Problem 8-06 Solution of weak base – acidity and dissociation constants

The measurement of pH of methylamine solution of the concentration 0.002 mol dm^{-3} at the temperature of 30.1 °C yielded the value pH = 10.87. Calculate the acidity constant of $CH_3NH_3^+$ and the dissociation constant of methylamine (both for standard state of infinite dilution, c^{st} = 1 mol dm^{-3}). Ionic product of water at 30.1 °C is $K_w = 1.484{\cdot}10^{-14}$ and all the activity coefficients can be taken as equal to one.

[$K_{BH+} = 1.104{\cdot}10^{-11}$, $K_{dis} = 1.344{\cdot}10^{-3}$]

Řešení:

Base is a substance accepting a proton: (notation: $CH_3NH_2 \equiv B$):

$$CH_3NH_2 + H^+ = CH_3NH_3^+ \qquad \text{reaction extent } \xi_1, \quad K_1 = \frac{c_{BH^+}}{c_B \cdot c_{H^+}} \cdot c^{st}, \qquad c^{st} = 1 \text{ mol dm}^{-3}$$

At the same time occurs the dissociation of water:

$$H_2O = H^+ + OH^- \qquad \text{reaction extent } \xi_2, \quad K_v = \frac{c_{H^+} \cdot c_{OH^-}}{(c^{st})^2} = 1.484{\cdot}10^{-14}$$

Acidity constant is the equilibrium constant of the reaction

$$CH_3NH_3^+ = CH_3NH_2 + H^+ \qquad K_{(CH_3NH_3^+)} (= K_{BH^+}) = \frac{1}{K_1}$$

$$(\ BH^+ \ = \ B \ + H^+)$$

Balance:

$$c_B = c_0 - x_1 \quad , \quad c_0 = 0.002 \text{ mol dm}^{-3} \quad , \quad x_1 = \xi_1/V$$

$$c_{BH^+} = x_1$$

$$c_{H^+} = x_2 - x_1 = 10^{-pH} = 10^{-10.87} = 1.349{\cdot}10^{-11} \text{ mol dm}^{-3}$$

$$c_{OH^-} = x_2 = \frac{K_v}{c_{H^+}} = \frac{1.484 \cdot 10^{-14}}{1.349 \cdot 10^{-11}} = 0.0011 \text{ mol dm}^{-3}$$

$$x_1 = x_2 - c_{H^+} = 0.0011 - 1.349 \cdot 10^{-11} \doteq 0.0011 \text{ mol dm}^{-3}$$

Acidity constant of BH^+

$$K_{BH^+} = \frac{1}{K_1} = \frac{c_B \cdot c_{H^+}}{c_{BH^+}} = \frac{(0.002 - 0.0011) \cdot 1.349 \cdot 10^{-11}}{0.0011} = 1.104 \cdot 10^{-11}$$

Dissociation constant of methylamine:

$$CH_3NH_2 + H_2O = CH_3NH_3^+ + OH^- \qquad K_{dis} = \frac{K_w}{K_{BH^+}} \left(= \frac{c_{B^+} \cdot c_{OH^-}}{c_B} \right) \quad (a_{H_2O} = 1)$$

$$K_{dis} = \frac{K_w}{K_{BH^+}} = \frac{1.484 \cdot 10^{-14}}{1.104 \cdot 10^{-11}} = 1.344 \cdot 10^{-3}$$