

Problem 8-12 Balance of simultaneous equilibria in electrolyte solutions

2 dm³ of aqueous solution contain 0.2 mol of HCl and 0.4 mol of NH₄Cl. What is pH of this solution at the temperature of 25 °C? Acidity constant of NH₃ 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:



conversion x

$$K_a = \frac{a_{\text{NH}_3} \cdot a_{\text{H}^+}}{a_{\text{NH}_4^+}} = 5.6 \cdot 10^{-10}$$



conversion y

$$K_w = a_{\text{OH}^-} \cdot a_{\text{H}^+} = 1.008 \cdot 10^{-14}$$

$$c_0(\text{NH}_4\text{Cl}) = n(\text{NH}_4\text{Cl})/V = 0.4/2 = 0.2 \text{ mol dm}^{-3}$$

$$c_0(\text{NH}_3) = n(\text{NH}_3)/V = 0.2/2 = 0.1 \text{ mol dm}^{-3}$$

$$c(\text{NH}_4^+) = c_0(\text{NH}_4\text{Cl}) - x$$

$$c(\text{NH}_3) = c_0(\text{NH}_3) + x$$

$$c(\text{H}^+) = x + y$$

$$c(\text{OH}^-) = y$$

$$K_a = \frac{c_{\text{NH}_3} \cdot c_{\text{H}^+}}{c_{\text{NH}_4^+}} = \frac{(c_0(\text{NH}_3) + x) \cdot (x + y)}{c_0(\text{NH}_4\text{Cl}) - x} = 10^{-9.25} = 5.6234 \cdot 10^{-10}$$

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

$$x \ll c_0(\text{NH}_4\text{Cl}) \text{ , } x \ll c_0(\text{NH}_3)$$

$$K_a = \frac{c_{\text{NH}_3} \cdot c_{\text{H}^+}}{c_{\text{NH}_4^+}} \cong \frac{c_0(\text{NH}_3) \cdot c_{\text{H}^+}}{c_0(\text{NH}_4\text{Cl})}$$

$$c_{\text{H}^+} \cong K_a \cdot \frac{c_0(\text{NH}_4\text{Cl})}{c_0(\text{NH}_3)} = 10^{-9.25} \cdot \frac{0.2}{0.1} = 1.12468 \cdot 10^{-9}$$

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