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Some Solution Equilibria Involving Calcium Sulfite and Carbonate

II. The Equilibrium between Calcium Sulfate and Calcium Sulfite in Aqueous Solutions[1]

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The equilibrium constant for the reaction $CaSO_4(H_2O)_2(s) + SO_3^{2-} \rightleftharpoons CaSO_3(H_2O)_{\frac{1}{2}}(s) + SO_4^{2-} + 1.5\ H_2O$ has been determined at 25°C, 35°C, and 75°C, with Na^+ concentrations 1 m and 3.5 m, and ClO_4^- as neutral anion. The average values for log K are, for both Na^+ concentrations; at 25°C 1.88; at 35°C 1.96; and at 75°C 2.23; thus $K = [SO_4^{2-}]\,[SO_3^{2-}]^{-1} = 76$, 91, and 170 at the three temperatures.

The measurements suggest $\log K_S = -6.5 \pm 0.2$ for the activity solubility product of $CaSO_3(H_2O)_{\frac{1}{2}}$ at 25°C.

The present paper will describe studies of the equilibrium

$$CaSO_4(s) + SO_3^{2-} = CaSO_3(s) + SO_4^{2-};\ K = [SO_4^{2-}]\,/\,[SO_3^{2-}] \qquad (1)$$

The available literature data that could be used for estimating K are in very bad agreement, giving values of K ranging from about 1 to several hundreds.

ESTIMATION OF K FROM LITERATURE DATA

The equilibrium constant K in (1) is the ratio of the concentrations of two binegative ions of practically the same size. The activity factors of these ions can be expected to be approximately equal although their values will, of course, vary very much with the ionic medium. If this is so, the apparent K in any aqueous solution will not be far from the real activity constant, and K will be fairly independent of ionic strength.

We made an attempt to estimate K from the relevant literature data, summarized in Table 1. The solubility of $CaSO_4(H_2O)_2$ in water at temperatures below 100°C has been very accurately measured by several workers, whose results agree well. The last column in Tab. 1 gives the concentration of the saturated aqueous solutions[2] in mM.

Table 1. Literature data on the solubilities of $CaSO_3(H_2O)_{\frac{1}{2}}$ in water and in saturated $CaSO_4(H_2O)_2$, expressed in mg $CaSO_3$ per 1 000 g solution.

Temp. °C	$CaSO_3$ in pure water			$CaSO_3$ in saturated $CaSO_4$ solutions		$CaSO_4$ in water mM
	R	L	W+S	L	W+S	
10						14.177
15	1 670					
18						14.817
20			99.5	29.0		
25						15.295
30		49.2 (64)		23.8 (31)		15.361
40		48.5 (63)	92.7	22.3 (29)	32.8	15.413
45						15.310
50	1 710	43.9 (57)		19.2 (25)		
55						14.765
60		46.9 (61)	83.1	14.6 (19)	36.6	
65.3						14.20
70		34.6 (45)		9.2 (12)		
75						13.575
80		23.8 (31)	59.0	6.9 (9)	43.0	
90		20.8 (27)		6.2 (8)		
100	1 590	8.5 (11)		4.6 (6)		11.900

R = Robart 1913.
L = van der Linden 1916 (The values in parentheses are the original data, expressed as mg of "$CaSO_3(H_2O)_2$" per 1 000 g solution).
W+S = Wurz and Swoboda 1948.

On the other hand, the data on $CaSO_3$ (really $CaSO_3(H_2O)_{\frac{1}{2}}$) are scarce and contradictory as seen from Table 1 where the data of Robart [3], van der Linden [4] and Wurz and Swoboda [5] are compared. The constant K could be estimated from them in two ways.

From the solubilities of $CaSO_3$ and $CaSO_4$ in pure water, we calculated the solubility products, making reasonable assumptions regarding the activity factors; K was then obtained as the ratio of the solubility products of $CaSO_4$ and $CaSO_3$. For both salts we used the activity factors for $ZnSO_4$ as given by Harned and Owen [6] on the basis of data of Cowperthwaite and LaMer [7] and Bray [8]; the activity factors for all metal(II) sulfates seem to vary with concentration in practically the same way [6].

In this way we obtained the following very approximate values for K:

from Robart's data	1.2(15°C) to 0.8(100°C)
from van der Linden's data	200(30°C) to 6 000(100°C)
from Wurz and Swoboda's data	70(20°C) to 140(80°C)

If, instead, one uses Kielland's activity factor tables [9], the constants in the two latter cases will be multiplied with a factor of about 1.5, and thus become 300 to 9 000, and 100 to 200; however, the $ZnSO_4$ values seem preferable.

We may also use the solubility of $CaSO_3$ in saturated calcium sulfate solutions. In these experiments one may expect $[SO_4^{2-}]$ to be practically the same as in a saturated solution of $CaSO_4(H_2O)_2$ in pure water; since the two binegative ions are in the same solution no activity factor correction is needed, and the constant K is obtained as the ratio SO_4^{2-}/SO_3^{2-} in the solution. The values so obtained are approximately

from van der Linden's data	80(30°C) to 300(100°C)
from Wurz and Swoboda's data	65(20°C) to 40(80°C)

Not only do van der Linden's and Wurz-Swoboda's values disagree with each other; in each paper the two sets of data seem to lead to disagreeing results.

Robart's solubility values are so much higher than those given in the two other papers that one may suspect they are misquoted; since, however, Latimer and Hildebrand [10] had selected Robart's data we felt we should not discard them without making experiments of our own.

EXPERIMENTAL

The equilibrium (1) was studied in solutions with 1 m Na+ at 25°C, 35°C, and 75°C, and with 3.5 m Na+ at 25°C and 35°C (with one stray experiment at 75°C).

At the two lower temperatures, the solutions were shaken to equilibrium in 100 ml glass bottles in a water thermostat. At 75°C the solution was kept in an Erlenmeyer flask with a magnetic stirrer; the flask was kept in an air thermostat at 75°C.

The solutions were generally made up by adding to a sodium sulfite solution an excess of $CaSO_4(H_2O)_2$. In one case, the equilibrium was approached from the other direction, solid $CaSO_3(H_2O)$ being added to a sodium sulfate solution. As in part I [1] the solutions contained perchlorate ions as balance.

Especially at the lower temperatures, the time of contact was very long, 5—38 days, to assure that equilibrium was obtained. — At the end of an experiment, the stirring was stopped but the flask was still left in the thermostat. After a few hours, the solids had settled, and samples of the solution were sucked out through a glass filter-stick. The samples were weighed and analysed for sulfate and sulfite ions.

Sulfite was determined iodometrically (part I). Since the sulfite concentration in our solutions was low, the accuracy was only about 5 % at the lowest concentrations.

For determining *sulfate* the standard gravimetric method could not be used here because of the fear of the coprecipitation of sodium owing to the high Na+ concentration in the solutions. Instead, a volumetric method with the following principle [11] was used. The sulfite ions are first bound as a formalin complex and then sulfate precipitated with barium chloride at room temperature after adding acetic acid. The precipitate of $BaSO_4$ is washed, centrifuged, and then converted to $BaCO_3$ by means of a strong sodium carbonate solution. This reaction takes about 1 h at 100°C. The barium carbonate precipitate is washed till the reaction is neutral, and then the carbonate content determined by dissolving in a known excess of hydrochloric acid, and back-titrating with sodium hydroxide. The accuracy of the sulfate determination is better than 1 %, which is satisfactory considering the much larger uncertainty in the sulfite determination.

The solid phases. In order to make sure in what form calcium sulfite and sulfate were present, X-ray powder photographs were taken of the powder mixture in a number of the equilibrium solutions at 25°C and 75°C and compared with photographs of synthetic specimens. Calcium sulfate proved to be present in the form of the dihydrate $CaSO_4(H_2O)_2$, gypsum. Calcium sulfite was present in one and the same form at 25°C and 75°C; this phase was also prepared synthetically. The diffraction lines of this phase agreed very well with the data of Matthews and McIntosh [12]; these authors state that the composition of the phase is $CaSO_3(H_2O)_{\frac{1}{2}}$.

Table 2. Experiments on the equilibrium

$$CaSO_4(s) + SO_3^{2-} \rightleftharpoons CaSO_3(s) + SO_4^{2-}$$

Temp. °C	Na+ mole/kg H_2O	Time days	SO_4^{2-} mmole/kg	SO_3^{2-} solution	K	log K
25	1.0	19	455	6.28	72.4	1.86
25	1.0	23	455	6.28	72.4	1.86
25	3.5	5	349	5.05	69.1	1.84
25	3.5	9	354	4.73	74.8	1.87
25	3.5	24	354	3.61	98	1.99
35	1.0	28	461	5.25	87.8	1.94
35	1.0	35	466	5.17	90.1	1.95
35 *	1.0	10	500	5.46	91.6	1.96
35	3.5	28	355	3.57	99.4	2.00
35	3.5	38	357	3.94	90.7	1.96
75	1.0	0.1	456	3.16	144	2.16
75	1.0	0.3	453	2.73	166	2.22
75	1.0	1.0	459	2.76	166	2.22
75	1.0	4.0	464	2.25	206	2.31
75	3.5	0.1	743	4.31	172	2.24

RESULTS

Our results are given in Table 2. Since the equilibrium constant K of the reaction studied is a pure number, it is immaterial whether we express the concentrations in m, in M, or in mole/kg of solution. It is the latter unit we have chosen in the table, since it gives the easiest calculations, and thus the smallest chance of computation errors.

The columns of Table 2 are: temperature °C; concentration of Na^+, in mole/kg of water; time of equilibration, days; final concentration of SO_4^{2-}; final concentration of SO_3^{2-}; equilibrium constant K, and log K.

The single experiment where the equilibrium was approached starting with calcium sulfite is marked with an asterisk.

The correction for the hydrolysis of the sulfite ion according to

$$SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + OH^-$$

can be shown to be negligible in comparison with the other experimental errors; it is less than 1 %.

The equilibrium constant K is found to increase with temperature. There may be a slight increase with increasing ionic strength, though the accuracy of the data does not allow a certain conclusion. We prefer to give an average K for both ionic strengths:

$$\begin{array}{lll} 25°\mathrm{C} & \log K = 1.88 & K = 76 \\ 35°\mathrm{C} & \log K = 1.96 & K = 91 \\ 75°\mathrm{C} & \log K = 2.23 & K = 170 \end{array}$$

If we compare these values with the literature data given above, our data are found to be in complete disagreement with Robart's. The best agreement is with the K values from Wurz and Swoboda's solubilities in pure water, and with those from van der Linden's solubilities in calcium sulfate solutions.

The accuracy of our values for log K is, we hope, better than ± 0.10.

If we assume that the log K so obtained represents the true activity equilibrium constant, we can find the true activity solubility product for $CaSO_3$ by combination with the activity solubility product[13] $[Ca^{2+}]\ [SO_4^{2-}] = 10^{-4.63}$ at 25°C

$$[Ca^{2+}]\ [SO_3^{2-}] = K_s = 10^{-6.51}$$

The uncertainty in log K_s is estimated as ± 0.2.

From this value of K_s we may calculate the solubility of $CaSO_3(H_2O)_{\frac{1}{2}}$ at 25°C in pure water to be around 0.76 mM or 91 mg $CaSO_3$/l.

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