Ammonia-Hydrochloric Acid Equilibrium Product

over Solid and Aqueous Ammonium Chloride at 25 °C

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Relative humidity dependence of the equilibrium product of NH_3 and HCl was thermodynamically calculated for ammonium chloride at 25 °C. This compound was found to be deliquescent at relative humidity greater than 77%, where the product began to decrease steeply. When the solution was treated as ideal, the product was mispredicted several factors higher than that for non-ideal solution.

Ammonium chloride and nitrate are of the major inorganic components of the urban aerosol. Their concentrations have been measured as those of fine-mode (particle diameter < 2 μm) chloride and nitrate, which exhibit a seasonal variation[1,2] associated with the change of air temperature.[2] These compounds are volatile and deliquescent under atmospheric conditions. Their thermodynamics is the key to interpret their atmospheric behaviors[3] such as the temperature dependence of the gas-particle distribution factors for chloride and nitrate species.[4] For solid and aqueous ammonium nitrate, the thermodynamics is fairly well studied in the atmospheric context[3,6] and some comparisons were made between the observed results and theoretical predictions.[5,7]

On the thermodynamics of ammonium chloride, however, few papers have been published so far. The temperature dependence of the equilibrium vapor pressure product, $P_{NH3} \cdot P_{HCl}$ over solid ammonium chloride has been calculated by some groups.[4,8,9,10,11] In this study, the equilibria for solid and aqueous ammonium chloride, shown in Reactions (1) and (2), are thermodynamically investigated.

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g) \qquad\qquad (1)$$

$$NH_4Cl(aq) \rightleftharpoons NH_3(g) + HCl(g) \qquad\qquad (2)$$
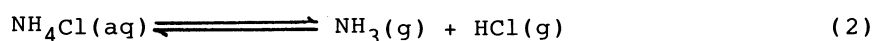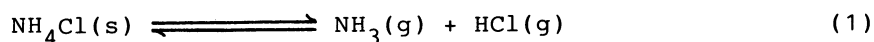
Expressions for the individual ammonia and hydrochloric acid partial pressures

over non-ideal ammonium chloride solution are derived by using the method presented by Stelson and Seinfeld for ammonium nitrate.[6]

Recent available free energy data for the NH_3-HCl-NH_4Cl system at 298 K are as follows:[12] $NH_3(g)$; -16.45, $HCl(g)$; -95.299, $NH_4Cl(s)$; -202.87, $NH_4Cl(aq)$; -210.52, $Cl^-(aq)$; -131.228, $H^+(aq)$; 0.0, $NH_4^+(aq)$; -79.31, $H_2O(l)$; -237.129, $NH_4OH(aq)$; -263.65 kJ mol^{-1}. These data yield the equilibrium constants for the NH_3-HCl-NH_4Cl system (Table 1). The equilibrium constants in Table 1 are thermodynamic equilibrium constants where pressure is reference to one atmosphere and aqueous solute concentration to unit molality.

Table 1. Equilibrium Constants for the NH_3-HCl-H_2O System at 298 K

No.	Reaction	Equilibrium constant
(1)	$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$	1.088×10^{-16}
(2)	$NH_4Cl(aq) \rightleftharpoons NH_3(g) + HCl(g)$	4.970×10^{-18}
(3)	$H^+(aq) + Cl^-(aq) \rightleftharpoons HCl(g)$	5.077×10^{-7}
(4)	$NH_4OH(aq) \rightleftharpoons H_2O(l) + NH_3(g)$	1.721×10^{-2}
(5)	$NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_4OH(aq)$	5.584×10^4
(6)	$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$	9.886×10^{13}

The internal consistency of the calculated equilibrium constants was examined in two ways as Stelson and Seinfeld did for the ammonium nitrate system:[6] First, K_2 should equal $K_3K_4K_5/K_6$. From the corresponding values in Table 1, $K_3K_4K_5/K_6$ becomes 4.935×10^{-18} whereas K_2 is 4.970×10^{-18}, which shows a good agreement with an error of 2.7%. Second, K_1 should equal K_2 a $_{NH4Cl}$ where a_{NH4Cl} is the activity for the saturated ammonium chloride solution. The value of Hamar and Wu[13] and K_2 in Table 1 give 8.70×10^{-17} for K_2 a $_{NH4Cl}$. This is 13% smaller than the value of K_1 in Table 1. The extent of the present internal consistency is almost the same as that for ammonium nitrate of Stelson and Seinfeld where the corresponding discrepancy are 9.2 and 3.6% for the first and second examinations, respectively.[6]

For ammonium chloride at 25 °C below 77% relative humidity (r.h.), the equilibrium product is K_1. Above 77% r.h., the equilibrium concentration product is given by[6]

$$P_{NH3} \cdot P_{HCl} = K_2 \gamma_{NH4^+} \gamma_{Cl^-} \, m_{NH4^+} \, m_{Cl^-}$$
$$= K_2 \, (\gamma_\pm)^2_{NH4Cl} \, m^2_{NH4Cl} \qquad (7)$$

where P, γ, and m are the partial pressure, activity coefficient, and molality of the chemical species indicated as the suffix, respectively, and $\gamma_\pm$ is the mean activity coefficient for NH_4Cl. The solution activity coefficient data are available,[13] and the product can be calculated for NH_4Cl molality. The relative humidity over the solution can be calculated as a function of NH_4Cl molality from the molal osmotic coefficient data.[6]

$$r.h. = 100.0 \, a_w = 100.0 \, \exp(-3.6031 \times 10^{-2} \, m_{NH4Cl} \, \phi_m) \qquad (8)$$

where a_w is the water activity and ϕ_m is the molal osmotic coefficient at m_{NH4Cl}. The equilibrium concentration product and the relative humidity are now both functions singly of m_{NH4Cl}. The equilibrium product is eventually expressed as a function of r.h. in ppb^2 for practical purpose (Fig. 1). The equilibrium product is found to be reduced rapidly over 77% r.h.: the product decreases to be one tenth at 90% r.h.

When the solution is treated as ideal, the broken line is obtained, predicting a larger value for the product at r.h.> ca. 77%. Misprediction of the deliquescence relative humidity is not so great as that for ammonium nitrate,[6] where the deliquescence relative humidity grossly decreased from 62% to 39% and that the equilibrium product was overestimated almost by an order of magnitude.

The present prediction for the logarithmic equilibrium product, $\log(P_{NH3} P_{HCl}/ppb^2)$= LEP = 2.037, over the solid state is somewhat higher than the non-ideal NH_4Cl solution curve at saturation (LEP=1.940). The measured vapor pressure extraporated to 25 °C,[8] LEP=1.994 is closer to the non-ideal prediction
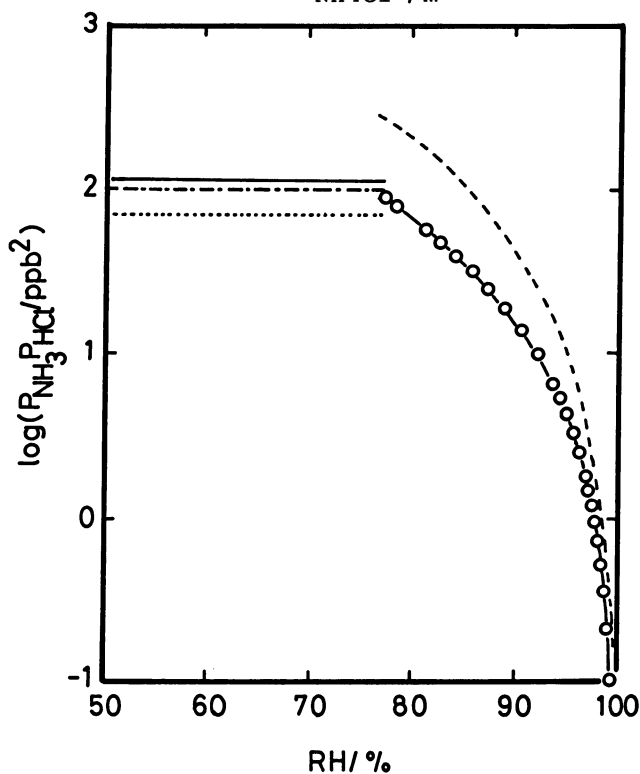

Fig. 1. Relative humidity dependence of the equilibrium product.

———— : non-ideal, ------ : ideal,

----------- : calc,[8]   —-—-—-— : meas.[8]

at saturation. However, a strictly calculated value[8] (LEP =1.839) for solid ammonium chloride is considerably lower than the non-ideal prediction. Less elaborated calculations have yielded closer results: 2.007,[4] 1.980,[9] and 1.990[10] for LEP. Further vapor pressure measurements for ammonium chloride under atmospheric temperature and relative humidity are required to be done.

The present calculation would help to interpret the observed concentration product, $P_{NH3} \cdot P_{HCl}$. This work is to be extended to temperatures other than 25 °C.

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