tube was kept at a temperature of 875°. The hydrogen thus purified was absorbed into ordinary degassed titanium contained in a heated silica tube L. After absorption and cooling, the resulting hydride was evacuated briefly at 200–300°, following which pure hydrogen was obtained as needed by heating to above 500°.

Helium.—This gas was used for volume calibration and was dried over Drierite and purified by passage through a tube containing zirconium powder heated to 875°.

Apparatus.—The dissociation measurements were made by observing the equilibrium pressure of hydrogen over a sample at a given temperature. The hydrogen content was determined by calculation from the pressure and known volume of the system. Changes in the volume of the sample due to the presence of hydrogen were found to have a negligible effect and were ignored. The equipment used is shown in Fig. 4. A weighed sample of pure titanium was placed in a 347-alloy stainless steel crucible which had previously been subjected to a blank run. The crucible was placed in the silica tube B in furnace F and degassed in high vacuum overnight at room temperature. The temperature was raised to 1000° over 17 hr. and a pressure of 0.1 μ maintained. A known volume of hydrogen at known pressure was admitted to the isolated sample from storage vessel E, the furnace allowed to cool overnight to 400° and then slowly at 25°.

After evacuation the volume of the measuring portion of the system was determined by admitting a known volume of helium from H and observing the pressure at C. The system was evacuated through V, then heated to the temperature of the desired isotherm. Known volumes of hydrogen were added or removed from the sample tube B *via* the double gas buret D. Equilibrium pressures were measured by manometer C and recorded by a Brown Instrument Co. pressure gage G. The Hoskins FA 120 furnace F was controlled to 0.5° by a reflection-galvanometer and phototube relay system connected to thermocouple T_1. The other thermocouple, T_2 (chromel-alumel), was frequently calibrated *vs.* a Bureau of Standards Pt-Pt, 10% Rh thermocouple and was used for measurement of temperature to 0.5°.

Equilibrium pressures were usually attained in a matter of minutes and could be maintained without change over a period of days. In general 45 min. was allowed after a constant pressure was noted. Diffusion losses were negligible and within experimental error over a period of weeks, as evidenced by constancy and reproducibility of readings. Contamination of the sample by mercury vapor was prevented by keeping the U-tubes adjoining the gas buret and each manometer immersed in Dry Ice-acetone.

Stoichiometric hydride TiH_2 was prepared in the above equipment, by cooling slowly to room temperature, and also in a large vacuum furnace consisting of a welded 347-alloy, stainless steel retort within a Hevi-Duty 1200° muffle furnace. Crucibles of the same alloy were broken in by trial runs. Titanium was degassed below 450° for 8–48 hr. to avoid fixation of adsorbed gases, then at 1000° for several hours in high vacuum. Hydrogen purified by passage through red hot Ti–Zr mixture was admitted and the furnace cooled over a period of 12–24 hr. A titanium getter layer was used to protect the sample from traces of oxygen and nitrogen which were always detected by slight discoloration of the getter. Hydrogen pressure was atmospheric throughout the absorption process.

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Summary

Stoichiometric titanium hydride was prepared and its density determined. The dissociation pressure was measured for the Ti–H system over the range 500–800°, 50–800 mm. and an hysteresis noted in the 600° isotherm. X-Ray diffraction patterns were observed for several compositions in the range $TiH_{0.86}$ to TiH_2 and two evanescent lines were found in the pattern of the stoichiometric hydride. A nearly linear relation of density to composition was found in this system from Ti to TiH_2. Titanium containing small quantities of interstitial hydrogen was found to react rapidly with pure hydrogen at room temperature and atmospheric pressure.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PHILADELPHIA QUARTZ COMPANY]

The System $Na_2O-SiO_2-H_2O$ at 50, 70 and 90°*

BY C. L. BAKER, L. R. JUE AND J. H. WILLS

The only available information on phase stability in the system $Na_2O-SiO_2-H_2O$ from 50 to 100° is the solubility curve for sodium metasilicate hydrates[1] and some data on phases separating at 60 and 100° determined by Leidenroth.[2] Leidenroth reported a compound $3Na_2O \cdot 2SiO_2 \cdot 6H_2O$ which is certainly the $3Na_2O \cdot 2SiO_2 \cdot 5H_2O$ or $Na_3HSiO_4 \cdot 2H_2O$ found at lower temperatures.[3] His data at 60° indicate that he obtained $Na_3HSiO_4 \cdot 1H_2O$ as well as the other hydrates. At 100° his data usually approach the $Na_3HSiO_4 \cdot 1H_2O$ composition rather than that of the dihydrate. Jordis[4] reported $Na_2SiO_2 \cdot 1.5H_2O$ formed at 100°.

Fairly complete isotherms at 50 and 70° are here reported. An incomplete system showing the more alkaline silicates at 90° is included. The new compounds found are $\alpha Na_2SiO_3 \cdot 6H_2O$,

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* Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society 116th Meeting, Atlantic City, N. J., September, 1949.

(1) C. L. Baker and L. R. Jue, *J. Phys. Chem.*, **42**, 165 (1938).

(2) K. Leidenroth, "Ein Beitrag zur Kenntnis der Natrium Silikate," Inaugural Dissertation, Martin Luther University, Halle-Wittenberg, June 29, 1939.

(3) J. H. Wills, *J. Phys. Chem.*, **54**, 304 (1950).

(4) E. Jordis, *Chem. Ztg.*, **38**, 922 (1914).

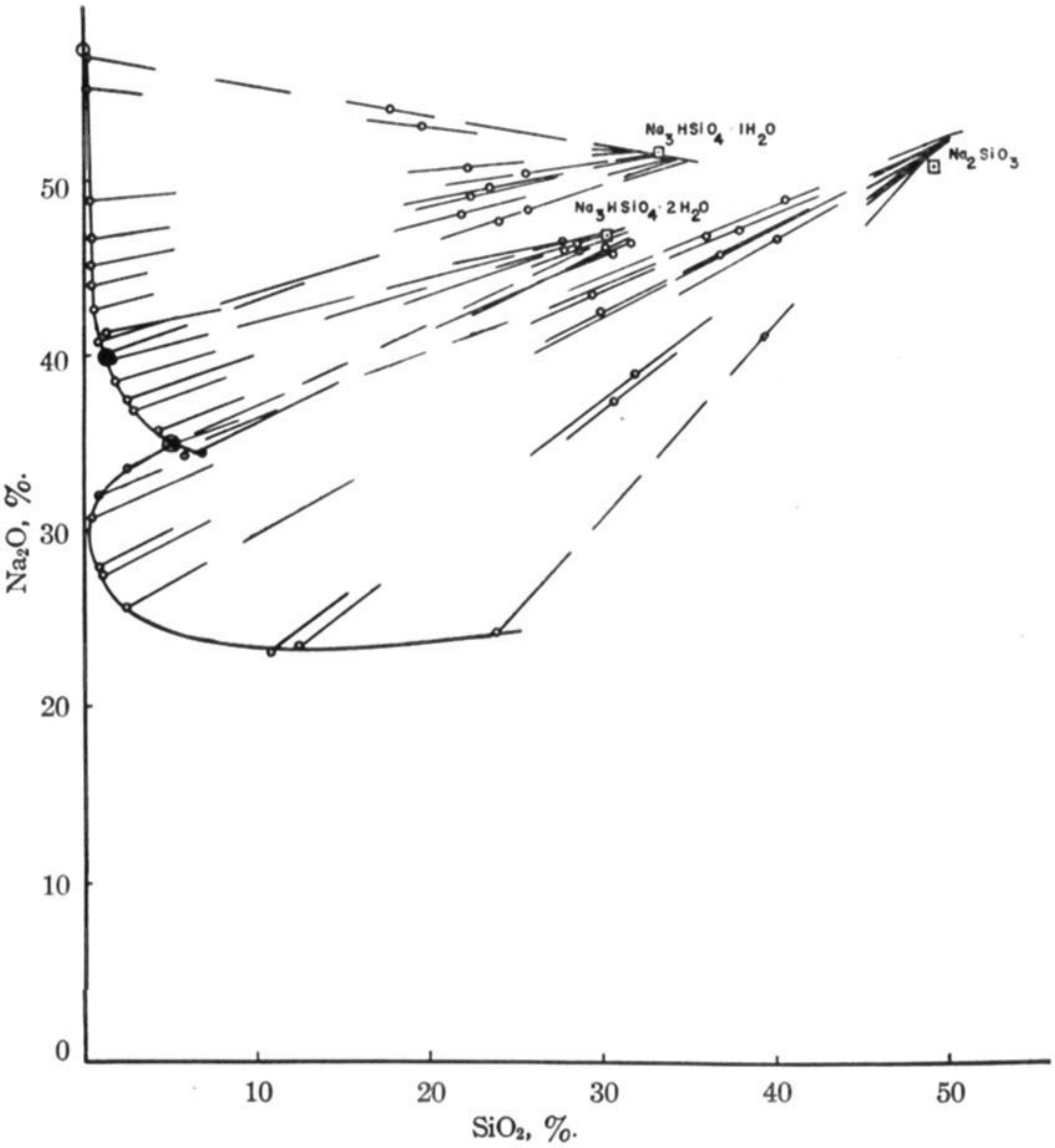


Fig. 1.—The system Na_2O–SiO_2–H_2O at 90°, alkaline salts only, weight per cent. basis: ⊗, points of isothermal invariance; ⊡, theoretical composition; O, experimental equilibrium points; -o-, wet residue determinations; — —, field boundaries.

$Na_3HSiO_4\cdot 1H_2O$ and an unidentified salt which may be $Na_2SiO_3\cdot 1H_2O$.

The Isotherm at 90°

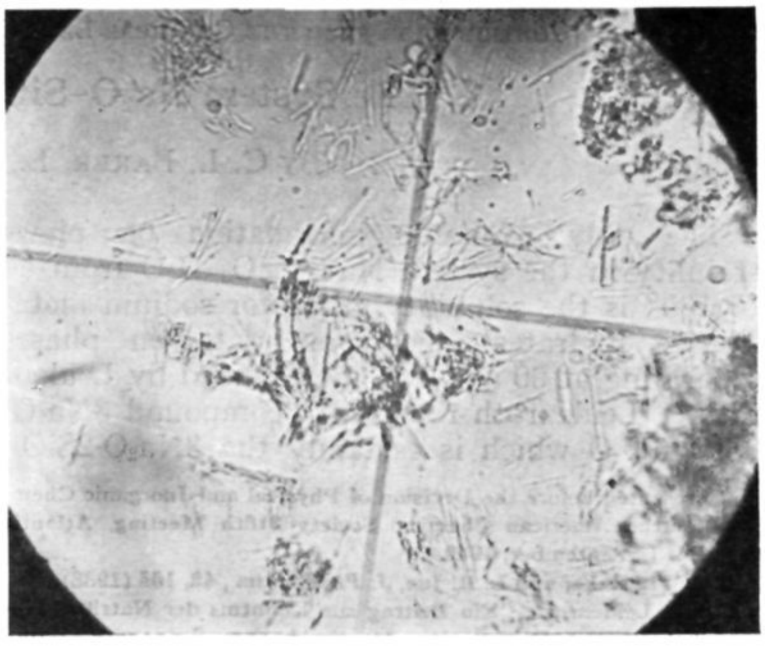
At 90 ± 0.3° only the metasilicate and more alkaline salts have been studied (Table I, Fig. 1). At this temperature the crystalline compound, anhydrous Na_2SiO_3, has a long stable range. The fact that this salt is stable at 90° in contact with solutions containing considerably less SiO_2 and Na_2O than any of the solutions in equilibrium with other salts at 70° probably explains the difficulty experienced with solutions at that temperature as due to contamination with anhydrous Na_2SiO_3. Sample crystals prepared at 100° (Illust. 1) had refractive indices 1.513, 1.520, 1.528, corresponding to crystals formed from an anhydrous melt.

By very careful operation according to the methods detailed in the section on analytical methods the solubility of NaOH was found to be 57.5 ± 0.1% Na_2O. If data given by Pickering[5] are interpolated, a figure of 60% Na_2O is found. His methods are open to question.

No isothermally invariant point was obtained for NaOH–$Na_3HSiO_4\cdot H_2O$. Such an invariant point probably lies within the range between 57.0 and 57.5% Na_2O. The solubility curve is considered accurate to about ±0.15% Na_2O and 0.05% SiO_2.

At one time there was thought to be some indication of the existence of an orthosilicate, but in every case the materials secured were finally proven to be $Na_3HSiO_4\cdot H_2O$ and NaOH.

It was noticed that when a portion of the solution in equilibrium with $Na_3HSiO_4\cdot 2H_2O$ at 90° was removed and allowed to cool at room temperature, crystals of $Na_3HSiO_4\cdot 2H_2O$ continued to separate and appeared to be quite stable even at room temperature and underwent transition to the pentahydrate only in rare cases. This observation of stability corroborates findings of Harman and Leidenroth. Working in the neighborhood of the invariant point between $Na_3HSiO_4\cdot 2H_2O$–Na_2SiO_3 one could easily pass from a suspension containing $Na_3HSiO_4\cdot 2H_2O$ to one containing Na_2SiO_3. However, the slow rate of solution of Na_2SiO_3 apparently impeded change in the opposite direction. The accuracy of the data on the $Na_3HSiO_4\cdot 2H_2O$ curve is considered as ±0.2% Na_2O and ±0.1% SiO_2.



Illust. 1.—Anhydrous Na_2SiO_3 grown at 100°, 140 ×.

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(5) S. U. Pickering, *J. Chem. Soc.*, **63**, 890 (1893).

The curve for Na_2SiO_3 was approached from supersaturation. Satisfactory results could not be obtained by preparing an undersaturated solution and depending upon the Na_2SiO_3 crystals to dissolve until equilibrium was reached. The accuracy of this portion of the curve is thought to be ±0.3% Na_2O and ±0.3% SiO_2.

Since approach from supersaturation took several weeks, there is some likelihood that a slow reaction with the silver containers later observed in very alkaline solutions, and described in the section on analytical procedures, may have depressed the alkali content so rapidly as to make impossible the true determination of the Na_2SiO_3 solubility near its invariant point with $Na_3HSiO_4 \cdot 2H_2O$. The latter curve was more readily established, and the invariant point suggested is considered accurate only to ±0.3% Na_2O and ±0.3% SiO_2. The actual determinations are given in Table I. Since for theoretical reasons[6] it is not possible for the tangent to a saturation curve to pass through the composition of the saturating solid, the curve is drawn slightly above the most alkaline point on the Na_2SiO_3 curve.

TABLE I[b]

THE SYSTEM Na_2O–SiO_2–H_2O AT 90°

Composition of soln.[b]		Composition of residue		
Na_2O	SiO_2	Na_2O	SiO_2	Stable solid phase
34.47	5.76	46.90	36.10	Na_2SiO_3
33.70	2.56	48.90	40.60	Na_2SiO_3
32.20	0.85	47.30	37.92	Na_2SiO_3
30.83	0.44	43.50	29.40	Na_2SiO_3
28.10	0.80	42.30	29.95	Na_2SiO_3
27.60	1.10	45.80	36.80	Na_2SiO_3
25.74	2.39	46.75	40.10	Na_2SiO_3
23.50	12.40	37.60	30.68	Na_2SiO_3
23.30	10.80	39.12	31.90	Na_2SiO_3
24.28	23.70	41.30	39.45	Na_2SiO_3
35.0	5.50			Na_2SiO_3 and $Na_3HSiO_4 \cdot 2H_2O$
41.30	1.34	46.60	27.72	$Na_3HSiO_4 \cdot 2H_2O$
39.88	1.65	46.60	27.70	$Na_3HSiO_4 \cdot 2H_2O$
39.85	1.64	46.60	28.96	$Na_3HSiO_4 \cdot 2H_2O$
38.60	1.80	46.60	28.65	$Na_3HSiO_4 \cdot 2H_2O$
38.45	1.95	46.75	28.95	$Na_3HSiO_4 \cdot 2H_2O$
37.60	2.47	46.15	27.85	$Na_3HSiO_4 \cdot 2H_2O$
37.30	2.70	46.05	27.65	$Na_3HSiO_4 \cdot 2H_2O$
36.95	2.87	46.15	28.65	$Na_3HSiO_4 \cdot 2H_2O$
35.80	4.33	45.90	30.65	$Na_3HSiO_4 \cdot 2H_2O$
35.30	4.52	44.80	30.18	$Na_3HSiO_4 \cdot 2H_2O$
35.10	5.02	46.60	31.65	$Na_3HSiO_4 \cdot 2H_2O$
34.60	6.95	46.25	30.30	$Na_3HSiO_4 \cdot 2H_2O$
34.60	7.45	46.10	28.70	$Na_3HSiO_4 \cdot 2H_2O$
40.0	1.50			$Na_3HSiO_4 \cdot 2H_2O$ and $Na_3HSiO_4 \cdot H_2O$
57.00	0.18	54.10	17.80	$Na_3HSiO_4 \cdot H_2O$
55.25	.20	53.15	19.75	$Na_3HSiO_4 \cdot H_2O$
55.50	.20	53.70	16.55	$Na_3HSiO_4 \cdot H_2O$
48.80	.26	50.80	22.30	$Na_3HSiO_4 \cdot H_2O$
46.75	.49	50.50	25.62	$Na_3HSiO_4 \cdot H_2O$
45.20	.44	49.70	23.52	$Na_3HSiO_4 \cdot H_2O$
44.10	.48	49.15	22.40	$Na_3HSiO_4 \cdot H_2O$
42.65	.62	48.15	21.95	$Na_3HSiO_4 \cdot H_2O$
40.85	.93	47.80	21.55	$Na_3HSiO_4 \cdot H_2O$
40.10	1.13	48.35	25.70	$Na_3HSiO_4 \cdot H_2O$
40.00	1.54	49.80	28.25	$Na_3HSiO_4 \cdot H_2O$
57.5 Na_2O[a]				Cryst. NaOH soly.

[a] Value by Pickering 60% Na_2O. [b] Numerical values in the tables are all per cent. by weight.

In developing the siliceous portion of the Na_2SiO_3 curve, solutions of high viscosity were encountered, and the points are probably accurate only to 0.4% Na_2O and 0.15% SiO_2.

The Schreinemakers[7] residue lines for Na_2SiO_3 converge at a point on the graph corresponding to a composition about 1% higher in Na_2O than the theoretical point. It may be that crystals of Na_2SiO_3 tend to include or adsorb an excess of Na_2O.

The Isotherm at 70°

The isotherm at 70° has been worked out more completely (Table II (a) and (b), Fig. 2). Solubility of NaOH at 70° was found to be 56.45 ± 0.05%, which is not far from the 56.75% obtained by interpolating the curve of Pickering,[5] but is definitely lower than the 56.97% found by Morey and Burlew[8] in a solution saturated with Na_2CO_3.

TABLE II (a)

THE SYSTEM Na_2O–SiO_2–H_2O AT 70°

Compn. of soln.		
Na_2O	SiO_2	Stable solid phase
0.32	0.80	$3Na_2O \cdot 13SiO_2 \cdot 11H_2O$
1.16	3.59	$3Na_2O \cdot 13SiO_2 \cdot 11H_2O$
2.41	5.00	$3Na_2O \cdot 13SiO_2 \cdot 11H_2O$
5.71	11.40	$3Na_2O \cdot 13SiO_2 \cdot 11H_2O$
8.08	16.57	$3Na_2O \cdot 13SiO_2 \cdot 11H_2O$
9.20	19.33	$3Na_2O \cdot 13SiO_2 \cdot 11H_2O$
11.84	24.06	$3Na_2O \cdot 13SiO_2 \cdot 11H_2O$
12.54	25.64	$3Na_2O \cdot 13SiO_2 \cdot 11H_2O$
12.66	25.98	$3Na_2O \cdot 13SiO_2 \cdot 11H_2O$
13.41	26.93	$3Na_2O \cdot 13SiO_2 \cdot 11H_2O$
13.73	29.86	$3Na_2O \cdot 13SiO_2 \cdot 11H_2O$
14.00	28.63	$3Na_2O \cdot 13SiO_2 \cdot 11H_2O$
16.34	33.66	$3Na_2O \cdot 13SiO_2 \cdot 11H_2O$
16.97	35.30	$3Na_2O \cdot 13SiO_2 \cdot 11H_2O$
17.69	36.34	$3Na_2O \cdot 13SiO_2 \cdot 11H_2O$
18.68	38.30	$3Na_2O \cdot 13SiO_2 \cdot 11H_2O$
20.44	41.40	$3Na_2O \cdot 13SiO_2 \cdot 11H_2O$
20.10	42.15	$3Na_2O \cdot 13SiO_2 \cdot 11H_2O$
22.5	47.0	$3Na_2O \cdot 13SiO_2 \cdot 11H_2O$ + $Na_2Si_2O_5$
22.02	42.59	$Na_2Si_2O_5$
24.11	39.95	$Na_2Si_2O_5$
23.00	40.65	$Na_2Si_2O_5$
22.80	40.38	$Na_2Si_2O_5$
22.08	41.16	$Na_2Si_2O_5$
25.6	40.4	Na_2SiO_3

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(6) E. D. Williamson and G. W. Morey, THIS JOURNAL, **40**, 56 (1918).

(7) F. A. H. Schreinemakers, *Z. physik. Chem.*, **11**, 75 (1893).

(8) G. W. Morey and J. S. Burlew, *Am. J. Sci.*, [V], XXXV-A, 212 (1938).

TABLE II (a) (*Continued*)

Compn. of soln. Na_2O	Compn. of soln. SiO_2	Stable solid phase
25.5	40.0	$Na_2SiO_3 + Na_2Si_2O_5$
24.97	34.66	$Na_2SiO_3 + \alpha\text{-}Na_2SiO_3\cdot 6H_2O$
25.34	34.15	Na_2SiO_3
23.98	27.11	Na_2SiO_3
23.90	25.66	Na_2SiO_3
23.93	25.01	Na_2SiO_3
24.14	25.00	Na_2SiO_3
23.68	24.38	Na_2SiO_3
23.59	20.50	Na_2SiO_3
23.28	12.50	Na_2SiO_3
23.16	11.68	Na_2SiO_3
22.98	9.81	Na_2SiO_3
23.69	9.24	Na_2SiO_3
22.69	8.84	Na_2SiO_3
22.28	8.93	Na_2SiO_3
23.16	7.87	Na_2SiO_3
23.45	6.38	Na_2SiO_3
23.56	5.60	Na_2SiO_3
23.95	5.04	Na_2SiO_3
22.94	3.98	Na_2SiO_3
25.02	2.45	Na_2SiO_3
25.68	1.47	Na_2SiO_3
28.19	1.08	Na_2SiO_3
29.36	0.71	Na_2SiO_3
30.11	0.47	Na_2SiO_3
35.86	0.30	Na_2SiO_3
38.75	0.26	Na_2SiO_3
25.0	34.8	$\alpha Na_2SiO_3\cdot 6H_2O + Na_2SiO_3$
23.74	34.28	$\alpha Na_2SiO_3\cdot 6H_2O + Na_2SiO_3$
23.27	33.47	$\alpha Na_2SiO_3\cdot 6H_2O + Na_2SiO_3$
21.22	31.08	$\alpha Na_2SiO_3\cdot 6H_2O + Na_2SiO_3$
20.61	24.49	$\alpha Na_2SiO_3\cdot 6H_2O + Na_2SiO_3$
18.99	22.72	$\alpha Na_2SiO_3\cdot 6H_2O + Na_2SiO_3$
19.50	18.55	$\alpha Na_2SiO_3\cdot 6H_2O + Na_2SiO_3$
18.21	14.80	$\alpha Na_2SiO_3\cdot 6H_2O + Na_2SiO_3$
18.45	12.54	$\alpha Na_2SiO_3\cdot 6H_2O + Na_2SiO_3$
18.76	11.21	$\alpha Na_2SiO_3\cdot 6H_2O + Na_2SiO_3$
20.19	7.35	$\alpha Na_2SiO_3\cdot 6H_2O + Na_2SiO_3$
22.03	6.45	$\alpha Na_2SiO_3\cdot 6H_2O + Na_2SiO_3$
23.45	6.10	$\alpha Na_2SiO_3\cdot 6H_2O + Na_2SiO_3$
23.75	6.00	$\alpha Na_2SiO_3\cdot 6H_2O$
28.80	6.28	$\alpha Na_2SiO_3\cdot 6H_2O$
30.5	6.70	$\alpha Na_2SiO_3\cdot 6H_2O + Na_3HSiO_4\cdot 5H_2O$

TABLE II (b)

THE SYSTEM Na_2O–SiO_2–H_2O AT 70°

Composition of soln. Na_2O	Composition of soln. SiO_2	Composition of residue Na_2O	Composition of residue SiO_2	Stable solid phase
27.80	29.70	28.75	28.75	$Na_2SiO_3\cdot 5H_2O$
26.58	25.85	29.05	28.25	$Na_2SiO_3\cdot 5H_2O$
26.40	24.50	29.08	27.70	$Na_2SiO_3\cdot 5H_2O$
27.00	21.97	29.08	27.70	$Na_2SiO_3\cdot 5H_2O$
27.85	21.55	28.22	28.05	$Na_2SiO_3\cdot 5H_2O$
28.95	22.12	29.25	28.12	$Na_2SiO_3\cdot 5H_2O$
29.47	22.60	29.37	28.02	$Na_2SiO_3\cdot 5H_2O$
29.70	23.25	29.25	27.75	$Na_2SiO_3\cdot 5H_2O$
30.6	24.8			$Na_3HSiO_4\cdot 5H_2O$
30.35	23.65	36.25	23.85	$Na_3HSiO_4\cdot 5H_2O$
29.81	21.20	36.72	23.70	$Na_3HSiO_4\cdot 5H_2O$
29.70	20.30	36.50	23.55	$Na_3HSiO_4\cdot 5H_2O$
29.55	17.75	34.35	21.88	$Na_3HSiO_4\cdot 5H_2O$
29.45	15.74	34.80	21.50	$Na_3HSiO_4\cdot 5H_2O$
29.51	12.45	35.35	21.75	$Na_3HSiO_4\cdot 5H_2O$
30.00	9.98	35.88	21.85	$Na_3HSiO_4\cdot 5H_2O$
30.35	7.35	36.38	22.72	$Na_3HSiO_4\cdot 5H_2O$
30.89	6.05			$Na_3HSiO_4\cdot 5H_2O$
30.91	5.35	36.18	21.65	$Na_3HSiO_4\cdot 5H_2O$
33.18	3.94	36.42	21.90	$Na_3HSiO_4\cdot 5H_2O$
34.65	3.57	36.68	22.85	$Na_3HSiO_4\cdot 5H_2O$
35.42	3.62	37.15	21.90	$Na_3HSiO_4\cdot 5H_2O$
36.05	3.84	36.67	21.12	$Na_3HSiO_4\cdot 5H_2O$
31.67	3.48	35.36	20.52	$Na_3HSiO_4\cdot 5H_2O$
31.66	3.90	35.09	19.87	$Na_3HSiO_4\cdot 5H_2O$
35.0	3.6			$Na_3HSiO_4\cdot 2H_2O$
34.90	2.52	45.45	27.30	$Na_3HSiO_4\cdot 2H_2O$
36.08	1.72	45.25	26.3	$Na_3HSiO_4\cdot 2H_2O$
36.80	1.33	46.15	27.52	$Na_3HSiO_4\cdot 2H_2O$
37.00	1.57			$Na_3HSiO_4\cdot 2H_2O$
37.60	1.18	45.60	25.50	$Na_3HSiO_4\cdot 2H_2O$
38.92	1.03	44.70	22.57	$Na_3HSiO_4\cdot 2H_2O$
39.52	0.76	46.50	26.68	$Na_3HSiO_4\cdot 2H_2O$
40.7	0.6			$Na_3HSiO_4\cdot H_2O$
43.50	.58	46.50	26.65	$Na_3HSiO_4\cdot H_2O$
39.30	.79	48.60	25.75	$Na_3HSiO_4\cdot H_2O$
41.90	.44	47.80	20.68	$Na_3HSiO_4\cdot H_2O$
45.50	.25	49.90	24.70	$Na_3HSiO_4\cdot H_2O$
46.60	.19	49.90	24.75	$Na_3HSiO_4\cdot H_2O$
48.00	.1	50.75	25.40	$Na_3HSiO_4\cdot H_2O$
48.85	.27	51.30	26.90	$Na_3HSiO_4\cdot H_2O$
49.60	.08	50.85	22.45	$Na_3HSiO_4\cdot H_2O$
55.10	.15	52.80	23.90	$Na_3HSiO_4\cdot H_2O$
56.45				NaOH
56.75				Pickering $Na_2O\cdot H_2O$
56.97				Morey & Burlew ($NaOH + Na_2CO_3$)

The invariant point between $Na_3HSiO_4\cdot H_2O$–$Na_3HSiO_4\cdot 2H_2O$ is also in some doubt, but is probably accurate to 0.2% Na_2O and 0.02% SiO_2. Solutions of original composition close to the invariant point invariably shifted to lower alkalinity along either one curve or the other. This also may be an effect of reaction with the silver flasks, as explained in the section on procedure.

The invariant point $Na_3HSiO_4\cdot 2H_2O$–$Na_3HSiO_4\cdot 5H_2O$ gave considerable difficulty. Any solution prepared with a Na_2O concentration less than 34.8% invariably led to the crystallization of $Na_3HSiO_4\cdot 5H_2O$. It is therefore thought that the value of 35.0% Na_2O is accurate to about ±0.2% Na_2O and the SiO_2 value to ±0.02%.

The invariant point $Na_3HSiO_4\cdot 5H_2O$–$Na_2SiO_3\cdot 5H_2O$ was obtained by the extrapolated intersection of two curves meeting at a small angle, and is therefore believed to be accurate only to about 0.3% Na_2O and 0.5% SiO_2.

The accuracy of each of the determinations for

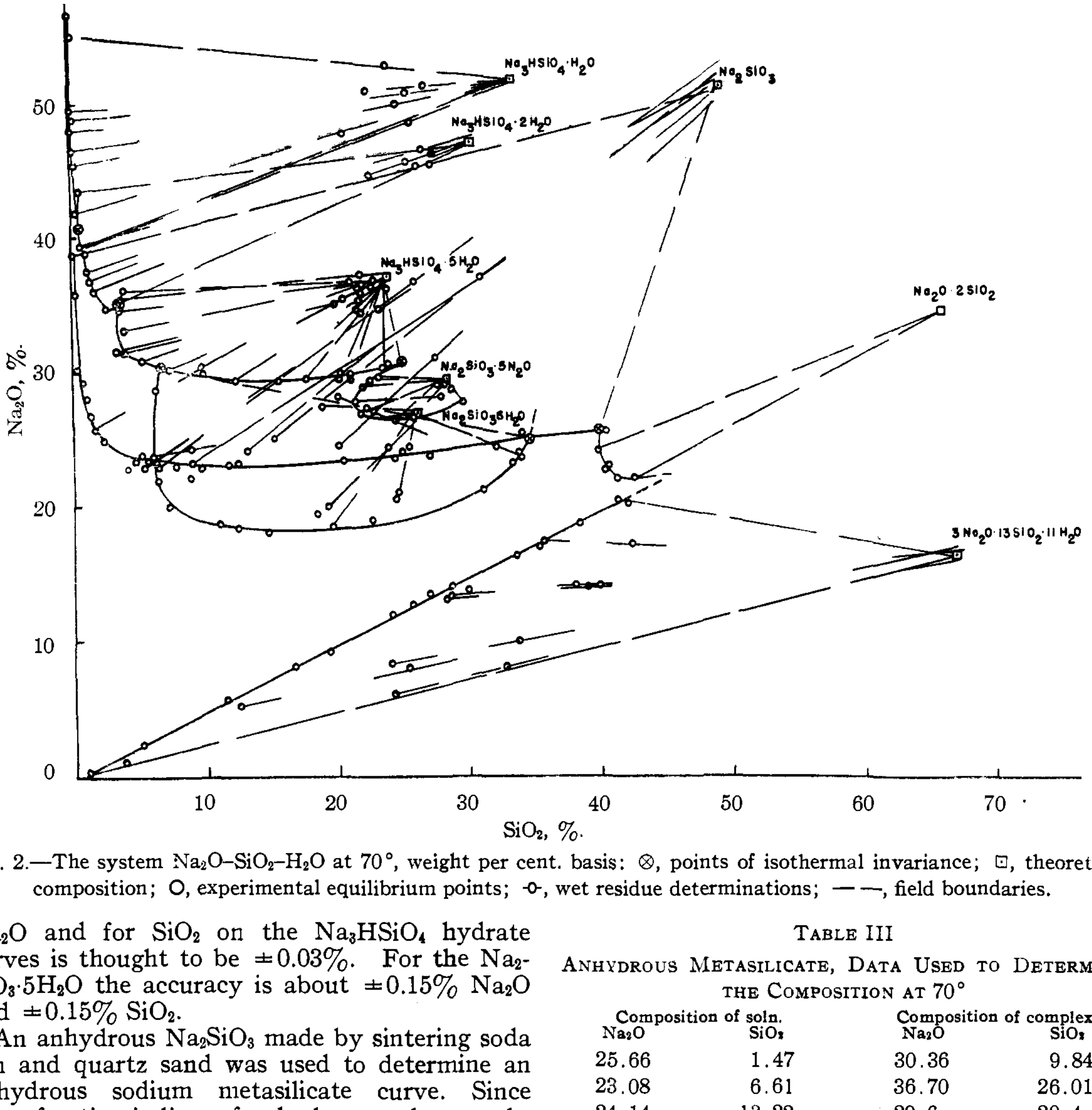

Fig. 2.—The system Na_2O-SiO_2-H_2O at 70°, weight per cent. basis: ⊗, points of isothermal invariance; ⊡, theoretical composition; O, experimental equilibrium points; -o-, wet residue determinations; ——, field boundaries.

Na_2O and for SiO_2 on the Na_3HSiO_4 hydrate curves is thought to be ±0.03%. For the $Na_2SiO_3 \cdot 5H_2O$ the accuracy is about ±0.15% Na_2O and ±0.15% SiO_2.

An anhydrous Na_2SiO_3 made by sintering soda ash and quartz sand was used to determine an anhydrous sodium metasilicate curve. Since the refractive indices of anhydrous melt crystals, of the sintered product, and of the residues in reaction flasks at 70 and 100° are the same, it is believed that the same solid phase was present. The curve extends from the disilicate almost to the Na_2O ordinate, and this salt is more stable than any of the others just mentioned. The solubility curve is in nearly the same position as at 90° and does not correspond to what one would expect from comparison with the retrograde solubility of the α-sodium metasilicate shown by Baker and Jue.[1] Analyses by the Hill–Ricci[9] method and the Schreinemakers wet residue method (Table III, Fig. 2) indicate that this is an anhydrous product, although the extrapolations are long and not as precise as in some of the other work. The crystals are exceedingly small, usually rectangles about 1 μ in width, and come out slowly from supersaturated solutions.

TABLE III

ANHYDROUS METASILICATE, DATA USED TO DETERMINE THE COMPOSITION AT 70°

Composition of soln. Na_2O	Composition of soln. SiO_2	Composition of complex Na_2O	Composition of complex SiO_2
25.66	1.47	30.36	9.84
23.08	6.61	36.70	26.01
24.14	13.22	29.6	20.4
		Wet residue	
25.07	15.27	36.92	30.96
22.95	5.43	34.65	23.22
24.51	20.07	31.09	27.56

It was also noted that in the most alkaline regions the reaction with the silver flasks mentioned earlier occurred, and an appreciable quantity of the silver compound was found in the residue after long periods of reaction.

Equilibrium was established from above and below saturation except at the siliceous end, where the viscosity was so great that approach from supersaturation was exceedingly slow. The accuracy of this anhydrous metasilicate curve is considered to be ±0.04% Na_2O and ±0.03% SiO_2. Illustration 2 shows a mass of crystals of the sintered product in solution. Crystals grown at 100° in a metasilicate ratio solution are more needle-like, as shown in Illust. 1.

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(9) A. E. Hill and J. E. Ricci, THIS JOURNAL, **53**, 4305 (1931).

Illust. 2.—Na_2SiO_3 at 70° from sintered seed, 140 ×.

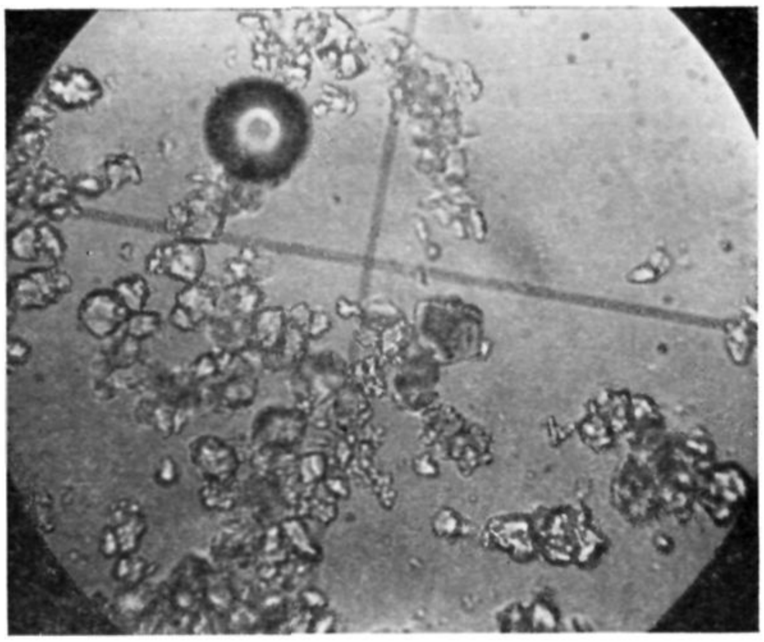
An interesting discovery in this system is that of a second form of $Na_2SiO_3 \cdot 6H_2O$ which has been termed the high temperature or alpha form (Illust. 3). The wet residue extrapolations make the composition rather certain (Table IV, Fig. 2). An X-ray diffraction pattern obtained by courtesy of G. W. Morey of the Geophysical Laboratories, Carnegie Institution of Washington, shown in Illust. 4 is different from that of other known hydrates.

Table IV

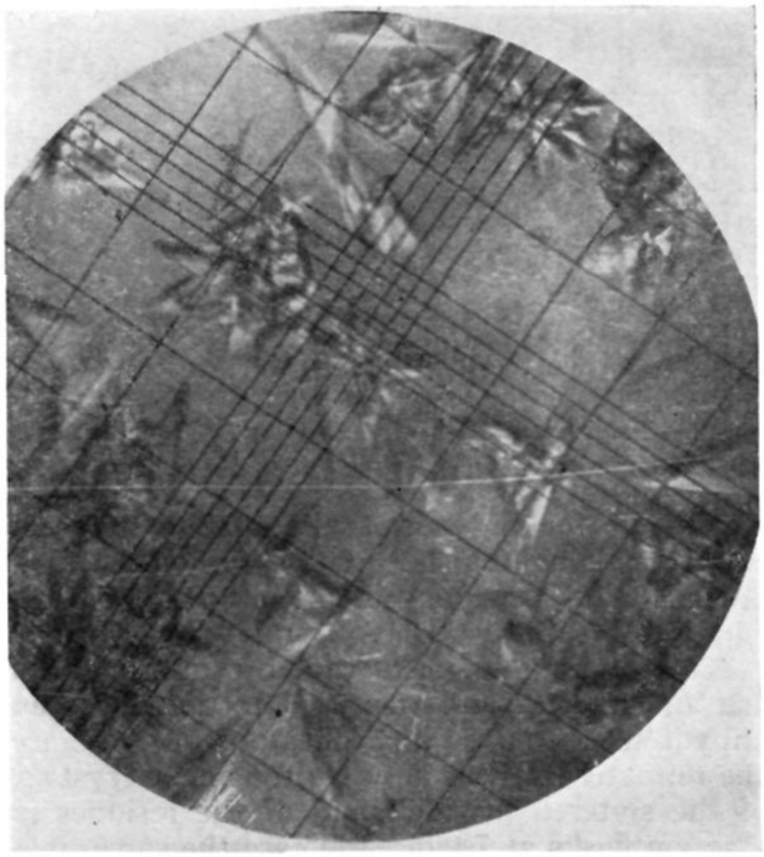
α-Sodium Metasilicate Hexahydrate, Data Used to Determine the Composition

Compn. of soln.		Compn. of wet residue	
Na_2O	SiO_2	Na_2O	SiO_2
20.86	24.66	24.49	25.57
21.01	25.00	24.71	25.88
19.69	18.51	24.38	23.87
20.07	19.28	24.41	23.99
28.21	20.22	27.08	22.83
27.52	19.03	27.31	22.31
23.95	33.76	24.5	32.1
23.61	4.82	24.3	8.9

Pressed and washed residues			
	Mole ratio		
Na_2O	SiO_2	H_2O	Remarks
1.02	1.00	6.13	Washed
1.02	1.00	5.75	Washed
0.95	1.00	5.97	Pressed



Illust. 3A.—$\alpha Na_2SiO_3 \cdot 6H_2O$ grown at 50°, 400 ×.



Illust. 3B.—$\beta Na_2SiO_3 \cdot 6H_2O$ grown at 50°, 90 ×.

This stable hexahydrate varies in both refractive indices and melting point from that described by previous workers, Baker, *et al.*,[10] Sprauer, *et al.*,[11] and Erdenbrecher.[12] All three reproduced photographs of the hexahydrate. The form obtained here is more nearly that shown by Sprauer, but he does not give any other properties by which identity may be established. The melting point has not been determined but it is thought to be about 80°. The highest and lowest indices are about 1.488 and 1.495[13] compared to 1.465, 1.473, 1.485.[10]

This salt is more stable than any of the other salts during most of its range. Its curve, however, has not been as carefully established as those of the other solutions excepting that of the disilicate. Certain solutions approached close to the limit from supersaturation, but they gener-

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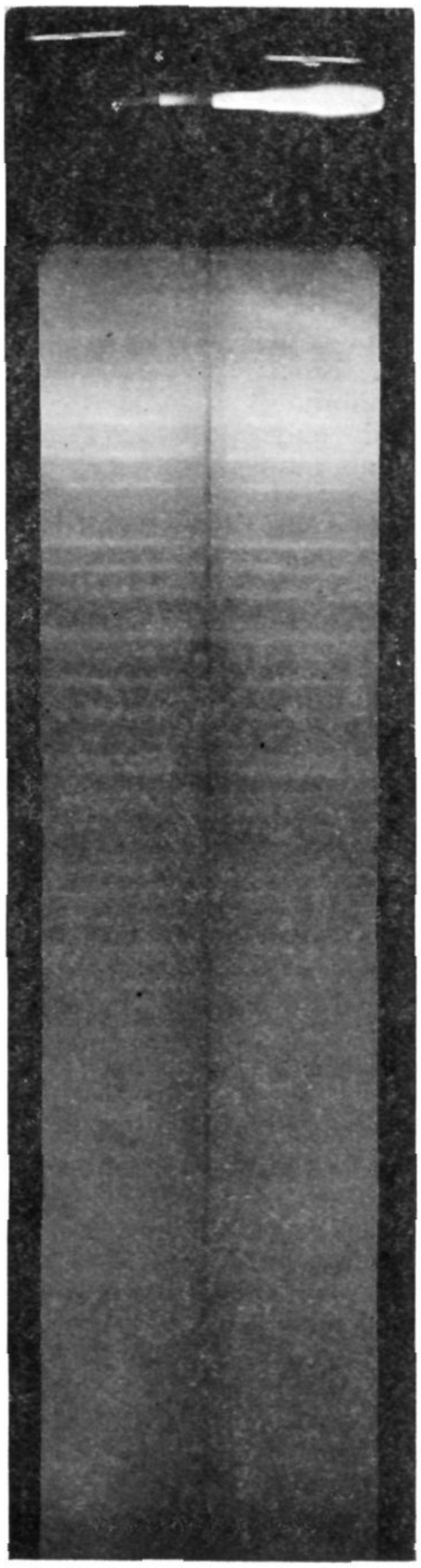
[10] C. L. Baker, H. T. Woodward and A. Pabst, *American Mineralogist*, **18**, 206 (1933).

[11] J. W. Sprauer and D. W. Pearce, *J. Phys. Chem.*, **44**, 909 (1940).

[12] A. H. Erdenbrecher, *Z. anorg. allgem. Chem.*, **124**, 339 (1922).

[13] Crystals sufficiently large and well formed for a complete optical examination were not obtained, but G. W. Morey in a personal communication reported these values and said that he did not recognize the salt.



Illust. 4.—X-Ray diffraction pattern of $\alpha Na_2SiO_3\cdot 6H_2O$ formed at 70°.

ally crystallized to a solid from which liquid samples could not be removed, before equilibrium could be determined. The points determined are thought accurate to ±0.1% Na_2O and ±0.1% SiO_2. In the alkaline section a drift with time was found which is attributed to the reaction with the silver flask.

This new form of hexahydrate appeared not to form spontaneously but only after seeding with the sintered metasilicate, which may then recrystallize slowly to the hexahydrate. Other examples of such inhibited crystallization are to be found in the work of Kracek[14a] and of Hill and Wills.[14b]

Some experiments from undersaturation were carried out with anhydrous sodium disilicate crystals obtained from an anhydrous melt. As far as could be observed, it was not possible to obtain growth from supersaturation but it is very difficult to work in this region of high viscosity. After long reaction one washed residue did appear to have a slightly altered index, but the crystals as shown in Illust. 5 did not appear to have changed. We do not feel capable of judging the accuracy of this curve. The solubility of $Na_2Si_2O_5$ does not fit a smooth curve made up from the data of Morey[15] and of Tuttle and Friedman,[16] and this fact may indicate a shift in phase.

Illust. 5.—$Na_2Si_2O_5$ crystals originally from a melt but after long immersion in solution (partially crossed nicol prisms, 193 ×).

In the most siliceous portion of the sodium tetrasilicate[17] region, a year or more may be required for equilibrium from supersaturation.

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[14] (a) F. C. Kracek, *Am. J. Sci.*, [V], XXXV-A, 143 (1938); (b) A. E. Hill and J. H. Wills, THIS JOURNAL, **60**, 1647 (1938).

[15] J. G. Vail, "Soluble Silicates in Industry," A.C.S. Monog. 46, (Chemical Catalog Co.), Reinhold Publ. Corp., N. Y., 1928, p. 116.

[16] O. F. Tuttle and I. I. Friedman, THIS JOURNAL, **70**, 919 (1948).

[17] W. F. Wegst and J. H. Wills, U. S. Reissue, 23,043 (1948).

Approach is much more rapid in the middle portion, where one or two weeks was sufficient in some cases. From undersaturation one or two weeks also seemed to be required, the time depending on the position of the initial solution. The accuracy of points on this solubility curve is considered to be ±0.04% Na_2O and ±0.04% SiO_2.

The composition was studied by various methods. Table V shows results for the wet residue extrapolation and for tracer ion experiments using NaCl. It is very difficult to obtain satisfactory extrapolations because the crystals are very fine, 1 to 15 μ in length by 0.2 to 5 μ wide, and hold the viscous liquid strongly. Furthermore, it is difficult to keep the solutions warm and thus maintain the viscosity near the original figure. The best approximation to the composition appears to be $3Na_2O \cdot 13SiO_2 \cdot 11H_2O$. Most wet residue studies for sodium tetrasilicate resulted in such long extrapolations that little weight could be placed on the results. The inert tracer (NaCl) results, Table V, are all a little high in water content. It is difficult to obtain the water content directly, since the equilibrium content as shown by constant weight determinations at any one temperature appeared to change gradually over the range from 62 to 100° and quite rapidly at about 100°. From then on equilibrium was reached only gradually up to about 150°, but at 250° equilibrium was reached in an hour. The dried salt takes up water rapidly even over sulfuric acid in a large desiccator.

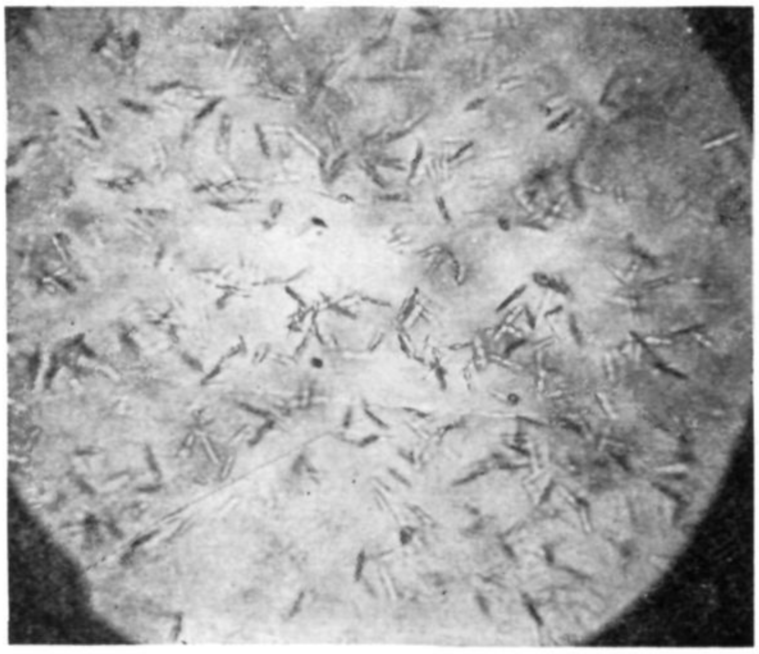
Table V

Sodium Tetrasilicate, Data Used to Determine the Composition

Liquor		Wet residue	
Na_2O	SiO_2	Na_2O	SiO_2
5.13	12.41	7.87	25.50
6.02	24.24	7.98	32.70
8.24	24.12	9.89	33.74
13.00	28.20	13.87	38.98
13.20	29.07	14.07	39.81
13.31	28.57	13.95	38.09
17.31	35.57	17.08	42.03

Composition by NaCl Tracer Extrapol. Method

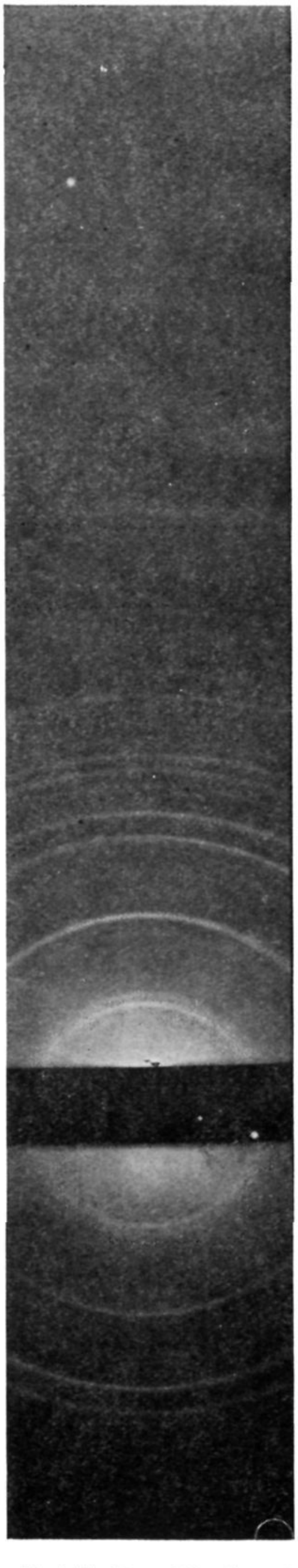
Na_2O	SiO_2	H_2O
16.04	65.78	18.18
16.53	65.68	17.78
15.90	64.69	19.40



Illust. 6.—$3Na_2O \cdot 13SiO_2 \cdot 11H_2O$ grown at 70°, 140 ×.

Illustration 6 gives an idea of the appearance of these crystals. In some cases they tend to form a structure similar to a chestnut burr. Illustration 7 shows an X-ray diffraction pattern of this sodium tetrasilicate.

For a long time it was thought that a simple formula such as $Na_2O \cdot 4SiO_2 \cdot 7H_2O$ would be correct. A damp specimen dried over partially dehydrated material did appear to reach this degree of hydration, but the weight of evidence for the complex form was finally convincing and the name has been retained because of usage, simplicity and the unlikelihood that a true tetrasilicate will be found. (It has been suggested that this compound may be considered as an isopolyacid salt having a cage-like structure.)



Illust. 7.—X-ray diffraction pattern of $3Na_2O \cdot 13SiO_2 \cdot 11H_2O$ grown at room temperature (courtesy Allis Chalmers Mfg. Co.).

The Isotherm at 50°

At 50° the two forms of $Na_2SiO_3\cdot 6H_2O$ were found, but not the $Na_3HSiO_4\cdot 1H_2O$. At this temperature, too, appeared the supposed $Na_2SiO_3\cdot 1H_2O$. Otherwise the same salts are present as at 70° (Table VI, Fig. 3).

TABLE VI

THE SYSTEM Na_2O–SiO_2–H_2O AT 50°

Composition of soln.		Composition of residue		
Na_2O	SiO_2	Na_2O	SiO_2	Stable solid phase
0.5	1.5			$3Na_2O\cdot 13SiO_2\cdot 11H_2O$
5.2	11.2			$3Na_2O\cdot 13SiO_2\cdot 11H_2O$
8.6	18.5			$3Na_2O\cdot 13SiO_2\cdot 11H_2O$
14.2	30.8			$3Na_2O\cdot 13SiO_2\cdot 11H_2O$
17.8	37.9			$3Na_2O\cdot 13SiO_2\cdot 11H_2O$
19.4	39.2			$Na_2Si_2O_5$
19.7	36.8			$Na_2iS_2O_5$
19.8	35.2			$Na_2Si_2O_5$
21.3	36.5			$Na_2Si_2O_5$
17.9	5.0	24.3	20.0	$\alpha\text{-}Na_2SiO_3\cdot 6H_2O$
19.3	30.4			$\alpha\text{-}Na_2SiO_3\cdot 6H_2O$
18.4	26.4			$\alpha\text{-}Na_2SiO_3\cdot 6H_2O$
18.7	25.0			$\alpha\text{-}Na_2SiO_2\cdot 6H_2O$
16.2	20.2			$\alpha\text{-}Na_2SiO_3\cdot 6H_2O$
14.7	15.3	22.7	22.5	$\alpha\text{-}Na_2SiO_3\cdot 6H_2O$
12.5	8.1			$\alpha\text{-}Na_2SiO_3\cdot 6H_2O$
13.5	4.8			$\alpha\text{-}Na_2SiO_3\cdot 6H_2O$
13.6	4.6			$\alpha\text{-}Na_2SiO_3\cdot 6H_2O$
15.3	3.3	23.7	19.6	$\alpha\text{-}Na_2SiO_3\cdot 6H_2O$
18.4	2.9			$\alpha\text{-}Na_2SiO_3\cdot 6H_2O$
21.8	2.7			$\alpha\text{-}Na_2SiO_3\cdot 6H_2O$
23.0	3.1			$\alpha\text{-}Na_2SiO_3\cdot 6H_2O$
25.1	3.9			$\alpha\text{-}Na_2SiO_3\cdot 6H_2O$
25.6	4.4			$\alpha\text{-}Na_2SiO_3\cdot 6H_2O$
20.2	35.3			$\alpha\text{-}Na_2SiO_3\cdot 6H_2O$ + $Na_2SiO_3\cdot H_2O$
19.2	30.6			$Na_2SiO_3\cdot H_2O$
16.8	22.0			$\alpha\text{-}Na_2SiO_3\cdot 6H_2O$ + $Na_2SiO_3\cdot H_2O$
16.2	19.6			$Na_2SiO_3\cdot H_2O$
14.7	15.3			$Na_2SiO_3\cdot H_2O$
15.0	15.1			$Na_2SiO_3\cdot H_2O$
15.2	10.4			$Na_2SiO_3\cdot H_2O$
16.7	8.4			$Na_2SiO_3\cdot H_2O$
18.3	6.7			$Na_2SiO_3\cdot H_2O$
21.9	4.3			$Na_2SiO_3\cdot H_2O$
24.0	3.4			$Na_2SiO_3\cdot H_2O$ + $\alpha\text{-}Na_2SiO_3\cdot 6H_2O$
26.2	2.5			$Na_2SiO_3\cdot H_2O$
37.0	0.5			$Na_2SiO_3\cdot H_2O$
24.2	39.4			Na_2SiO_3
23.4	38.4			Na_2SiO_3
24.25	37.34			Na_2SiO_3
23.81	34.44			Na_2SiO_3
23.3	30.6			Na_2SiO_3
23.6	30.3			Na_2SiO_3 + $\beta\text{-}Na_2SiO_3\cdot 6H_2O$
23.10	30.30	26.32	26.37	$\beta\text{-}Na_2SiO_3\cdot 6H_2O$
22.42	26.92	25.75	26.17	$\beta\text{-}Na_2SiO_3\cdot 6H_2O$
21.21	24.10	26.37	26.30	$\beta\text{-}Na_2SiO_3\cdot 6H_2O$
20.28	19.55	26.54	25.52	$\beta\text{-}Na_2SiO_3\cdot 6H_2O$
19.98	16.90	26.88	25.70	$\beta\text{-}Na_2SiO_3\cdot 6H_2O$
19.80	15.57	26.87	25.78	$\beta\text{-}Na_2SiO_3\cdot 6H_2O$
19.96	13.25	26.91	25.52	$\beta\text{-}Na_2SiO_3\cdot 6H_2O$
20.02	12.45	26.90	25.67	$\beta\text{-}Na_2SiO_3\cdot 6H_2O$
20.28	10.72	26.78	25.53	$\beta\text{-}Na_2SiO_3\cdot 6H_2O$
20.61	10.00	26.89	25.52	$\beta\text{-}Na_2SiO_3\cdot 6H_2O$
20.88	9.96	26.75	25.49	$\beta\text{-}Na_2SiO_3\cdot 6H_2O$
21.03	9.94			$Na_2SiO_3\cdot 5H_2O$ + $\beta\text{-}Na_2SiO_3\cdot 6H_2O$
21.01	10.15	29.0	27.34	$Na_2SiO_3\cdot 5H_2O$
21.30	8.68	29.05	27.47	$Na_2SiO_3\cdot 5H_2O$
21.68	8.16	28.80	27.05	$Na_2SiO_3\cdot 5H_2O$
21.82	7.82	28.83	27.00	$Na_2SiO_3\cdot 5H_2O$
23.01	6.47	29.03	27.24	$Na_2SiO_3\cdot 5H_2O$
23.25	6.17	29.08	27.28	$Na_2SiO_3\cdot 5H_2O$
24.93	5.65	28.95	27.00	$Na_2SiO_3\cdot 5H_2O$
26.31	5.90	29.08	27.75	$Na_2SiO_3\cdot 5H_2O$
26.45	6.03			$Na_3HSiO_4\cdot 5H_2O$ + $Na_2SiO_3\cdot 5H_2O$
26.45	5.98	36.00	22.87	$Na_3HSiO_4\cdot 5H_2O$
27.20	3.82	36.20	22.47	$Na_3HSiO_4\cdot 5H_2O$
30.10	1.51	36.30	22.28	$Na_3HSiO_4\cdot 5H_2O$
33.00	1.10	36.30	22.00	$Na_3HSiO_4\cdot 5H_2O$
36.87	1.15	36.80	21.57	$Na_3HSiO_4\cdot 5H_2O$
36.90	1.11	36.63	21.62	$Na_3HSiO_4\cdot 5H_2O$
37.32	1.15	36.45	21.63	$Na_3HSiO_4\cdot 5H_2O$
37.0	1.15			$Na_3HSiO_4\cdot 2H_2O$ + $Na_3HSiO_4\cdot 5H_2O$
37.38	0.75	45.60	25.90	$Na_3HSiO_4\cdot 2H_2O$
37.62	.80	45.10	26.00	$Na_3HSiO_4\cdot 2H_2O$
37.97	.64	45.40	25.25	$Na_3HSiO_4\cdot 2H_2O$
38.83	.55	45.00	22.57	$Na_3HSiO_4\cdot 2H_2O$
39.07	.59	45.35	26.57	$Na_3HSiO_4\cdot 2H_2O$
39.80	.50	45.30	26.35	$Na_3HSiO_4\cdot 2H_2O$
39.90	.50	46.60	26.85	$Na_3HSiO_4\cdot 2H_2O$
40.30	.42	46.00	24.67	$Na_3HSiO_4\cdot 2H_2O$
41.50	.26	46.15	25.62	$Na_3HSiO_4\cdot 2H_2O$
41.75	.26	45.90	23.10	$Na_3HSiO_4\cdot 2H_2O$
42.00	.26			$NaOH\cdot H_2O$ + $Na_3HSiO_4\cdot 2H_2O$
42.40	.26			$NaOH\cdot H_2O$
43.70	.20			$NaOH\cdot H_2O$
45.00	.00			$NaOH\cdot H_2O$

As before, the work may be divided into two sections. The curves for the metastable more readily crystallizable alkalies were determined first. The solubility of $NaOH\cdot H_2O$ was found to be 45.00 ± 0.05% Na_2O. This may be compared to 45.7% as obtained by Pickering.[5] The transformation from this sodium hydroxide hydrate to $Na_3HSiO_4\cdot 2H_2O$ was not determined exactly, because the two curves are quite parallel to each other. The invariant point is taken at about 42.0 ± 0.3% Na_2O and 0.26 ± 0.02% SiO_2. Attempts to establish isothermally invariant points using mixtures of the two solid phases were unsuccessful, either because of the slowness with which equilibrium was attained in the viscous

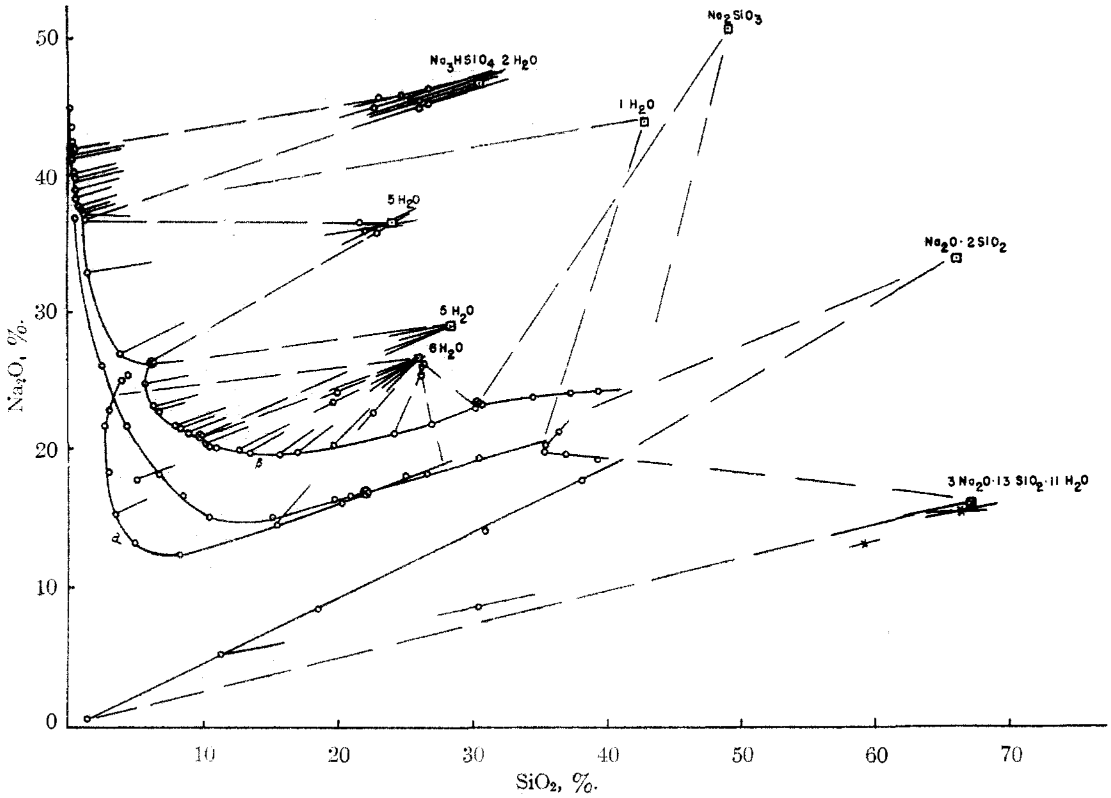


Fig. 3.—The system Na_2O–SiO_2–H_2O at 50°, weight per cent. basis: ⊗, points of isothermal invariance; ⊡, theoretical composition; O, experimental equilibrium points; -o-, wet residue determinations; ×, composition of washed and dried solid phase; — —, field boundaries.

solution or because of reaction of the alkali with the silver flask.

The invariant point between $Na_3HSiO_4 \cdot 5H_2O$ and $Na_3HSiO_4 \cdot 2H_2O$ was obtained by extrapolation. Transformation invariably occurs at about 37.0 ± 0.1% Na_2O and 1.15 ± 0.03% SiO_2.

Conditions for transformation of $Na_3HSiO_4 \cdot 5H_2O$ to $Na_2SiO_3 \cdot 5H_2O$ were established quite accurately. The metasilicate has a considerably shorter curve than at 70°, and soon reaches the point of transformation to $\beta Na_2SiO_3 \cdot 6H_2O$, a salt with a very prominent curve.

The invariant point between the penta- and the hexahydrate of Na_2SiO_3 was established definitely by the crossing of the two curves. Equilibrium at the siliceous end of the β $Na_2SiO_3 \cdot 6H_2O$ curve was difficult to obtain and required at least four months. The accuracy of points on these solubility curves in the more alkaline range is thought to be about ±0.05% Na_2O and ±0.05% SiO_2.

A metastable curve for anhydrous sodium metasilicate was obtained from undersaturation, the sintered product being used as starting material. It is in about the same position and has about the same accuracy as at 70°, but the β $Na_2SiO_3 \cdot 6H_2O$ interferes.

A curve for the unidentified salt was found toward the close of the work and could not be studied carefully. The refractive indices, roughly about 1.49, 1.50 and 1.51, serve to distinguish it from other phases. The photographs show aggregates of small crystals grown from supersaturation (Illust. 8). One stock was grown at 65° from a 79% solution of $Na_2SiO_3 \cdot 5H_2O$, seeded with a small amount of solution which contained $\alpha Na_2SiO_3 \cdot 6H_2O$ crystals, but which had been prepared from supersaturation over a period of six months by seeding a solution of $Na_3HSiO_4 \cdot 5H_2O$ with sintered Na_2SiO_3 crystals.

Another batch of crystals was formed from melted $Na_2SiO_3 \cdot 9H_2O$ at 70° over a two-year period. The seed used was thought, according to its indices, to be $\alpha Na_2SiO_3 \cdot 6H_2O$. The mother liquor of both batches was metastable to the $\alpha Na_2SiO_3 \cdot 6H_2O$ curve, but the solid phase appeared to consist mainly of the unidentified salt.

In this region, a similar batch of crystals underwent transition to $\alpha Na_2SiO_3 \cdot 6H_2O$ when seeded after reaching the new curve.

The stock of crystals obtained was used to obtain the alkaline section of the curve for the unidentified salt from undersaturation. The siliceous end had been obtained earlier and is considered highly questionable. Change of any kind seemed to be so slow as to defy interpretation. As crystals remained present it could only be assumed that some kind of equilibrium was established.

Since growth from supersaturation was obtained only in solutions near the metasilicate ratio line, wet residue extrapolations were of little help. Several attempts to wash and dry the solid phase for analysis were made, and the hydration was found to vary from 1.3 to 4.6. It is thought that some $\alpha Na_2SiO_3 \cdot 6H_2O$ was probably present in the solid portions of these metastable mixtures, and that the saturating solid phase may be either a low temperature form or βNa_2SiO_3, or a $Na_2SiO_3 \cdot 1H_2O$. The indices and the habit of the crystals both suggest some hydration.

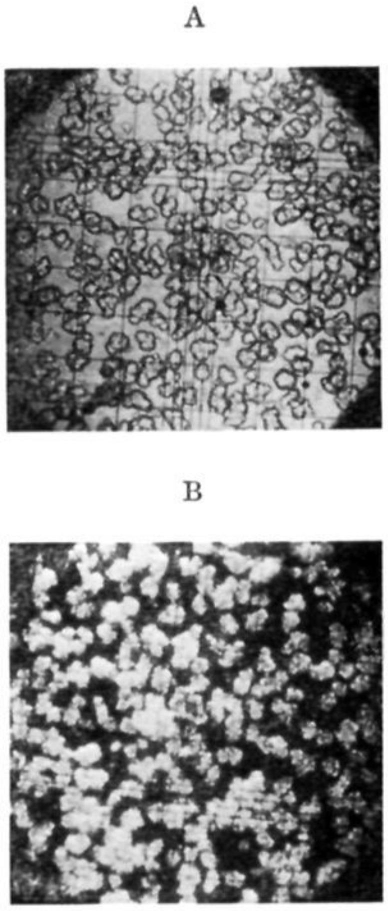
The curve is stable in both the more siliceous and the more alkaline ranges, and if time had permitted when ample seed stock was available, solutions prepared from undersaturation should have given useful wet residue extrapolations. It is thought that the transformation points at which $\alpha Na_2SiO_3 \cdot 6H_2O$ becomes stable are fairly well known by interpolation. There is no indication as to whether or not the curve would intersect any of the more alkaline curves other than that of $NaOH \cdot H_2O$. The probable intersection with a disilicate curve is not considered accurate.

The curve for $\alpha Na_2SiO_3 \cdot 6H_2O$, although this is still the most stable alkaline salt, is not as prominent as at 70°. Its accuracy is also at least about ±0.1% Na_2O and ±0.1% SiO_2. The small rate of growth of the alpha form is shown by an experiment in which a solution at about 15% SiO_2 on the $\beta Na_2SiO_3 \cdot 6H_2O$ curve was prepared, containing beta crystals. Its composition remained constant for at least one month, and beta crystals still remained in part four months later. In the course of five more months, the composition gradually shifted to the more stable curve.

One solution of initial composition 28.8% Na_2O and 6.3% SiO_2 fell to the $Na_3HSiO_4 \cdot 5H_2O$ curve, followed that curve to the intersection with the $Na_2SiO_3 \cdot 5H_2O$ curve, and then followed down that curve to 24.3% Na_2O and 6.0% SiO_2. This shift required 367 days; even a year later at 659 days it had not reached the stable phase, and at 799 days the analysis was 21.8% Na_2O and 4.7% SiO_2. Examination of the course showed that it took nearly a year for all of the $Na_2SiO_3 \cdot 5H_2O$ to transform to the stable $Na_2SiO_3 \cdot 6H_2O$.

A solubility curve for anhydrous sodium disilicate obtained from a furnace melt is given. Its X-ray diffraction pattern corresponds to the alpha form discussed by Kracek.[18] Solubility of this salt is extremely high, and solutions are viscous and difficult to handle. Equilibrium is established only slowly and we have not been able to determine any growth from supersaturation. The accuracy of the position of this curve cannot be estimated.

The curve for sodium tetrasilicate appears in approximately the same position as at 70°. It is not certain whether or not these crystals are congruently soluble. When dissolved in water, the ratio of Na_2O to SiO_2 in the liquid phase usually approximated that of the solid phase. Where considerable growth from supersaturation occurred, wet residue experiments indicated the same composition found at 70°. Washed and dried residues marked X on Fig. 3 also appear to indicate the same formula, although only the most thoroughly washed example shows a composition identical with that proposed. The accuracy of the position of this curve is thought to be about ±0.04% Na_2O and ±0.04% SiO_2.



Illust. 8.—(a) $Na_2SiO_3 \cdot 1H_2O$ formed at 50°, 70 ×. (b) With crossed nicol prisms shows that the particles are agglomerates.

It is very evident that there are still many interesting unsolved points in the knowledge of phase relations of the systems Na_2O–SiO_2–H_2O from 0 to 100°. This paper and previous ones may serve to point out these questions and make easier the work of later investigators.

Materials and Procedure

Standard methods of analysis were used. Na_2O was determined by volumetric titration with standard 0.2 *N* HCl, the traces of CO_2 by absorption and weighing on Ascarite in the usual train, and SiO_2 gravimetrically by precipitation with HCl. The residue of SiO_2 from such relatively pure soluble silicates does not require double precipitation and H_2F_2 treatment if care is taken to dry the initial precipitate thoroughly on a steam-bath.

Where H_2O was determined as a check on the other analyses, ignited loss was found by the following technique. The sample was allowed to filter into a bed of anhydrous sand in a weighed mullite or platinum crucible. Very viscous samples were wetted down with a little water to facilitate distribution through the sand. When dried slowly and ignited, the sand inhibits puffing or intumescence and aids in liberating CO_2.

One working with alkaline solutions is soon aware of the danger of contamination of his systems by absorption of CO_2. The effect of this added component on the equilibrium curves is uncertain, but must be considered. In very alkaline solutions the solubility of Na_2CO_3 is very low, but in general it increases with dilution. As SiO_2 concentration increases, CO_2 tends to fall. In this work we used two approaches, that described by Baker and Jue,[1,19] *i. e.*, avoiding contamination, and that used in our second section of allowing for its presence in determining the results.

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(18) F. C. Kracek, THIS JOURNAL, **61**, 2863 (1939).

(19) C. L. Baker and L. R. Jue, *J. Phys. Chem.*, **54**, 299 (1950).

Section 1.—The first section of this study, in which contamination was avoided, included the data at 90° and the data at 50 and 70° on the metastable alkaline salts, *i. e.*, the Na_3HSiO_4 hydrates, the $Na_2SiO_3 \cdot 5H_2O$ and β-$Na_2SiO_3 \cdot 6H_2O$.

The general methods and materials have been described.[1,19]

The determination of the curve for the new compound $Na_3HSiO_4 \cdot H_2O$ found at 70 and 90° involved many difficulties. In particular, care had to be taken to obtain a residue free from crystalline NaOH. Separation of residue by centrifuging was unsatisfactory. The residues were usually obtained by allowing the crystals to settle for twenty-four hours, a time which allowed most of the solid to reach the bottom of the flask. This much was then removed and pressed quickly between pieces of cloth to squeeze out as much of the excess solution as possible before the mass had an opportunity to cool. Filtration was slow because the highly alkaline solution swelled the fibers of the filter paper.

At 70° some difficulty was experienced in the early attempts to establish the solubility of $Na_3HSiO_4 \cdot 1H_2O$ in solutions of the highest alkalinity. Saturation with respect to NaOH at 70° was attained by rotating a flask containing a solution. When equilibrium had been established after several weeks, the flask was allowed to remain stationary until a clear supernatant liquid could be drawn off. The clear solution was placed in another flask, $Na_3HSiO_4 \cdot 5H_2O$ crystals were added, and the flask was allowed to rotate until equilibrium could be established.

In obtaining the curve for $Na_3HSiO_4 \cdot 2H_2O$ at 90° precautions had to be taken to exclude crystals of anhydrous Na_2SiO_3 because of the slow rate of solution of this latter salt. In other words, if crystals of $Na_2SiO_3 \cdot 5H_2O$ were added to bring the solution to a required composition, anhydrous Na_2SiO_3 might form at some points and would pass into solution slowly over a period of many weeks. For this reason a filtered solution of sodium silicate having a ratio of $1Na_2O:3.22SiO_2$, ordinarily referred to as Na_2O, $3.22SiO_2$, was used to adjust the SiO_2 content.

Difficulties at 70° in securing the Schreinemakers[7] residue lines passing through the point representing the theoretical composition $Na_3HSiO_4 \cdot 5H_2O$ were finally traced to the formation of crystals of anhydrous metasilicate during the preparation of the solution by evaporation. This difficulty was avoided by preparing solutions of approximately correct Na_2O concentrations but with the silica somewhat low. The solution was then brought to 70° and the SiO_2 concentration adjusted by the addition of a concentrated filtered solution of $Na_2O:3.22SiO_2$ sodium silicate.

Section 2.—In this section is included the work at 50 and 70° on the stable metasilicates, $\alpha Na_2SiO_3 \cdot 6H_2O$ and $Na_2SiO_3 \cdot 1H_2O$, as well as the more siliceous disilicate and tetrasilicate.

This second section differs principally from the first in allowing for the presence of traces of CO_2 in the starting materials which were the purest commercial silicates available, usually liquid commercial silicates clarified by filtration, crystals of $Na_2SiO_3 \cdot 5H_2O$ then available well crystallized rather than the granulated product of today, granulated $Na_3HSiO_4 \cdot 5H_2O$, liquid caustic (36% Na_2O) saturated with Na_2CO_3, anhydrous sodium metasilicate and disilicate from fused anhydrous materials. Somewhat different methods of sampling were used.

A vacuum-sealed "Red Top Thermo Regulator" from the H. B. Instrument Company was used to control the bath temperature at 50 and 70°. The regulator drifted toward higher temperature with time because the mercury evaporated and condensed above the contact. If this condensate was returned to the mercury reservoir at monthly intervals by a slight warming of the regulator the bath could be controlled to approximately 70.0 ± 0.1°. We believe it conservative to claim control to 70.0 ± 0.3°.

Samples of solutions in contact with the more stable metasilicates, sodium tetrasilicate and disilicate at 50 and 70° were obtained by forcing liquid out of silver reaction flasks using air pressure. Rubber stoppers holding a U-shaped glass tube with one short leg were wired fast to the flask mouth. Where solutions were very viscous or recrystallization on cooling was a problem, they were kept warm by heating the glass tube with a coil of Nichrome resistance wire. Care was necessary to avoid localized boiling in the tube.[20] The end of the tube in the solution was covered with a sheet of hardened #41 Whatman filter paper bound with rubber bands. With the most viscous solutions and high air pressures the paper was backed with 14XX nylon fabric. Some such solutions required two weeks to remove sufficient sample. Samples were protected from evaporation during slow filtrations by a rubber spark plug cap which closely fitted the tube and the small mouth of the erlenmeyer form of weighing bottle. To facilitate later removal of the sample for analysis and to promote rapid cooling of the sample, a small amount of water was placed in the bottle before sampling except for very viscous solutions in the disilicate region which required as many as ten hours for a sample. Eventually a platinum filter and tube was used.

Analyses were usually made about two weeks apart and more infrequently as found necessary where equilibrium was delayed. Sampling was continued until at least two and preferably more complete analyses agreed. In some cases in which equilibrium was not obtained for one to three years, samples were taken three months apart. Where a number of samplings were required, as in most cases, it was not possible to use the analysis of the original solution as one point in determining the solid phase by extrapolation.

There is one point of interest in the use of silver flasks and rubber stoppers. Where reactions were continued for a long time in solutions more alkaline than the $3Na_2O:2SiO_2$ ratio there developed an apparently amorphous material which was found to be a silver sulfide product and which gradually increased in amount and caused difficulty with wet residue and washed residue analyses after long runs. The effect was more noticeable in the more alkaline solutions. This product seemed to be correlated with reduction in alkalinity and brought about a continuous shift in composition so that the compositions of the liquid phase of solutions moved along the equilibrium curve. This silver salt could be removed during analysis of solid phases by washing the SiO_2 filter cake with 10% NH_4OH solution followed by concentrated hydrochloric acid and finally by distilled water.

During the course of investigation, the Schreinemakers[7] wet residue, the Hill–Ricci[9] extrapolation between original composition and final solution, and the Bijlert[21] tracer ion technique using NaCl were used to determine the composition of the solid phases.

Wet residue analyses were often made by removing samples of liquor and solid separately. However, in some cases it was difficult to obtain a sample of liquor by filtration and in these cases wet residue was bound in filter paper backed with clean, dry, weighed, desized cotton cloth and centrifuged inside a covering of dentists rubber dam reinforced with cellophane. The liquor sample on the cloth was analyzed and also the residual solid phase. In other cases, solid phase was pressed between filter paper on a Carver hydraulic press.

It was difficult to recover the residues of $Na_2SiO_3 \cdot 6H_2O$ and $Na_2SiO_3 \cdot 1H_2O$ successfully and a special technique was worked out to handle the small crystals which dissolved rapidly and held water tenaciously. In order to cut the viscosity, a solution of 15% Na_2O at 50–55° was used to dilute the magma and promote rapid, hot filtration. After filtration, the crystals were redispersed in the hot alkali solution, filtered, and then redispersed in, and filtered from acetone twice and from ether twice.

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(20) A. E. Hill and N. S. Yanick, THIS JOURNAL, **57**, 645 (1935).

(21) A. van Bijlert, *Z. physik. Chem.*, **8**, 343 (1891).

The crystals were then dried at 50–55° overnight and seed stock was stored at that temperature.

This treatment of the stable metasilicate crystals with a caustic solution close to the region of minimum solubility did not appear to affect the crystal shape as observed by the microscope or the composition as compared to wet residue analyses. The crystals were much less rapidly soluble in the alkali than in water and the resulting wash liquor could be filtered at a reasonable rate leaving an appreciable residue of fairly dry crystals. Moreover they could be washed with acetone since the concentration of soluble silicate had been reduced. Water alone did not have these effects and no water–organic solvent mixture was found which worked as well. In some cases the redispersion was made with a mixture of caustic solution and acetone.

Analysis of the sodium tetrasilicate required some special precautions as the alkali is not neutralized rapidly. For complete reaction it was necessary to heat the titrated solution for intervals as on a steam-bath, and continue titration after cooling. This cycle method was continued until the indicator did not change color. Since the neutralized silicate remaining absorbs indicator and turns pink it was necessary to differentiate between the liquid and solid phase when determining the intermediate endpoints and additional indicator was usually needed. The following method which allows determination of ignited loss, alkali, and silica on the same sample was preferred for the analyses of very siliceous samples such as those containing the tetrasilicate. The sample was dried and fused. The fused glass was crushed and a known proportion weighed as a sample to be hydrated at a steam pressure of about 35 pounds for a half-hour or until no grit remained. The solution was then diluted and titrated. If the glass is more alkaline than the disilicate, Na_2O may be lost by evaporation under the conditions of strong ignition required and therefore if Na_2CO_3 was added to the dried solid to increase the rate of solution, care was taken to avoid an excess.

No effort was made to determine the solubility of SiO_2 in water. Quartz has a solubility of less than 0.005% even at 200° and amorphous silica may show a concentration of about 0.35% at 70°.[22]

A petrographic microscope was used constantly. Photomicrographs were usually taken when a sample was removed and, after equilibrium was established, samples of wet residue were washed and dried and the refractive index was measured or checked.

Accurate determinations of CO_2 in such small amounts as are present even in commercial sodium silicates required careful attention and standardization of details of operation. The sulfuric acid in the absorption tubes was changed frequently. If rubber connecting hose becomes coated with concentrated sulfuric acid, results may be in error. Solutions were brought only to a full boil, and Ascarite tubes were weighed after allowing 0.5 hour to reach equilibrium temperature in the balance case. A similar tube is best used as a counter-weight.

In order to be sure that allowance could be made for the traces of CO_2 with satisfactory results, a series of tests on samples with increasing CO_2 content were made by adding Na_2CO_3 to a solution. It was found that if the percentage of Na_2O were corrected by subtracting the Na_2O equivalent to the CO_2 present, and the sum of $Na_2O + SiO_2 + H_2O$ taken as 100% of the system (where H_2O is ignited loss less CO_2), the ratio and the concentration of Na_2O and SiO_2, recalculated to per cent. by weight of the new base sum, remained essentially constant with increasing CO_2, at least up to concentrations above 1% CO_2—a concentration far greater than the 0.1% CO_2 maximum usually present. Saturation was reached at about 2.2% CO_2.

Similarly, a series of analyses was made on solutions saturated with both $Na_2SiO_3 \cdot 5H_2O$ and $Na_2CO_3 \cdot 1H_2O$.

THE EFFECT OF ADDED Na_2CO_3 ON THE ANALYSIS OF Na_2O, SiO_2, H_2O

Time, days	0[a]	21	33	66
% Na_2O	19.90	21.42	21.98	22.11
% SiO_2	15.03	14.40	14.31	14.49
% H_2O	(64.74)			60.83
% CO_2	0.050	1.68	2.25	2.20
% Na_2O[b]	19.83	19.05	18.80	19.01
Total	(99.72)			99.63
Ratio[c]	0.756	0.673	0.651	0.655
	100% basis ($Na_2O + SiO_2 + H_2O = 100\%$)			
% Na_2O	19.91	19.87	19.90	20.15
% SiO_2	15.09	15.03	15.16	15.36
Ratio	0.758	0.756	0.762	0.762

[a] Average of two sets of duplicates taken two weeks apart. The other columns represent the average of duplicates, except at 66 days where only one set of analyses was made. The parentheses indicate that the total was taken from a solution of similar original composition. [b] Determined Na_2O corrected for Na_2O in Na_2CO_3. [c] Ratio by weight of SiO_2 to total Na_2O.

When plotted on the 100% basis these fall on the curve for $Na_2SiO_3 \cdot 5H_2O$ previously determined with solutions protected from CO_2. This fact shows that the presence of such small amounts of Na_2CO_3 would not prevent an accurate determination of the solubility curves.

SOLUTIONS SATURATED WITH $Na_2SiO_3 \cdot 5H_2O$ AND $Na_2CO_3 \cdot 1H_2O$ RECALCULATED TO 100% $Na_2O + SiO_2 + H_2O$

Time, days	8	23			
% Na_2O	26.94	26.91	27.09		
% SiO_2	26.10	25.94	26.28		
% CO_2	0.437	0.398	0.404		
	100% basis			$Na_2SiO_3 \cdot 5H_2O$ curve ±0.1	
% Na_2O	26.67	26.70	26.87	26.55	26.70
% SiO_2	26.44	26.28	26.63	26.30	26.60

In general, we believe normal analyses are precise to about ±0.1% of the stated value but in some of the more difficult analyses of wet residues such as with sodium tetrasilicate, the uncertainty is probably 0.5%. We make this statement which we believe conservative after a careful review of the known analytical errors and a comparison of results carried out in duplicate. The estimated accuracy of each of the individual solubility curves is given in the discussion.

Acknowledgment.—We are glad to have this opportunity to acknowledge the careful analytical and mechanical work of John H. Muth and Thomas R. Foltz who carried out most of the determinations at 50° for the curves of $3Na_2O \cdot 13SiO_2 \cdot 11H_2O$, $Na_2Si_2O_5$, Na_2SiO_3, $Na_2SiO_3 \cdot H_2O$, α-$Na_2SiO_3 \cdot 6H_2O$.

Conclusions

1. The very viscous colloidal Na_2O–SiO_2–H_2O system has a number of easily differentiated metastable curves. These have been worked out in detail at 50 and 70° and partially at 90°.
2. There are two forms of the $Na_2SiO_3 \cdot 6H_2O$ at 50 and 70°.
3. The existence of a possible $Na_2SiO_3 \cdot 1H_2O$ is indicated at 50°.

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[22] G. W. Morey and E. Ingerson, "Pneumatolytic and Hydrothermal Alteration and Synthesis of Silicates," *Economic Geology*, **32**, 607 (1937).

4. Solubility curves have been obtained for $Na_2Si_2O_5$ from undersaturation but they could not be checked from supersaturation.

5. The solubility curve for $\beta 3Na_2O\cdot 13SiO_2\cdot 11H_2O$ changes but slightly with temperature. This composition best fits the experimental data.

6. The solid phases observed at the temperatures used were: $3Na_2O\cdot 13SiO_2\cdot 11H_2O$, $Na_2Si_2O_5$, Na_2SiO_3, $Na_2SiO_3\cdot H_2O$, $\alpha Na_2SiO_3\cdot 6H_2O$, $\beta Na_2SiO_3\cdot 6H_2O$, $Na_2SiO_3\cdot 5H_2O$, $Na_3HSiO_4\cdot 5H_2O$, $Na_3HSiO_4\cdot 2H_2O$. $Na_3HSiO_4\cdot H_2O$, NaOH and $NaOH\cdot H_2O$.

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Preparation, Stability and Adsorptive Properties of the Carbides of Iron[1]

BY H. H. PODGURSKI, J. T. KUMMER, T. W. DEWITT AND P. H. EMMETT

Introduction

The possible importance of metallic carbides in the synthesis of hydrocarbons from hydrogen and carbon monoxide over catalytic Co, Ni or Fe was first suggested by Fischer and Tropsch.[2] They proposed that the carbides might be intermediates in the Fischer–Tropsch process by being formed by the reaction of carbon monoxide with the metals and reduced by hydrogen to form hydrocarbons. In recent years it seems to have been well established that for iron[3a,b] and probably for cobalt[4,5] the bulk carbides are not intermediates. Nevertheless, the carbides are known to be formed during synthesis. It seemed well, therefore, to obtain some information relative to the adsorptive properties of the carbides toward carbon monoxide and hydrogen with a view to assessing more accurately their part, if any, in the Fischer–Tropsch synthesis. The present paper reports such adsorption studies for the various iron carbides and also gives additional information relative to the preparation and properties of the iron carbides including the use of hydrocarbons as carbiding agents, the rate of carbiding as a function of surface area, and the relative stability of samples of Fe_3C, Hägg Fe_2C, and hexagonal Fe_2C.[6]

Experimental

The apparatus employed both for carbiding runs and for adsorption measurements was an adaptation of a standard adsorption apparatus such as has been used in surface area measurements by low-temperature adsorption isotherms and has been described on numerous occasions.[7,8] Surface area measurements with nitrogen at −195° were made on all samples of carbides and metals used in the present work.

The catalyst tube was held at a constant temperature (to within ±0.25°) in the range 100 to 500° by using a furnace control similar to that described by Benedict.[9] A thermocouple in a well down the center of the catalyst tube enabled one to detect any temperature rise in the catalyst during carbiding or adsorption runs. Liquid nitrogen, Dry Ice-alcohol, and ordinary ice were used for the −195, −78.5 and 0° baths, respectively. The bath at −46° was maintained by keeping chlorobenzene at its melting point.

Carbon monoxide was prepared from formic acid and phosphoric acid. Just before use, it was passed over hot copper at 300° to remove traces of oxygen; through soda-lime to remove carbon dioxide; and through a Dry Ice trap to remove water vapor. Helium and tank nitrogen were purified by standard procedures.

Hydrocarbons (Phillips hydrocarbon gases, pure grade) were employed for some of the carbiding in place of carbon monoxide. The hydrocarbons (usually either propane, butane or pentane) were further purified by being passed over hot reduced copper, through a tube containing ascarite and finally through a tube containing freshly-activated alumina. The pentane was carried over the iron catalyst with pure dry helium.

The iron catalysts used for preparing the adsorbents in the present work were fused synthetic ammonia-type catalysts. Except for catalyst 910, which was free of added components, promoted catalysts were used in this investigation. Most of the work was done on promoted catalyst 423 which, in addition to oxygen, contained 72.26% Fe, 2.26% Al_2O_3. 0.62% SiO_2 and 0.21% ZrO_2. The other catalysts employed were 435, with 72.2% Fe, 0.8% Al_2O_3 and 0.25% K_2O; and 422, with 73.26% Fe, 1.55% Al_2O_3 and 0.58% ZrO_2. These fused oxide catalysts were initially reduced with hydrogen at space velocities near 1000 and at successively higher temperatures starting at 350 and extending up to 500° for the promoted catalysts.

The samples carbided with carbon monoxide were prepared by passing carbon monoxide over the reduced catalysts at temperatures starting at 200° and increasing gradually to 275°. As is well known,[10,11,12] iron under these conditions will form a carbide that can be identified by its X-ray structure and that corresponds approximately in composition to Fe_2C. In the present work, the percentage carbiding was determined in two ways. During the carbiding process a sample of the exit gas was analyzed for carbon dioxide at various time intervals. An integration of this time *vs.* carbon dioxide curve gave values for the total carbon dioxide yield from which the extent of carbiding was calculated by assuming that the carbon monoxide reacted with the iron to form Fe_2C and carbon dioxide. The amount of carbide formed was checked by noting the increase in the weight of the sample. The two methods always agreed to within about ±0.1% carbide carbon when correction was made for a trace of oxygen

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(1) Joint contribution from the Gulf Research & Development Company's Multiple Fellowship, Mellon Institute, and the University of Pittsburgh, Pittsburgh, Pa.

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