TABLE I

AREAS OF SOLIDS CALCULATED BY THE NEW METHOD OF HARKINS AND JURA AND BY THAT OF BRUNAUER, EMMETT AND TELLER[a]

Areas in square meters per gram

	New method of Harkins and Jura				B.E.T. method				
	N_2	H_2O	*n*-Butane	*n*-Heptane	N_2 σ = 16.1	H_2O 14.8	H_2O 11.3	*n*-Butane 56.6	*n*-Heptane 64.0
TiO_2 (Standard)	13.8	13.8	13.8	13.8	13.8	13.8	10.5	13.8	13.8
TiO_2 II	8.7	8.4		8.7	8.6	11.7	8.8		8.7
SiO_2 (Quartz)	3.2	3.3		3.3	3.2	4.2	3.2		3.6
$BaSO_4$	2.4	2.3	2.2	2.3	2.4	2.8	2.1	2.7	2.4
$ZrSiO_4$	2.9	2.7			2.8	3.5	2.7		
$TiO_2 + Al_2O_3$	9.6	11.8			9.5	12.5	9.5		

[a] This is Table III of the paper by Harkins and Jura (ref. 3) with a column of calculations for the areas by B.E.T. method using water isotherms with an assumed cross-section of 11.3Å.^{2} for the water molecule.

Harkins and Jura plots where cross-sectional areas (in sq. Å. per molecule) of 14.8 for water; 56.6 for *n*-butane; and 64 for *n*-heptane are arbitrarily assigned. However, an assignment of 11.3 sq. Å. to water in place of 14.8 gives, as shown in Table I, substantially as good average agreement as obtained by Harkins and Jura, there being only one serious discrepancy in each comparison. Nevertheless, one gets such good agreement only by assigning values of 11.3, 56.6 and 64, for water, *n*-butane and *n*-heptane, rather than 10.5, 32 and 45 sq. Å. that one would calculate from the density of the liquids in the prescribed manner. It, therefore, seems that the cross-sectional areas that have to be assigned to adsorbate molecules to obtain areas agreeing with those calculated from nitrogen isotherms are sometimes larger than those calculated from liquid densities by factors of as much as 1.5. This is consistent with the results reported by Beebe, Beckwith and Honig[15] who found that values of about 19.5 sq. Å. had to be assigned to krypton molecules in measurements at −195° to obtain surface area values on a variety of adsorbents in agreement with those gotten from nitrogen isotherms. This value, 19.5, is about 30% larger than one would calculate in the normal way from the extrapolated value for the density of liquid krypton at −195°.

As pointed out above, until many more data are obtained, it is impossible to say which method will, on the average, give the more reliable and more nearly correct area measurements. Meantime, it will be well to keep in mind the various points raised in the present discussion and to proceed with caution in cross-comparing areas of porous or finely divided solids obtained by the use of different adsorbates.

Summary

A correlation has been pointed out between the heat of adsorption of nitrogen and the molecular area that has to be assigned to adsorbed nitrogen molecules to bring about agreement between the method of Brunauer, Emmett and Teller and that of Harkins and Jura for measuring the surface areas of finely divided or porous solids by low temperature nitrogen adsorption isotherms. The significance, usefulness and limitations of the two methods are discussed.

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[15] Beebe, Beckwith and Honig, THIS JOURNAL, **67**, 1554 (1945).

The System Sodium Carbonate–Sodium Sulfate–Sodium Hydroxide–Water at 100°[1]

BY STANLEY J. GREEN[2] AND FRANCIS J. FRATTALI[3]

Introduction

The pilot-plant investigations by the Federal Bureau of Mines covering the extraction of alumina from Pennsylvania high-iron, diasporic, nodular clays by the lime-soda sintering process presented a problem of sulfur elimination from the plant liquors. Oxidation of the pyrite which occurs in the clays and combustion of sulfur-containing fuel produce sulfates during the sintering treatment and account for the presence of sulfate in the leach liquors. Because these liquors are recycled in the process, the sulfate concentration gradually increases and affects the efficiency of the several operations. It has been proved experimentally in the laboratory that sulfate not only detrimentally affects the amount of alumina extracted but also interferes with the recovery of soda from the processed liquors. Efficient recovery of soda is necessary in order to make this method of alumina production economical.

The plant liquors from which soda is to be re-

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covered contain the sodium salts of aluminate, carbonate, hydroxide, sulfate and a small amount of silicate.

The presence of so many compounds in these solutions produces a complex system for phase-rule study. However, preliminary tests indicated that the alumina and silica do not attain saturation nor do they affect appreciably the solubility of the other constituents. Therefore, the Al_2O_3 and SiO_2 concentrations can be ignored in the phase study. It was essential to determine the 100° isotherm of the 4-component system Na_2CO_3–Na_2SO_4–NaOH–H_2O in order to develop methods of sulfate removal, as data for this system at the desired temperature were not available in the literature.

Related to the study of the 4-component system, neglecting silicate and aluminate, are the three ternary systems, namely: (1) the system Na_2CO_3–NaOH–H_2O; (2) the system Na_2SO_4–Na_2CO_3–H_2O; and (3) the system Na_2SO_4–NaOH–H_2O. At 60° and at lower temperatures, system 1 was studied by Freeth,[4] and in the range of 50 to 140° by Prichodko.[5] Several investigators[6,7,8,9] reported on system 2 at various temperatures from 25 to 70° and from 150 to 350°, but their data do not include solubility at 100°. System 3 was studied by Prichodko at temperatures of 50 to 140°. The work conducted by Schroeder, *et al.*,[9] on the effect of sodium hydroxide and sodium carbonate on the solubility equilibria of sodium sulfate at temperatures of 150 to 350° suggested a discrepancy in Prichodko's data. Taking these into consideration, it was necessary that all three ternary systems be determined together with the 4-component system at 100°.

Experimental Methods

The work was carried out in four 2.5-liter iron vessels suitably constructed for the removal of samples, measurement of temperature and agitation. A few trial runs showed that a scraper blade resting nearly flush with the walls of the vessel was necessary to eliminate caking and to provide efficient agitation. The agitators were driven at approximately 240 r. p. m., and the temperature was maintained constant, in an electrically heated oil-bath, at 100 ± 1°

The reagents employed in the experiments were Baker C.P. analyzed chemicals. These consisted of anhydrous sodium carbonate, crystals of sodium carbonate monohydrate, anhydrous sodium sulfate, and sodium hydroxide (special). In addition to these compounds, it was necessary to prepare the double salt, burkeite, $2Na_2SO_4{\cdot}Na_2CO_3$, which was done by evaporating a solution containing the single salts in the proper ratio.

The ternary systems were determined by preparing first a saturated solution of one of the components and then placing it in the thermostat with about 10% excess solids to ensure saturation. By limiting the solids in contact with solution to this value, equilibrium was attained in a reasonable time, as found by tests. This was done by withdrawing samples of solutions periodically for analysis until no change in composition was evident. Thereafter, the phase study was conducted by the method described by Teeple,[7] which consisted of making small additions of the third component to the saturated solution. After each addition, samples were removed and analyzed. During most of the work, it was found that twenty hours was sufficient time to reach equilibrium when a simple salt comprised the solid phase, and two or three times this amount of time for complexes in which the solid phase consisted of a solid solution.

Liquid samples at the temperature of the solution were obtained by introducing a fritted-glass crucible (10 mm. diameter) connected to a 10-ml. pipet into the solution vessel and then forcing a fixed volume of filtered solution to enter the pipet by blowing compressed air into the vessel. This filtered solution was delivered into a weighing bottle, then weighed and diluted for chemical analysis. For samples of solid phase, however, the pipet was replaced with a 20-mm.-bore tubing connected to a 250-ml. Erlenmeyer flask into which slurry was delivered and immediately filtered on a Buchner funnel.

The method of initial complexes of known composition was also used to determine several points of the system Na_2CO_3–Na_2SO_4–H_2O and especially the invariant points; this method served as a check on the method employed by Teeple.

The 4-component system was obtained according to the method of Teeple by determining only its univariant lines. Complexes at the two invariant points in the Na_2CO_3–Na_2SO_4–H_2O system were prepared, and to these complexes small quantities of solid sodium hydroxide were added, thus developing the univariant lines. As the field of high sodium hydroxide was not pertinent to our problem, these two lines were sufficient to define the major portion of the 4-component system.

Chemical analysis of the liquids having no sodium hydroxide present consisted in determining carbonate as CO_2 by the gravimetric absorption method; sulfate gravimetrically by precipitating in acid solution as $BaSO_4$; and total Na_2O gravimetrically by the triple acetate method. The Na_2O determination served as a check on the accuracy of the other analytical results and where results varied by more than 3%, these were rejected and the experiment repeated. Solutions containing both the carbonate and hydroxide of sodium were analyzed by the Winkler method. Thus by titrating one portion of a sample to the methyl orange endpoint the total alkalinity was determined, and by titrating the second portion against phenolphthalein after precipitation of carbonate with barium chloride, the alkalinity due to sodium hydroxide was found. From the difference of these two titrations the carbonate present was calculated.

The wet residues were analyzed as such, and their compositions were plotted in conformity with Schreinemakers' rest method of establishing the nature of the solid phases. The chemical compositions of the wet residues were determined from an analysis of their water, carbon dioxide, sulfur trioxide and total Na_2O contents; the sodium hydroxide in the solids were established by calculations. A portion of these wet residues was dried in air for a period of eighteen hours or more and examined by the powder immersion method under the petrographic microscope. Values of the optical properties of the salts encountered in this study appear in standard texts on petrography.[10] Utilizing this technique, chemical analysis of the solids was confirmed, and this method alone would have been sufficient for identification had it not been for solid solutions. In those cases, where solid solutions were encountered, the microscope could not be relied upon solely because variations occurred in the relative amounts of the constituents in solid solution and consequently corresponding variations in optical properties were observed which introduced uncertainties in this method of detection.

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(4) F. A. Freeth, *Trans. Roy. Soc.*, **223B**, 35 (1922).

(5) G. V. Prichodko, *J. Applied Chem.*, U. S. S. R., **5**, 31 (1932).

(6) W. A. Caspari, *J. Chem. Soc.*, **125**, 2381 (1924).

(7) J. E. Teeple, "The Industrial Development of Searles Lake Brines," A. C. S. Monograph 49, pp. 66–72.

(8) N. S. Kurnakov and S. Z. Makarov, *Ann. Inst. Anal. Phys. Chem.* (Leningrad), **4**, No. 2, 307–363 (1930).

(9) Schroeder, *et al.*, THIS JOURNAL, **58**, 843 (1936).

(10) Winchell, "Microscopic Characters of Artificial Minerals," John Wiley and Sons, Inc., New York, N. Y., 1931.

The temperature of the solution in the reaction vessel was measured at the time of sampling. These readings indicated that the temperature was maintained at 100 ± 1.0° throughout the experimental work.

Experimental Results and Discussion

Solubility of Na_2CO_3 in Aq. NaOH.—The data for this system are calculated in Table I, and a plot of the solution compositions appears in Fig. 1. No attempt was made to define the system in the region of saturated solution of sodium hydroxide because the plant liquors, as explained previously, never would reach such high alkali concentrations. In the concentration range studied, the solid phase in equilibrium with the solution was examined under the petrographic microscope and identified as $Na_2CO_3 \cdot H_2O$. The chemical analyses of the wet residues in Table I further confirm this conclusion.

A comparison of our data with those of Prichodko[5] was made graphically, and our values for the Na_2CO_3 concentrations were found to be 1 to 3% higher. Although no explanation can be proposed for this disagreement, it should be mentioned that this author used at 100° the ampule technique, whereby a sealed ampule containing the complex is subjected to temperature changes and the points of appearance and disappearance of heterogeneity are recorded; the average temperature is taken as the saturation temperature. Good agreement however, exists with Freeth's[4] 60° isotherm, indicating that there is a very small change in solubility between 60 and 100°.

TABLE I

SOLUBILITIES IN AQ. NaOH AT 100°

Solid phase	Solution composition, weight per cent. Na_2CO_3	NaOH	Wet residue composition, weight per cent.[a] Na_2CO_3	NaOH
$Na_2CO_3 \cdot H_2O$	30.8	0.0	..	...
$Na_2CO_3 \cdot H_2O$	28.9	1.1	..	0
$Na_2CO_3 \cdot H_2O$	27.5	2.0	82.2	0
$Na_2CO_3 \cdot H_2O$	23.8	4.6	87.6	0
$Na_2CO_3 \cdot H_2O$	20.3	7.5	..	...
$Na_2CO_3 \cdot H_2O$	20.2	7.6[b]	80.0	0
$Na_2CO_3 \cdot H_2O$	16.6	10.5	71.7	2.6
$Na_2CO_3 \cdot H_2O$	12.8	13.8	84.3	0
$Na_2CO_3 \cdot H_2O$	9.4	17.1	83.5	0.7
$Na_2CO_3 \cdot H_2O$	7.6	19.0	83.7	3.8
$Na_2CO_3 \cdot H_2O$	5.5	21.9	81.0	2.0
$Na_2CO_3 \cdot H_2O$	4.8	24.2	78.0	5.0
$Na_2CO_3 \cdot H_2O$	3.6	27.0	71.8	7.7
$Na_2CO_3 \cdot H_2O$	2.7	29.7	69.2	8.8
Na_2SO_4	Na_2SO_4	NaOH	Na_2SO_4	NaOH
Na_2SO_4	30.0	0	..	...
Na_2SO_4	22.9	4.0	..	...
Na_2SO_4	16.2	8.6	65.6	0
Na_2SO_4	12.7	12.1	..	...
Na_2SO_4	9.5	15.4	..	...
Na_2SO_4	6.8	18.4	..	...
Na_2SO_4	4.7	22.9	..	...
Na_2SO_4	2.9	27.4	..	...
Na_2SO_4	2.1	31.6	..	...
Na_2SO_4	1.7	35.2	80.9	4.8

[a] NaOH calculated by difference. [b] Agitation time forty-four hours, all others twenty hours.

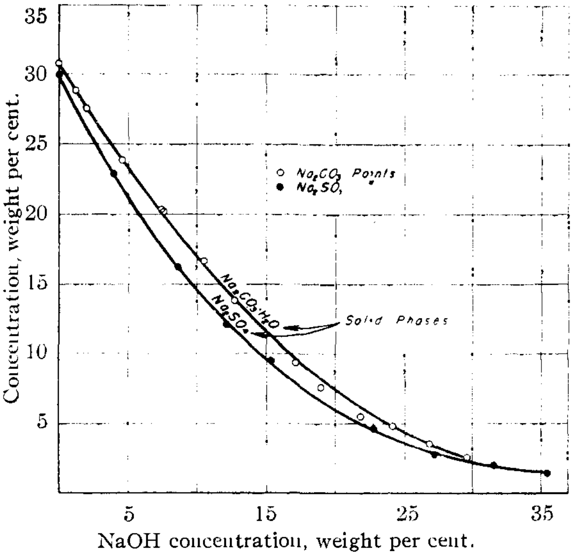

Fig. 1.—Solubilities in aq. NaOH at 100°.

Solubility of Na_2SO_4 in Aq. NaOH.—The data for this system are shown in Table I and plotted in Fig. 1. The solid phase in the range of concentrations studied was anhydrous sodium sulfate.

The wet residues of this system primarily were identified by means of the petrographic microscope. Crystals were obtained from the fritted glass crucible and were immediately pressed between filter paper to remove as much of the adhering mother liquor as was possible before the microscopic examination. Several chemical analyses were made and these confirm the results obtained petrographically.

The authors' solution analyses were compared to Prichodko's[5] results and, here again, his values are about 2% lower in most instances, his points, moreover, being on a line essentially parallel to the one resulting from this work.

System Na_2CO_3-Na_2SO_4-H_2O.—The data for this ternary system are presented in Table II and were obtained by essentially four different methods. Method A consisted in adding increments of anhydrous Na_2SO_4 to a saturated solution of Na_2CO_3 in equilibrium with $Na_2CO_3 \cdot H_2O$; Method B employed the commonly used initial complex of known composition technique; while Method C involved the addition of Na_2SO_4 to a solution just past the invariant point in the high Na_2CO_3 field in contact with virtually pure burkeite and Method D consisted of adding Na_2CO_3 to a saturated Na_2SO_4 solution in contact with excess solid. By analyzing the solution on successive days, sufficient time was allowed for the attainment of equilibrium; the time utilized for each method is indicated in the footnotes of Table II.

TABLE II

THE SYSTEM Na_2CO_3–Na_2SO_4–H_2O AT 100°

Solution	Method of detns.[a]	Solution composition, weight per cent. Na_2CO_3	Solution composition, weight per cent. Na_2SO_4	Wet residue composition, weight per cent. Na_2CO_3	Wet residue composition, weight per cent. Na_2SO_4	Solid phase[b]
1	..	30.8	0	..	..	$Na_2CO_3·H_2O$
2	A	29.6	2.1	84.8	0.8	$Na_2CO_3·H_2O$
3	A	28.8	3.4	78.7	1.9	$Na_3CO_3·H_2O$, S.S.
4	B	28.4	3.2	54.6	21.5	$Na_2CO_3·H_2O$, S.S.
5	B	28.6	3.4	51.4	26.8	$Na_2CO_3·H_2O$, S.S.
6	C	24.8	5.4	32.9	58.3	.... S.S.
7	C	22.6	6.6	..	..	.... S.S.
8[c]	C	18.5	9.4	30.1	56.5	.... S.S.
9[c]	C	17.3	10.3	29.0	59.5	.... S.S.
10	C	14.9	13.1	27.5	59.2	.... S.S.
11	B	13.6	14.0	25.6	63.0	.... S.S.
12	C	8.8	19.4	25.2	64.8	.... S.S.
13	C	6.8	22.0	24.3	68.1	.... S.S.
14[d]	C	6.8	22.2	24.4	68.9	.... S.S.
15	B	4.0	26.6	19.3	70.5	Na_2SO_4, S.S.
16	D	4.2	26.4	8.5	79.8	Na_2SO_4, S.S.
17	D	2.9	28.0	0.7	99.1	Na_2SO_4
18	D	1.5	28.3	1.6	98.2	Na_2SO_4
19	..	0	30.0	..	..	Na_2SO_4

[a] Agitation time: A, 20 hours; B, 72 hours; C, 44 hours; D, 20 hours. [b] S.S. is abbreviation for solid solution. [c] Agitation time 68 hours. [d] Agitation time 116 hours.

A ternary plot of the system is shown in Fig. 2 wherein is noted a 3-branched curve. The two outer branches represent equilibrium with $Na_2CO_3·H_2O$ and Na_2SO_4, respectively. The middle branch represents equilibrium with a sulfate compound of varying composition approximating that of burkeite $2Na_2SO_4·Na_2CO_3$ and having a range in composition of (1.4–2.2) $Na_2SO_4·Na_2CO_3$.

Solid Phase Composition.—Figure 3 shows the relations between the salt ratios of liquid and solid phases. The solution data were obtained by simple calculations while the percentages of total solids for the solid phase were obtained by extrapolating the tie lines between the solution and wet residue compositions as indicated on Fig. 2. The two limits of the solid solution are designated as Solid Solution A and Solid Solution B and have the composition $1.4Na_2SO_4·Na_2CO_3$ and $2.2Na_2SO_4·Na_2CO_3$, respectively.

The Na_2CO_3–Na_2SO_4–NaOH–H_2O System.—The data describing this system are presented in Table III and illustrated in Fig. 4. The relative amounts of the three salts in solution, expressed in per cent. of total solids on a weight basis, are indicated in this ternary plot. The three corners of the diagram indicate saturated solutions of the respective salts, while the three sides represent the related three-component systems previously described. All points inside the triangle, therefore, represent solutions saturated with respect to a particular solid phase. The two

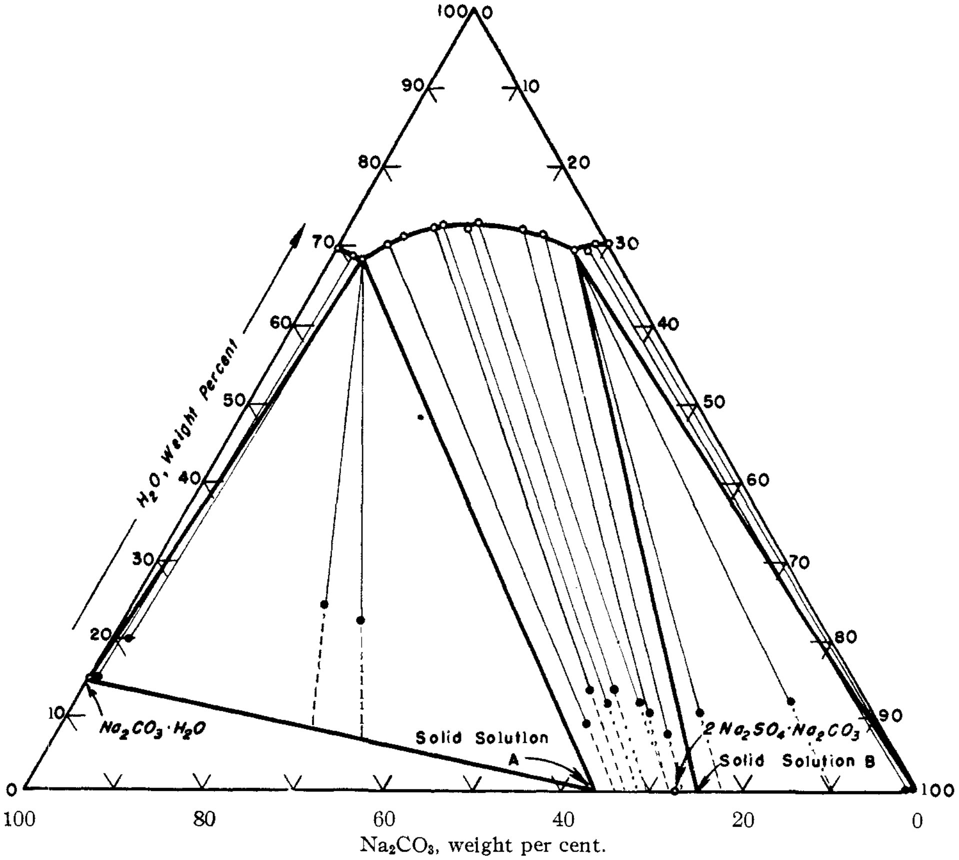

Fig. 2.—The system Na_2CO_3–Na_2SO_4–H_2O at 100°: O, saturated solution; ●, wet residues.

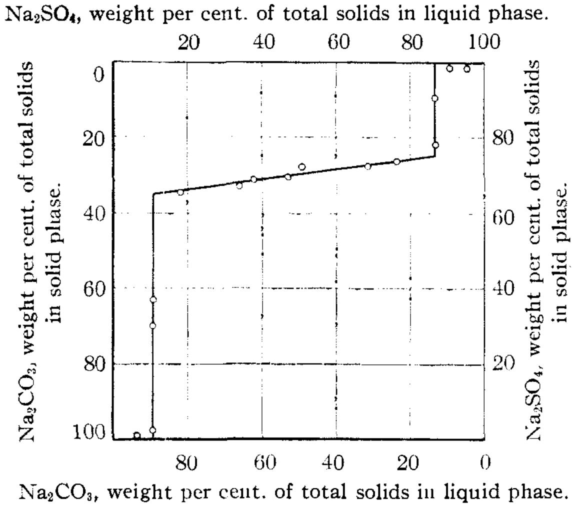

Fig. 3.—Solid phase composition in the system Na_2CO_3–Na_2SO_4–H_2O at 100°.

univariant lines A and B represent solutions in equilibrium with two salts. In order to indicate actual salt concentrations on a two-dimensional plot of this type, lines of constant total dissolved solids are presented. For example, a saturated solution illustrated by point P represents a solution having a total solids content of 28.3% of which Na_2CO_3 is 67.5%, Na_2SO_4 is 20% and NaOH is 12.5%. The salt concentrations, therefore, are 19.1% Na_2CO_3, 5.7% Na_2SO_4 and 3.5% NaOH.

The two solid phases in equilibrium along univariant line A are $Na_2CO_3 \cdot H_2O$ and a sulfate-rich solid solution designated as Solid Solution A while univariant line B represents solutions in equilibrium with Solid Solution B and Na_2SO_4. These solid phases were identified petrographically. Also the chemical analysis of the wet residue confirmed this conclusion because in all instances along line "A" the tie-line drawn between the solution and wet residue compositions intersected the Na_2CO_3–Na_2SO_4 axis at some point be-

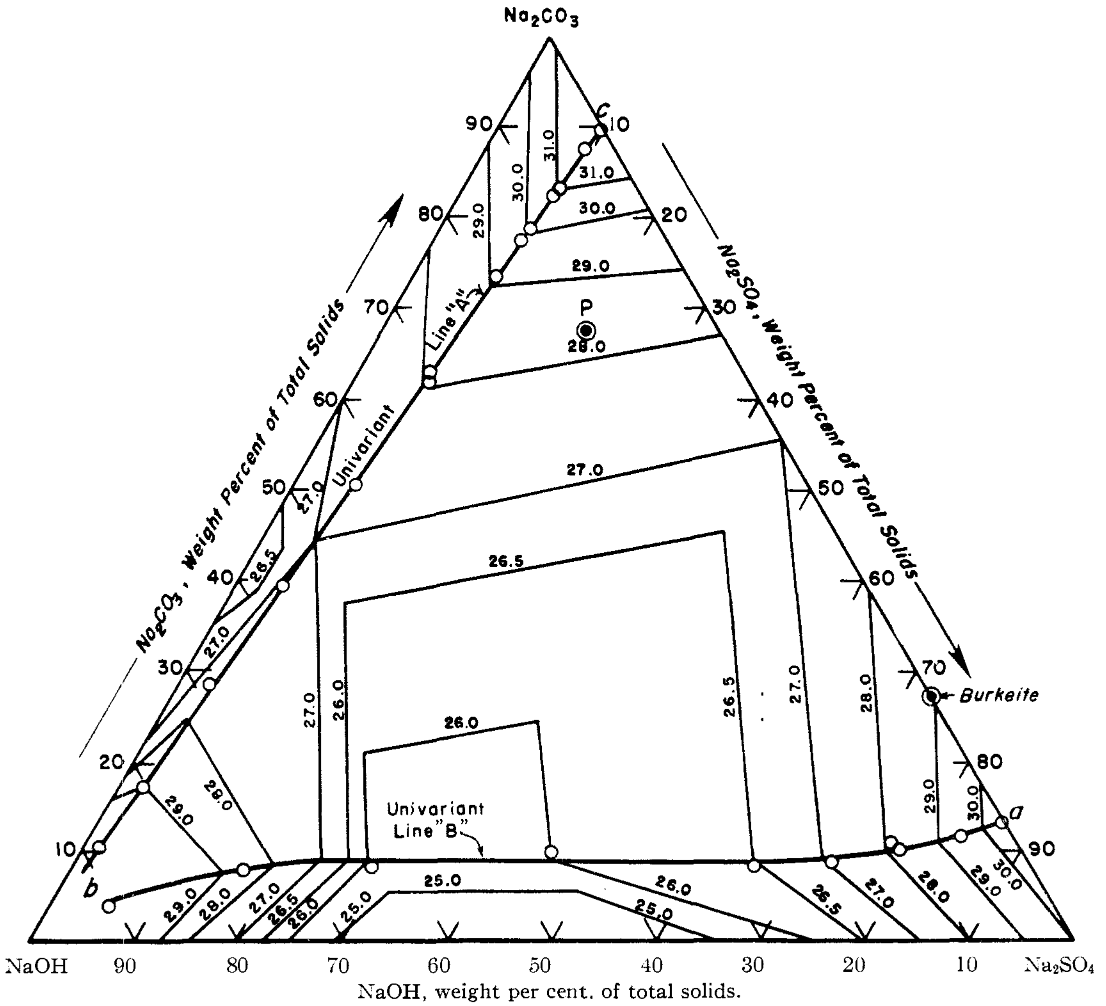

Fig. 4.—Solubility curves for the system Na_2CO_3–Na_2SO_4–NaOH–H_2O at 100°: area below ab = Na_2SO_4 field; area abc = solid solution of Na_2SO_4 and Na_2CO_3; area above bc = $Na_2CO_3 \cdot H_2O$ field; O, points fixing equilibria.

tween the composition of Solid Solution A and Na_2CO_3.

TABLE III

THE SYSTEM Na_2CO_3–Na_2SO_4–NaOH–H_2O AT 100°

Soln.	Solution composition, weight per cent. Na_2CO_3	Na_2SO_4	NaOH	Wet residue composition, weight per cent. Na_2CO_3	Na_2SO_4	NaOH[a]	Solid phase identification
				Univariant Line A			
1	28.5	3.2	0	49.8	37.3	0	$Na_2CO_3\cdot H_2O$, S.S.
2	28.0	3.1	0.9	53.5	24.5	1.0	$Na_2CO_3\cdot H_2O$, S.S.
3	26.4	2.9	2.5	54.6	22.0	2.5	$Na_2CO_3\cdot H_2O$, S.S.
4	25.4	2.8	2.6	61.6	23.8	0	$Na_2CO_3\cdot H_2O$, S.S.
5	23.3	2.6	4.2	..	..	..	$Na_2CO_3\cdot H_2O$, S.S.
6[b]	23.8	2.5	3.8	62.6	18.4	0.9	$Na_2CO_3\cdot H_2O$, S.S.
7	21.5	2.3	5.4	56.9	16.8	2.3	$Na_2CO_3\cdot H_2O$, S.S.
8	17.9	1.9	8.6	67.1	13.6	0.6	$Na_2CO_3\cdot H_2O$, S.S.
9	17.4	2.0	8.7	61.5	15.3	1.6	$Na_2CO_3\cdot H_2O$, S.S.
10	14.0	1.7	12.0	68.7	12.6	0	$Na_2CO_3\cdot H_2O$, S.S.
11	10.8	1.2	15.4	..	..	..	$Na_2CO_3\cdot H_2O$, S.S.
12	8.0	0.8	18.9	55.2	8.3	0.2	$Na_2CO_3\cdot H_2O$, S.S.
13	5.0	0.6	23.2	50.9	7.1	9.2	$Na_2CO_3\cdot H_2O$, S.S.
14	3.2	0.5	26.9	51.9	6.8	11.0	$Na_2CO_3\cdot H_2O$, S.S.
				Univariant Line B			
1	4.0	26.6	0	19.3	70.5	0	Na_2SO_4, S.S.
2	3.4	24.5	1.5	18.3	71.8	1.8	Na_2SO_4, S.S.
3	3.0	21.8	3.4	..	..	..	....
4[c]	2.9	21.9	3.3	15.2	84.8	0	Na_2SO_4, S.S.
5	2.4	19.6	5.1	15.3	78.8	0	Na_2SO_4, S.S.
6	2.2	17.3	7.0	12.9	79.7	0.4	Na_2SO_4, S.S.
7	2.5	11.7	11.8	..	..	..	Na_2SO_4, S.S.
8	2.1	7.5	16.3	12.0	73.5	0.2	Na_2SO_4, S.S.
9	2.3	4.7	21.4	12.9	71.9	2.6	Na_2SO_4, S.S.
10	1.3	2.9	30.4	11.0	65.6	8.0	Na_2SO_4, S.S.

[a] NaOH calculated by difference. [b] Solution 5 given 68 hours agitation time, all others 20 hours. [c] Solution 3 given 68 hours agitation time, all others 20 hours.

Similarly along line "B" the extrapolated tie lines intersected the Na_2SO_4–Na_2CO_3 axis at points between Na_2SO_4 and Solid Solution B. No attempts was made to study completely the composition of the solid phase in the area of $xNa_2SO_4\cdot Na_2CO_3$ which covers the major portion of the diagram, since it was felt that an adequate estimate of this composition could be made by utilizing the data illustrated in Fig. 3.

Acknowledgment.—The authors wish to express their appreciation to Albert Kauffman and Howard Jaffee of the Petrographic Department at this station for doing the microscopic work, and to Richard A. Brown, Chemical Engineer, in charge of the Alkaline Alumina Project, and John E. Conley, Chief of the Chemical Engineering Unit, for valuable suggestions and criticisms during the investigation.

Summary

1. The major portion of the 4-component system Na_2CO_3–Na_2SO_4–NaOH–H_2O at 100° has been determined, involving the determination of parts of the three related 3-component systems, namely: (1) Na_2CO_3–NaOH–H_2O (2) Na_2SO_4–NaOH–H_2O and (3) Na_2CO_3–Na_2SO_4–H_2O at the same temperature. Ordinary chemical methods were used in solution and solid phase analyses and the petrographic microscope was employed to identify the solid phases.

2. In this system for the concentration range studied, three fields were encountered which are $Na_2CO_3\cdot H_2O$, solid solution of the varying composition, $(1.4–2.2)Na_2SO\cdot_4Na_2CO_3$ and Na_2SO_4.

3. The results of this study are presented conveniently on a ternary diagram with lines of constant total dissolved solids.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

Dipole Moments of Linear and Cyclic Polymethylpolysiloxanes

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In connection with an extended study in this Laboratory of the physical properties[1] of polysiloxanes we have had occasion to investigate the dielectric behavior of the pure liquid polymethylpolysiloxanes reported recently by Patnode and Wilcock.[2] We sought to gain an insight into the structure of the polysiloxanes, and we hoped, in particular, to obtain at least an approximate value for the silicon–oxygen–silicon bond angle from the dipole moments computed by means of Onsager's equation.[3] Upon evaluation of the accepted physical constants appearing in this equation it reduces to

$$\mu^2 = 0.0482 \times 10^{-36} \left[V \cdot \frac{2\epsilon + n^2}{\epsilon(n^2 + 2)^2} (\epsilon - n^2) \right] \text{(e. s. u.)} \qquad (1)$$

at 20.0°, in which

μ = dipole moment (gas phase) of the molecule
V = the molar volume
ϵ = dielectric constant of the pure liquid substance, and
n = the refractive index

Although, according to Onsager, the refractive index should include the contribution of the atomic polarization as well as that of the electron polarization we have set $n = n^{20}\text{D}$. Equation 1 may be condensed to the form

$$\mu = 0.220 \times 10^{-18}\sqrt{P^*} \text{ (e. s. u.)} \qquad (2)$$

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(1) The properties so far discussed include: (a) crystal habit and configuration [Burkhard, Decker and Harker, THIS JOURNAL, **67**, 2174 (1945)]; (b) molar volume and viscosity [Hurd, *ibid.*, **68**, 364 (1946)]; (c) vapor pressure and viscosity relations [Wilcock, *ibid.* **68**, 691 (1946)]; (d) molar and group refraction [Sauer, *ibid.*, **68**, 954 (1946)].

(2) Patnode and Wilcock, THIS JOURNAL, **68**, 358 (1946).

(3) Onsager, THIS JOURNAL, **58**, 1490 (1936). Böttcher [*Physica*, **6**, 59 (1939)] has analyzed a large amount of experimental work in the light of the Onsager formula. In general, results are obtained which check well with those found by the usual methods.