Equilibrium Constants in the Ammonium Carbonate–Carbaminate System. The Acid Dissociation Constant of Carbamic Acid

FINN CHRISTENSSON, HANS C. S. KOEFOED, ALLAN C. PETERSEN and KAJ RASMUSSEN

Chemistry Department, Royal Veterinary and Agricultural University, 40 Thorvaldsensvej, DK-1871 Copenhagen V, Denmark

The equilibrium constant for the reaction

\[ \text{NH}_3 + \text{HCO}_3^- \rightleftharpoons \text{NH}_2\text{COO}^- + \text{H}_2\text{O} \]

the acid dissociation constant of carbamic acid, and the acid dissociation constant of the hydrogen carbonate ion, at the ionic strength 0.5 M and temperatures from 25 to 70 °C, have been determined from carbamate contents in equilibrated mixtures of ammonium chloride and sodium carbonate.

The formalism of the carbamic acid, ammonia, carbon dioxide equilibrium is well known and frequently given in textbooks. Despite its widespread occurrence and its simple formalism, the thermodynamics and kinetics of carbamate formation have not been studied since the early work of Faurschou in 1921–1924.

Faurschou estimated the equilibrium constant \( K_1 \) of

\[ \text{NH}_3 + \text{HCO}_3^- \rightleftharpoons \text{NH}_2\text{COO}^- + \text{H}_2\text{O} \]

to be \( 10^{9.36} \) M\(^{-1}\) at 18 °C and zero concentration from measurements in various \( \text{NH}_4^+ / \text{NH}_3 \) buffered solutions. The temperature dependence of \( K_1 \) was found to be small. An upper limit of \( 10^{-6} \) M\(^{-1}\) for the dissociation constant \( K_2 \) of carbamic acid at 0 °C was estimated from colorimetric measurements. The constants necessary for the calculation of \( K_1 \) and \( K_2 \) were estimated at the existing ionic strength by means of the cube root activity coefficient law.

In the present work \( K_1 \) and \( K_2 \) and the acid dissociation constant \( K_3 \) of the hydrogen carbonate ion were measured indirectly from analytic determinations of the carbamate contents in equilibrated mixtures of aqueous solutions of ammonium chloride and sodium carbonate. The ionic strength was kept constant at 0.5 M. The temperature was kept constant at different values from 25 to 70 °C. The constants are based on concentrations, and no corrections for activity coefficients have been made.

METHOD

The equilibrium constants in aqueous mixtures of \( \text{NH}_4\text{Cl} \) and \( \text{Na}_2\text{CO}_3 \) are defined as follows

\[ K_1 = [\text{NH}_2\text{COO}^-]/([\text{NH}_3][\text{HCO}_3^-]) \]  \hspace{1cm} (1)
\[ K_2 = [\text{H}^+][\text{NH}_2\text{COO}^-]/[\text{NH}_2\text{COOH}] \]  \hspace{1cm} (2)
\[ K_3 = [\text{H}^+][\text{CO}_3^-]/[\text{HCO}_3^-] \]  \hspace{1cm} (3)
\[ K_4 = [\text{H}^+][\text{NH}_3]/[\text{NH}_2^+] \]  \hspace{1cm} (4)
\[ K_5 = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2] \]  \hspace{1cm} (5)
\[ K_6 = [\text{H}^+][\text{OH}^-] \]  \hspace{1cm} (6)

In eqn. (5) and in the following, \([\text{CO}_2] \) means \([\text{CO}_2] + [\text{H}_2\text{CO}_3] \). The remaining equations connecting concentrations are

\[ C_{\text{NH}_4\text{Cl}} = [\text{NH}_4^+] + [\text{NH}_3] + [\text{NH}_2\text{COOH}] + [\text{NH}_2\text{COO}^-] \]  \hspace{1cm} (7)
\[ C_{\text{Na}_2\text{CO}_3} = [\text{CO}_3^-] + [\text{HCO}_3^-] + [\text{CO}_2] + [\text{NH}_2\text{COOH}] + [\text{NH}_2\text{COO}^-] \]  \hspace{1cm} (8)
\[ C_{\text{carbam.}} = [\text{NH}_2\text{COOH}] + [\text{NH}_2\text{COO}^-] \]  \hspace{1cm} (9)
\[ [\text{Na}^+] + [\text{H}^+] + [\text{NH}_2^+] = [\text{Cl}^-] + 2[\text{CO}_3^-] + [\text{HCO}_3^-] + [\text{NH}_2\text{COO}^-] \]  \hspace{1cm} (10)
Eqns. (7), (8) and (9) are trivial and eqn. (10) is obtained from the principle of electroneutrality. In all the mixtures \( C_{\text{NH}_4\text{Cl}} = \text{[Cl}^-\text{]} \) and \( C_{\text{Na}_2\text{CO}_3} = \frac{1}{2} [\text{Na}^+] \) are known from preparation. \( C_{\text{carbonate}} \) is determined as described below.

On the basis of the ten equations, where \( K_4, K_5, \) and \( K_6 \) are known, and under the assumption of constants independent of anything but ionic strength and temperature, it follows that \( K_1, K_2, \) and \( K_3 \) can be found from \( C_{\text{NH}_4\text{Cl}}, C_{\text{Na}_2\text{CO}_3} \) and \( C_{\text{carbonate}} \) in three different mixtures of ammonium chloride and sodium carbonate, if they have equal ionic strength and temperature. The equations are solved iteratively since no explicit expression for the calculation can be made.

The three mixtures were prepared with a choice of \( C_{\text{NH}_4\text{Cl}} \) and \( C_{\text{Na}_2\text{CO}_3} \) so as (1) to make the result nearly independent of \( K_5 \) and \( K_6, \) (2) to minimize the error on \( K_2, \) and (3) to obtain an ionic strength \( I = 0.5 \) M. However, such a choice can be made only if all equilibrium constants are known in advance. The first three mixtures were therefore chosen on the basis of estimated values of \( K_1, K_2, \) and \( K_3. \) The new values of \( K_1, K_2, \) and \( K_3 \) obtained from these mixtures were used for the next choice of mixtures and so forth. Generally three consecutive choices of mixtures (nine different solutions) were necessary at each temperature to obtain the constants in solutions with ionic strength calculated to be 0.50 M.

\( K_4 \) is the only constant needed with higher accuracy in advance and during the calculation. The assumption of constants independent of anything but ionic strength holds inside two decimal places for the literature values of \( pK_4. \) Therefore we assume that the literature values of \( pK_4 \) estimated for 0.5 M NaNO\(_3\) or NaClO\(_4\) are applicable here with an error less than 0.01.

EXPERIMENTAL

The mixtures were prepared from stock solutions of NH\(_4\)Cl (B.D.H. analytical reagent) and Na\(_2\)CO\(_3\) (Merck analytical). A small content (about 2\%) of NaHCO\(_3\) in the stock solutions of Na\(_2\)CO\(_3\) was determined by a combination of acidimetric and gravimetric (BaCO\(_3\)) determinations.

The slow conversion of carbaminate to carbonate in cold alkaline solution makes it possible to determine \( C_{\text{carbonate}}. \)

The aqueous solutions of NH\(_4\)Cl and Na\(_2\)CO\(_3\) were equilibrated at constant temperature in 100 ml closed bottles (24 – 72 h). Further standing did not change the result. The equilibrated mixtures were poured into an excess of cold 0.2 M NaOH in order to fix the total carbaminate content. The temperature after mixing should never exceed 20 °C, therefore in some experiments it was necessary to supercool the NaOH solution to about -6 °C. 1 M BaCl\(_2\) was then added in excess to total added Na\(_2\)CO\(_3\), and BaCO\(_3\) was filtered off by suction. The filtrate was heated in a closed bottle to about 90 °C for 3 h, cooled and filtered again. The last precipitated BaCO\(_3\), which is equivalent to \( C_{\text{carbonate}} \), was determined acidimetrically. 0.01 M BaCl\(_2\) was used at all quantitative transfers and washings of solid BaCO\(_3\).

As shown in Table 1, the analysis has been carried out with high accuracy. All measured volumina have been taken from modern piston burettes with a reproducibility of 0.002 ml or better (which was checked). All measurements were repeated at least six times and \( C_{\text{carbonate}} \) in Table 1 are averages.

RESULTS

The result appears from Tables 1 and 2. The variations of \( K_1 \) and \( K_3 \) with temperature correspond to the enthalpy changes of \(-10(1) \) and \(-11(2) \) kJ mol\(^{-1}\), respectively. In Table 2, the standard deviations of the constants \( K_1, K_2, \) and \( K_3 \) illustrate the reproducibility of the analytical results and some supposed

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>( C_{\text{NH}_4\text{Cl}} ) M</th>
<th>( C_{\text{Na}_2\text{CO}<em>3} + C</em>{\text{NaHCO}_3} ) (2.3 mol % NaHCO(_3)) M</th>
<th>( C_{\text{carbonate}}^a ) M × 10(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.0493</td>
<td>0.1817</td>
<td>3.623(3)</td>
</tr>
<tr>
<td>25</td>
<td>0.1755</td>
<td>0.1849</td>
<td>18.759(5)</td>
</tr>
<tr>
<td>25</td>
<td>0.4340</td>
<td>0.0596</td>
<td>5.461(6)</td>
</tr>
<tr>
<td>35</td>
<td>0.0496</td>
<td>0.1826</td>
<td>3.599(9)</td>
</tr>
<tr>
<td>35</td>
<td>0.1801</td>
<td>0.1896</td>
<td>20.334(7)</td>
</tr>
<tr>
<td>35</td>
<td>0.4355</td>
<td>0.0597</td>
<td>5.277(8)</td>
</tr>
<tr>
<td>50</td>
<td>0.0500</td>
<td>0.1842</td>
<td>3.179(11)</td>
</tr>
<tr>
<td>50</td>
<td>0.1881</td>
<td>0.1981</td>
<td>21.049(10)</td>
</tr>
<tr>
<td>50</td>
<td>0.4378</td>
<td>0.0601</td>
<td>4.602(11)</td>
</tr>
<tr>
<td>70</td>
<td>0.0505</td>
<td>0.1858</td>
<td>2.849(11)</td>
</tr>
<tr>
<td>70</td>
<td>0.2006</td>
<td>0.2113</td>
<td>24.016(13)</td>
</tr>
<tr>
<td>70</td>
<td>0.4411</td>
<td>0.0555</td>
<td>4.254(9)</td>
</tr>
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</table>

\( ^a \) Standard deviations on \( C_{\text{carbonate}} \) are based on mean of six measurements.

Table 2. Equilibrium constants in aqueous mixtures of NH₄Cl and Na₂CO₃ at ionic strength 0.5 M.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>pK₁</th>
<th>pK₂</th>
<th>pK₃</th>
<th>pK₄*</th>
<th>pK₅*</th>
<th>pK₆*</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>−0.328(4)</td>
<td>6.76(5)</td>
<td>9.58(1)</td>
<td>9.30(1)</td>
<td>6.02(2)</td>
<td>13.75(5)</td>
</tr>
<tr>
<td>35</td>
<td>−0.288(4)</td>
<td>6.61(7)</td>
<td>9.43(1)</td>
<td>9.00(1)</td>
<td>6.02(2)</td>
<td>13.45(5)</td>
</tr>
<tr>
<td>50</td>
<td>−0.182(6)</td>
<td>6.56(5)</td>
<td>9.26(2)</td>
<td>8.59(1)</td>
<td>6.02(2)</td>
<td>13.05(5)</td>
</tr>
<tr>
<td>70</td>
<td>−0.079(11)</td>
<td>6.49(2)</td>
<td>9.18(2)</td>
<td>8.10(0)</td>
<td>5.9(2)</td>
<td>12.5(5)</td>
</tr>
</tbody>
</table>

* Interpolated to I = 0.5 M from Refs. 4–6. † Interpolated to I = 0.5 M from Ref. 8.

Estimated errors on pK₄, pK₅, and pK₆ are the assumed uncertainties of literature values, used for the calculation of errors on pK₁, pK₂, and pK₃.

Fig. 1. The acid dissociation constant of HCO₃⁻.

Symbol | Ionic strength | Medium | Method | Ref.
---|---|---|---|---
■ 0 | — | H/AgCl | 8 |
▼ 0.08 | NaCl | H/AgCl | 8 |
△ 0.16 | NaCl | H/AgCl | 8 |
▲ 0.5 | NaCl | H/H | 11 |
+ 1.0 | NaClO₄ | H/H | 12 |
〇 0.5 | Na₂CO₃/ NH₄Cl | conc. | This work |

errors on K₄, K₅, and K₆. We have no check on the assumption of constants independent of anything but ionic strength and temperature, and therefore these standard deviations do not reflect the true error. However, as the values of K₃ are near the values expected from literature (Fig 1), we suppose that K₁ and K₂ are close to the true ones.

REFERENCES


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