

Summary

Illumination automatically constant over long periods is obtained from a spark struck between adjacent edges of two square bars moving in horizontal planes at right angles to each other. Conduction and radiation of heat are so rapid that erosion is at a minimum. A simplified method of following total energy at the exit slit of a monochromator is suggested and proved to be accurate. The monochromatic energies obtainable, under specified conditions, from zinc, cadmium and aluminum sparks, are listed at several wave lengths.

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THE SOLUBILITY OF CALCIUM HYDROXIDE IN AQUEOUS SALT SOLUTIONS¹

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There have been numerous investigations of the solubility of a sparingly soluble electrolyte in a solution of another electrolyte and attempts to formulate more or less rigorous expressions for the behavior of such solutions. While most of the previous workers along this line have used as the saturating substance a uni-univalent electrolyte of very low solubility, we have investigated the solubility relations, in a series of salt solutions, of a univalent substance of considerably greater solubility, namely, calcium hydroxide, which is readily obtainable in the form of large, well-defined crystals of a high degree of purity. The fact that it is a strong base lends it further interest since it may exhibit phenomena peculiar to substances which dissociate to produce hydroxyl ion.

The salts used were selected with the purpose of obtaining series, such as the chlorides of the alkali metals, which might be expected to show some definite relationships or systematic differences, such as the effect of different valence types. To this end the solubility of crystalline calcium hydroxide was determined at 25° in solutions of each of the following salts, at a series of concentrations extending well toward saturation of the salt: sodium chloride, potassium chloride, lithium chloride, cesium chloride, strontium chloride, barium chloride, sodium bromide, potassium bromide, sodium iodide, sodium nitrate, sodium nitrite, sodium chlorate, sodium perchlorate and sodium acetate. An attempt was made to use calcium chloride but the formation of hydrated double salts vitiated the results.

In all of these cases the solubility of calcium hydroxide increases with the salt concentration to a maximum, which ranges from about 1.35 to

¹ From the dissertation presented by Clinton Grove to the Graduate School of Yale University, June, 1928, in candidacy for the degree of Doctor of Philosophy.

2.8 times its solubility in pure water, though in one case (barium chloride) the solubility had not begun to fall at the highest salt concentration studied. Some of these results may be of interest to industry because of the widespread commercial uses and importance of lime.

Preparation of Materials

In the preparation of a substance on which physico-chemical measurements are to be made, it is essential that the product be not only of the highest degree of purity but also that it have a definite crystal form and be in the form of particles of such size that the determinations shall be reproducible. The failure of previous investigators to obtain consistent and reproducible results on the solubility of calcium hydroxide in water may be traced to the fact that their solid phase was composed of small particles—in part, at least, approaching colloidal dimensions—of indeterminate crystal form prepared by the slaking of calcium oxide from the calcination of calcium carbonate. We used definitely crystalline material, prepared by the diffusion method outlined by Johnston² in which solutions of calcium chloride and of sodium hydroxide are allowed to diffuse into each other and the crystals of calcium hydroxide are built up slowly, the degree of virtual supersaturation of the solution being automatically controlled by the rates of diffusion of the reacting substances. The standard procedure was as follows. In a quart Mason jar were placed two 50-cc. beakers, in one of which there was 50 cc. of a solution containing 600 g. of recrystallized $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ per liter, and in the other 50 cc. of a solution containing 240 g. per liter of sodium hydroxide which had been freed from carbonate by the addition to the hot solution of a very slight excess of a saturated solution of barium hydroxide; water was then carefully introduced into the jar until the beakers were covered to a depth of about two centimeters, after which the jar was sealed and allowed to stand until reaction was complete, about four weeks. The crystals of calcium hydroxide were deposited on the beakers and on the jar in hexagonal pyramids up to a centimeter in length. The growth of the crystals often caused the jars and beakers to crack or even break; this breakage led us to abandon the original use of desiccators as diffusion chambers. By the use of a large number of jars, an almost unlimited supply of the crystals was made available. The crystals, after removal from the diffusion chambers, were collected in an empty Gooch crucible and rapidly washed successively with water, dilute hydrochloric acid, water, alcohol, and ether. Any adherent wash was driven off by heating for a short time in an oven at 110° . The crystals were then sealed in glass tubes to protect them from atmospheric carbon dioxide, by which they are readily attacked unless kept dry.

Representative samples of these crystals were analyzed by converting

² Johnston, *This Journal*, 36, 16 (1914).

to calcium oxide by heating them in a platinum crucible at the full heat of the blast lamp, and also by precipitation as calcium oxalate and weighing as the carbonate as recommended by Foote and Bradley.³ Concordant results by these two methods indicated that the samples contained 99.92% calcium hydroxide. A qualitative test showed the presence of chloride and a quantitative determination as silver chloride showed 0.075% chloride reckoned as sodium chloride or 0.071% as calcium chloride. These hexagonal crystals of calcium hydroxide have been studied crystallographically by Ashton and Wilson,⁴ who used the same method of preparation.

During the initial stage of the preparation as above described, a mass of long acicular crystals was formed in the beaker which originally contained the calcium chloride solution, but as more hydroxide diffused in, these crystals were gradually changed to the hydroxide. A sample of these crystals was removed from the beaker, centrifuged, and analyzed for chlorine, alkalinity, and water of crystallization. Although the tendency of these crystals to decompose rapidly in the presence of anything other than the solution with which they were in equilibrium precluded any very exact analysis, the best analyses we could make showed the compound to be identical with that reported by Milikan⁵ as $\text{CaCl}_2 \cdot 3\text{CaO} \cdot 16\text{H}_2\text{O}$. Since, however, the water lost on drying to constant weight at 110° corresponds in the formula to $13\text{H}_2\text{O}$ rather than to $16\text{H}_2\text{O}$, it would appear preferable to write the formula as $\text{CaCl}_2 \cdot 3\text{Ca}(\text{OH})_2 \cdot 13\text{H}_2\text{O}$.

In the selection of salts for these measurements, it was obviously necessary to use only such that the solubility product of the hydroxide of its cation, or of the calcium salt of its anion, would bear such a relation to the solubility product of calcium hydroxide that, at the concentration used, there would be no alteration of the solid phase and change of the solubility equilibrium, as would, for instance, happen in the presence of sulfate, even at comparatively low concentration. The salts used were standard c. p. preparations recrystallized three or four times from distilled water. The sodium iodide was recrystallized only once and then in an atmosphere of carbon dioxide to prevent oxidation. The cesium chloride was a preparation of special purity obtained through the generous coöperation of Professor H. W. Foote.

Apparatus and Method of Experiment

In the design of the apparatus in which to saturate the solution with calcium hydroxide, it was necessary to meet certain special requirements, in particular, rigidly to exclude carbon dioxide. Although the presence of calcium carbonate is not necessarily harmful, owing to its extremely low

³ Foote and Bradley, *THIS JOURNAL*, **48**, 676 (1926).

⁴ Ashton and Wilson, *Am. J. Sci.*, [5] **13**, 209 (1927).

⁵ Milikan, *Z. physik. Chem.*, **92**, 59 (1918).

solubility, especially in the presence of a large excess of the hydroxide, its formation at the expense of the hydroxide in solution and the consequent disturbance of the equilibrium would vitiate the results of the measurements made. Johnston and Williamson⁶ have shown that, in order to maintain the hydroxide as the *stable* phase, it is necessary to have a partial pressure of carbon dioxide less than about 10^{-13} atmospheres. To achieve this, it was necessary to eliminate cork and rubber stoppers and rubber tubing since these are permeable to carbon dioxide.

Since, in this investigation, we have used quite large, well-defined crystals of the hydroxide which are attacked and dissolved much more slowly than smaller, less well-defined crystals, it was necessary to have the crystals in contact with the solution for a considerable length of time instead of passing the solution only once through a column packed with the crystals, as has been done by Brönsted in his work on the activity of electrolytes in solutions of other electrolytes. To this end, an apparatus was devised in which the liquid flows back and forth through a column of the crystals held rigidly in place. In the course of this work it has been observed that calcium hydroxide, like calcium sulfate, has little tendency to crystallize except from greatly supersaturated solutions, so that there is danger that, if the crystals were allowed to disintegrate by abrasion, the small particles formed would cause supersaturation which the presence of the large crystals might not readily remove. It was for this reason that special care was taken to keep the crystals fixed rigidly in place while the solution flowed over them. In addition to these requirements, it was thought desirable to have some arrangement whereby the liquid would not be in contact with the solid phase when the apparatus was removed from the thermostat for sampling and subjected to temperature changes. Since the solubility of calcium hydroxide increases with decreasing temperature, there is no danger of precipitation on removal from the thermostat at 25°. Consequently we could with safety remove the apparatus and take samples simply by drawing off the solution through a stopcock into weighed flasks, avoiding use of a pipet.

The apparatus as finally used was similar to that used for the determination of the solubility of calcium carbonate by Frear and Johnston.⁷ It resembles an hour-glass both in shape and mode of operation. As shown in Fig. 1, it consists of two bulbs separated by a middle compartment H, the constriction of the hour-glass, in which the crystals of the hydroxide are packed; this compartment is closed by the ground-glass stopper V to which a touch of vaseline has previously been applied to prevent the sticking often caused by alkaline solutions. The ends of the compartment H are the closely fitting porcelain filter plates F, held in place by indentations on the glass around the edges of the plate; the perforations of the porcelain plates are large enough to permit the ready flow of the solution but do not permit the passage of the crystals into either bulb. The

⁶ Johnston and Williamson, *THIS JOURNAL*, **38**, 975 (1916).

⁷ Frear and Johnston, *ibid.*, **51**, 2082 (1929).

bulbs are also connected through a circuit of tubing as shown; its purpose is to permit the air to flow from the lower into the upper bulb as the solution flows from the upper through the column of crystals into the lower bulb. In order to prevent the liquid from entering this circuit of tubing, the tube ends in two tips curved backward as shown at A. The amount of the solution, drawn in through X by suction applied at Z, was such that when it was all in the lower bulb, the ends of the tips were not covered. Z is a three-way stopcock, allowing maintenance of the circuit while closing the system to the outside; samples were taken by opening this stopcock to admit air to the apparatus and drawing off the solution through X.

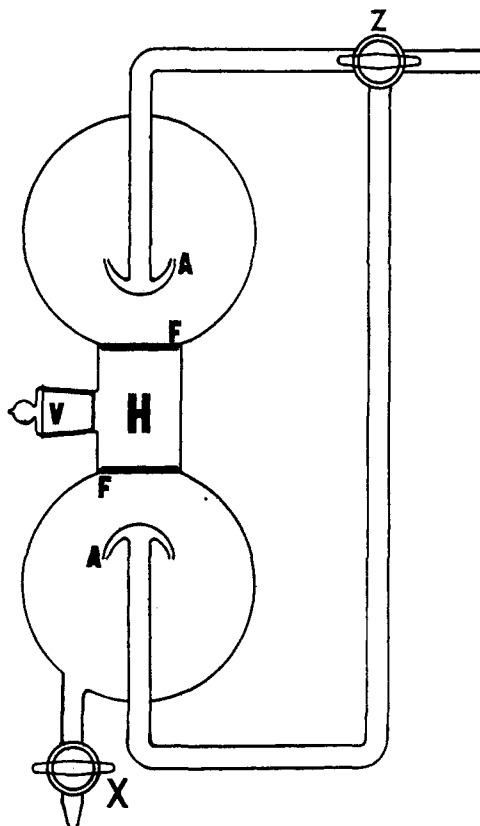


Fig. 1.

The two halves of the groove are, as shown, semicircular and concentric but of different radius. They are connected on opposite sides so that a roller D operating in this groove passes from one semicircle to the other as the cam slowly rotates. The brass strip B, which can move only vertically on the extension of the shaft on which the cam rotates, being held by a brass collar, carries the rigidly held roller D, which fits into the groove G and, as the cam rotates, causes the strip to move alternately up and down as the roller is lifted to the inner semicircle or is lowered to the outer one. The reciprocating motion of B is transmitted by a slotted bar to the 20-cm. cog wheel O and causes it to turn through a small arc; this, in turn, causes the small cog wheel O₁ and the holder to which it is attached to turn through 180° and back again as the strip is alternately raised and lowered by the rotation of the cam. The whole mechanism here described

to the outside; samples were taken by opening this stopcock to admit air to the apparatus and drawing off the solution through X.

The solution was made to flow back and forth through the column of crystals by alternate oscillation through 180° of the apparatus about H as a center; that is, the apparatus was turned counter-clockwise through 180° from the position shown in the figure, allowed to remain in this position until all the solution had passed through H and was then returned clockwise to the original position. The speed was adjusted so that the half-revolution in each direction required about five seconds and the apparatus remained in each upright position for about forty seconds. This alternating motion is effected by clamping the apparatus into a holder which is alternately turned, as above described, by a motor operating through the cam and gears shown in Fig. 2. The cam Y was driven by a half-horsepower motor running at 1750 r. p. m., connection to the cam being through two 48 to 1 speed reducers; this cam is a circular plate of steel, 19 mm. thick and 20 cm. in diameter, in which a groove G 12.5 mm. deep has been very carefully cut.

was held in a rigid frame attached to the sides of the thermostat. The lower part of the mechanism and the holder for the apparatus was immersed in the water of the thermostat; the water was kept at $25 \pm 0.02^\circ$. This complete set-up was used for a period of six months with practically no trouble after the initial adjustments and with no attention except oiling of the bearings of the moving parts at frequent intervals.

In carrying out the measurements, the crystals of the hydroxide were placed in the middle compartment, the solvent was drawn into the lower bulb, and, after closing the stopcocks, the apparatus was clamped into the holder and allowed to rotate for twenty-four hours, which period preliminary experiments had shown was sufficient for saturation. The usual procedure was to start with a concentrated salt solution, and, after withdrawing the samples for analysis, draw in an equal amount of water, thereby securing a lower salt concentration for the solubility determination following; repetition of this procedure obviated the necessity of replacing the entire solution after each sampling.

Analytical Methods.—All analyses were made on a weight basis; the samples were weighed to 0.1 milligram and the solutions used for the titrations were weighed to the nearest centigram.

The calcium hydroxide was determined by a simple titration with 0.05 *N* hydrochloric acid. At first, attempts were made to use phenolphthalein as indicator but this yielded results which were low when compared with a gravimetric determination of the calcium present; this led to the substitution of methyl red, which gave results checking the gravimetric determination. It was found that overtitration could easily be avoided by adding a few drops of phenolphthalein, titrating to its end-point and then, after the addition of two drops of methyl red, proceeding cautiously to the development of a faint pink color. The difference in the amount of acid used, of the order of a few tenths of a cc., with the two indicators must be due

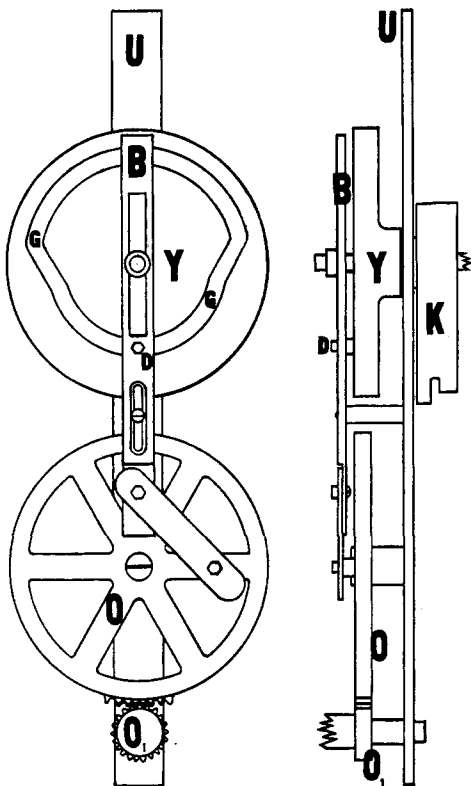


Fig. 2.

to the carbon dioxide contained in the sampling flask and that absorbed from the air during the titration for, with the same procedure, this difference was practically constant. With salts such as sodium nitrite and sodium acetate, the use of methyl red was not possible; in these cases, phenolphthalein only was used, but to the amount of acid required at its end-point was added the average difference between the methyl red and phenolphthalein end-points. The constancy of the correction in the case of the salts of the strong acids and strict adherence to a standard procedure made this correction quite valid, as was proved by gravimetric determination of the calcium in solution.

Chloride and bromide were determined by Mohr's method, titration with tenth normal silver nitrate using potassium chromate as indicator in neutral solution; iodide was determined by the well-known Volhard method. The other salts were determined by evaporating a weighed portion of the solution with sulfuric acid, driving off the excess acid by heating the dish containing the salts in a current of air which had been passed through a wash-bottle containing ammonium hydroxide and weighing the resulting mixed sulfates; from the total weight of salt was subtracted the amount of calcium sulfate equivalent to the calcium hydroxide as determined by titration and the remainder was calculated to the salt used.

Previous Investigations

The literature reveals no attempt to measure the solubility of calcium hydroxide in the form of well-defined crystals large enough to eliminate surface effects, either in water or in salt solutions. In fact, of the measurements previously made, the only ones which seem to be highly accurate have been made using pure water as the solvent, with the exception of a series of measurements in ammonium chloride solutions made by Noyes and Chapin.⁸ These measurements are, however, not comparable with ours since in this case there is formed by metathesis a slightly ionized, volatile base which sets up a number of secondary equilibria involving both the liquid and the gaseous phases, the latter of which they did not investigate.

In many of the measurements in presence of a salt the salt was a compound such as calcium chloride or calcium nitrate which causes alteration of the solid phase and consequently shows abnormal results when viewed from the standpoint of the theory of solutions. The solubility of calcium hydroxide in solutions of sodium hydroxide has been measured by d'Anselme⁹ but the accuracy of these measurements is rather doubtful. Cabot¹⁰ published graphs which indicate that the solubility in solutions of sodium

⁸ Noyes and Chapin, *Z. physik. Chem.*, **28**, 518 (1899).

⁹ d'Anselme, *Bull. soc. chim.*, [3] **29**, 938 (1903).

¹⁰ Cabot, *J. Soc. Chem. Ind.*, **16**, 417 (1897).

and potassium chlorides goes through a maximum when the salt concentration is about molal. Cameron and Bell¹¹ measured the solubility of calcium hydroxide and of calcium sulfate in the presence of each other, necessarily over a very limited range.

Of the values given for the solubility in pure water at 25°, the following seem the most reliable, all data having been calculated to millimoles per 1000 g. of water.

20.89	Cameron and Bell, <i>J. Phys. Chem.</i> , 15 , 67 (1911)
20.85	Cameron and Bell, <i>THIS JOURNAL</i> , 28 , 1220 (1906)
20.55	Moody and Leyson, <i>J. Chem. Soc.</i> , 93 , 1767 (1908)
20.53	Bassett and Taylor, <i>ibid.</i> , 105 , 1926 (1914)
20.29	Noyes and Chapin, <i>Z. physik. Chem.</i> , 28 , 518 (1899)

The difference between these figures and our value of 19.76 millimoles of calcium hydroxide per kilo of water is undoubtedly due to the difference in nature of the saturating phases in the different measurements. With calcium hydroxide in the form of large well-defined crystals, the solubility in water should be less than for materials of indefinite particle size and crystalline form.

Experimental Results

In Table I are given the observations on the solubility of calcium hydroxide in solutions of various salts. Each datum is the mean of duplicate analyses made after the apparatus containing the saturating hydroxide and the solvent solution had been allowed to rotate at 25° for at least twenty-four hours, a period which preliminary experiments had shown to be sufficient for the attainment of equilibrium.

In these tables the concentration of the salt, M , is given in the first column as moles per 1000 g. of water; that of calcium hydroxide, S , in the second column as millimoles per 1000 g. of water. For each determination there is also given, in column 3, the corresponding ionic strength; and of the fourth and fifth columns, respectively, the ratio of the solubility and in the activity coefficient of calcium hydroxide in the given solution to that in the solution when no salt is present. The last mentioned were calculated by means of the following equations, where a is the activity of any ion, m its concentration, γ its activity coefficient, and the subscript 0 refers to the solution containing no added salt.

$$a_{\text{Ca}^{2+}} a_{\text{OH}^{-}}^2 = K = a_{\text{Ca}^{2+}} a_{\text{OH}^{-}}^2$$

$$\gamma_{\text{Ca}^{2+}} m_{\text{Ca}^{2+}} \gamma_{\text{OH}^{-}}^2 m_{\text{OH}^{-}}^2 = \gamma_{\text{Ca}^{2+}} m_{\text{Ca}^{2+}} \gamma_{\text{OH}^{-}}^2 m_{\text{OH}^{-}}^2$$

$$\frac{\gamma_{\pm}(\text{Ca}(\text{OH})_2)_1}{\gamma_{\pm}(\text{Ca}(\text{OH})_2)_0} = \left(\frac{\gamma_{\text{Ca}^{2+}} \gamma_{\text{OH}^{-}}^2}{\gamma_{\text{Ca}^{2+}} \gamma_{\text{OH}^{-}}^2} \right)^{1/3} = \left(\frac{m_{\text{Ca}^{2+}} m_{\text{OH}^{-}}^2}{m_{\text{Ca}^{2+}} m_{\text{OH}^{-}}^2} \right)^{1/3}$$

¹¹ Cameron and Bell, *THIS JOURNAL*, **28**, 1220 (1906).

TABLE I
THE SOLUBILITY OF CALCIUM HYDROXIDE IN SALT SOLUTIONS AT 25°

Salt	M moles/kg. H ₂ O	S millimoles/kg. H ₂ O	μ	S/S_0	$100\gamma_{\pm}/\gamma_0^{\pm}$
None	0.000	19.76	0.059	1.000	100.0
NaCl	0.012	20.65	0.074	1.045	95.7
	.064	22.68	.132	1.148	87.1
	.121	24.02	.193	1.216	82.3
	.366	27.18	.448	1.376	72.7
	.763	29.11	.850	1.473	67.9
	1.21	29.66	1.30	1.501	66.6
	1.75	29.33	1.84	1.489	67.4
	2.15	28.57	2.24	1.446	69.2
	2.24	28.33	2.33	1.434	69.7
	2.81	26.69	2.89	1.351	74.0
	3.76	24.10	3.83	1.220	82.0
	KCl	0.038	21.57	0.103	1.092
.076		22.73	.145	1.150	86.9
.264		25.50	.341	1.290	77.5
.527		27.08	.608	1.370	73.0
.989		27.66	1.07	1.400	71.4
1.08		27.68	1.16	1.401	71.4
1.28		27.44	1.36	1.389	72.0
1.62		26.96	1.70	1.364	73.3
1.96		26.10	2.04	1.321	75.7
2.87		23.51	2.94	1.190	84.0
CsCl		0.073	22.36	0.140	1.132
	.199	24.51	.273	1.240	80.6
	.537	26.84	.617	1.358	73.6
	.862	27.24	.944	1.379	72.5
	1.25	27.03	1.33	1.368	73.1
	1.56	26.47	1.64	1.340	74.7
	3.55	20.56	3.62	1.040	96.1
LiCl	0.054	22.66	0.122	1.147	87.2
	.115	24.73	.189	1.257	79.9
	.249	27.99	.333	1.417	70.6
	.465	31.72	.560	1.605	62.3
	.830	35.73	.937	1.808	55.3
	1.37	39.90	1.49	2.019	49.5
	1.85	42.39	1.98	2.145	46.6
	2.25	44.05	2.38	2.229	44.8
	3.03	46.43	3.16	2.350	42.6
	3.81	47.62	3.96	2.410	41.5
	5.36	48.45	5.51	2.452	40.7
10.37	44.72	10.51	2.263	44.2	
BaCl ₂	0.019	22.83	0.125	1.155	86.6
	.037	24.70	.185	1.250	80.0
	.066	26.83	.278	1.358	73.5
	.111	29.45	.422	1.490	67.1
	.159	31.57	.570	1.598	62.6

TABLE I (Continued)

Salt	M moles/kg. H ₂ O	S millimoles/kg. H ₂ O	μ	S/S_0	$100\gamma_{\pm}/\gamma_0^*$
	0.287	35.78	0.969	1.811	55.2
	.425	39.10	1.39	1.979	50.5
	.624	42.46	2.00	2.149	64.5
	1.29	49.16	4.03	2.488	40.2
	1.44	49.91	4.48	2.526	39.6
	1.59	50.22	4.93	2.541	39.4
SrCl ₂	0.053	26.24	0.237	1.328	75.3
	.120	30.43	.451	1.540	64.9
	.283	37.02	.961	1.873	53.4
	.445	41.35	1.46	2.093	47.8
	.823	48.19	2.61	2.439	41.0
	1.33	53.36	4.17	2.700	37.0
	2.19	56.22	6.75	2.845	35.2
	2.23	56.23	6.85	2.846	35.2
	3.18	55.37	9.72	2.802	35.7
NaClO ₃	0.189	24.66	0.263	1.248	80.1
	.386	26.43	.465	1.338	74.8
	.716	27.55	.798	1.394	72.1
	.814	27.65	.897	1.399	71.5
	1.14	27.76	1.22	1.405	71.2
	1.59	27.31	1.67	1.382	72.4
	1.97	26.18	2.04	1.325	75.5
	2.96	23.52	3.03	1.190	84.0
	4.56	18.99	4.62	0.961	104.1
NaClO ₄	0.118	23.25	0.188	1.177	85.0
	.399	25.38	.475	1.284	77.9
	.476	25.62	.553	1.297	77.1
	.776	25.66	.853	1.299	77.0
	1.16	24.79	1.24	1.255	79.7
	1.58	23.53	1.65	1.191	84.0
	2.40	20.46	2.46	1.035	96.6
	3.57	16.24	3.62	0.822	121.7
NaBr	0.189	24.85	0.264	1.258	79.5
	.348	26.41	.428	1.337	74.8
	.721	28.05	.805	1.420	70.4
	.979	28.47	1.06	1.441	69.4
	1.30	28.41	1.39	1.438	69.6
	1.77	27.80	1.90	1.407	71.1
	2.90	24.78	2.98	1.254	79.7
KBr	0.162	24.04	0.234	1.217	82.2
	.270	25.09	.345	1.270	78.8
	.453	26.08	.531	1.320	75.8
	.759	26.69	.840	1.351	74.0
	.930	26.70	1.01	1.351	74.0
	1.27	26.36	1.35	1.334	75.0
	1.55	25.96	1.63	1.314	76.1
	2.09	24.41	2.16	1.235	81.0
	3.24	20.58	3.30	1.042	96.0

TABLE I (Concluded)

Salt	M moles/kg. H ₂ O	S millimoles/kg. H ₂ O	μ	S/S_0	$100\gamma_{\pm}/\gamma_0^{\pm}$
NaNO ₃	0.176	25.38	0.252	1.284	77.9
	.217	25.92	.295	1.312	76.2
	.351	27.67	.434	1.400	71.4
	.510	29.15	.598	1.475	67.8
	.838	30.98	.931	1.568	63.8
	1.35	32.30	1.45	1.635	61.2
	1.76	32.75	1.86	1.657	60.4
	2.27	32.74	2.37	1.657	60.4
	2.81	32.31	2.91	1.638	61.2
	3.78	30.79	3.87	1.558	64.2
	4.72	29.31	4.81	1.483	67.4
	NaNO ₂	0.252	26.65	0.332	1.349
.455		28.94	.542	1.465	68.3
.854		31.27	.948	1.582	63.2
1.30		32.55	1.40	1.647	60.7
2.03		33.21	2.13	1.681	59.5
2.90		33.22	3.00	1.681	59.5
4.12		32.04	4.21	1.621	61.7
5.82		29.64	5.91	1.500	66.7
NaI	0.085	22.61	0.153	1.144	87.4
	.159	24.10	.231	1.220	82.0
	.356	25.90	.434	1.311	76.3
	.605	26.78	.685	1.355	73.8
	.904	27.02	.985	1.367	73.2
	1.33	26.62	1.41	1.367	73.2
	1.60	26.05	1.68	1.318	75.9
	1.83	25.41	1.91	1.286	77.8
	2.11	24.66	2.18	1.248	80.1
	2.86	22.28	2.93	1.128	88.7
	4.21	18.71	4.77	0.947	105.6
NaC ₂ H ₃ O ₂	0.188	26.33	0.267	1.332	75.0
	.588	32.43	.685	1.641	60.9
	.692	32.95	.791	1.668	60.0
	.972	33.83	1.07	1.712	58.4
	1.01	34.92	1.12	1.766	56.6
	1.67	36.48	1.78	1.846	54.2
	3.26	37.18	3.37	1.862	53.7
	3.64	36.79	3.75	1.862	53.7
	4.88	34.97	4.99	1.770	56.5

Discussion

It was observed by Harned and James¹² that, in contrast to the behavior of hydrochloric acid in salt solutions, potassium hydroxide exhibits a higher activity coefficient in solutions of those salts which in the pure solvent have the lower activity coefficient. Their measurements of the activity

¹² Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).

coefficients of potassium hydroxide in solutions of potassium iodide, potassium bromide, and potassium chloride showed that

$$\gamma_{\text{KOH}(\text{KCl})} > \gamma_{\text{KOH}(\text{KBr})} > \gamma_{\text{KOH}(\text{KI})}$$

while

$$\gamma_{\text{KI}} > \gamma_{\text{KBr}} > \gamma_{\text{KCl}}$$

A survey of the influence of the alkali metal chlorides on the activity coefficients of the corresponding hydroxides shows the following values for 0.1 molal hydroxide in 0.2 molal salt solution.

Metal	$\gamma_{0.1 M \text{ MeOH}}$	$\gamma_{0.1 M \text{ MeOH}(0.2 M \text{ MeX})}$	Lowering	% Lowering
Li	0.744 ^a	0.662 ^a	0.082	11.0
Na	.775 ^b	.700 ^c	.075	10.7
K	.789 ^d	.706 ^e	.083	10.7
K	.772 ^f	.706 ^e	.066	8.5

^a Harned and Swindells, *THIS JOURNAL*, 48, 126 (1926). ^b Harned, *ibid.*, 47, 676 (1925). ^c Harned, *ibid.*, 47, 684 (1925). ^d Knobel, *ibid.*, 45, 70 (1923). ^e Harned, *ibid.*, 47, 689 (1925). ^f Scatchard, *ibid.*, 47, 648 (1925); a recalculation of Knobel's data.

On the basis of Scatchard's recalculation of Knobel's results, the effect of the halide in depressing the activity of the hydroxide is greater, the higher the activity coefficient of the salt in aqueous solution, just as is the case with variable anion and identical cation. For a similar salt series in which the anion of the several salts remains the same, the behavior of calcium hydroxide is the same, for it, too, shows the higher activity coefficient in a solution of the salt of lower activity coefficient. On the other hand, in a series of salts with a common cation, as the sodium halides, we find that calcium hydroxide has the higher activity coefficient in a solution of the salt having a higher activity coefficient, just the reverse of the results of Harned and James on the activity coefficient of potassium hydroxide in solutions of the potassium halides.

Harned¹³ suggests that the decrease in activity coefficient of hydroxides in the presence of salts of high activity coefficient is due to the further deformation, in these solutions, of the already highly unsymmetrical hydroxyl ion. Not only does our work support this view but it indicates that Brönsted's theory of specific interaction is applicable, to some extent at least, in concentrated solutions. Brönsted has shown that bivalent ions are affected to a much greater extent than univalent ions by the presence of the same concentration of an electrolyte. If we assume that the activity of an ion is influenced mainly by the presence of ions of opposite charge, as does Brönsted, the rise in activity coefficient of the hydroxide with lower activity coefficient of the salt as the cation only is varied, may be accounted for by the influence of the cation on the hydroxyl ion as in the case of the uni-univalent hydroxides. When the anion, however, is varied, no such

¹³ Harned, *Trans. Faraday Soc.*, 23, 462 (1927).

rise in activity coefficient of the calcium hydroxide is observed, since there is present here a bivalent cation from the hydroxide whose activity coefficient is affected sufficiently in the opposite direction by change of anion to reverse the sequence of the series.

Bozorth,¹⁴ measuring the solubility of potassium perchlorate in aqueous salt solutions, demonstrated that the effects of the ions of the solvent salts are specific and additive. That this is corroborated by our results may be seen by inspection of Table II, in which interpolated values, at even values of the ionic strength, of the solubility of calcium hydroxide in solutions of potassium chloride have been subtracted from the corresponding values in solutions of sodium chloride, and similarly for the pair potassium bromide and sodium bromide. Comparison of these two series of values reveals that substitution of one cation for the other, the anion remaining the same, gives rise to the same differences in solubility of calcium hydroxide regardless of the halogen ion present. If a similar comparison is made by subtracting the corresponding values for sodium bromide from sodium chloride and for potassium bromide from potassium chloride, the difference in solubility of calcium hydroxide occasioned by the difference in the anion is likewise constant regardless of the cation with which it is combined. In so far as can be determined, then, the effects of the ions are specific and additive to the extent that the differences for a pair of univalent ions of like sign are the same regardless of the univalent ion of opposite sign with which they are associated.

TABLE II
INTERPOLATED VALUES

Ionic strength	Difference in solubility of calcium hydroxide in			
	NaCl-KCl	NaBr-KBr	NaCl-NaBr	KCl-KBr
0.2	0.25	0.22	0.50	0.47
.4	.56	.52	.78	.74
.6	.80	.74	1.06	1.10
.8	.92	.84	1.47	1.39
1.0	1.00	.94	1.73	1.67
1.2	1.07	1.02	1.95	1.90
1.5	1.26	1.12	2.32	2.18
1.8	1.48	1.25	2.69	2.46
2.0	1.52	1.62	2.81	2.74
2.5	1.65	1.66	2.87	2.88
3.0	1.66	1.69	3.00	3.03

In considering the experimental data in the light of the more recent theories of solutions, we may remark that the solutions cannot be said to fall within the range postulated as dilute by these theories. Indeed, a saturated solution of calcium hydroxide in water at 25° itself can hardly be considered a dilute solution. For this reason, it is to be expected that the

¹⁴ Bozorth, THIS JOURNAL, 45, 2653 (1923).

experimental results would approach those required by the original theory of Debye and Hückel¹⁵ only in the most dilute of the salt solutions; and this proves to be the case.

In his well-known extension of the original interionic attraction theory of solutions to the more concentrated range, Hückel¹⁶ proposed an equation for change of activity coefficient with ionic strength of the form

$$-\log \gamma = \frac{0.708 \sqrt{\mu}}{1 + A \sqrt{\mu}} + B\mu$$

where γ is the activity coefficient, μ is the ionic strength, A is a constant dependent on the ionic diameter and B is an empirical constant. It has been pointed out by Brönsted,¹⁷ however, that this equation, as originally proposed, cannot adequately describe the behavior of such solutions owing to its failure to take into account the great complexity of the system involved, while Harned¹⁸ states that, although an equation of the form given will describe the behavior of concentrated solutions, the constants used cannot, in general, be calculated by Hückel's method, particularly in the case of hydroxides, but must be varied arbitrarily to fit the data at hand. Since the present work includes no direct measurements of activity coefficients and since the concentrations used are too high to permit of safe extrapolation of the solubility of calcium hydroxide to zero ionic strength in order to evaluate the activity coefficients as suggested by Lewis and Randall,¹⁹ it became necessary to express the activity coefficients at the various ionic strengths in terms of the unknown activity coefficient of calcium hydroxide in pure water and then, for one salt series, to solve for A , B , and γ_0 , the activity coefficient of calcium hydroxide in pure water, by simultaneous solution of three equations involving the above constants. The values so derived for these three constants, for the solutions of each of the salts studied, are brought together in Table III. As might be expected from an equation whose theoretical basis is none too firm, the value of γ_0 varies somewhat.

The equation, with the constants given in Table III expresses with considerable accuracy the change of activity coefficient with ionic strength for some of the salts, though for others the agreement is not so good. It can be used, within these limits of accuracy, for the calculation at any ionic strength of the activity coefficient ratio and its reciprocal the solubility ratio.

In Table IV a comparison is made for strontium chloride and for sodium nitrite of the values of the activity coefficient as calculated by use of the

¹⁵ Debye and Hückel, *Physik. Z.*, 21, 185 (1923).

¹⁶ Hückel, *ibid.*, 26, 93 (1926).

¹⁷ Brönsted, *Trans. Faraday Soc.*, 23, 416 (1927).

¹⁸ Harned, *ibid.*, 23, 462 (1927).

¹⁹ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances." McGraw-Hill Book Co., Inc., 1923, p. 369.

TABLE III

VALUES OF THE CONSTANTS AS EVALUATED BY SOLUTION OF SIMULTANEOUS EQUATIONS

Salt	γ_0	A	B
NaCl	0.722	0.70	0.098
KCl	.728	.83	.100
CsCl	.731	.90	.095
LiCl	.709	.54	.031
BaCl ₂	.710	.58	.030
SrCl ₂	.708	.58	.020
NaClO ₃	.730	.85	.096
NaClO ₄	.735	.94	.122
NaBr	.725	.75	.105
KBr	.730	.90	.100
NaNO ₃	.720	.75	.060
NaNO ₂	.722	.78	.054
NaI	.732	.90	.100
NaOOCCH ₃	.711	.54	.070

constants given in Table III with "observed" values arrived at by multiplying the calculated value at zero salt concentration by the activity coefficient ratios as obtained by direct measurement. In the case of strontium chloride it will be noted that the agreement between the two sets of values is good over the entire range while the two sets of values for sodium nitrite diverge at higher ionic strengths.

TABLE IV

A COMPARISON OF CALCULATED AND "OBSERVED" VALUES OF THE ACTIVITY COEFFICIENTS FOR STRONTIUM CHLORIDE AND FOR SODIUM NITRITE

Ionic strength	Strontium chloride		Ionic strength	Sodium nitrite	
	Activity coefficient Calcd.	Obs.		Activity coefficient Calcd.	Obs.
0.059	0.708	0.708	0.059	0.720	0.720
.237	.544	.534	.332	.545	.534
.451	.464	.460	.542	.498	.492
.961	.378	.378	.948	.456	.455
1.46	.337	.338	1.40	.437	.437
2.61	.290	.290	2.13	.428	.429
4.17	.264	.262	3.00	.437	.429
6.75	.252	.250	4.21	.466	.444
6.85	.252	.250	5.91	.530	.480
9.72	.256	.252			

In general the values of the activity coefficient of calcium hydroxide, calculated by the use of an equation of the Hückel type for solutions of salts of low activity coefficient, agree with the observed values rather better than for solutions of salts of higher activity coefficient. This implies that, in the cases of the salts with high activity coefficient, we are dealing with systems in which the factors neglected by Hückel in the formulation of his equation have assumed a relatively greater importance than in solutions of salts which exhibit better conformity with his equation.

Summary

1. Calcium hydroxide of a high degree of purity in the form of well-defined crystals has been prepared by a diffusion method. The solubility of this calcium hydroxide was measured at 25° in pure water and in solutions of various strengths of sodium chloride, potassium chloride, lithium chloride, cesium chloride, strontium chloride, barium chloride, sodium bromide, potassium bromide, sodium iodide, sodium nitrate, sodium nitrite, sodium chlorate, sodium perchlorate, and sodium acetate.

2. A new type of solubility apparatus in which the solid is held rigidly in place and the solution to be saturated flows over it has been developed and used in this work.

3. The solubility of crystalline calcium hydroxide in pure water at 25° has been found to be 19.76 millimoles per 1000 g. of solvent.

4. The solubility of calcium hydroxide in solutions of neutral salts goes through a maximum unless limited by the solubility of the salt and then decreases to a point which may be less than that of the compound in pure water.

5. The change in the solubility and in the activity coefficient of the hydroxide with change in the ionic strength follows, to a greater or less extent, values calculated by the use of equations of the type suggested by Hückel but employing empirical constants. Agreement of calculated and observed values is usually better in solutions of salts with low activity coefficients than in solutions of those with high coefficients. The constants for each salt which when introduced into the Hückel equation describe the change of the activity coefficient of calcium hydroxide with change of the ionic strength are given.

6. In a series of salts with a common anion, the activity coefficient of the calcium hydroxide is higher in the salt of lower activity coefficient, while in a series of salts with a common cation, the activity coefficient of the calcium hydroxide is higher in the salt with higher activity coefficient. Uni-univalent hydroxides have the higher activity coefficient in solutions of salts with lower activity coefficients in all cases. This unusual behavior is presumably due to the greater specific sensitivity of the bivalent calcium ion to changes in anion.

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