Some Solution Equilibria Involving Calcium Sulfite and Carbonate

III. The Acidity Constants of $H_2CO_3$ and $H_2SO_3$, and $CaCO_3 + CaSO_3$
Equilibria in $NaClO_4$ Medium at $25^\circ C$

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A number of equilibrium constants have been determined, involving aqueous solutions, solid $CaSO_4(H_2O)_n$, $CaCO_3$ and $CaSO_4(H_2O)_4^+$ 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 $CO_3^-$ 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 $[H^+] = h$, and a silver-silver ion electrode as reference electrode:

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

$E_o$ 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).

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The main experiments were made as titrations of 200 mM Na$_2$CO$_3$ or 100 mM Na$_2$CO$_3$ (balance NaClO$_4$) with HClO$_4$, with careful addition and mechanical stirring, to prevent loss of CO$_3^2$-. For each point one could calculate, from the analytical data, $Z = [HCO_3^-] / ([HCO_3^-] + [CO_3^{2-}])$, 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 obtained. 3.

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:

- for [Na$^+$] = 1 000 mm ~ 950 mM: $K_{a2} = 10^{-9.59}$ M = 10$^{-9.57}$ m
- for [Na$^+$] = 3 500 mm ~ 3 000 mM: $K_{a2} = 10^{-9.63}$ M = 10$^{-9.56}$ 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-fitting 4 was applied, this error was immediately discovered because the apparent $Z$ curve was shifted (cf. Fig. 2 d in Ref 3); a correction could then easily be applied.

Titrations of NaHCO$_3$ with NaOH, applying mechanical stirring, gave somewhat smaller corrections, but we preferred the titrations of Na$_2$CO$_3$ 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 $E_1$.

FIRST ACIDITY CONSTANT OF CARBONIC ACID

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

$$\text{CO}_2(\text{g}) + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+; \text{K}_p\text{K}_{al} = [\text{H}^+][\text{HCO}_3^-] \rho_{\text{CO}_3^2}$$

In each point of the titration, one knows [H$^+$] = $h$ from the emf measurement, and [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 $E_1$.

After correction to $\rho_{\text{CO}_2} = 1$ atm, the following results were obtained from two experiments with each ionic strength, starting with 200 mM HCO$_3^-$:

- for Na$^+$ = 1 000 mm ~ 950 mM: $K_p\text{K}_{al} = 10^{-7.59}$ M$^2$ atm$^{-1} = 10^{-7.55}$ m$^2$ atm$^{-1}$
- for Na$^+$ = 3 500 mm ~ 3 000 mM: $K_p\text{K}_{al} = 10^{-8.62}$ M$^2$ atm$^{-1} = 10^{-8.88}$ m$^2$ atm$^{-1}$

These values may be combined with the values for $K_p$ found in part I,
- for 1 m Na$^+$, -1.51, -1.55 for 3.5 m Na$^+$, to give
- $-\log K_{al} = -6.04$ for 1 m Na$^+$, $-6.33$ for 3.5 m Na$^+$

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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 5), and \(-6.51\) (Kauko and Carlberg 6); \( \log K_{a2} = -10.25\) (MacInnes and Belcher 7) and \(-10.24\) (Kauko and Airola 8).

THE ACIDITY CONSTANTS OF \( \text{H}_2\text{SO}_3 \)

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 \( \text{SO}_2 \), from 0.16 to 1.2 M, and of the desired sodium concentration. By this procedure, losses of \( \text{SO}_2 \) 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 Leppla 9) 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

\[
\text{SO}_3^{2-} + \text{H}_2\text{SO}_3 \rightleftharpoons 2 \text{HSO}_3^{-}
\]

Table 1. Logarithms of measured and derived equilibrium constants.

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

Note: \(\text{CO}_2\) and \(\text{SO}_2\) are gaseous (pressure in atm), \(\text{H}_2\text{CO}_3\) and \(\text{H}_2\text{SO}_3\) are in aqueous solution. 
'\(\text{CaSO}_4\)' = \(\text{CaSO}_4(\text{H}_2\text{O})_2\), '\(\text{CaSO}_3\)' = \(\text{CaSO}_3(\text{H}_2\text{O})_4\) \(\text{CaCO}_3\) = calcite.

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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):

1 atm CO₂: log [H₂CO₃] = —1.51
log (HCO₃⁻) = pH — 7.55
CaCO₃(s): log [Ca²⁺] = —4.91 — 2 log [HCO₃⁻] = 10.19 — 2 pH
log [HSO₃⁻] = log [SO₃²⁻] — pH + 6.34 = pH — 8.65
log [H₂SO₃] = log [HSO₃⁻] — pH + 1.37 = — 7.28

From equilibrium 2 we see that log pSO₂ is less than — 7.
Provided that we have started with a pure sodium sulfite solution before

absorbing SO₂, we find the following condition on the concentrations (the charge, or electroneutrality condition):

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

It will be immediately seen from the diagram that if [Na⁺] is 0.5 m or higher, [Ca²⁺] can certainly be neglected. The two predominant anionic species will be HCO₃⁻ and SO₃²⁻; since the ratios [HSO₃⁻]/[HCO₃⁻] = 10⁻¹.1⁰ ≈ 0.079 and [CO₃²⁻]/[SO₃²⁻] = 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 SO₂ is sorbed in a Na₂SO₃ solution, and excess CaSO₃ added, so much CaSO₃ will precipitate that the solution will finally contain a considerable amount of HCO₃⁻.

Kinetic experiments on the reaction of CaCO₃ with SO₃²⁻ + HSO₃⁻ solutions have confirmed that the reaction goes quickly to an equilibrium state corresponding to a mixture HCO₃⁻ + SO₃²⁻. In the temperature interval studied, the times for establishment of equilibrium were of the order of minutes or tens of minutes.

CHECK ON CaCO₃ + CaSO₃ EQUILIBRIUM

First a series of experiments were made, where solid CaCO₃ and CaSO₃ were shaken with various SO₃²⁻ + CO₃²⁻ solutions in order to study the equilibrium CaCO₃(s) + SO₃²⁻ ⇌ CaSO₃(s) + CO₃²⁻. However, in these alkaline solutions, the reactions proved to be very slow, and even after several weeks had not reached equilibrium. The analytical ratios CO₃²⁻/SO₃²⁻ 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 CaCO₃ was inhibited, as may sometimes occur especially in the presence of traces of heavy metal ions (Erga and Terjesen 11).

Attempts were made instead to study equilibria such as those described in Fig. 1, in the presence of CaSO₃, CaCO₃ and CO₂(g) of 1 atm pressure. In

**Table 2. Equilibrium with CO₂(g), solid CaCO₃ + CaSO₃(H₂O)₄ at 25°C.**

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<thead>
<tr>
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</thead>
<tbody>
<tr>
<td></td>
<td>(a)</td>
<td>(b)</td>
<td></td>
<td>(a)</td>
<td>(b)</td>
<td>(a)</td>
</tr>
<tr>
<td>1.0</td>
<td>0.1064</td>
<td>0.0140</td>
<td>6.52</td>
<td>-1.08</td>
<td>-2.22</td>
<td>-2.24</td>
</tr>
<tr>
<td>1.0</td>
<td>0.1334</td>
<td>0.0168</td>
<td>6.61</td>
<td>-0.99</td>
<td>-2.17</td>
<td>-2.22</td>
</tr>
<tr>
<td>3.5</td>
<td>0.1326</td>
<td>0.0193</td>
<td>6.99</td>
<td>-1.04</td>
<td>-2.30</td>
<td>-2.38</td>
</tr>
<tr>
<td>3.5</td>
<td>0.1333</td>
<td>0.0262</td>
<td>6.95</td>
<td>-1.08</td>
<td>-2.18</td>
<td>-2.22</td>
</tr>
<tr>
<td>3.5</td>
<td>0.0928</td>
<td>0.0228</td>
<td>6.81</td>
<td>-1.22</td>
<td>-2.25</td>
<td>-2.17</td>
</tr>
</tbody>
</table>

Note: Concentrations on M scale, except [Na⁺], which is 1.0 or 3.5 m.

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

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

\[ \text{pH} = - \log [\text{H}^+] \]
this case, the equilibrium was established quite rapidly. From the original composition of the solution (a M NaHSO₃ or 2 a M Na₂SO₃) one knows

\[ a = [\text{HSO}_3^-] + 2[\text{SO}_4^{2-}] + [\text{HCO}_3^-] \]

One may neglect [CO₃²⁻].

The solutions were analysed for Ca²⁺ (which was negligible) and total sulfite

\[ b = [\text{HSO}_3^-] + [\text{SO}_4^{2-}] \]

as described in Part I. For the calculations it was necessary to know the "pH" (as above, −log b) which was measured for a sample of the equilibrium solution, still keeping it in 1 atm CO₂ 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):

\[
[\text{HCO}_3^-] = \frac{p_{\text{CO}_2} \cdot 10^{\text{pH}-7.59}}{a - [\text{HCO}_3^-] + 2.10^{\text{pH}-6.36}} \text{ or } [\text{HSO}_3^-] = \frac{b}{1 + 10^{\text{pH}-6.36}}
\]

Table 2 gives the values of log K for

\[
\text{CaCO}_3(s) + \text{HSO}_3^- \rightleftharpoons \text{CaSO}_3(s) + \text{HCO}_3^- \quad K = [\text{HCO}_3^-]/[\text{HSO}_3^-]
\]

calculated with [HSO₃⁻] 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 SO$_2$ and 0.20 atm for CO$_2$. By applying the equilibrium constants 2, 9, 10, 4, 7, and 8 for 25°C and 1 m Na$^+$ in Table 1 we find

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

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 HSO$_3^-$ ions.

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