Problem 8-05 Solution of weak base – pH

What is pH value of the ammonia solution with concentration of 0.002 mol dm^{-3} at the temperature of 20 °C. The value of acidity constant of ion NH_4^+ is $5.56\cdot10^{-10}$ and the ionic product of water is $K_w = 6.8\cdot10^{-15}$ (both for standard state of infinite dilution, c^{st} = 1 mol dm^{-3}). You can assume that the amount of hydrogen ions formed by water autoprotolysis is negligible small and all activity coefficients are equal to one.

[pH = 10.345]

Solution:

NH_4^+ acidity constant is the equilibrium constant of the reaction

$NH_4^+ = NH_3 + H^+$ $\qquad K_{(NH_4^+)} = 5.6\cdot10^{-10}$

We take into consideration two simultaneous reaction:

- base NH_3 accepts proton
  $NH_3 + H^+ = NH_4^+$ $\qquad K = 1/K_{(NH_4^+)}$ ..... reaction extent ξ_1 , $x_1 = \xi_1/V$
- water dissociation
  $H_2O = H^+ + OH^-$ $\qquad K_v = 6.8\cdot10^{-15}$ ..... reaction extent ξ_2 , $x_2 = \xi_2/V$

Balance:

$$c_{NH_3} = c_0 - x_1 \quad , \quad c_0 = 0.002 \text{ mol dm}^{-3}$$

$$c_{NH_4^+} = x_1$$

$$c_{OH^-} = x_2$$

$$c_{H^+} = x_2 - x_1 \to 0 \qquad \Rightarrow \quad x_1 \approx x_2 \equiv x$$

$$K_w \approx c_{H^+} \cdot c_{OH^-}$$

$$K = \frac{1}{K_{NH_4^+}} = \frac{c_{NH_4^+}}{c_{NH_3} \cdot c_{H^+}}$$

$$\frac{K_w}{K_{NH_4^+}} = \frac{c_{NH_4^+} \cdot c_{OH^-}}{c_{NH_3}} = \frac{x^2}{c_0 - x}$$

$$\frac{6.8\cdot10^{-15}}{5.56\cdot10^{-10}} = \frac{x^2}{0.002 - x}$$

$$1.223\cdot10^{-5}\cdot0.002 - 1.223\cdot10^{-5}\cdot x = x^2$$

$$x = -6.115\cdot10^{-6} \pm (3.73945\cdot10^{-11} + 2.446\cdot10^{-8})^{1/2} =$$

$$= -6.115\cdot10^{-6} + 1.56516\cdot10^{-4} = 1.504\cdot10^{-4} \text{ mol dm}^{-3}$$

pOH = –log $1.504\cdot10^{-4}$ = 3.82275

pH = –log K_w – pOH = –log ($6.8\cdot10^{-15}$) – 3.82275 = –(–14.16749) – 3.82275 = 10.3447

pH = 10.345

Note: Acidity constant and dissociation constant are connected by a relation:

$NH_3 + H_2O = NH_4^+ + OH^-$ $\qquad K = \dfrac{K_w}{K_{ac\,(NH_4^+)}} = \dfrac{c_{NH_4^+} \cdot c_{OH^-}}{c_{NH_3} \cdot c^{st}} \qquad (a_{H_2O} = 1)$