Problem 8-07 Solution of the salt of the weak base and weak acid

Aqueous solution of the salt of weak acid (AH) and weak base (BOH) at the temperature of 25 °C and concentration of 0.0025 mol dm^{-3} has pH = 9.65. Calculate the dissociation constant of the weak acid in question, if you know that the dissociation constant conjugated to the weak base BOH has the value of $K_{B+} = 1.32 \cdot 10^{-9}$ (all for standard state of infinite dilution, $c^{st} = 1$ mol dm^{-3}, and unit activity coefficients).

[$K_{dis\,(HA)} = 3.26 \cdot 10^{-11}$]

Solution:

The salt of weak base and weak acid BA is completely dissociated to ions

$$BA = B^+ + A^-$$

which undergo by further reactions with water:

(1) $A^- + H_2O = AH + OH^-$ $\quad x_1 = \xi_1/V$ $\quad K_1 = \dfrac{K_w}{K_{dis\,(HA)}}$

$AH = H^+ + A^-$ $\quad K_{dis(HA)}$

$H_2O = H^+ + OH^-$ $\quad K_w$

(2) $B^+ + H_2O = BOH + H^+$ $\quad x_2 = \xi_2/V$ $\quad K_2 = K_{B+}$ (dissociation constant conjugated acid B^+)

(3) $H_2O = H^+ + OH^-$ $\quad x_3 = \xi_3/V$ $\quad K_3 = K_w$

Balance:

Initial concentration of the salt BA: $c_0 = 0.0025$ mol dm^{-3}

$c_{A^-} = c_0 - x_1$

$c_{B^+} = c_0 - x_2$

$c_{HA} = x_1$

$c_{BOH} = x_2$

$c_{H^+} = x_2 + x_3$ $\quad$ pH = 9.65 $\Rightarrow$ $c_{H^+} = 10^{-9.65} = 2.26872 \cdot 10^{-10}$ mol dm^{-3}

$c_{OH^-} = x_1 + x_3$ $\quad K_v = 1 \cdot 10^{-14} = c_{H^+} \cdot c_{OH^-}$ $\quad (c^{st} = 1$ mol dm$^{-3})$

$$c_{OH^-} = \frac{K_w}{c_{H^+}} = \frac{10^{-14}}{2.23872 \cdot 10^{-10}} = 4.467 \cdot 10^{-5} \text{ mol dm}^{-3}$$

$$K_1 = \frac{K_w}{K_{dis\,(HA)}} = \frac{c_{AH} \cdot c_{OH^-}}{c^{st} \cdot c_{A^-}} = \frac{x_1 \cdot (x_1 + x_3)}{c^{st} \cdot (c_0 - x_1)} \quad , \quad (c^{st} = 1 \text{ mol dm}^{-3})$$

$$\frac{1 \cdot 10^{-14}}{K_{dis\,(HA)}} = \frac{x_1 \cdot 4.467 \cdot 10^{-5}}{2.5 \cdot 10^{-3} - x_1}$$

$$K_2 = K_{ac\,(BOH)} = \frac{c_{BOH} \cdot c_{H^+}}{c_{B^+}} = \frac{x_2 \cdot (x_2 + x_3)}{c_0 - x_2}$$

$$1.32 \cdot 10^{-9} = \frac{x_2 \cdot 2.23872 \cdot 10^{-5}}{2.5 \cdot 10^{-3} - x_2}$$

$$1.32 \cdot 10^{-9} \cdot 2.5 \cdot 10^{-3} - 1.32 \cdot 10^{-9} \cdot x_2 = x_2 \cdot 2.23872 \cdot 10^{-10}$$

$$x_2 = \frac{1.32\cdot10^{-9}\cdot2.5\cdot10^{-3}}{1.32\cdot10^{-9}+2.23872\cdot10^{-10}} = 2.1375\cdot10^{-3}$$

$$c_{OH^-} - c_{H^+} = x_1 + x_3 - x_2 - x_3 = x_1 - x_2$$

$$x_1 = c_{OH^-} - c_{H^+} + x_2 = 4.467\cdot10^{-5} - 2.23872\cdot10^{-10} + 2.1375\cdot10^{-3} = 2.18217\cdot10^{-3}$$

$$K_{dis\,(HA)} = \frac{K_w}{x_1\cdot c_{OH^-}}\cdot(c_0 - x_1) = \frac{1\cdot10^{-14}}{2.18217\cdot10^{-3}\cdot4.467\cdot10^{-5}}\cdot(0.0025 - 2.18217\cdot10^{-3})$$

$K_{dis\,(HA)} = 3.26\cdot10^{-11}$