compound indicated on the solubility curves of Fig. 1 at 250 and 300°.

The petrographic findings have been substantiated by x-ray examination of the series, using the powder method, for which the authors are indebted to Professor Lewis S. Ramsdell, Mineralogical Laboratory, University of Michigan. The x-ray data confirm the hypothesis that the compound $Na_2CO_3 \cdot 2Na_2SO_4$ forms solid solutions with both of its constituents. Although the

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[9] W. F. Foshag, *Am. Min.*, **20**, 50 (1935).

[10] Rogers, *Am. J. Sci.*, **11**, 473 (1926).

[11] Private communication.

change in the dimensions of the unit cell is not great, patterns for the solid phases from solutions high in sodium sulfate have a distinctly larger spacing than those from solutions high in sodium carbonate. Also, the spacings for the latter are distinctly less than those of the pure compound. The indications are that the spacings for the compound containing excess sodium sulfate are very slightly larger than those of the pure compound. The x-ray examination further supports the study with the petrographic microscope which shows that sodium sulfate will dissolve a limited amount of sodium carbonate at the higher temperatures.

Effect of Sodium Hydroxide on the System

Before studying the effect of sodium hydroxide on the sodium sulfate–sodium carbonate–water system, some data on the solubility of sodium carbonate in solutions of sodium hydroxide were collected. These data are given in Table III and are plotted in Fig. 3. At 150 and 250°, the sodium hydroxide decreases the solubility of the sodium carbonate, but at 350° it increases the solubility quite sharply, as in the case of sodium sulfate.[5]

TABLE III

SOLUBILITY OF SODIUM CARBONATE IN SOLUTIONS OF SODIUM HYDROXIDE AT 150, 250 AND 350°

Temp., °C.	G./100 g. H_2O NaOH	G./100 g. H_2O Na_2CO_3
150	7.2	26.2
	19.5	13.4
250	8.1	14.2
	21.4	11.5
350	8.1	4.9
	7.2	9.7[a]
	20.2	12.7

[a] Value high.

Two investigators in Russia[12,13] have secured values for the solubility of sodium carbonate in solutions of sodium hydroxide at temperatures from 50 to 140°. At temperatures from 50 to 105° the results show a very large disagreement, and it is not possible to decide definitely, from the data available, which values are the most accurate. Allowing for a temperature difference of 10°, the values obtained by Prikhodko[12] at 140°, with the exception of one point, are in agreement with the results obtained in the present study at 150°. The one value that does not agree is also inconsistent with the rest of the data and the solubility for sodium carbonate in water.

Russian investigators have also collected data for the system sodium carbonate–sodium chloride–water at temperatures from −21.4 to 60°.[14]

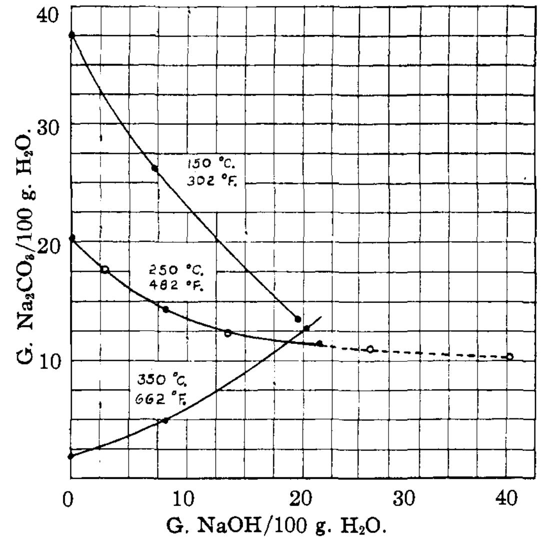

Fig. 3.—Solubility of sodium carbonate in solutions of sodium hydroxide at 150, 250 and 350°: ○, F. G. Straub; ●, present data.

F. G. Straub[15] has reported several values for the solubility of sodium carbonate in solutions of sodium hydroxide at 215 and 250°. These values are expressed in terms of grams per liter and cannot be converted directly to grams per 100 g. of water, especially in view of the fact that some of the solutions may be supersaturated at room temperature. If it is assumed, however, that the solutions can exist and that, on a basis of weight concentration, sodium carbonate and sodium hydroxide have additive effects on the density of the solution, comparison can be made. This latter assumption is not unreasonable up to moderate concentrations of dissolved solid, inasmuch as data are available to show that equal weight concentrations of sodium carbonate or sodium hydroxide do produce solutions of about the same density. When calculated in this manner, Straub's results for 250°, as shown in Fig. 3, are in extremely good agreement with the values secured in the present investigation.

Table IV gives data for the system Na_2SO_4–Na_2CO_3–NaOH–H_2O at temperatures of 150, 250, and 350° for two concentrations of sodium hydroxide. No evidence was found to indicate that the addition of the sodium hydroxide caused a change

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[12] G. W. Prikhodko, *J. Applied Chem.* (U. S. S. R.), **5**, 31–3 (1932).

[13] Udintzeva and Popovich, *ibid.*, **4**, 219–27 (1931).

[14] Makarov, *J. Gen. Chem.* (U. S. S. R.), **3**, 234–248 (1933).

[15] F. G. Straub, Embrittlement in Boilers, Univ. Ill. Eng. Expt. Sta. *Bull.* **216** (1930), 128 pp., p. 75, 76.

in solid phase at either 150 or 250° and the phases are believed to be the same as given for these temperatures in Fig. 2. The addition of the sodium hydroxide at 350° caused a large increase in solubility and allowed a more accurate determination of the position of the curve than was possible in the system Na_2SO_4–Na_2CO_3–H_2O at this temperature. A short branch of the curve indicates equilibrium with sodium sulfate containing dissolved sodium carbonate; the second long branch is probably in equilibrium with the compound $Na_2CO_3 \cdot 2Na_2SO_4$ containing dissolved sodium sulfate or sodium carbonate and the final branch corresponds to equilibrium with sodium carbonate. Another solid phase may also exist between the compound and the final sodium carbonate branch. Comparison of the data in Table IV with those in Table II for corresponding temperatures will show that the addition of sodium hydroxide at 150 and 250° for any given sodium carbonate concentration causes a decrease in the amount of sodium sulfate dissolved in the solution. In other words the addition of sodium hydroxide progressively shifts the curves toward lower concentrations. At 350° the addition of sodium hydroxide causes a pronounced shift toward higher concentrations.

TABLE IV

EFFECT OF SODIUM HYDROXIDE ON THE SYSTEM SODIUM SULFATE–SODIUM CARBONATE–WATER AT 150, 250 AND 350°

G./100 g. H_2O		
NaOH	Na_2CO_3	Na_2SO_4
	150°	
7.7	0.9	28.7
7.6	1.4	29.0
7.7	1.5	28.8
7.8	1.6	28.8
7.7	1.7	28.9
7.6	2.2	25.7
7.8	5.1	18.1
8.0	9.2	12.2
8.0	13.8	8.8
7.6	24.8	4.5
7.8	25.1	4.5
7.5	25.6	2.3
19.5	0.7	16.3
19.5	1.0	16.5
19.2	1.1	16.2
19.4	1.2	16.7
19.4	1.2	16.4
19.4	1.2	16.2
19.4	2.0	11.6
19.6	2.7	9.7
19.2	9.1	4.3
19.3	13.2	2.7
19.4	13.5	1.5
	250°	
7.9	0.5	33.6
7.9	1.3	32.1
7.6	1.6	31.7
7.8	1.9	28.3[a]
8.0	2.4	25.0
7.8	2.6	23.6[a]
8.0	3.6	18.4[a]
7.8	5.1	14.6
7.8	5.5	13.8[a]
8.0	6.0	13.6[a]
8.1	7.9	11.7
8.0	12.6	8.6
7.9	12.6	9.3
7.8	15.1	8.0[a]
7.8	16.0	6.8
7.9	15.7	6.7
8.1	16.3	6.4
8.0	14.4	2.9
7.8	14.7	2.9
19.8	0.6	29.8
18.8	1.3	28.9
19.7	1.9	25.3
19.0	2.1	19.0
19.0	3.0	16.0
19.7	3.8	12.7
19.6	8.6	7.7
19.9	11.7	6.8
20.0	12.8	5.9
20.2	11.9	3.0
	350°	
8.0	0.3	17.1
8.1	.7	16.0
8.3	1.2	12.0
8.1	2.0	8.8
8.6	4.0	6.6
8.6	4.9	3.8
8.5	5.1	2.8
8.5	4.9	1.5
20.9	0.7	46.3
20.7	1.1	43.4
20.4	2.6	35.0
20.9	4.7	28.0
20.1	7.9	20.9
20.7	13.0	15.2
19.9	13.3	12.1
20.5	13.5	7.2[a]
19.7	12.6	4.6

[a] Calculated from initial concentrations.

Straub[15] also has reported a series of values at 175, 250 and 300° for the system sodium sulfate–sodium carbonate–sodium hydroxide–water, at 100 g. of sodium hydroxide per liter of solution. Again assuming additive effects equal to that of the sodium hydroxide for all of the dissolved solids, these values at 250° were compared with those in Table IV. Good agreement existed at low concentrations of sodium carbonate, but the data diverged very widely at the higher concentrations. This difference may result from the fact that Straub did not agitate his bombs, and consequently failed to reach equilibrium. Agitation would be especially important at the higher sodium carbonate concentrations in this system, as the sodium carbonate and sodium sulfate charged into the bomb must all go into solution and reprecipitate as a new solid phase.

Three methods of analysis were used during the present work for the determination of carbonate. When only sodium sulfate and sodium carbonate were present, the carbonate was determined by titration to the methyl red end-point in the cold, then the sample was heated to the boiling point and the titration finished.

When sodium sulfate, sodium carbonate and sodium hydroxide were present in the sample, the carbonate was determined either by the titration of two samples, from one of which the carbonate has been precipitated; or by acidifying the sample, evolving the carbon dioxide and absorbing it in standard barium hydroxide. In the method using two samples an excess of standard acid was added to one sample, it was boiled very gently for two to three minutes to drive off the carbon dioxide, and was then back-titrated to the phenolphthalein end-point with standard sodium hydroxide. A slight excess of strontium chloride over that necessary to precipitate all the carbonate was added to the second sample; it was brought to a boil in a stoppered flask, cooled, and then titrated to the phenolphthalein end-point with standard acid. From these two titrations, both the hydroxide and carbonate could be calculated. Strontium chloride was used to precipitate the carbonate instead of barium chloride in order to avoid precipitation of the sulfate with consequent errors from occlusion.[16]

When the sodium carbonate present was determined by the evolution method the sample was acidified with sulfuric acid and a stream to gas was circulated through the sample, through the standard barium hydroxide and then recirculated through the sample until complete absorption of the carbon dioxide in the barium hydroxide had been secured.[17] After this absorption, the excess of barium hydroxide was titrated with acid to determine the carbonate. The hydroxide was determined by titrating a separate sample to the methyl red end-point and making a deduction for the carbonate present.

Table V gives the results obtained on five samples that were analyzed for carbonate by the evolution method and by the method using strontium chloride. Satisfactory agreement is shown.

TABLE V

COMPARISON OF EVOLUTION METHOD AND STRONTIUM CHLORIDE METHOD FOR THE DETERMINATION OF CARBONATE

Grams Na_2CO_3 present Evolution method	 Strontium chloride method
1.52	1.54
0.58	0.56
.128	.128
.242	.235
.380	.383

The total solid was determined in all the samples by conversion of the carbonate to sulfate, evaporation to dryness, ignition and weighing. If the total solid obtained in this manner did not check the total solid as calculated from the analysis within 1%, the analysis of the sample was repeated.

Acknowledgments.—The authors wish to acknowledge the assistance of Lewis S. Ramsdell, of the University of Michigan, in the x-ray examination of the solid phases; and the suggestions of Dr. Everett P. Partridge, formerly of the Bureau of Mines, in the collection of the data and the preparation of the manuscript.

Conclusions

1. Complete data have been presented for the system sodium sulfate–sodium carbonate–water at intervals of 50° from 150 to 350°.

2. Three solid phases have been found to exist at 150 and 200°—(a) sodium sulfate, (b) a compound ($Na_2CO_3 \cdot 2Na_2SO_4$ containing dissolved sodium sulfate or sodium carbonate and (c) sodium carbonate. At 250 and 300°, the solid phases appear to be (a) a solid solution of sodium carbonate in sodium sulfate, (b) a compound ($Na_2CO_3 \cdot 2Na_2SO_4$) containing dissolved solved sodium sulfate or sodium carbonate, (c) a possible second compound with a higher ratio of sodium carbonate to sodium sulfate, stable only over a very narrow range and (d) sodium carbonate. At the higher temperatures the sodium sulfate and sodium carbonate have a higher solubility in the compound than at the lower temperatures.

3. Curves have been given to show the effect of sodium hydroxide on the system. At 150 and 250°, sodium hydroxide up to 20 g. per 100 g. H_2O lowers the concentrations of both sodium carbonate and sodium sulfate with respect to all solid phases; at 350° sodium hydroxide increases the concentrations very greatly.

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(16) W. C. Schroeder, *Ind. Eng. Chem., Anal. Ed.*, **5**, 389 (1933).

(17) E. P. Partridge, W. C. Schroeder and L. F. Collins, *ibid.*, **4**, 271 (1932).