Problem 8-12 Balance of simultaneous equilibria in electrolyte solutions

2 dm^3 of aqueous solution contain 0.2 mol of HCl and 0.4 mol of NH_4Cl. What is pH of this solution at the temperature of 25 °C? Acidity constant of NH_3 has the value of $K_a = 5.6 \cdot 10^{-10}$, ionic product of water $K_w = 1.008 \cdot 10^{-14}$.

[pH = 8.949]

Solution:

$NH_4Cl = NH_4^+ + Cl^-$

$NH_4^+ = NH_3 + H^+$ conversion x $\quad K_a = \dfrac{a_{NH_3} \cdot a_{H^+}}{a_{NH_4^+}} = 5.6 \cdot 10^{-10}$

$H_2O = OH^- + H^+$ conversion y $\quad K_w = a_{OH^-} \cdot a_{H^+} = 1.008 \cdot 10^{-14}$

$c_0(NH_4Cl) = n(NH_4Cl)/V = 0.4/2 = 0.2$ mol dm^{-3}
$c_0(NH_3) = n(NH_3)/V = 0.2/2 = 0.1$ mol dm^{-3}

$c(NH_4^+) = c_0(NH_4Cl) - x$
$c(NH_3) = c_0(NH_3) + x$
$c(H^+) = x + y$
$c(OH^-) = y$

$$K_a = \frac{c_{NH_3} \cdot c_{H^+}}{c_{NH_4^+}} = \frac{(c_0(NH_3) + x) \cdot (x + y)}{c_0(NH_4Cl) - x} = 10^{-9.25} = 5.6234 \cdot 10^{-10}$$

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

$x << c_0(NH_4Cl)$, $x << c_0(NH_3)$

$$K_a = \frac{c_{NH_3} \cdot c_{H^+}}{c_{NH_4^+}} \cong \frac{c_0(NH_3) \cdot c_{H^+}}{c_0(NH_4Cl)}$$

$$c_{H^+} \cong K_a \cdot \frac{c_{0(NH_4Cl)}}{c_{0(NH_3)}} = 10^{-9.25} \cdot \frac{0.2}{0.1} = 1.12468 \cdot 10^{-9}$$

pH = –log c_{H^+} = –log $(1.12468 \cdot 10^{-9})$ = 8.949