

Some Solution Equilibria Involving Calcium Sulfite and Carbonate

III. The Acidity Constants of H_2CO_3 and H_2SO_3 , and $\text{CaCO}_3 + \text{CaSO}_3$ Equilibria in NaClO_4 Medium at 25°C

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A number of equilibrium constants have been determined, involving aqueous solutions, solid $\text{CaSO}_4(\text{H}_2\text{O})_2$, CaCO_3 and $\text{CaSO}_3(\text{H}_2\text{O})_{\frac{1}{2}}$ and gaseous CO_2 and SO_2 . The equilibria have been studied at Na^+ concentrations 1 m and 3.5 m and at the temperatures 25, 35 and 75°C . The results are summarized in Table 1; applications to practical cases are given in the diagrams, Fig. 1 and Fig. 2.

In connection with the work in parts I and II, the acidity constants of H_2CO_3 and H_2SO_3 were determined for the ionic media studied, 1 m and 3.5 m Na^+ , with ClO_4^- as neutral anion. Although some preliminary experiments were made at higher temperatures, only those at 25°C had an accuracy that made them worth publishing.

The experiments were carried out as potentiometric titrations, using a glass electrode for measuring $[\text{H}^+] = h$, and a silver-silver ion electrode as reference electrode:

— glass electrode/1 m NaClO_4 /0.01 m AgClO_4 , ($I=0.01$) m $\text{NaClO}_4/\text{Ag} +$
 $E = E_o + E_j - 59.15 \log h$

E_o and the liquid junction potential E_j were determined by comparison with solutions of the same ionic strength $I = 1$ or 3.5, but with some Na^+ replaced by H^+ . These solutions either occurred naturally at one end of the titration, or were specially prepared and inserted in the cell before or after a titration. The procedure has been described in several papers from this laboratory, *e.g.* Refs.^{1,2}.

THE SECOND ACIDITY CONSTANT OF CARBONIC ACID

For convenience in the titrations, all concentrations were expressed in M units for the calculations (although, of course, the Na^+ concentration was always 1 m or 3.5 m).

The main experiments were made as titrations of 200 mM Na_2CO_3 or 100 mM Na_2CO_3 (balance NaClO_4) with HClO_4 , with careful addition and mechanical stirring, to prevent loss of CO_2 . For each point one could calculate, from the analytical data, $Z = [\text{HCO}_3^-]/([\text{HCO}_3^-] + [\text{CO}_3^{2-}])$, the number of protons bound per CO_3 group, and plot it as a function of $\log h$. The experimental curve $Z(\log h)$ was fitted to a calculated normalized curve, $Z = v(1 + v)^{-1}$ versus $v (= \log h - \log K)$, and from the position of best agreement, $\log K$ was obtained³.

For each of the two ionic media used, two titrations were carried out with 200 mM CO_3^{2-} , and one with 100 mM CO_3^{2-} . The curves $Z(\log h)$ coincided, as one might expect for a mononuclear process. The best values found were, at 25°C:

$$\text{for } [\text{Na}^+] = 1\,000 \text{ mm} \sim 950 \text{ mM: } K_{a2} = 10^{-9.59} \text{ M} = 10^{-9.57} \text{ m}$$

$$\text{for } [\text{Na}^+] = 3\,500 \text{ mm} \sim 3\,000 \text{ mM: } K_{a2} = 10^{-9.63} \text{ M} = 10^{-9.56} \text{ m}$$

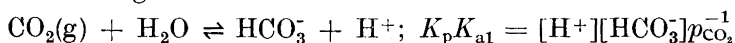
with an uncertainty of less than ± 0.02 in $\log K$.

In a few preliminary experiments, we were thoughtless enough to start with an NaHCO_3 solution and stir with a stream of nitrogen. This led to losses of CO_2 with the gas stream, amounting to about 10 % of the whole carbonate content. When the curve-fitting³ was applied, this error was immediately discovered because the apparent Z curve was shifted (*cf.* Fig. 2 d in Ref³); a correction could then easily be applied.

Titration of NaHCO_3 with NaOH , applying mechanical stirring, gave somewhat smaller corrections, but we preferred the titrations of Na_2CO_3 with HClO_4 , since they gave immediately Z curves of the right shape and, moreover, could be easily extended to an acid-base titration giving E_0 and E_j .

FIRST ACIDITY CONSTANT OF CARBONIC ACID

In titrations of HCO_3^- — H_2CO_3 buffers, it is always hard to avoid the escape of some CO_2 . It was decided to titrate instead NaHCO_3 with H^+ , keeping $[\text{H}_2\text{CO}_3]$ constant by equilibrating with $\text{CO}_2(\text{g})$ at 1 atm. The constant obtained will be the following:



In each point of the titration, one knows $[\text{H}^+] = h$ from the emf measurement, and $[\text{HCO}_3^-]$ from the original amount of HCO_3^- and from the amount of H^+ added.

The experiments were carried out in the same way as for K_{a2} , adding H^+ to a known amount of HCO_3^- , and bubbling CO_2 through the solution. The points after the equivalence point, when all the HCO_3^- had been consumed, could be used for determining E_0 and E_j .

After correction to $p_{\text{CO}_2} = 1$ atm, the following results were obtained from two experiments with each ionic strength, starting with 200 mM HCO_3^- :

$$[\text{Na}^+] = 1\,000 \text{ mm} \sim 950 \text{ mM; } K_p K_{a1} = 10^{-7.59} \text{ M}^2 \text{ atm}^{-1} = 10^{-7.55} \text{ m}^2 \text{ atm}^{-1}$$

$$[\text{Na}^+] = 3\,500 \text{ mm} \sim 3\,000 \text{ mM; } K_p K_{a1} = 10^{-8.02} \text{ M}^2 \text{ atm}^{-1} = 10^{-7.88} \text{ m}^2 \text{ atm}^{-1}$$

These values may be combined with the values for K_p found in part I, —1.51 for 1 m Na^+ and —1.55 for 3.5 m Na^+ , to give

$$-\log K_{a1} = -6.04 \text{ for } 1 \text{ m } \text{Na}^+, -6.33 \text{ for } 3.5 \text{ m } \text{Na}^+$$

The accuracy is estimated to be ± 0.02 . Literature values for 25°C and at infinite dilution are $\log K_{a1} = -6.366$ (Shedlovsky and MacInnes ⁴), -6.352 (Harned and Davis ⁶), and -6.51 (Kauko and Carlberg ⁵); $\log K_{a2} = -10.25$ (MacInnes and Belcher ⁷) and -10.24 (Kauko and Airola ⁸)

THE ACIDITY CONSTANTS OF H₂SO₃

After a number of preliminary experiments, we chose to start the titrations with initial [OH⁻] from 20 to 100 mM, and to titrate with a solution of SO₂, from 0.16 to 1.2 M, and of the desired sodium concentration. By this procedure, losses of SO₂ were avoided.

The average values were:

for 1 m Na⁺: $K_{a1} = 10^{-1.39}$ M = $10^{-1.37}$ m; $K_{a2} = 10^{-6.36}$ M = $10^{-6.34}$ m
 for 3.5 m Na⁺: $K_{a1} = 10^{-1.79}$ M = $10^{-1.72}$ m; $K_{a2} = 10^{-6.43}$ M = $10^{-6.36}$ m

The limits of error of these figures are somewhat higher, about ± 0.05 for $\log K_{a2}$ and ± 0.10 for $\log K_{a1}$. Literature values for 25°C and infinite dilution are $\log K_{a1} =$ from -1.89 (Johnstone and Leppla⁹) to -1.76 (Tartar and Garretson ¹⁰), and $\log K_{a2} = -7.20$ (Tartar and Garretson ¹⁰)

CHECK OF CONSTANTS

Table 1 gives a summary of the $\log K$ values determined in the present work. At 25°C, it is possible to make a check on the constants, since the equilibrium constant of the reaction



Table 1. Logarithms of measured and derived equilibrium constants.

No.	Reaction	1 m			3.5 m		
		25°C	35°C	75°C	25°C	35°C	75°C
1	$\text{CaSO}_4 \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2-}$	-2.92	-2.91	-2.94	-3.16	-3.09	-3.34
2	$\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_3$	0.03	-0.13	-0.53	0.06	-0.09	-0.50
3	$\text{CaSO}_3 + \text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2 \text{HSO}_3^-$	0.09	-0.26	-1.30	-0.52	-0.91	-1.89
4	$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$	-1.51	-1.59	-1.78	-1.55	-1.62	-1.78
5	$\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2 \text{HCO}_3^-$	-4.91	-5.10	-5.56	-5.50	-5.80	-6.49
6	$\text{CaSO}_4 + \text{SO}_3^{2-} \rightleftharpoons \text{CaSO}_3 + \text{SO}_4^{2-}$	1.88	1.96	2.23	1.88	1.96	2.23
7	$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	-7.55			-7.88		
8	$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$	-9.57			-9.56		
9	$\text{H}_2\text{SO}_3 \rightleftharpoons \text{H}^+ + \text{HSO}_3^-$	-1.37			-1.72		
10	$\text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^{2-}$	-6.34			-6.36		
1-6	$\text{CaSO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{SO}_3^{2-}$	-4.80	-4.87	-5.17	-5.04	-5.05	-5.57
3-2	$\text{CaSO}_3 + \text{H}_2\text{SO}_3 \rightleftharpoons \text{Ca}^{2+} + 2 \text{HSO}_3^-$	0.06	-0.13	-0.77	-0.58	-0.82	-1.39
(3-2)- (1-6)	$\text{SO}_3^{2-} + \text{H}_2\text{SO}_3 \rightleftharpoons 2 \text{HSO}_3^-$	4.86	4.74	4.40	4.46	4.23	4.18
9-10		4.97			4.64		
7-4	$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	-6.04			-6.33		

Note: CO₂ and SO₂ are gaseous (pressure in atm), H₂CO₃ and H₂SO₃ are in aqueous solution. "CaSO₄" = CaSO₄(H₂O)₂, "CaSO₃" = CaSO₃(H₂O)_½, CaCO₃ = calcite.

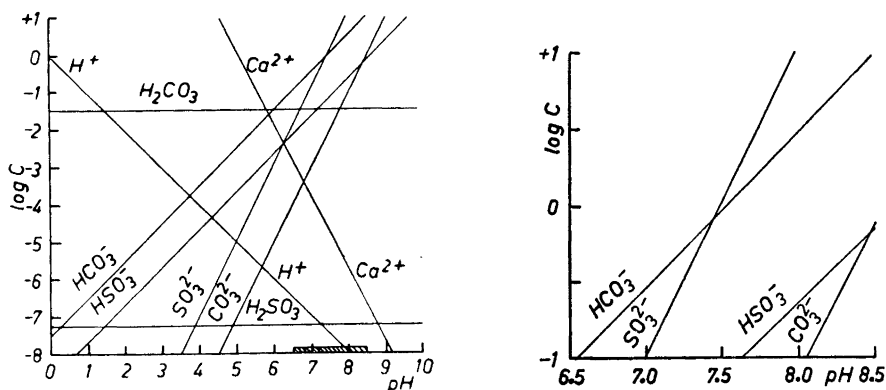


Fig. 1. Logarithmic diagram for aqueous solution (25°C, 1 m NaClO₄) in equilibrium with solid CaCO₃ and CaSO₃, and CO₂ of 1 atm. Horizontal axis: pH (= -log [H⁺]). Vertical axis: log of concentration of species in question. The approximate pH range of practical interest is marked out on the pH scale.

can be calculated in two independent ways, namely by combining the reactions 3 + 6 — 2 — 1 or 9 — 10 (Table 1). For 1 m Na⁺ the results of the two calculations are 4.86 and 4.97; for 3.5 m Na⁺ they are 4.46 and 4.64. The difference is 0.11 (0.18) in the logarithm, which is not too bad, considering the spread in the individual determinations, and the fact that for reactions 2 and 3 the ionic medium in the equilibrium solution differs substantially from the original one.

LOGARITHMIC EQUILIBRIUM DIAGRAMS

We shall now construct logarithmic diagrams, using the equilibrium constants we have found for 25°C and 1 m Na⁺. First let us study the conditions imposed on the concentrations, if the solution is in equilibrium with CO₂ of 1 atm, solid CaCO₃, and solid CaSO₃. This is the state one may obtain by adding excess of calcium carbonate to a sulfite solution which has already absorbed some SO₂. We shall use the equilibrium constants for 4, 7, 8, 5, (1—6), 10 and 9. We use (1 minus 6), rather than (3 minus 2), which are slightly more uncertain. We find the following equilibrium conditions (Fig. 1):

$$\begin{aligned}
 &1 \text{ atm CO}_2: \log [\text{H}_2\text{CO}_3] = -1.51 \\
 &\quad \log [\text{HCO}_3^-] = \text{pH} - 7.55 \\
 &\quad \log [\text{CO}_3^{2-}] = \log [\text{HCO}_3^-] + \text{pH} - 9.57 = 2 \text{ pH} - 17.12 \\
 \text{CaCO}_3(\text{s}): \quad &\log [\text{Ca}^{2+}] = -4.91 - 2 \log [\text{HCO}_3^-] = 10.19 - 2 \text{ pH} \\
 \text{CaSO}_3(\text{s}): \quad &\log [\text{SO}_3^{2-}] = -4.80 - \log [\text{Ca}^{2+}] = 2 \text{ pH} - 14.99 \\
 &\log [\text{HSO}_3^-] = \log [\text{SO}_3^{2-}] - \text{pH} + 6.34 = \text{pH} - 8.65 \\
 &\log [\text{H}_2\text{SO}_3] = \log [\text{HSO}_3^-] - \text{pH} + 1.37 = -7.28
 \end{aligned}$$

From equilibrium 2 we see that log p_{SO_2} is less than — 7.

Provided that we have started with a pure sodium sulfite solution before

absorbing SO_2 , we find the following condition on the concentrations (the charge, or electroneutrality condition):

$$2 [\text{Ca}^{2+}] + [\text{Na}^+] + [\text{H}^+] = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{HSO}_3^-] + 2 [\text{SO}_3^{2-}] (+ [\text{OH}^-])$$

It will be immediately seen from the diagram that if $[\text{Na}^+]$ is 0.5 m or higher, $[\text{Ca}^{2+}]$ can certainly be neglected. The two predominant anionic species will be HCO_3^- and SO_3^{2-} ; since the ratios $[\text{HSO}_3^-]/[\text{HCO}_3^-] = 10^{-1.10} = 0.079$ and $[\text{CO}_3^{2-}]/[\text{SO}_3^{2-}] = 10^{-2.13} = 0.0074$, the charge condition will be:

$$[\text{Na}^+] = 1.079 [\text{HCO}_3^-] + 1.007 [\text{SO}_3^{2-}] \approx [\text{HCO}_3^-] + [\text{SO}_3^{2-}]$$

We may thus expect the processes suggested in part I to be favored by equilibrium: if SO_2 is sorbed in a Na_2SO_3 solution, and excess CaCO_3 added, so much CaSO_3 will precipitate that the solution will finally contain a considerable amount of HCO_3^- .

Kinetic experiments on the reaction of CaCO_3 with $\text{SO}_3^{2-} + \text{HSO}_3^-$ solutions have confirmed that the reaction goes quickly to an equilibrium state corresponding to a mixture $\text{HCO}_3^- + \text{SO}_3^{2-}$. In the temperature interval studied, the times for establishment of equilibrium were of the order of minutes or tens of minutes.

CHECK ON $\text{CaCO}_3 + \text{CaSO}_3$ EQUILIBRIUM

First a series of experiments were made, where solid CaCO_3 and CaSO_3 were shaken with various $\text{SO}_3^{2-} + \text{CO}_3^{2-}$ solutions in order to study the equilibrium $\text{CaCO}_3(\text{s}) + \text{SO}_3^{2-} \rightleftharpoons \text{CaSO}_3(\text{s}) + \text{CO}_3^{2-}$. However, in these alkaline solutions, the reactions proved to be very slow, and even after several weeks had not reached equilibrium. The analytical ratios $\text{CO}_3^{2-}/\text{SO}_3^{2-}$ kept changing and differed from each other and from any constant that could be calculated from the constants in Table 1. One reason may have been that the dissolution of CaCO_3 was inhibited, as may sometimes occur especially in the presence of traces of heavy metal ions (Erga and Terjesen¹¹).

Attempts were made instead to study equilibria such as those described in Fig. 1, in the presence of CaSO_3 , CaCO_3 and $\text{CO}_2(\text{g})$ of 1 atm pressure. In

Table 2. Equilibrium with $\text{CO}_2(\text{g})$, solid $\text{CaCO}_3 + \text{CaSO}_3(\text{H}_2\text{O})_{\frac{1}{2}}$ at 25°C.

$[\text{Na}^+]$	a	b	pH	$\log [\text{HCO}_3^-]$	$\log [\text{HSO}_3^-]$ (a), (b),	$\log K$ (a), (b)
1.0	0.1064	0.0140	6.52	-1.08	-2.22 -2.24	1.14 1.16
1.0	0.1334	0.0168	6.61	-0.99	-2.17 -2.22	1.18 1.23
3.5	0.1326	0.0193	6.99	-1.04	-2.30 -2.38	1.26 1.34
3.5	0.1333	0.0262	6.95	-1.08	-2.18 -2.22	1.10 1.14
3.5	0.0928	0.0228	6.81	-1.22	-2.25 -2.17	1.03 0.97

Note: Concentrations on M scale, except $[\text{Na}^+]$, which is 1.0 or 3.5 m.

$$a = [\text{HSO}_3^-] + 2 [\text{SO}_3^{2-}] + [\text{HCO}_3^-]$$

$$b = [\text{HSO}_3^-] + [\text{SO}_3^{2-}]$$

$$\text{pH} = -\log [\text{H}^+]$$

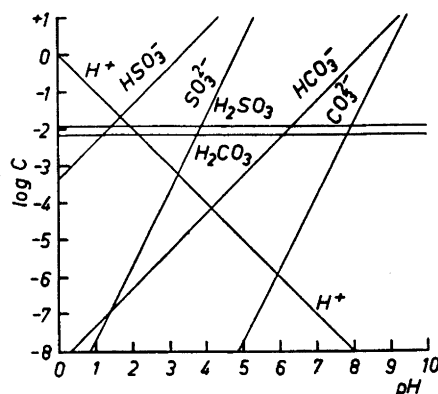


Fig. 2. Logarithmic diagram for aqueous solution in equilibrium with CO_2 of partial pressure 0.20 atm, and SO_2 of partial pressure 0.01 atm. Horizontal scale: pH, range of practical interest is between 2.5 and 4. Vertical axis: log of concentration of the various species.

this case, the equilibrium was established quite rapidly. From the original composition of the solution (a M NaHSO_3 or $2a$ M Na_2SO_3) one knows

$$a = [\text{HSO}_3^-] + 2[\text{SO}_3^{2-}] + [\text{HCO}_3^-]$$

One may neglect $[\text{CO}_3^{2-}]$.

The solutions were analysed for Ca^{2+} (which was negligible) and total sulfite

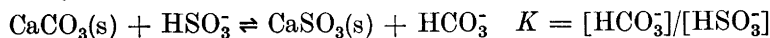
$$b = [\text{HSO}_3^-] + [\text{SO}_3^{2-}]$$

as described in Part I. For the calculations it was necessary to know the "pH" (as above, $-\log h$) which was measured for a sample of the equilibrium solution, still keeping it in 1 atm CO_2 atmosphere. Our experimental data are given in Table 2.

One could then calculate, using M units and the log K values 7.59 and 6.36 for 1 m Na^+ (for 3.5 m Na^+ 8.02 and 6.43):

$$\begin{aligned} [\text{HCO}_3^-] &= p_{\text{CO}_2} \cdot 10^{\text{pH}-7.59} \\ [\text{HSO}_3^-] &= \frac{a - [\text{HCO}_3^-]}{1 + 2 \cdot 10^{\text{pH}-6.36}} \quad \text{or} \quad [\text{HSO}_3^-] = \frac{b}{1 + 10^{\text{pH}-6.36}} \end{aligned}$$

Table 2 gives the values of log K for



calculated with $[\text{HSO}_3^-]$ obtained in the two ways above, from a or from b . The average values are 1.18 ± 0.05 (1 m Na^+) and 1.15 ± 0.20 (3.5 m Na^+). We may also calculate this constant by means of two combinations:

(5—7) + (10 + 6 — 1) gives log $K = 1.10$ (1 m Na^+) and 1.06 (3.5 m Na^+)
 (5—7 + (2 + 9 — 3) gives log $K = 1.21$ (1 m Na^+) and 1.24 (3.5 m Na^+)

The agreement with the direct equilibrium data is as good as might be expected.

SORPTION EQUILIBRIUM

We shall finally look at the equilibria in the sorption process. Let us suppose that the solution is brought to equilibrium with a flue gas with the partial pressures 0.01 atm for SO₂ and 0.20 atm for CO₂. By applying the equilibrium constants 2, 9, 10, 4, 7, and 8 for 25°C and 1 m Na⁺ in Table 1 we find

$$\begin{aligned}\log [\text{H}_2\text{SO}_3] &= -1.97 \\ \log [\text{HSO}_3^-] &= \log [\text{H}_2\text{SO}_3] + \text{pH} - 1.37 = \text{pH} - 3.34 \\ \log [\text{SO}_3^{2-}] &= \log [\text{HSO}_3^-] + \text{pH} - 6.34 = 2 \text{ pH} - 9.68 \\ \log [\text{H}_2\text{CO}_3] &= -1.51 - 0.70 = -2.21 \\ \log [\text{HCO}_3^-] &= -7.55 - 0.70 + \text{pH} = \text{pH} - 8.25 \\ \log [\text{CO}_3^{2-}] &= \log [\text{HCO}_3^-] + \text{pH} - 9.57 = 2 \text{ pH} - 17.82\end{aligned}$$

The corresponding logarithmic diagram is given in Fig. 2. The charge condition will be:

$$[\text{H}^+] + [\text{Na}^+] + 2 [\text{Ca}^{2+}] = [\text{HSO}_3^-] + 2 [\text{SO}_3^{2-}] + [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] (+ [\text{OH}^-])$$

It is easily seen from Fig. 2 that under these conditions any ions of carbonic acid will be very thoroughly removed from the solution and replaced by HSO₃⁻ ions.

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