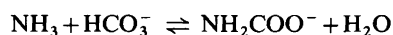


Equilibrium Constants in the Ammonium Carbonate–Carbaminate System. The Acid Dissociation Constant of Carbamic Acid

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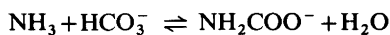
The equilibrium constant for the reaction



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 Faurholt in 1921–1924.^{1–2}

Faurholt estimated the equilibrium constant K_1 of



to be $10^{0.36} \text{ M}^{-1}$ 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.³

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 equi-

librated 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 NH_4Cl and Na_2CO_3 are defined as follows

$$K_1 = [\text{NH}_2\text{COO}^-]/([\text{NH}_3][\text{HCO}_3^-]) \quad (1)$$

$$K_2 = [\text{H}^+][\text{NH}_2\text{COO}^-]/[\text{NH}_2\text{COOH}] \quad (2)$$

$$K_3 = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] \quad (3)$$

$$K_4 = [\text{H}^+][\text{NH}_3]/[\text{NH}_4^+] \quad (4)$$

$$K_5 = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2] \quad (5)$$

$$K_6 = [\text{H}^+][\text{OH}^-] \quad (6)$$

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

$$C_{\text{NH}_4\text{Cl}} = [\text{NH}_4^+] + [\text{NH}_3] + [\text{NH}_2\text{COOH}] + [\text{NH}_2\text{COO}^-] \quad (7)$$

$$C_{\text{Na}_2\text{CO}_3} = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{CO}_2] + [\text{NH}_2\text{COOH}] + [\text{NH}_2\text{COO}^-] \quad (8)$$

$$C_{\text{carbam.}} = [\text{NH}_2\text{COOH}] + [\text{NH}_2\text{COO}^-] \quad (9)$$

$$[\text{Na}^+] + [\text{H}^+] + [\text{NH}_4^+] = [\text{Cl}^-] + 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{NH}_2\text{COO}^-] \quad (10)$$

Eqns. (7), (8) and (9) are trivial and eqn. (10) is obtained from the principle of electroneutrality. In all the mixtures $C_{\text{NH}_4\text{Cl}} = [\text{Cl}^-]$ and $C_{\text{Na}_2\text{CO}_3} = \frac{1}{2} [\text{Na}^+]$ are known from preparation. C_{carbam} 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_{carbam} 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 $\text{p}K_4$.⁴⁻⁶ Therefore we assume that the literature values of $\text{p}K_4$ 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_4Cl (B.D.H. analytical reagent) and Na_2CO_3 (Merck analytical). A small content (about 2%) of NaHCO_3 in the stock solutions of Na_2CO_3 was determined by a combination of acidimetric and gravimetric (BaCO_3) determinations.

The slow conversion of carbamate to carbonate in cold alkaline solution makes it possible to determine C_{carbam} .

The aqueous solutions of NH_4Cl and Na_2CO_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 carbamate 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_2CO_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_{carbam} , 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_{carbam} in Table 1 are averages.

RESULTS

The result appears from Tables 1 and 2. The variations of K_1 and K_2 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 1. Final experimental data.

Temp. °C	$C_{\text{NH}_4\text{Cl}}$ M	$C_{\text{Na}_2\text{CO}_3} + C_{\text{NaHCO}_3}$ (2.3 mol % NaHCO_3) M	C_{carbam}^a $\text{M} \times 10^3$
25	0.0493	0.1817	3.623(3)
25	0.1755	0.1849	18.759(5)
25	0.4340	0.0596	5.461(6)
35	0.0496	0.1826	3.599(9)
35	0.1801	0.1896	20.334(7)
35	0.4355	0.0597	5.277(8)
50	0.0500	0.1842	3.179(11)
50	0.1881	0.1981	21.049(10)
50	0.4378	0.0601	4.602(11)
70	0.0505	0.1858	2.849(11)
70	0.2006	0.2113	24.016(13)
70	0.4411	0.0555	4.254(9)

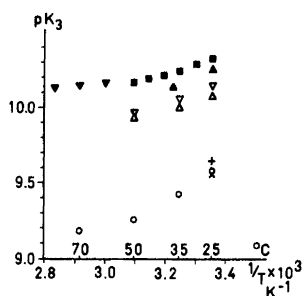
^a Standard deviations on C_{carbam} are based on mean of six measurements.

Table 2. Equilibrium constants in aqueous mixtures of NH_4Cl and Na_2CO_3 at ionic strength 0.5 M.

Temp. °C	$\text{p}K_1$	$\text{p}K_2$	$\text{p}K_3$	$\text{p}K_4^a$	$\text{p}K_5^b$	$\text{p}K_6^b$
25	-0.328(4)	6.76(5)	9.58(1)	9.30(1)	6.0(2)	13.7(5)
35	-0.288(4)	6.61(7)	9.43(1)	9.00(1)	6.0(2)	13.4(5)
50	-0.182(6)	6.56(5)	9.26(2)	8.59(1)	6.0(2)	13.0(5)
70	-0.079(11)	6.49(2)	9.18(2)	8.10(0)	5.9(2)	12.5(5)

^a Interpolated to $I=0.5$ M from Refs. 4–6. ^b Interpolated to $I=0.5$ M from Ref. 8.

Estimated errors on $\text{p}K_4$, $\text{p}K_5$, and $\text{p}K_6$ are the assumed uncertainties of literature values, used for the calculation of errors on $\text{p}K_1$, $\text{p}K_2$, and $\text{p}K_3$.

Fig. 1. The acid dissociation constant of HCO_3^- .

Symbol	Ionic strength	Medium	Method	Ref.
■	0	—	H/AgCl	8
▼	0	—	glass	9
▽	0.08	NaCl	H/AgCl	8
△	0.16	NaCl	H/AgCl	8
▲	0	—	H/H	10
+	0.5	NaCl	H/H	11
×	1.0	NaClO_4	glass	12
○	0.5	$\text{Na}_2\text{CO}_3/\text{NH}_4\text{Cl}$	conc.	This work

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errors on K_4 , K_5 , and K_6 . 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 K_3 are near the values expected from literature (Fig. 1), we suppose that K_1 and K_2 are close to the true ones.

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