Problem 8-10 Balance of simultaneous equilibria in electrolyte solutions

0.2 mol of salmiac (NH_4Cl) together with 0.001 mol of ammonia (NH_3) were dissolved in 2 dm^3 of water.

(a) Write the equations which would permit to calculate pH. Don't solve.

(b) Calculate pH of the solution assuming that the water protolysis can be neglected. Acidity constant of NH_3 has the value of $5.6 \cdot 10^{-10}$ (standard state of infinite dilution, $c^{st} = 1$ mol dm^{-3}).

[(a) $K_1 = \dfrac{(c_{A0} + x)\cdot(x + y)}{(c_{S0} - x)}$, $K_2 = y \cdot (x + y)$; (b) pH = 6.951]

Solution:

$NH_4Cl = NH_4^+ + Cl^-$

$NH_4^+ = NH_3 + H^+$ conversion x $\quad K_1 = \dfrac{a_{NH_3} \cdot a_{H^+}}{a_{NH_4^+}}$

$H_2O = OH^- + H^+$ conversion y $\quad K_2 = a_{OH^-} \cdot a_{H^+}$

(a) Balance: NH_4Cl = S , NH_3 = A

$c_{S0} = 0.2/2 = 0.1$ mol dm^{-3}

$c_{A0} = 0.001/2 = 0.0005$ mol dm^{-3}

$c(NH_4^+) = c_{S0} - x$

$c(NH_3) = c_{A0} + x$

$c(H^+) = x + y$

$c(OH^-) = y$

$$K_1 = \frac{(c_{A0} + x)\cdot(x + y)}{(c_{S0} - x)}$$

$$K_2 = (x + y) \cdot y$$

$$pH = -\log (x + y)$$

(b) Neglecting water protolysis:

$K_1 = 5.6 \cdot 10^{-10}$

$$a_{H^+} = K_1 \cdot \frac{a_{NH_4^+}}{a_{NH_3}} \cong K_1 \cdot \frac{c_{S0}}{c_{A0}} = 5.6 \cdot 10^{-10} \cdot \frac{0.1}{0.0005} = 1.12 \cdot 10^{-7}$$

$pH = -\log a_{H^+} = 6.9508$