

THE SOLUBILITY OF CALCIUM CARBONATE IN AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE AND POTASSIUM SULPHATE AT 25°¹

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The solubility of calcium carbonate in various aqueous solutions of electrolytes has been investigated in this laboratory.²

In this paper are given results obtained for the solubility of calcium carbonate in aqueous solutions of potassium chloride and of potassium sulphate; first, where carbon dioxide has been excluded from the atmosphere, and secondly, where carbon dioxide alone formed the gas phase under a pressure equal to that of the atmosphere.

For the experimental part of this work, bottles were filled with solutions of the chloride or the sulphate of potassium of varying concentrations, using distilled water recently boiled. To each solution an excess of calcium carbonate was added and the bottles were then shaken in a thermostat at 25° for a period of ten weeks.

At the end of this time the contents of the bottles were allowed to settle and 25 cc portions of the supernatant solution were analyzed for calcium. The sulphates or chlorides were estimated in the usual manner. Tables I and II contain the data obtained for these systems.

The figures obtained for potassium chloride solutions may be compared with the results of Cantoni and Goguelia.³ They found that after 98 days at 12°–18° solutions containing 7.45, 10 and 20 percent potassium chloride had dissolved 0.00748, 0.00742 and 0.00828 gram of calcium carbonate, respectively, to 100 cc of solution.

Carbon dioxide was forced into the previously prepared solutions at one and one-half atmospheres pressure at a

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² Cameron and Seidell: *Jour. Phys. Chem.*, 6, 50 (1902).

³ *Bull. Soc. Chim., Paris* [3], 33, 13 (1905).

TABLE I

The solubility of calcium carbonate in aqueous solutions of potassium chloride at 25°

Specific gravity, $\frac{25^\circ}{25^\circ}$	KCl	CaCO ₃
	Percent	Percent
1.000	0.00	0.0013
1.024	3.90	0.0078
1.046	7.23	0.0078
1.072	11.10	0.0076
1.092	13.82	0.0072
1.101	15.49	0.0076
1.122	18.21	0.0070
1.133	19.84	0.0072
1.179	26.00	0.0060

TABLE II

The solubility of calcium carbonate in aqueous solutions of potassium sulphate at 25°

Specific gravity, $\frac{25^\circ}{25^\circ}$	K ₂ SO ₄	CaCO ₃
	Percent	Percent
1.010	1.60	0.0104
1.021	3.15	0.0116
1.033	4.73	0.0132
1.048	6.06	0.0148
1.061	7.85	0.0168
1.069	8.88	0.0192
1.083	10.18	0.0192
1.084	10.48	0.0188

temperature slightly above 0°. As soon as these solutions were saturated with carbon dioxide under the conditions imposed, they were removed to the constant temperature bath 25°. After shaking for a week the stoppers were occasionally removed, for a moment only, allowing the pressure of the gas phase to adjust itself to that of the atmosphere, but not at the same time displacing the carbon dioxide with the atmosphere.

It was observed that the solutions of potassium sulphate of higher concentrations were capable of dissolving much more carbon dioxide than the corresponding solutions of potassium chloride and that in such solutions there was a change in the solid phase.

After the bottles had shaken for eight days at constant pressure of the carbon dioxide, they were allowed to settle and the clear solutions analyzed for the same constituents as before. The data are presented in Tables III and IV.

TABLE III

The solubility of calcium carbonate in aqueous solutions of potassium chloride at 25° saturated with carbon dioxide at atmospheric pressure

KCl	CaCO ₃
Percent	Percent
3.90	0.145
7.23	0.150
11.10	0.166
13.82	0.165
15.49	0.167
18.21	0.154
19.84	0.140
26.00	0.126

TABLE IV

Solubility of calcium carbonate and syngenite in aqueous solutions of potassium sulphate at 25° saturated with carbon dioxide at atmospheric pressure

SO ₃	CaO
Percent	Percent
0.0	0.062
0.69	0.69
1.37	0.69
1.67	0.47
2.18	0.30
2.99	0.24

From these figures it can be seen that there is a change in the solid phase. This change occurs at a concentration of

1.37 percent sulphuric anhydride. In solutions more concentrated than this the solid is composed of fine acicular crystals. When washed with water they are decomposed, yielding gypsum and a solution of potassium sulphate, thus showing them to be syngenite.

To confirm this conclusion a solution was prepared containing 7.5284 grams potassium sulphate to 100 grams water. To this solution 0.4318 gram calcium carbonate was added. Carbon dioxide was then forced into the system till the carbonate had changed into the double salt and the supernatant solution was analyzed for calcium oxide, sulphuric acid, and potash. Table V gives the composition of the solution before and after the precipitation.

TABLE V

The composition of a solution of potassium sulphate before and after precipitating with a weighed amount of calcium carbonate in the presence of an excess of carbon dioxide

	Before precipitation	After precipitation
Grams K_2O	4.0728 to 100 gm. H_2O	3.6988 to 100 gm. H_2O
" SO_3	3.4556 " " "	2.8406 " " "
" CaO	0.2418 added	0.0188 found in solution

These figures show that the precipitate was composed of 0.223 gram calcium oxide, 0.374 gram potash, and 0.615 gram sulphuric anhydride, corresponding in reacting weights to $1CaO:1K_2O:1.94 SO_3$.

In this paper we have shown that calcium carbonate is much more soluble in aqueous solutions of potassium sulphate than of potassium chloride; that the solubility curve for calcium carbonate in potassium chloride solutions passes through a maximum; and in potassium sulphate solutions above 1.37 percent sulphuric anhydride, or 2.98 percent potassium sulphate, syngenite is formed.

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