ing for suggesting the study of ammonium paramolybdate.

Summary

The lattice constants, space groups and density of crystalline ammonium paramolybdate were determined. From the weight of the unit of structure it is concluded that the compound is a heptamolybdate, with the formula $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

The Solubilities of Barium and Strontium Carbonates in Aqueous Solutions of Some Alkali Chlorides

BY R. W. TOWNLEY AND W. B. WHITNEY WITH W. A. FELSING

Object of the Investigation

A number of investigations dealing with the change in solubilities of the alkaline earth carbonates in aqueous salt solutions have been recorded. In each case an increase in solubility was noted. Muir[1] studied the solubility of calcium carbonate in sodium chloride solutions. Cameron and Robinson,[2] Cantoni and Goguelia,[3] and Dubrisay and François[4] studied the influence of potassium chloride upon the solubility of calcium carbonate and the last-named investigators also studied the influence of potassium chloride upon the barium carbonate solubility. De Coninck and Arzalier[5] briefly mention their study of the solubility of strontium carbonate in the presence of potassium chloride. In no case, however, was the study made with the view of determining the activity of these alkaline earth carbonates by the method outlined by Lewis and Randall.[6]

The purpose of this investigation, hence, was the determination of the influence of increasing concentrations of lithium, sodium, and potassium chlorides upon the solubilities of the normal carbonates of barium and strontium. It was hoped that the data obtained would yield information of value regarding the activities of these carbonates.

Previous Investigations

The solubility of barium carbonate in pure water has been reported[7] at various temperatures; McCoy and Smith's value at 25°, as calculated from their solubility product, is 0.90×10^{-4} g. moles/1000 g. of water. The solubility of strontium carbonate is also recorded by several investigators.[8] McCoy and Smith's value at 25° is 0.396×10^{-4} g.-moles/1000 g. water.

Experimental Methods

The method of this investigation consisted of saturating solutions of lithium, sodium, and potassium chlorides at different concentrations (approx. 0.02, 0.06, 0.10, 0.2, 0.3, 0.5, 1.0, and 3.0 *M*) with the solid barium and strontium carbonates at both 25 and 40°. The finely divided solids, in large excess, were agitated with the various solutions in a shaking device immersed in a thermostat maintained at 25 ± 0.02° and at 40 ± 0.04°. After an interval of twenty-four to forty-eight hours of agitation (some samples were shaken for much longer periods without yielding different results, however), the flasks were allowed to stand for several hours in the thermostat; filtered samples were withdrawn at the thermostat temperature and were immediately titrated against hydrochloric acid, using phenolphthalein as indicator; each sample was heated to the boiling point as the end-point was approached. Weight burets were used throughout. Duplicate equilibrium determinations were made for each concentration and each determination was made in duplicate.

Water.—The best grade of conductivity water was used throughout, the final distillation being made from and into quartz. All water and solutions were protected against carbon dioxide.

The Carbonates.—(a) The barium carbonate was prepared from Merck C. P. precipitated barium carbonate. The carbonate was converted into the bicarbonate to form a very dilute solution; it was then re-precipitated by boiling, collected on a filter, washed with conductivity water, and dried for twelve hours at 250°. (b) The strontium carbonate was prepared from C. P. strontium chloride by the addition, in hot dilute solution, of the required amount of ammonium carbonate of reagent grade. The carbonate was repeatedly washed, filtered and dried for twelve hours at 250°.

The Chlorides.—(a) The lithium chloride was obtained by recrystallizing E. & A. "Pure" lithium chloride. The

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(1) Muir, *J. Chem. Soc.*, **37**, 60 (1880).

(2) Cameron and Robinson, *J. Phys. Chem.*, **11**, 577 (1907).

(3) Cantoni and Goguelia, *Bull. soc. chim.*, [3] **33**, 13 (1905).

(4) Dubrisay and François, *Compt. rend.*, **192**, 741 (1931).

(5) De Coninck and Arzalier, *Bull. acad. roy. Belg.*, 577 (1908).

(6) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, Chapter XXVIII.

(7) (a) Kohlrausch and Rose, *Z. physik. Chem.*, **12**, 241 (1893); (b) McCoy and Smith, THIS JOURNAL, **33**, 468 (1911); (c) Seidell, "Solubilities," D. Van Nostrand Co., New York, 1919, p. 107.

(8) (a) Holleman, *Z. physik. Chem.*, **12**, 135 (1893); (b) Kohlrausch and Rose, *ibid.*, **12**, 241 (1893); (c) ref. 7b, p. 473.

solution was concentrated by slow evaporation in a vacuum desiccator containing concd. sulfuric acid. The filtered crystals were dried for ten hours at 250°. (b) The sodium chloride was prepared from Baker reagent grade by precipitation from solution by means of hydrogen chloride; the product was dried and then heated to the "crackling" point in a platinum dish. (c) The potassium chloride was recrystallized twice from conductivity water, washed, and dried for ten hours at 250°.

Hydrochloric Acid.—Constant boiling acid was used in preparing the 0.01 *M* acid for the titration of the equilibrium filtrates.

The Salt Solutions.—The chloride solutions were prepared by adding weighed quantities of water to carefully weighed quantities of the dried salts.

Experimental Data

The experimentally determined solubilities, both at 25 and 40°, were plotted to large scale against the molalities of the added chlorides. A "best" line was drawn through each set of data points; the data of Tables I and II at rounded concentrations were read off this best line.

Table I

Solubility of Barium Carbonate

Molality of added salt	"*C*," g. moles/1000 g. water ($\times 10^4$) at 25° in			"*C*," g. moles/1000 g. water ($\times 10^4$) at 40° in		
	LiCl	NaCl	KCl	LiCl	NaCl	KCl
0.00	0.9114	0.9114	0.9114	1.2217	1.2217	1.2217
.02	1.345	1.170	1.083	1.670	1.705	1.670
.05	1.970	1.515	1.330	2.175	2.220	2.075
.10	2.895	2.030	1.700	2.875	2.810	2.500
.20	4.325	2.875	2.260	4.060	3.680	3.025
.30	5.390	3.570	2.685	5.090	4.295	3.355
.40	6.260	4.180	3.005	6.075	4.655	3.590
.50	6.980	4.735	3.285	7.015	5.130	3.760
1.00	10.05	6.900	4.160	11.505	6.210	4.190
3.00	24.84	9.950	4.685	29.795	8.615	4.950

Table II

Solubility of Strontium Carbonate

Molality of added salt	"*C*," g. moles/1000 g. water ($\times 10^4$) at 25° in			"*C*," g. moles/1000 g. water ($\times 10^4$) at 40° in		
	LiCl	NaCl	KCl	LiCl	NaCl	KCl
0.00	0.5525	0.5525	0.5525	0.7026	0.7026	0.7026
.02	.957	.737	.672	1.164	.888	.975
.05	1.203	.965	.835	1.494	1.140	1.190
.10	1.455	1.320	1.055	1.845	1.505	1.415
.20	1.750	1.965	1.375	2.260	2.195	1.690
.30	1.925	2.485	1.570	2.525	2.780	1.870
.40	2.040	2.915	1.685	2.717	3.280	1.980
.50	2.135	3.285	1.756	2.870	3.710	2.055
1.00	2.440	4.415	1.900	3.390	5.145	2.205
3.00	3.405	6.855	2.176	5.060	8.665	2.480

Discussion and Treatment of Results

The solubilities of barium carbonate at 25 and 40° in pure water, as determined during this investigation, were 0.9114 and 1.2217 $\times 10^{-4}$ g. moles/1000 g. of water, respectively. The value at 25° agrees well with the value of McCoy and Smith,[7b] indicating that the method of analysis of this investigation yielded satisfactory results. The solubilities of strontium carbonate at 25 and 40° in pure water were found to be 0.5525 and 0.7026 $\times 10^{-4}$ g. moles/1000 g. of water, respectively. The value at 25° lies between that of Kohlrausch and Rose[8b] at 24° and that of McCoy and Smith[8c] at 25°. The average heats of solution for barium carbonate and strontium carbonate into their saturated solutions are, from these solubilities, 3625 and 2973 cal./mole, respectively.

The normal carbonate hydrolyzes in solution to form the bicarbonate ion

$$CO_3^{=} + H_2O = HCO_3^- + OH^-$$

A correction must be applied for this hydrolysis in the various salt solutions. If x is the concentration (moles per liter) of HCO_3^- and of OH^- produced, then $(C - x)$ is the *true* concentration of the carbonate ion (from barium carbonate or strontium carbonate). Consideration of the hydrolytic equation above leads to the relation $x^2/(C - x) = K'_w/K'_2$, where K'_w is the stoichiometric ion product for water and K'_2 is the second ionization constant (stoichiometric) for carbonic acid at any particular value of the ionic strength.

Values of K'_w at 25 and 40° at different values of the ionic strength were found in the work of Harned[9] and Harned and Hamer.[10] At 25°, Harned gives values for K'_w for solutions of potassium and sodium chlorides. These values were plotted against values of the square root of the ionic strength, $\mu^{1/2}$; values of K'_w could be read off this large scale plot for any value of $\mu^{1/2}$ for both of these salts. For lithium chloride solutions, for which no K'_w data were given, the values of K'_w for sodium chloride solutions were assumed to yield data sufficiently accurate for our purposes. At 40°, Harned and Hamer gave only K'_w data for potassium chloride solutions. Again, these data were taken as sufficiently accurate for our solutions in lithium and sodium chloride solutions.

Values for K'_2 for carbonic acid at 25 and 40° (38°) were taken from the papers by MacInnes and Belcher;[11] they give empirical equations relating K'_2 and $\mu^{1/2}$ for solutions of potassium carbonate, bicarbonate and chloride. They do

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(9) Harned, This Journal, **47**, 930 (1925).

(10) Harned and Hamer, *ibid.*, **55**, 2194 (1933).

(11) MacInnes and Belcher, *ibid.*, **55**, 2630 (1933); **57**, 1685 (1935).

not give data at 40 but at 38°; these values of K_2' are *assumed* to hold at 40°.

Corrections were then applied by means of the relation $x^2/(C - x) = K'/K_2'$ for each value of "C" listed in Tables I and II and for each value of $\mu^{1/2}$. The resulting values of $(C - x)$, the true $[CO_3^=]$, were then related to the ionic strength by plotting $1/m\pm$ against $\mu^{1/2}$. Extrapolation of these curves to zero value of $\mu^{1/2}$ yielded the following values.

TABLE III

EXTRAPOLATED VALUES OF $1/m\pm$ AT $\mu^{1/2} = 0$

Salt	$BaCO_3$		$SrCO_3$	
Temp., °C.	25	40	25	40
$[1/m\pm]_{\mu=0}$	42,880	58,100	95,800	151,500

These extrapolated values of $1/m\pm$ were used to calculate the values of the activity coefficients of the carbonates in their various solutions, according to the method of Lewis and Randall,[6] by means of the relation

$$f = [1/m\pm]_\mu/[1/m\pm]_{\mu=0}$$

The following tables present these calculated values, in which "Total m" is the ionic strength.

TABLE IV

ACTIVITY COEFFICIENTS OF BARIUM CARBONATE IN ALKALI CHLORIDE SOLUTIONS

Total	Act. coeff. at 25° in			Act. coeff. at 40° in		
m	LiCl	NaCl	KCl	LiCl	NaCl	KCl
0.001	0.919	0.933	0.944	0.873	0.864	0.873
.002	.877	.909	.930	.824	.811	.823
.005	.797	.863	.901	.732	.711	.730
.010	.716	.807	.865	.633	.611	.628
.020	.581	.716	.802	.513	.492	.508
.050	.338	.501	.606	.330	.321	.356
.100	.196	.326	.415	.211	.217	.260
.200	.110	.193	.263	.119	.138	.184
.500	.056	.091	.147	.050	.076	.118
1.000	.033	.054	.098	.024	.050	.084

TABLE V

ACTIVITY COEFFICIENTS OF STRONTIUM CARBONATE IN ALKALI CHLORIDE SOLUTIONS

Total	Act. coeff. at 25° in			Act. coeff. at 40° in		
m	LiCl	NaCl	KCl	LiCl	NaCl	KCl
0.001	0.881	0.931	0.946	0.840	0.892	0.876
.002	.815	.903	.933	.761	.856	.827
.005	.690	.847	.897	.596	.784	.725
.010	.566	.783	.856	.484	.700	.614
.020	.449	.678	.783	.363	.576	.486
.050	.321	.455	.568	.236	.372	.346
.100	.238	.278	.390	.161	.229	.251
.200	.175	.149	.251	.110	.117	.177
.500	.121	.067	.159	.069	.046	.111
1.000	.089	.041	.122	.043	.025	.078

Summary

1. The solubilities at 25 and 40° of barium and strontium carbonates have been determined in pure water and in solutions of lithium, sodium and potassium chlorides. The solubilities in solutions of the alkali chlorides are presented tabularly.

2. The activity coefficients of these carbonates in the alkali chloride solutions have been calculated and recorded.

3. The average heats of solution of these carbonates into their saturated solutions have been calculated for the temperature range 25–40°.

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The Magnetic Properties and Structure of Ferrihemoglobin (Methemoglobin) and Some of its Compounds

BY CHARLES D. CORYELL, FRED STITT AND LINUS PAULING

Our studies of the magnetic properties of hemoglobin derivatives containing ferrous iron,[1,2] including ferroheme, several hemochromogens, hemoglobin, and carbonmonoxyhemoglobin, led to the discovery that in two of these substances (ferroheme, hemoglobin) there are four unpaired electrons per heme, indicating that the bonds attaching the iron atoms to the rest of the molecule are essentially ionic in character, whereas the others contain no unpaired electrons, each iron atom being attached to six adjacent atoms by essentially covalent bonds. We have now investigated ferrihemoglobin[3] (acid methemoglobin), ferrihemoglobin hydroxide (alkaline methemoglobin), ferrihemoglobin fluoride, ferrihemoglobin cyanide, and ferrihemoglobin hydrosulfide, and have found a variety in magnetic properties greater than that for the ferrohemoglobin derivatives; the magnetic susceptibilities

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(1) L. Pauling and C. D. Coryell, *Proc. Nat. Acad. Sci.*, **22**, 159 (1936).

(2) L. Pauling and C. D. Coryell, *ibid.*, **22**, 210 (1936).

(3) The nomenclature used in this paper is described in ref. 2.