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Some Solution Equilibria Involving Calcium Sulfite and Carbonate

I. Simple Solubility Equilibria of CO_2, SO_2, $CaCO_3$, and $CaSO_4$

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Equilibrium constants for the reactions: 1) $CaSO_4(H_2O)_2(s) \rightleftharpoons Ca^{2+} + SO_4^{2-} + 2H_2O$ 2) $SO_2(g) + H_2O \rightleftharpoons H_2SO_3$ 3) $CaSO_3\,(H_2O)_{\frac{1}{2}}\,(s) + SO_2(g) + \frac{1}{2}\,H_2O \rightleftharpoons Ca^{2+} + 2\ HSO_3^-$ 4) $CO_2(g) + H_2O \rightleftharpoons H_2CO_3$ 5) $CaCO_3(s) + CO_2(g) + H_2O \rightleftharpoons Ca^{2+} + 2\ HCO_3^-$ were determined at 25, 35, and 75°C, using 1 m and 3.5 m $NaClO_4$ as ionic medium. The log K values (m scale) are given in Table 1.

The impetus to the work to be described below was a process once proposed for sulfur recovery in sulfite pulp mills. The principle is as follows:

(1) The sulfite waste liquor is burned and the SO_2 of the flue gases is absorbed in an ammonium sulfite solution; (2) or (2a) from this solution, calcium sulfite is precipitated by the addition of calcium carbonate.

$$SO_3^{2-} + SO_2(g) + H_2O \rightarrow 2\ HSO_3^- \tag{1}$$
$$2\ HSO_3^- + CaCO_3(s) \rightarrow CaSO_3(s) + CO_2(g) + H_2O + SO_3^{2-} \tag{2}$$
$$HSO_3^- + CaCO_3(s) \rightarrow CaSO_3(s) + HCO_3^- \tag{2a}$$

The calcium sulfite would then be separated and used for making fresh liquor; the remaining solution would be sent back to the absorber, to take up new SO_2, according to (1) or

$$HCO_3^- + SO_2(g) \rightarrow HSO_3^- + CO_2(g) \tag{1a}$$

The process might be advantageous in such mills where the excess steam available does not suffice for stripping the ammonium sulfite solution in the traditional way.

To study the feasibility of this process, a number of equilibria were studied involving solid $CaSO_3$ or $CaCO_3$ and a solution containing SO_3^{2-} ions. Since some oxidation to sulfate is unavoidable, the behavior of $CaSO_4$ and its hydrates in the solutions was also studied.

The main results of these equilibrium studies will now be published since the equilibrium constants may have an interest independent of the special process described. Even if the accuracy might have been better, it is thought that these data will give more precise information than was possible on the basis of previously published data, which were often conflicting.

Choice of experimental conditions

Three *temperatures* were studied, namely 25°C, 35°C, and 75°C. The first, 25°C, was chosen because it is a standard temperature for physicochemical measurements, and so makes our data directly comparable with a large amount of data compiled by other workers. It was kept constant by keeping the reaction vessel in a water thermostat of 25.0 ± better than 0.1°C. The experiments were moreover carried out in a thermostat room with 25.0 ± 0.5°C. The temperature 75°C was maintained by keeping the apparatus in an air thermostat of 75°C ± 1°; in the aqueous solutions the fluctuations were smoothed out so that the variations were considerably less.

As an intermediate temperature, one might have proposed 50°C; however, 35°C was chosen since it allows working with water thermostats without too much trouble from condensation of water vapor.

The *ionic medium* was kept constant, as far as possible, by making the solutions always contain either 1 m Na^+ or 3.5 m Na^+ (m = mole per 1 000 g of H_2O). The concentrations were given on a weight rather than a volume basis because the reactions would be considered at several temperatures. At 25°C, 3.5 m $NaClO_4$ is practically the same as 3.0 M $NaClO_4$. As anions the solutions contained sulfite, sulfate, and carbonate ions, depending upon which equilibria were to be studied; the balance was ClO_4^-.

As inert positive ion, Na^+ was chosen rather than NH_4^+, to avoid the necessity of making small corrections for the formation of NH_3, which would complicate the calculations unnecessarily without being essential for the process.

In the usual absorption process [1], combined with steam stripping, high concentration is an advantage, and the ionic concentrations are usually chosen above 10 m. However, in the precipitation processes to be studied, it would be preferable to work with a lower concentration, since this makes it easier to separate a pure precipitate. This was our reason for choosing 1 m and 3.5 m.

EXPERIMENTAL

Substances

Sulfur dioxide and *carbon dioxide* were taken from gas cylinders, and then washed first with water and then with a $NaClO_4$ solution of the desired concentration and temperature, to get the right water vapor pressure. Sodium carbonate, sodium sulfite, sodium sulfate, perchloric acid 70—72 %, calcium chloride, calcium sulfate dihydrate, and calcium carbonate were all of p. a. purity of Baker's, Kahlbaum's, or Merck's make.

Sodium perchlorate was prepared from sodium carbonate and perchloric acid. *Calcium sulfite* was precipitated from calcium chloride and sodium sulfite solutions, washed and sucked dry, all in a nitrogen atmosphere.

Ammonia was taken from a cylinder and purified only by being washed with distilled water.

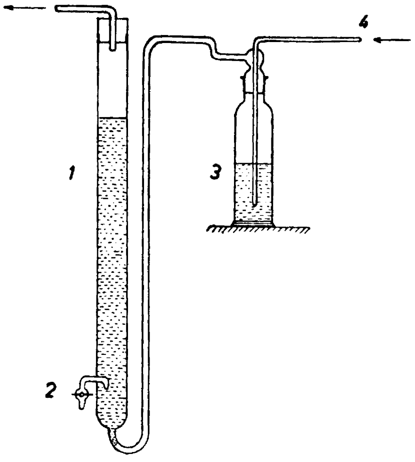

Fig. 1. Sketch of apparatus for equilibrating gas and solution (suspension). 1: glass tube, diameter 3 cm. 2: stop-cock for taking samples. 3: washing-bottle for preliminary equilibration with water vapor. 4: inlet for purified gas.

To avoid the oxidation of sulfite to sulfate by the oxygen of the air, all equilibrium experiments were carried out in an atmosphere of nitrogen from which oxygen had been removed by Meyer and Ronge's method[2], if a CO_2 or SO_2 atmosphere was not used. Moreover, the solutions contained 0.3 ml of benzyl alcohol per liter; this is an efficient chain inhibitor for the oxidation of SO_3^{2-} as found by Bäckström[3].

Apparatus

The central, thermostated, part of the apparatus is indicated in Fig. 1. The glass tube is about 60 cm long with an inner diameter of 3 cm. Like the washing bottle, it contains $NaClO_4$ solution, 1 m or 3.5 m. In some experiments, the tube also contained a solid in excess, $CaCO_3$(s) or $CaSO_3(H_2O)_{\frac{1}{2}}$(s).

The gas to be studied, CO_2 or SO_2, was first bubbled through the wash bottle, to become approximately saturated with water vapor, and then through the long tube. The solid phases were added only after the stream of gas had been started.

When no solid phase was present, samples were taken from the stop-cock at the lower part of the tube. Otherwise, samples were sucked very cautiously with an inverted bicycle pump (to avoid excessive under-pressure) through a pipette provided with a sintered-glass filter-stick.

In our 35°C thermostat, there was not enough room for this apparatus. Instead, a 500 ml bottle, provided with a stirrer, inlet and outlet tubes for the gas was used. Samples were taken by sucking, if necessary through a filter-stick.

The solubility of calcium sulfate, really $CaSO_4(H_2O)_2$, was determined simply by shaking 1 m or 3.5 m $NaClO_4$ solution with excess calcium sulfate dihydrate in bottles.

Analysis

Calcium was precipitated as oxalate, which was dissolved in sulfuric acid and titrated with $KMnO_4$.

To analyse for *sulfite*, excess of 0.05 M I_2 solution was added, the solution was acidified (if necessary), and excess iodine was titrated with thiosulfate.

Table 1. Summary of results (averages of two or more measurements).

	1 m $NaClO_4$			3.5 m $NaClO_4$		
	25°C	35°C	75°C	25°C	35°C	75°C
1. $CaSO_4$ (s) $\rightleftharpoons Ca^{2+} + SO_4^{2-}$						
mmole/kg solution	30.8	31.3	29.9	18.5	19.9	15.0
mmole/kg H_2O	34.7	35.3	33.7	26.4	28.4	21.4
log *K*	−2.92	−2.91	−2.94	−3.16	−3.09	−3.34
2. $SO_2(g) + H_2O \rightleftharpoons H_2SO_3$						
mmole/kg solution	1 040	727	209	825	594	170
mmole/kg H_2O	1 256	860	238	1 234	883	245
log *K*	0.03	−0.13	−0.53	0.06	−0.09	−0.50
3. $CaSO_3(s) + SO_2(g) + H_2O \rightleftharpoons Ca^{2+} + 2\ HSO_3^-$						
mmole Ca/kg solution	497	395	168	260	198	87.7
mmole Ca/kg H_2O	667	507	198	417	308	129
log *K*	0.09	−0.26	−1.30	−0.52	−0.91	−1.89
4. $CO_2(g) + H_2O \rightleftharpoons H_2CO_3$						
mmole/kg	26.5	21.7	9.25	19.2	16.0	7.75
mmole/kg H_2O	29.8	24.4	10.4	27.4	22.9	11.1
log *K*	− 1.51	− 1.59	− 1.78	− 1.55	− 1.62	− 1.78
5. $CaCO_3(s) + CO_2(g) + H_2O \rightleftharpoons Ca^{2+} + 2\ HCO_3^-$						
mmole Ca/kg solution	12.8	10.9	6.72	6.42	5.05	2.64
mmole Ca/kg H_2O	14.4	12.3	7.55	9.18	7.22	3.77
log *K*	− 4.91	− 5.10	− 5.56	− 5.50	− 5.80	− 6.49

The *total carbonate* of the solution was precipitated by excess of barium hydroxide, the precipitate was washed in a centrifuge, and dissolved in excess of 0.1 M HCl. This solution was boiled and then the excess HCl was determined by titration with 0.1 M NaOH.

Sulfate was determined gravimetrically as $BaSO_4$.

RESULTS

The results of this part of our work are summarized in Table 1.

In the second reaction formula for brevity, H_2SO_3 means the uncharged molecular species present in the aqueous solution, whether it be H_2SO_3, SO_2, or $SO_2(H_2O)_n$. The same holds for H_2CO_3 in the fourth reaction. The formulas $CaCO_3$, $CaSO_3$, and $CaSO_4$ stand for the solid phase present at equilibrium, under our conditions they were $CaCO_3$ (calcite), $CaSO_3(H_2O)_{\frac{1}{2}}$ (see part II), and $CaSO_4(H_2O)_2$ (gypsum).

For each reaction, the first line gives the average of the data primarily obtained. Since the samples were weighed before analysis, the unit is mmole/kg solution. Each value is the average of two or more separate experiments; the difference was less than 1 % for the experiments involving SO_2, and less than 1.5 % for the others. The figures are the uncorrected analytical data: total solubility for the gases, and total Ca in the experiments with solid phases.

The second line of figures, for each equilibrium, gives the primary data corrected to the unit mmole/kg H_2O.

To obtain the figures in the third line, log *K* of the reaction, one must consider that the partial pressures of SO_2 and CO_2 were 1.00 atm minus the equilibrium pressure of water vapor, 0.031 atm at 25°C, 0.055 atm at 35°C, and 0.380 atm at 75°C, for pure water, which should be multiplied by the activity of water, which we calculated from Jones' osmotic coefficients [4] as 0.96_8 in 1 m $NaClO_4$ and 0.88_4 in 3.5 m $NaClO_4$.

Moreover, in the second equilibrium, the solubility of SO_2 in water, one should correct for the dissociation of H_2SO_3, which is a fairly strong acid. For 25°C, according to part III, log K_a is —1.37 in 1 m and —1.72 in 3.5 m $NaClO_4$. Assuming the same temperature dependence of log K as at zero ionic strength [6], we estimate —1.46 and —1.81 for 35°C, and —1.83 and —2.18 at 75°C. The corresponding correction can be neglected for H_2CO_3.

The spread of the experimental data corresponds to an uncertainty of about 0.01 in the first, third and fourth log K_a and $\pm$ 0.02 in the fifth. The systematic error in the constant for SO_2 solubility, because of the uncertainty of the K_a, may be of the same order of magnitude for 25°C, and larger for the other temperatures. The solubility of $CaSO_3$ is so large that the ionic medium is considerably changed, introducing an unknown error in the activity factors.

Comparison with literature data

There is an abundant literature on the solubility of gypsum in water and aqueous solutions [5]. Although there are no data that can be directly compared with ours, the general trend, with a solubility maximum around 40—50°C, agrees with our data. The value for the activity-solubility product at 25°C, according to Latimer *et al.*[8], is log $K_s = -4.625$ which, with our values, would give reasonable activity coefficients.

The solubilities of CO_2 and SO_2 agree well with previous determinations [6,7], with due regard to the salting-out effect.

The equilibrium $CaCO_3(s) + H_2O + CO_2(g) \rightleftharpoons Ca^{2+} + 2\ HCO_3^-$ has been studied carefully by Frear and Johnston [9]. Their value for log K at 25°C is —5.83, using activities.

The equilibrium $CaSO_3\ (H_2O)_{\frac{1}{2}}(s) + \frac{1}{2}H_2O + SO_2(g) \rightleftharpoons Ca^{2+} + 2\ HSO_3^-$ has been studied by Conrad and Beuschlein [10] who, however, did not try to calculate the equilibrium constants. Their ionic strengths varied, and were too high for extrapolation to zero. Their lowest concentrations, 0.142 M $Ca(HSO_3)_2$ and $p_{SO_2} = 16.2$ torr at 25°C would give log $K = -0.27$ (M, atm units), which compares reasonably well with our value.

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