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The System Calcium Oxide–Silica–Water at 30°. The Association of Silicate* Ion in Dilute Alkaline Solution

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Knowledge of the compounds of hydrated calcium silicate and their equilibria is important in cement technology and in regard to the use of siliceous minerals in cement.

Hydrated calcium silicate is gelatinous at room temperature, regardless of method of preparation or time. However, the units of physical structure may be well-organized and definite, since X-ray analysis has shown that most inorganic gelatinous or amorphous materials are in reality crystalline, while all are crystalline (to X-rays) whose atoms or radicals are di- or monovalent.[1] A diffraction pattern has in fact been reported by Chassevant[2] for hydrous calcium silicate and has been corroborated by Foret.[3]

A high adsorption will be expected of the gelatinous silicate because of the minute size of the particles. Kolthoff and Moskovitz[4] observed that hydrous $Fe(OH)_3$ adsorbed $Cu(OH)_2$ up to 0.42 mole per mole. Weiser[5] found that gelatinous cupric ferrocyanide adsorbed potassium ferrocyanide continuously up to 0.85 mole per mole. The constancy of the x-ray diffraction pattern of the gel with varying ratios of alkali to copper[6] furnished direct proof of the adsorption character of the combination, although the possibility of a small amount of solid solution was not excluded. Similar results were obtained with the ferrocyanides of cobalt, nickel and manganese. A low adsorption was exhibited by lead ferrocyanide, which conformed to its coarsely crystalline character.

In general, owing to fineness of the microcrystals, solubility values for hydrous calcium silicate may be high. However, they will be generally reproducible if a similar state of growth of the microcrystals persists, so that active, or conversely normal, peripheral atoms are consistently dominant. The exclusively gelatinous character of calcium silicate formed at room temperature and lack of evidence of aging indicate the possibility of a fairly definite physical configuration and corresponding fairly definite solubilities.

The time required to reach equilibrium depends on the mode of experiment, the character of the starting materials and the degree of agitation. Fused calcium silicate may be decomposed with water, or, conversely, silica may be combined with dissolved calcium hydroxide. In both cases, observers have found that weeks or months may be required for complete reaction, particularly if agitation is poor; in side experiments with continuously rotated mixtures of silica gel and lime water of limited concentration we noticed that the concentration was decreasing appreciably after seven days. To expedite reaction, steel balls have been recommended for breaking up the

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(1) J. Böhm and H. Niclassen, *Z. anorg. Chem.*, **132**, 1–9 (1923).

(2) L. Chassevant, *Compt. rend.*, **199**, 673–675 (1934).

(3) J. Foret, *ibid.*, **203**, 80–83 (1936).

(4) I. M. Kolthoff and B. Moskovitz, *J. Phys. Chem.*, **41**, 629–644 (1937).

(5) H. B. Weiser, *J. Phys. Chem.*, **34**, 335–351 (1930).

(6) H. B. Weiser, W. O. Milligan and J. B. Bates, *J. Phys. Chem.*, **42**, 945–954 (1938).

coagula.[7,8] A third method of experiment consists in precipitating hydrous calcium silicate and treating this with lime water. Because in this method the initial solid phase is a hydrous compound more or less closely related to the final products of equilibrium, a comparatively rapid approach to equilibrium would be expected. This in fact has been realized in the present work.

Chemical analysis has in the past frequently neglected the correction due to dissolved silica. The solubility of silica is relatively high at the lower lime concentrations and so will affect acid titration, conductivity measurement, and the apparent composition of the solid phase if the latter is estimated by difference. In the present work, separate analysis has been made for CaO and SiO_2 in the liquid and solid phases.

Experimental

The preparation of the calcium silicate and the equilibrium experiments were carried out in a three-necked flask which was contained in a water-bath controlled at 30.2° and was protected at all times from air by tested soda-lime tubes appropriately placed. The solid was prepared by the slow addition from a buret of 15–40 cc. of sodium metasilicate solution, preheated to 30.2°, to 2 liters of 15–50% saturated lime water, the mixture being stirred vigorously by means of a mercury-seal stirrer during the addition. About 300 mg. of flocculent precipitate was thus formed in the presence of excess calcium hydroxide in solution. After the precipitate had settled, the supernatant liquid was decanted, and the precipitate was washed by decantation and settling seven times with 500-cc. portions of lime water. The solid was then stirred with 2 liters of lime water of known concentration for twelve hours to five days until equilibrium had been well established. The supernatant liquid was then drawn off, filtered through a Jena G3 filter, and its analysis begun immediately. The wet solid was next drawn off for analysis into a stoppered centrifuge tube. In this tube it was washed with 10 times its volume of aqueous acetone of such concentration (50% or stronger) that a precipitate of calcium hydroxide just was avoided. Activity of calcium hydroxide in the wash solution was secured in this way sufficient for avoiding decomposition of the solid. The second wash was made with a stronger solution of acetone, or with pure acetone; this was followed by three washings with acetone and three with ether, after which the solid was filtered and allowed to dry. For solid phases in equilibrium with very dilute lime water (3 mmole of $Ca(OH)_2$/l. or less) the washing with acetone was omitted and a slight correction made for the calcium oxide in the centrifuged wet residue. The dry solid contained only about 0.05% Na_2O by spectrographic test.[8a]

All reagents were C. P. and were examined under the microscope for noticeable impurity. The lime water was made up by dilution, in the absence of carbon dioxide, of a filtered solution. The sodium metasilicate crystals were kept in a tightly stoppered bottle in a desiccator; 200 cc. of solution was made up as required. The solution always contained a small amount of carbonate that was determined by a sensitive turbidimetric method described elsewhere.[9] The carbonate was assumed to have reacted with the calcium hydroxide in solution, so that the equivalent amount of calcium oxide was subtracted in determining the composition of the solid phase. The correction amounted rather uniformly to 0.07%.

Hydroxyl was estimated by titrating 50 to 200 cc. with 0.1 *N* hydrochloric acid in the presence of phenolphthalein. Calcium was determined in the usual manner by precipitating as calcium oxalate, and titrating hot with 0.1 *N* potassium permanganate solution. Silica in solution was determined by the colorimetric method of King and Dolan[10] in which silicomolybdate is reduced with 1:2:4 aminonaphtholsulfonic acid containing sulfite. The solution of the reagent was kept in a refrigerator as directed. The standard silica solution was made up by dilution of a gravimetrically analyzed solution of sodium metasilicate. For constancy of standard it was found absolutely necessary to paraffin the bottles containing the metasilicate solutions. A calibration curve was used, and the precision of estimating silica was ±0.8%.

The solid phase was analyzed by dissolving in hydrochloric acid, evaporating to dryness in a platinum dish, and determining the silica by repeated dehydration in the usual way. The ignited silica was treated with hydrogen fluoride and the insoluble residue corrected for. The silica filtrate was analyzed for calcium as described.

Equilibrium and Reversibility.—The ratio CaO/SiO_2 in the solid phase (written for short C/S) is shown in Table I and Fig. 1 as a function of the concentration of Ca^{++} at equilibrium. There are four phase ranges, I, II, III and IV, of which II and IV are invariant with respect to concentration. All experimental points are included, except one in range IV where the initial washing out of the alkali had been neglected. In range I, which differs from IV in its much higher *p*H, omission of the same wash in two instances did not affect the consistency of the values obtained, and they were included in the total.

In these experiments, three factors were involved in the attainment of equilibrium: the time of contact (column 6), the direction of approach to equilibrium (column 7), and the nature of the solid phase. The direction is labeled S (synthesis) when the final solid phase was formed by combination of the initial solid with lime from

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[7] W. M. Shaw and W. H. MacIntire, *Soil Sci.*, **29**, 429–456 (1930).

[8] T. Thorvaldson and V. A. Vigfusson, *Trans. Roy. Soc. Canada*, Ser. 3, **22**, 423–431 (1928).

[8a] Made by M. Slavin, of this Station.

[9] P. S. Roller and G. Ervin, Jr., *Ind. Eng. Chem., Anal. Ed.*, **11**, 150–153 (1939).

[10] E. J. King and M. Dolan, *Can. Med. Assoc. J.*, **31**, 21–26 (1934).

TABLE I

EQUILIBRIUM CONCENTRATIONS OF CALCIUM ION AT DIFFERENT RATIOS OF CaO TO SiO_2 IN THE SOLID PHASE

Phase range	Expt.	Millimoles/liter Ca^{++}	Millimoles/liter Activity Ca^{++}	CaO/SiO_2	Time of contact, days	Approach
I	1	20.67	6.87	1.401	5	S
	2	19.96	6.75	1.447	1	S
	3	19.90	6.74	1.417	5	S
	4	19.60	6.70	1.427	8	S
	5	17.51	6.32	1.387	1	S
	6	14.98	5.81	1.326	5	S
	7	13.53	5.51	1.309	5	S
	8	12.08	5.14	1.267	0.5	S
	9	9.81	4.54	1.235	1	D
	10	7.49	3.80	1.187	5	S
	11	6.99	3.62	1.168	1	D
	12	6.60	3.49	1.164	5	S
	13	4.89	2.82	1.116	5	S
	14	4.02	2.45	1.100	1	D
II	15	3.11	1.99	1.053	1	D
	16	3.10	1.99	1.048	5	S
	17	3.05	1.97	1.008	4	D
	18	3.11	1.99	1.014	1	S
	19	3.07	1.98	1.000	2	S
III	20	2.84	1.87	0.955	2	D
	21	2.69	1.79	.957	2	D
	22	2.57	1.72	.955	4	D
	23	2.24	1.54	.964	1	D
	24	2.09	1.46	.936	1	D
	25	2.07	1.44	.933	2	D
	26	1.64	1.19	.910	2	S
	27	1.60	1.17	.918	1	D
	28	1.60	1.17	.919	1	D
	29	1.37	1.03	.921	1	D
	30	1.18	0.902	.901	1	D
	31	0.990	.768	.895	2	D
IV	32	.897	.705	.869	4	D
	33	.923	.724	.854	4	D
	34	.900	.707	.852	2	D
	35	.900	.707	.819	2	D

a more concentrated solution than that in which the solid was formed. Conversely, the direction is labeled D (decomposition) when calcium oxide was released to a more dilute solution.

In range I, the same results were obtained after three hours as after five days, as may be seen from the following data (S direction):

	3 hr.	5 d.	3 hr.	5 d.	3 hr.	5 d.
Concn. Ca^{++} (mml./l.)	4.85	4.93	7.49	7.48	15.18	14.78
C/S in solid	1.110	1.116	1.188	1.186	1.326	1.326

To test reversibility in range I, a D approach was effected by diluting the mixture of expt. 5 (Table I). After one day of contact the results of expt. 11 were obtained, which agree very closely with those obtained by the reverse approach.

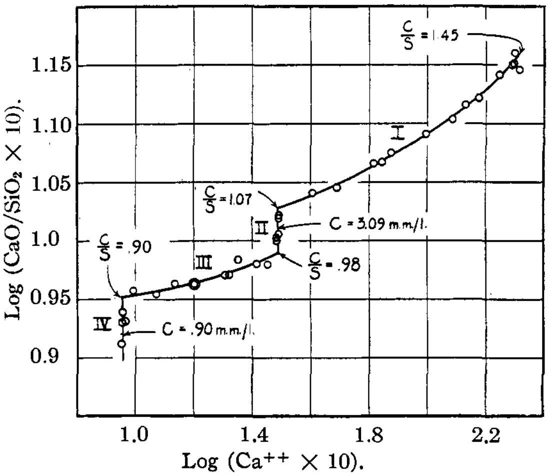

Fig. 1.—Mole ratio of CaO to SiO_2 in solid against concentration of calcium ion in solution (millimoles/liter).

The rapid and reversible equilibrium observed for range I also has been observed by Baylis.[11]

In range II no special tests were made, but the two directions of approach, and widely varying times, were used (Table I).

In range III, after one day of contact (D approach) a concentration of 2.57 mml./l. and a C/S ratio of 0.957 were obtained; the result after four days was 2.43 and 0.954, so that one day appeared adequate for attainment of equilibrium. However, in the reverse approach in the same region, it seemed that two days were required, since the results of expt. 26, which are comparable with those of expt. 27, were arrived at in not less than this time.

In range IV at least two days were required in a D approach to reach the invariant concentration, the greater time being due no doubt to comparative slowness of the compound transformation. It did not seem feasible to test reversibility in this range because of complete solution of the solid when it was treated with water in attempting to obtain a sufficiently low C/S ratio in preparation for an S approach.

The above tests indicate that the stirring times listed in Table I were sufficient; the consistency of the results for widely varying times and different directions of approach attests further to the establishment of equilibrium.

Nature of the Solid Phases

Because of their gelatinous adsorptive character, the composition of compounds in the solid phases may not be determined in the usual way.

[11] J. R. Baylis, *J. Phys. Chem.*, **32**, 1236–1262 (1928).

However, they may be identified by the application of physical chemical considerations. Two of these are: adsorption isotherm and ion product constant.

Evidence of Adsorption Isotherm.—The continuously changing composition and the rapid approach to equilibrium in ranges I and III are characteristic of adsorption. However, only part of the calcium oxide in the solid phase is adsorbed; the rest is combined in an adsorbing compound. Since in range I the C/S ratio was 1.07 to 1.45, the absorbent may be a 1/1, 4/5, 2/3 or 1/2 compound, etc. For a given ratio, the moles of calcium oxide adsorbed may be calculated with reference to any one of these possible combinations. In Fig. 2, the adsorption per mole of 2/3, 4/5 and 1/1 compound has been plotted against log concentration of Ca^{++} and against log activity of Ca^{++}, as for a Freundlich isotherm. Activity coefficient of Ca^{++} was calculated by the usual Debye–Hückel formula, $-\log \gamma_2 = 2.02 \sqrt{\mu} - 0.40 \mu$, the coefficient 0.40 being deduced from the data of Fosbinder[12] for calcium hydroxide.

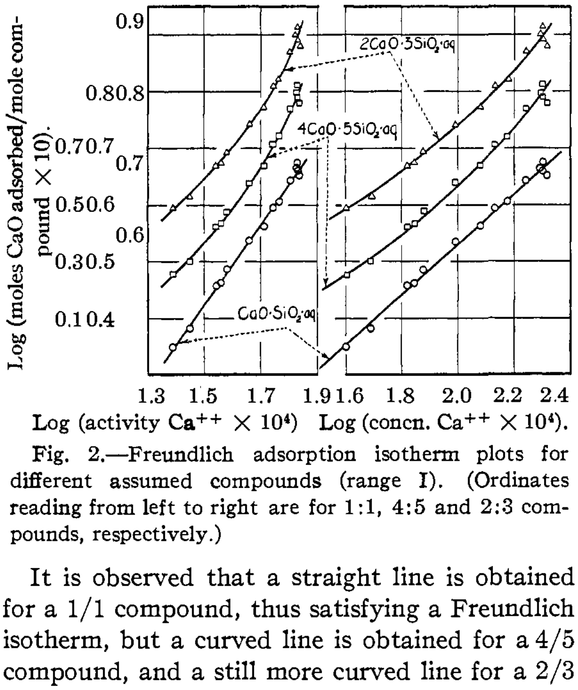

Fig. 2.—Freundlich adsorption isotherm plots for different assumed compounds (range I). (Ordinates reading from left to right are for 1:1, 4:5 and 2:3 compounds, respectively.)

It is observed that a straight line is obtained for a 1/1 compound, thus satisfying a Freundlich isotherm, but a curved line is obtained for a 4/5 compound, and a still more curved line for a 2/3 compound. Due to a fortuitous rate of increase in the activity coefficient for Ca^{++}, the same relations are obtained for concentration or activity but the distinctions are more pronounced for activity. It is inferred, therefore, that the adsorbing compound in range I is, empirically, $CaO{\cdot}SiO_2{\cdot}aq$. The value of n in the Freundlich equation ($x/m = ac^{1/n}$) is 0.70 for activity and 1.13 for concentration.

According to Lefol[13] and to Cirilli,[14] calcium silicate retains one mole of water at high temperatures, and so this molecule is constitutional. The empirical monosilicate is probably, therefore, structurally the acid salt of orthosilicic acid, or $CaH_2SiO_4{\cdot}aq$. The existence of orthosilicic acid is known from vapor tension measurements.[15,16] Its existence is demonstrated further by the wet preparation of thallous orthosilicate by Vesterberg and Willers.[17] For these and other reasons, we shall consistently adhere to the orthosilicate, rather than the metasilicate, terminology. However, the terminology is essentially immaterial as far as our conclusions are concerned.

The adsorption isotherm holds right up to lime saturation, so there is no indication of a silicate higher than the 1/1 compound. Furthermore, the mean maximum C/S ratio, corresponding to 20.7 mml. CaO/l. (somewhat in excess of true lime saturation, or 19.4 mml./l.),[18] was only 1.45, whereas even for a 3/2 compound a ratio more nearly equal to 2 would be expected due to adsorption. The apparent non-existence at 30° of $3CaO{\cdot}2SiO_2{\cdot}aq.$, or of $2CaO{\cdot}SiO_2{\cdot}aq.$, may be explained by the difficulty of displacing the first two hydrogens of orthosilicic acid. Britton[19] found no break in the titration curve that would correspond to dissociation of these. Sodium orthosilicate has never been crystallized, even in the presence of a great excess of sodium hydroxide. Although Vesterberg and Willers obtained insoluble thallous orthosilicate, this occurred only under unusually favorable conditions, as by digestion of the insoluble 1:1 compound with concentrated thallous hydroxide.

Nacken and Mosebach[20] believed that they had prepared hydrated calcium orthosilicate on treating tricalcium silicate with water; however, on prolonging the experiment (which involved intermittent shaking) from 30 to 278 days, the C/S ratio dropped to 1.55 and 1.68 in two experi-

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(12) R. J. Fosbinder, This Journal, **51**, 1345–1356 (1929).

(13) J. Lefol, *Compt. rend.*, **201**, 669–672 (1935); *Compt. rend. 17 Congr. Chim. Ind., Paris*, Sept.-Oct. 1937, 562–571.

(14) V. Cirilli, *Ann. chim. applicata*, **28**, 239–244 (1938).

(15) R. Spychalski, *Z. anorg. allgem. Chem.*, **239**, 317–320 (1938).

(16) P. A. Thiessen and O. Koerner, *Z. anorg. Chem.*, **189**, 168–182 (1930).

(17) K. A. Vesterberg and C. U. Willers, *Arkiv. Kemi Mineral. Geol.*, **9**, 1–8 (1926); *Chem. Abs.*, **20**, 1963 (1926).

(18) H. Bassett, *J. Chem. Soc.*, 1270–1275 (1934).

(19) H. T. S. Britton, *J. Chem. Soc.*, 425–436 (1927).

(20) R. Nacken and R. Mosebach, *Z. anorg. allgem. Chem.*, **223**, 161–173 (1935).

ments.[21] Beitlich[22] obtained a ratio of 1.95, from which he inferred the existence of an orthosilicate; however, he added solid lime to his mixture, and this may have become entangled in the gel or for some other reason did not dissolve completely. Moreover, a 2/1 compound would again require an appreciably higher ratio than 1.95 owing to adsorption.

In addition to the above, the following maximum ratios, corresponding to approximate lime saturation, have been reported: 1.4–1.5,[7,8,11,23,24] 1.5–1.6,[25,26] 1.6–1.7.[27,28,29] The adsorption character of the continuously increasing C/S ratio has generally been recognized, and usually a 1/1 compound has been assumed to be the adsorbent.

Range III was insufficiently large and the data insufficiently accurate to permit discrimination of the nature of the adsorbing compound by means of a Freundlich isotherm. The C/S ratio in this range was 0.98 to 0.90, so that the solid might be a 5/6, 4/5, 3/4, 2/3 or 1/2 compound.

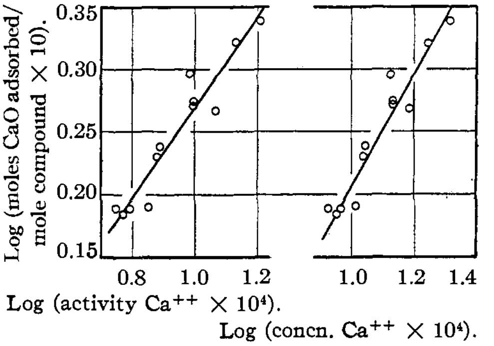

Fig. 3.—Freundlich adsorption isotherm plot for $3CaO \cdot 4SiO_2 \cdot aq.$ (range III).

It is observed from Fig. 3 that the assumption of an adsorbing compound having the formula $3CaO \cdot 4SiO_2 \cdot aq.$ satisfies the requirements of the isotherm. The value of the exponent n is for activity as variable, 2.2, and for concentration as variable, 2.7. The apparent agreement for a 3/4 compound does not exclude the possibility of any of the others. Its existence was independently inferred from an ion product study that will now be considered.

Evidence of Solubility Product Constant.—During the course of an adsorption isotherm, the concentrations of the ions are continuously changing, but if the adsorbent is one and the same compound, AB_n, then the product of the ion activities, $A \times B^n$, should be constant, and a plot of log A against log B should give a straight line of slope, n. The fulfillment of this condition may be used to ascertain the composition of the adsorbing compound. The activities A and B must of course be accurately determined as a prerequisite to the application of the method.

For the purpose of calculating the activities of the silicate ions, accurate values for dissolved silica were obtained in a special series of experiments in which the reaction flask was paraffined. After ample time, based on previous experience, had been allowed for equilibrium, the solution phase was analyzed. The paired values of silica and Ca^{++} are shown in Table II and plotted in Fig. 4. (The two lowest values for silica are in parentheses, as the color during analysis was unstable and the result therefore unreliable.) It is observed that silica increases continuously with decrease in Ca^{++}. The absence of a sharp change in passing from range I to range III may be due to the fact that the dissolved silica consists of several ions and molecules, so that a discontinuity for one of these is dulled by the presence of the others.

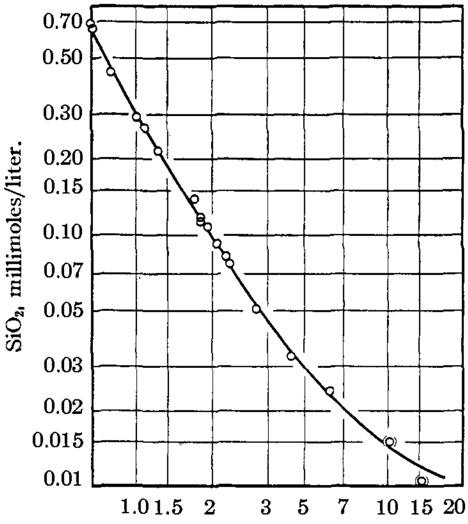

Fig. 4.—Variation of concentration of silica with concentration of calcium ion.

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(23) H. Kühl and A. Mann, *Tonind. Ztg.*, **58**, 862, 896, 918, 930, 944, 955, 990, 1003, 1014 (1934).

(24) A. J. P. van der Burgh, *Chem. Weekblad*, **29**, 616–618 (1932).

(25) B. Tavasci, *Ann. chim. applicata*, **23**, 413–427 (1933).

(26) P. Jolibois and L. Chassevant, *Compt. rend.*, **188**, 452–454 (1929).

(27) H. Le Chatelier, "Constitution of Hydraulic Mortars," trans. by J. L. Mack, McGraw-Hill Book Co., Inc., New York, N. Y., 1905.

(28) E. P. Flint and L. S. Wells, *Bur. Standards J. Research*, **12**, 751–783 (1934).

(29) F. Klasse, *Zement*, **17**, 2–9, 49–56 (1928).

TABLE II

EQUILIBRIUM CONCENTRATIONS OF CALCIUM ION, HYDROXYL ION, AND SILICA, AND CALCULATED CONCENTRATIONS OF SILICIC ACID COMPONENTS

Millimoles/liter				Activity coefficients			Millimoles/liter									
							Non-association		Association							
Ca^{++}	SiO_2	OH^- (exptl.)	OH^- (by diff.)	γ_1	γ_2	γ_3	$H_3SiO_4^-$	$H_2SiO_4^=$	H_4SiO_4	$H_3SiO_4^-$	$H_2SiO_4^=$	$H_3Si_2O_6^-$	$H_2Si_2O_6^=$	$HSi_2O_6^{\equiv}$	SiO_2 (Sum)	% Devn. in SiO_2
								Range I								
20.47	(0.0105)	40.81	40.93	0.876	0.334	0.21	0.0_2313	0.0_2737	0.0_5660	0.0_2270	0.0110	0.0_7392	0.0_4369	0.0_4210	(0.0138)	(−23.9)
15.36	(.0151)	30.70	30.70	.876	.384	.24	$.0_2596$	$.0_2920$	$.0_4135$	$.0_2417$	.0111	$.0_6124$	$.0_4765$	$.0_4316$	(.0156)	(− 3.2)
8.76	.0238	17.50	17.50	.885	.482	.33	.0139	$.0_2990$	$.0_4572$	.0100	.0124	$.0_5126$	$.0_3360$	$.0_4809$	.0234	+ 1.6
6.24	.0337	12.45	12.45	.894	.538	.40	.0229	.0106	$.0_3139$	.0174	.0139	$.0_5532$	$.0_3983$	$.0_3148$	.0337	± 0
4.54	.0510	8.94	9.03	.904	.592	.46	.0386	.0121	$.0_3317$	.0292	.0159	$.0_4210$	$.0_2262$	$.0_3275$	.0512	− 0.4
3.52	.0777	6.85	6.96	.910	.629	.51	.0624	.0145	$.0_3651$	.0454	.0181	$.0_4654$	$.0_2599$	$.0_3469$	.0772	+ 0.6
3.41	.0821	6.66	6.74	.912	.632	.51	.0664	.0148	$.0_3714$	.0480	.0186	$.0_4755$	$.0_2669$	$.0_3511$	.0819	+ 0.2
3.16	.0924	6.18	6.23	.914	.642	.52	.0757	.0154	$.0_3880$	.0548	.0194	$.0_3107$	$.0_2861$	$.0_3605$	.0937	− 1.4
								Range III								
2.92	0.108	5.72	5.73	0.915	0.653	0.54	0.0895	0.0165	0.0_2118	0.0677	0.0216	0.0_3176	0.0129	0.0_3820	0.118	− 8.5
2.84	.112	5.38	5.57	.916	.657	.55	.0933	.0168	$.0_2125$	.0698	.0216	$.0_3192$	.0137	$.0_3835$	.122	− 8.2
2.81	.107	5.50	5.51	.917	.660	.55	.0895	.0159	$.0_2128$	.0704	.0215	$.0_3199$	.0139	$.0_3842$	.123	−13.0
2.70	.114	5.27	5.29	.918	.660	.55	.0959	.0162	$.0_2140$	.0740	.0218	$.0_3228$	.0154	$.0_3896$	.130	−12.3
2.69	.119	5.25	5.26	.918	.660	.55	.100	.0170	$.0_2141$	.0741	.0218	$.0_3230$	.0155	$.0_3898$	.131	− 9.2
2.55	.140	4.90	4.96	.920	.672	.57	.119	.0186	$.0_2158$	.0783	.0214	$.0_3273$	.0170	$.0_3916$	.138	+ 1.4
1.83	.215	3.46	3.44	.930	.714	.63	.190	.0199	$.0_2329$	.113	.0206	$.0_3820$	.0342	$.0_2124$	.209	+ 2.9
1.64	.267	3.12	3.01	.932	.729	.65	.237	.0214	$.0_2430$	.129	.0202	$.0_2122$	.0438	$.0_2137$	.246	+ 8.5
1.52	.293	2.63	2.75	.934	.738	.66	.262	.0214	$.0_2516$	.142	.0202	$.0_2161$	.0525	$.0_2150$	.279	+ 5.0
1.18	.442	2.08	1.92	.940	.764	.70	.398	.0223	.0103	.197	.0191	$.0_2447$	.0992	$.0_2195$	.438	+ 0.9
1.01	.660	1.69	1.36	.944	.777	.73	.595	.0233	.0190	.259	.0177	.0108	.169	$.0_2231$	.659	+ 0.2
.99	.690	1.82	1.29	.945	.779	.73	.620	.0233	.0208	.268	.0173	.0123	.182	$.0_2236$	.698	− 1.1

It is usually assumed that the silica in dilute alkaline solution is made up simply of $SiO_3^=$, $HSiO_3^-$, and H_2SiO_3. Following the orthosilicate terminology, we shall write these components $H_2SiO_4^=$, $H_3SiO_4^-$ and H_4SiO_4, respectively. The presence of the ions $SiO_4^{==}$ and $HSiO_4^{\equiv}$ will be neglected on the basis of a trifling dissociation of the hydrogens from $H_2SiO_4^=$. If CaH_2SiO_4 is the adsorbing compound in range I, as the adsorption isotherm shows, then the product of the activities of Ca^{++} and $H_2SiO_4^=$ should be constant over the whole range of adsorption. To calculate the concentration of $H_2SiO_4^=$, it is necessary to know the ionization constants of the acid anions. These have been determined only approximately. For the ionization of $H_3SiO_4^-$ ($HSiO_3$), K_2 has been given as 10^{-12}(30,31) and 10^{-13}(32) and for the ionization of H_4SiO_4 (H_2SiO_3), K_1 has been given, respectively, as 10^{-10}, $10^{-9.7}$ and 10^{-9}. We have chosen for the calculation $K_1 = 10^{-9.8}$ and $K_2 = 10^{-12.4}$; these values are slightly less than the mean of the reported values, but the difference was partly premeditated since the thermodynamic constants, with which we are concerned, are smaller than the constants calculated, as in these citations, from *p*H measurement without correction for activity coefficients of the ions. K_W was taken equal to $10^{-13.8}$ from "International Critical Tables." OH^- was estimated by difference, assuming one charge per SiO_2. This assumption could be corrected on the basis of the calculated proportions of the silicate ions and a second approximation made, but the original assumption proved sufficiently accurate both in the present and in

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(30) H. F. Joseph and H. B. Oakley, *J. Chem. Soc.*, **127**, 2813–2818 (1925).

(31) W. D. Treadwell and W. Wieland, *Helv. Chim. Acta*, **13**, 842–864 (1930).

(32) G. Hägg, *Z. anorg. allgem. Chem.*, **155**, 21–41 (1926).

subsequent calculations. In view of the dilute character of the solutions and lacking better information, the same activity coefficient was used for all ions of the same charge. γ_1, or that for singly charged anions and for OH^-, was taken from the equation of Flint and Wells[33] for OH^- in a solution of $Ca(OH)_2$. γ_2 was the same as that for Ca^{++}, and γ_3 (for use in subsequent calculations) was assumed by comparison with the values for a trivalent ion.[34]

From the above known values, the concentrations of $H_2SiO_4^=$, $H_3SiO_4^-$ and H_4SiO_4 have been calculated, as shown in Table II (case of non-association). For range I, a plot of log activity $H_2SiO_4^=$ against log activity Ca^{++} gives a straight line of slope equal to $-1/1$ (plot I′ of Fig. 5). This shows that the product of the activities of Ca^{++} and $H_2SiO_4^=$ is constant, and that the adsorbing compound is CaH_2SiO_4, or calcium monosilicate, in agreement with the adsorption data.

$H_3SiO_4^-$ being the only remaining silicate ion, one would expect that the compound of range III would be $Ca(H_3SiO_4)_2$, so that a plot of log activity $H_3SiO_4^-$ against log activity Ca^{++} should give a straight line of slope $-{}^1/_2$. Plot III′ of Fig. 5 shows that a straight line is obtained, but the slope instead of being $-{}^1/_2$ is much too high at about $-{}^2/_1$. The impossible compound $Ca_2H_3SiO_4$ is therefore indicated, and the apparent linearity of the plot is fortuitous.

The reason for the high slope is that the silica in solution is increasing much more rapidly with decreasing Ca^{++} than it should in order for an acid silicate to be satisfied. The consequent high rate of increase in calculated $H_3SiO_4^-$ could be reduced by choice of a smaller constant than $10^{-9.8}$ for K_1, which would transfer the silica to H_4SiO_4 from $H_3SiO_4^-$. Calculation shows, however, that to approach the theoretical slope of $-{}^1/_2$, K_1 would have to be reduced to a very low value, 10^{-12} or less. This is about equal to or less than K_2, which is not only untenable, but would lead to predictions of very high hydrolysis for sodium disilicate ($Na_2O \cdot 2SiO_2$ or $NaHSiO_3$), instead of only 5% or so obtained by Bogue[35] and by Harmon.[36]

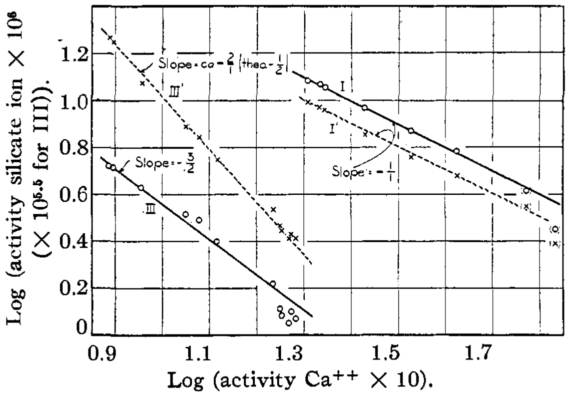

Fig. 5.—Test of compound by solubility product constant.

An alternative to the compound $Ca(H_3SiO_4)_2$ is an addition compound of the type $nCaH_2SiO_4 \cdot Ca(H_3SiO_4)_2$. For this the ion product $(Ca^{++} \times H_2SiO_4^=)^n \times (Ca^{++} \times [H_3SiO_4^-]^2)$ would have to be constant. However, in order to approach a steady value of the product, n, it is found, would have to be unreasonably large. Substituting the activities of $H_2SiO_4^=$, $H_3SiO_4^-$ and Ca^{++} of Table II, n would have to be about 8 for a reasonably steady value of the product. This corresponds to the hypothetical compound $9CaO \cdot 10SiO_2 \cdot aq.$, which is not only unexpected and irregular, but is so close to the molar ratio of calcium oxide to silica in the solid phase as to allow for practically none of the undoubted adsorption by the gelatinous solid.

We were thus led to the presumption that association of silicate ion takes place, even at the high dilution of silicon dioxide and high pH of the solutions. However, association could not be considered as having advanced to the colloid stage. The proof of this is as follows. A solution of $Na_2O \cdot 2SiO_2$ has a pH that is about the same as for the present solutions, about 10.7 and up, depending on the concentration;[35,36] comparison may therefore be made with $Na_2O \cdot 2SiO_2$ solution as respects the properties of dissolved silica. Harmon[37] and Ganguly[38] found for such a solution practically complete molecular diffusion at concentrations up to 0.3 N. Ganguly[39] and Burgess and Krishnamurti[40] observed no colloidal scattering at concentrations of the order of 2 N. Finally, Main[41] saw in the results of viscosity measurement no evidence of colloidality for concentrations up to 3 N.

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[33] E. P. Flint and L. S. Wells, *Bur. Standards J. Research*, **11**, 163–171 (1933).

[34] G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923.

[35] R. H. Bogue, THIS JOURNAL, **42**, 2575–2582 (1920).

[36] R. W. Harmon, *J. Phys. Chem.*, **30**, 1100–1111 (1926).

[37] R. W. Harmon, *ibid.*, **31**, 616–625 (1927).

[38] P. B. Ganguly, *ibid.*, **31**, 407–416 (1927).

[39] P. B. Ganguly, *ibid.*, **30**, 706–712 (1926).

[40] L. L. Burgess and K. Krishnamurti, *Trans. Faraday Soc.*, **26**, 574–577 (1930).

[41] V. R. Main, *J. Phys. Chem.*, **30**, 535–561 (1926).

It seemed reasonable therefore to assume that association was confined to a molecular-type of compound, and in the first instance to a dimer, so that corresponding to $SiO_4^{==}$, $HSiO_4^{\equiv}$, $H_2SiO_4^{=}$, $H_3SiO_4^{-}$ and H_4SiO_4, a new series of ions was to be considered, which in the order of decreasing alkalinity is $Si_2O_6^{==}$, $HSi_2O_6^{\equiv}$, $H_2Si_2O_6^{=}$, $H_3Si_2O_6^{-}$, and $H_4Si_2O_6$. As far as the possibility of combination of Ca^{++} with any of the latter ions to form a compound in range III is concerned, we may rule out $Si_2O_6^{==}$, the most alkaline anion, because the ratio CaO/SiO_2 would be 1/1 which is greater than any of the experimental ratios in range III. Compound formation with the next most alkaline ion, $HSi_2O_6^{\equiv}$, is feasible, as will be shown. For the sake of completeness we have also considered in great detail the independent possibility of combination with the still more acid anion, $H_2Si_2O_6^{=}$, and also the possibility of combination with $H_3SiO_4^{-}$ in the new situation of association. The former compound would require a slope of $-1/1$ in plotting log activity $H_2Si_2O_6^{=}$ against log activity Ca^{++}. However, here again, as for the case of nonassociation, the rate of increase of silica in solution is so great that a very small ionization constant would be required for $H_3Si_2O_6^{-}$ and for H_4SiO_4. The expected hydrolysis of $Na_2O \cdot 2SiO_2$ would again then be very much greater than is actually found. The postulate of a tetra polymer did not avoid the calculated high degree of hydrolysis. With respect to the possible compound $Ca(H_3SiO_4)_2$, the same impasse of high hydrolysis existed as before.

The combination of $HSi_2O_6^{\equiv}$ with Ca^{++} to give $Ca_3(HSi_2O_6)_2 \cdot aq.$ (or empirically $3CaO \cdot 4SiO_2$) would require a slope of $-3/2$. This slope was readily realized in preliminary test. The problem that remained was to determine accurately the magnitude of the various equilibrium constants. For this purpose we have the four ionization constant equations for H_4SiO_4 (K_1), $H_3SiO_4^{-}$ (K_2), $H_3Si_2O_6^{-}$ (K_{II}) and $H_2Si_2O_6^{=}$ (K_{III}), the equations of association (1), of solubility product constant (2) and (3), and of conservation of mass (4).

$$\frac{\gamma_2 H_2Si_2O_6^{=}}{\gamma_1^2 (H_3SiO_4^{-})^2} = K_S \qquad (1)$$

$$\gamma_2^3 \gamma_3^2 (Ca^{++})^3 \times (HSi_2O_6^{\equiv})^2 = K_{S.P.}\,(C_3S_2) \qquad (2)$$

$$\gamma_2^2\, Ca^{++} \times H_2SiO_4^{=} = K_{S.P.}\,(CS) \qquad (3)$$

$$H_4SiO_4 + H_3SiO_4^{-} + H_2SiO_4^{=} + 2H_3Si_2O_6^{-} + 2H_2Si_2O_6^{=} + 2HSi_2O_6^{\equiv} = SiO_2 \qquad (4)$$

By substituting into (4), equation (5) is obtained for range III in which each of the silicic acid unknowns is replaced one by one by a function of the different constants as unknown, whose coefficient is a function of Ca^{++}, OH^{-} and the activity coefficients.

$$\frac{MK_W/K_1}{o^{3/2}c^{3/4}} + \frac{M}{\gamma_1 o^{1/2} c^{3/4}} + \frac{o^{1/2} M K_2/K_W}{\gamma_2 c^{3/4}} + \frac{NK_W/K_{II}}{\gamma_1 o^2 c^{3/2}} + \frac{N}{\gamma_2 o c^{3/2}} + \frac{K_{S.P.}(C_3S_2)}{\gamma_3 c^{3/2}} = SiO_2 \qquad (5)$$

in which, $M = (K_W/K_{III})^{1/2} K_{S.P.}^{1/4}(C_3S_2) K_S^{-1/2}$, $N = 2K_W/K_{III}K_{S.P.}^{1/2}(C_3S_2)$, o = activity OH^{-}, c = activity Ca^{++}.

By making use of (3) instead of (2), a similar equation is obtained for range I

$$\frac{AK_W/K_1}{o^2 c} + \frac{A}{\gamma_1 o c} + \frac{K_{S.P.}(CS)}{\gamma_2 c} + \frac{BK_W/K_{II}}{\gamma_1 o^3 c^2}\; \frac{B}{\gamma_2 o^2 c^2} + \frac{BK_{III}/K_W}{\gamma_3 o c^2} = SiO_2 \qquad (6)$$

in which $A = K_W/K_2 K_{S.P.}(CS)$, $B = 2K_S \cdot (K_W/K_2\, K_{S.P.}(CS))^2$.

Since the same ultimate unknowns enter in both equations (5) and (6), their solution is not independent, but is conditional and based on successive approximations. In equation (6), the unknown terms of greatest weight are the second and third, so this equation is solved for $K_{S.P.}(CS)$ and K_2 (from A) after substituting for the other unknowns their values obtained from a previous sufficiently close solution of (5). By combining in the latter the second and the less important third term containing the substituted value of K_2, the number of unknowns is reduced to five. The general solution of the resultant equation led however to absurd negative values. This is due to the fact that in the range of pH under consideration, H_4SiO_4, $H_3Si_2O_6^{-}$ and $HSi_2O_6^{\equiv}$ are very small (compare Table II under association), so that treating the corresponding terms as independent unknowns was virtually the same as introducing arbitrary unknowns whose effect on the solution of an inexact (observational) equation is arbitrary. Therefore these terms were converted into knowns by substituting for K_1, K_{II} and K_{III} values based on the electrometric titration results previously referred to. Naturally the solution depends upon the substituted values, but since the combined magnitude of these averaged only 4% of the total, small errors of quantitation would be immaterial. The solution of the reduced equation (5) gave values for $K_{S.P.}(C_3S_2)$ and for $K_W/K_{III}K_{S.P.}^{1/2}(C_3S_2)$ (from N).

In every case the actual solution was carried out by applying the method of least squares to the observational equations and solving the resultant normal equations simultaneously. The precision was estimated from the residuals,[42] or the differences in silica found and calculated.

The results of the solution may be summarized as follows: $K_S = 2200 \pm 150$; $K_2 = 10^{-12.16 \pm .02}$; $K_{S.P.}(CS) = 2.53 \pm 0.10 \times 10^{-8}$; $(K_W/K_{III})^2 \cdot K_{S.P.}(C_3S_2) = 1.37 \pm 0.10 \times 10^{-23}$; $K_{S.P.} \cdot (C_3S_2) = 1.37 \times 10^{-21}$ (based on $K_{III} = 10^{-12.8}$); $K_1 = K_{II} = 10^{-9.8}$, and $K_{III} = 10^{-12.8}$ (all assumed from electrometric results).

K_{III} in the above tabulation was taken as different from the determined value of K_2 because of anomalies[19,31] observed in the titration of sodium silicate in the range of pH dominated by the second ionization constant, and it was taken as less because of the somewhat high value of K_2 compared to the mean of the electrometric values.

K_2 it may be noted is very much smaller than K_{II} even though the valence of the respective acids $H_3SiO_4^-$ and $H_3Si_2O_6^-$ is the same. The greater ionization of $H_3Si_2O_6^-$ may be explained by the electrical screening effect of the additional SiO_2 in the dimer ion.

From the above values of the equilibrium constants, the concentrations of the different silicic acids have been calculated in Table II under association; also given is their sum and the percentage deviation of the experimental silica from the latter. From the table, log activity $H_2SiO_4^{=}$ and log activity $HSi_2O_6^{\equiv}$, corrected to zero deviation, have been plotted in Fig. 5 against log activity Ca^{++}. The resultant graphs, I and III, respectively, are within the limit of error straight lines of theoretically correct slope $-1/1$ and $-{}^3/_2$. That the correct slope was previously gotten in range I for the case of non-association is explained by the small degree of association in this range due to the relatively low concentration of SiO_2.

In view of its non-existence (non-precipitation) in range III, the product of the ion activities for CaH_2SiO_4 should be less than $K_{S.P.}(CS)$ in this range. Making use of the values of Table II, this is confirmed for each of the determinations of range III, except that the low group of first five determinations (*cf.* Fig. 5) deviates in the wrong direction by an average of 3%. Likewise the product of the ion activities for $Ca_3(HSi_2O_6)_2$ should be less than $K_{S.P.}(C_3S_2)$ in range I. Surmounting the obstacle raised by the approximate character of K_{III} and hence of $HSi_2O_6^{\equiv}$ (and this alone), the equivalent condition is $(\gamma_2 Ca^{++})^3(\gamma_2 H_2Si_2O_6^{=})^2 \cdot (\gamma_1 OH^-)^2 < N^2/4 < 1.37 \times 10^{-23}$. This is found to be satisfied by each of the determinations of range I.

By comparison of the respective $K_{S.P.}$, it is noted that the (intrinsic) solubility of CaH_2SiO_4 is 1.7 times that of $CaCO_3$. If the monosilicate were crystalline instead of gelatinous, its solubility product would presumably be less. The solubility of $Ca_3(HSi_2O_6)_2$ (based on K_{III} equal to $10^{-12.8}$) is slightly less than that of $CaCO_3$.

The association of silicate ion explains the peculiar result of a decided increase in pH with increase in concentration, even for solutions of buffer character.[35,36] By equation (1) an increase in concentration results in the loss of two acid anions and gain of only one acid anion of nearly equal ionization constant, so the pH must also increase with concentration.

Because of the high value of 2200 for the association constant, comparatively much $H_2Si_2O_6^{=}$ and little $H_3SiO_4^-$ should be present in a solution of $Na_2O \cdot 2SiO_2$. This condition is indicated by the comparatively low depression of the freezing point of a solution of this substance. Harmon[43] found, for example, that in a solution that is 0.102 molar with respect to Na_2O the depression is 0.548° for sodium metasilicate but only 0.415° for the disilicate. However, (in the orthosilicate terminology) since $Na(H_3SiO_4)$ dissociates into four ions per mole of Na_2O (or more depending on hydrolysis and dissociation), while $Na_2(H_2SiO_4)$ dissociates into three ions (or more), a greater depression would be expected for the disilicate. Thus, for the comparable salt Na_2CO_3, at a concentration that is 0.10 molar with respect to Na_2O the depression is 0.444°, whereas for $NaHCO_3$ the depression is 0.702° and therefore considerably higher ("International Critical Tables"). The difference in behavior between HCO_3^- and a supposedly exclusive $H_3SiO_4^-$ is too great to be explained by differences in ionization constant or activity coefficient, but is accounted for by molecular association of $H_3SiO_4^-$. An abnormally low depression of the freezing point by sodium disilicate is also seen in the measurements of Kahlenberg and Lincoln.[44] The vapor pressure lowering[43] and the dew-point depression[45] are also comparatively low.

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[42] T. W. Wright and J. F. Hayford, "Adjustment of Observations," D. Van Nostrand Co., New York, N. Y., 1906.

[43] R. W. Harmon, *J. Phys. Chem.*, **31**, 355–373 (1927).

[44] L. Kahlenberg and A. T. Lincoln, *J. Phys. Chem.*, **2**, 77–90 (1898).

[45] A. N. C. Bennett, *J. Phys. Chem.*, **31**, 890–896 (1927).

TABLE III

INVARIANT CONCENTRATIONS AND SOLID PHASES IN EQUILIBRIUM

Millimoles/liter		Compounds (Hydrated)	
CaO	SiO_2	Ratios	Formulas
3.09	0.090	$CaO \cdot SiO_2 + 3CaO \cdot 4SiO_2$	$CaH_2SiO_4 + Ca_3(HSi_2O_6)_2$
.900	.931	$3CaO \cdot 4SiO_2 + CaO \cdot 2SiO_2$	$Ca_3(HSi_2O_6)_2 + CaH_2Si_2O_6$ or $Ca(HSiO_3)_2$

Invariant Ranges.—The invariant concentrations and the compounds in equilibrium therewith are given in Table III. The silica concentration for the upper invariant point was interpolated from the curve of Fig. 4. The value for the lower invariant point was the average of two accurate analyses carried out in the paraffined flask. A solution containing 0.924 millimole of CaO/l. was diluted one-third with water; after four days of stirring the concentration of Ca^{++} was 0.900 millimoles/l. and of SiO_2, 0.936 millimole/l. On a one-fold dilution of the latter solution, the concentrations after three days were, respectively, 0.900 and 0.926. The *p*H of the solutions, measured colorimetrically with acyl red, was 10.3–10.5. The values for Ca^{++} agree with those independently obtained when analyzing for the solid phase (Table I).

The existence of an invariant concentration corresponding to our value of 3.09 millimoles CaO/l. is indicated by the work of Thorvaldson and Vigfusson,[8] who decomposed tri- and dicalcium silicate with water till a steady state was reached. When their results are replotted as C/S ratio in the solid against concentration, a large break is observed at about 4 millimoles/l. for the trisilicate and at 2 millimoles/l. for the disilicate, both at a C/S ratio as in the present work close to 1/1. Shaw and MacIntire[7] found that uniform adsorption of calcium hydroxide by silica gel held to approximately 2.5 millimoles/l. when an arrest occurred; an arrest at about 3.5 millimoles/l. is shown by the results of Maffei[46] and at about 2 millimoles/l. by the results of van der Burgh,[24] who used twenty-four hour shaking periods. In treating silicate melts with lime water, Kühl and Mann[23] observed an arrest at 2.3 millimoles/l. and C/S ratio of 1/1.

The lower invariant concentration was early recognized by Le Chatelier,[27] who repeatedly extracted precipitated calcium silicate and obtained an arrest at 0.93 millimole CaO/l. The results of Baylis[11] in the same type of experiment show invariance at about the same concentration. Tavasci,[25] in decomposing tricalcium silicate with water, corroborated Le Chatelier's value; he believed, however, that an arrest occurred also at 0.55 millimole/l. In treating silica gel with lime water over a long period of time, Jolibois and Chassevant[26] obtained an invariant concentration of 0.95 millimole/l. The value obtained by Beitlich[22] in the same reaction was 0.75 millimole/l.; this, however, is low because the author did not take into account, in the conductivity measurements, the presence of silica in solution.

If the new solid that makes its appearance in range IV were silica, the concentration of silica would be expected to be equal to or greater than the solubility of gelatinous silica in water, which according to Lenher and Merrill[47] is 2.7 millimoles/l., and according to Hitchen[48] is 3.3 millimoles/l. However, the actual value of 0.931 millimoles/l. (Table III) is much lower, so the solid phase is not silica. The next less alkaline anion after $HSi_2O_6^{=}$ is $H_2Si_2O_6^{=}$, and, in the monomer series, $H_3SiO_4^-$. Combination of either of these anions with Ca^{++} would result in the compound $CaO \cdot 2SiO_2 \cdot aq$. Having eliminated silica, calcium disilicate is therefore strongly indicated to be the compound that makes its appearance in the second invariant range. It may be noted that hydrated calcium disilicate occurs naturally as the mineral okenite.

It is easily shown that the ion activity product for $CaH_2Si_2O_6$ is equal to

$$\frac{N}{2} \frac{1}{\gamma_1 OH^-} \frac{1}{\gamma_2^{1/2} Ca^{++1/2}}$$

and that the product for the other possible form of the disilicate, namely, $Ca(H_3SiO_4)_2$, is $1/K_S$ times this. Substituting for Ca^{++} and OH^- (assuming one charge per SiO_2) from Table III, $K_{S.P.}$ for $CaH_2Si_2O_6$ is calculated to be $1.69 \pm 0.06 \times 10^{-7}$, and $K_{S.P.}$ for $Ca(H_3SiO_4)_2$ $7.68 \pm 0.60 \times 10^{-11}$. The mean activity of the solute at saturation is given by the square and cube roots of the respective $K_{S.P.}$, and is, respectively, 4.11×10^{-4} and 4.25×10^{-4}. The practical identity

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(46) A. Maffei, *Gazz. chim. ital.*, **66**, 197–204 (1936).

(47) V. Lenher and H. B. Merrill, THIS JOURNAL, **39**, 2630–2638 (1917).

(48) C. S. Hitchen, *Bull. Inst. Mining and Met.* No. **364**, 26 pp. (1935).

of the values shows that the free energy of formation of calcium disilicate is the same whether the solid arises from the monomer or dimer forms; it would appear, therefore, that there is only one disilicate which may be formed indifferently from one or the other of the anions. The disilicate is intrinsically 2.6 times as soluble as the monosilicate. The ion product in range III is less than $K_{S.P.}$ for either $Ca_2H_2Si_2O_6$ or $Ca(H_3SiO_4)_2$, as is proper.

In view of the consistent rapid approach to equality of the CaO/SiO_2 ratio in solid and in solution, and the closeness of the ratios in invariant range IV, it is likely that calcium disilicate dissolves congruently in the next less-alkaline univariant range and is the last remaining compound. No hydrated silicate richer in silica than the disilicate is known in nature.

Summary

Hydrated calcium silicates are gelatinous. The effects to be expected from this in a phase rule study are discussed briefly.

Measurements were made of the ratio of CaO to SiO_2 in the solid phase, and of the concentrations of CaO and SiO_2 in solution at 30.2°. Equilibrium and reversibility were tested for.

Four phase ranges were distinguished; in two of these the concentrations were invariant. Adsorption of CaO by the solid phases occurred throughout. The compositions of the hydrated compounds, deduced from considerations of adsorption isotherm and solubility product constant, were: (1) $CaO \cdot SiO_2$ (CaH_2SiO_4), (2) $3CaO \cdot 4SiO_2$ ($Ca_3(HSi_2O_6)_2$), (3) $CaO \cdot 2SiO_2$ (indifferently either $CaH_2Si_2O_6$ or $Ca(HSiO_3)_2$). The invariant concentrations for the mixture of (1) and (2) were: 3.09 millimoles CaO/l. and 0.090 millimole SiO_2/l. and for the mixture of (2) and (3), 0.900 millimole CaO/l. and 0.931 millimole SiO_2/l.

The assumed exclusive presence of the simple ions $SiO_3^=$ and $HSiO_3^-$, or in the more rational and preferred orthosilicate terminology, $H_2SiO_4^-$ and $H_3SiO_4^=$, was inconsistent with the existence of the only alternatives of $Ca(H_3SiO_4)_2$ or any reasonable double compounds of the latter with CaH_2SiO_4. It was necessary to assume therefore that association took place in the dilute alkaline solutions. The postulate of two sets of silicate ions, based on an association equilibrium between $H_3SiO_4^-$ and $H_2Si_2O_6^=$, led to reasonable and concordant results. The association constant, solubility product constants, and one of the ionization constants, were calculated to a known precision. A high tendency toward association is evidenced.

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[CONTRIBUTION FROM THE PHYSICAL CHEMICAL RESEARCH LABORATORY OF NORTHWESTERN UNIVERSITY]

Isotopic Composition of Oxygen in Carbonate Rocks and Iron Oxide Ores

BY MALCOLM DOLE AND ROBERT L. SLOBOD[1]

Introduction

In recent years the isotopic composition of oxygen in various natural substances has been the subject of a number of investigations beginning with the research of Manian, Urey and Bleakney,[2] who studied stony meteorites and terrestrial silicate rocks. Unfortunately, after these workers had performed the difficult task of recovering the oxygen from these rocks by reaction with graphite and carbon tetrachloride vapors at 1000°, their methods of isotopic analysis were too inaccurate to demonstrate any significant differences between the various samples of oxygen; thus their specific gravity determinations of 0.47 cc. of water were accurate only to $\pm 63\ \gamma$[3] or 29% in the O^{18} abundance ratio while their more accurate mass spectrographic abundance measurements had for their average error 2.5%, which is equivalent to 6 γ. They found no significant variations in the isotopic composition of the oxygen between the stony meteorites and terrestrial silicate rocks, and they concluded that the absolute value of the abundance ratio O^{18}/O^{16} is 0.973/500. In a slightly more accurate mass spectrographic investigation of this abundance ratio in the oxygen from the thermal decomposition of

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[1] University Fellow, 1937–1938.

[2] S. H. Manian, H. C. Urey and W. Bleakney, THIS JOURNAL, **56**, 2601 (1934). This paper contains many references to earlier investigations concerning possible variations in the abundance of isotopic elements in meteors.

[3] The symbol refers to excess density of sample over that of normal water in parts per million; a negative value of γ means that the sample of water is lighter than normal. In this paper we shall take purified Lake Michigan water as being our standard of normal water.