Problem 6-03 Equilibrium constant, equilibrium mixture composition, temperature dependence

Lyases are enzymes catalyzing non-hydrolytic decompositions of substrates into two components:

$$\mathbf{AB = A + B}\ .$$

(a) Calculate the equilibrium constant of this reaction at the temperature of 25 °C for standard state infinite dilution at given temperature and pressure, $c^{st} = 1$ mol dm^{-3} if you know that in the solution initially containing 0.4 mol AB and 0.1 mol B in 1 dm^3, in equilibrium was found 22.4 mmol of A in 1 dm^3. You can assume that all activity coefficients are equal to one.

(b) What would be the values of equilibrium concentrations of AB, A, and B, if the initial solution contained only AB in concentration 7.6 mmol dm^{-3}?

(c) The reaction enthalpy has the value of 42.8 kJ mol^{-1}, and it can be taken as constant at the temperature interval under consideration. At which temperature will be the reaction yield twice larger than that reached ad (a) – i.e. at 25 °C?

[(a) $K_1 = 7.261 \cdot 10^{-3}$; (b) $c_A = c_B = 0.004638$ mol dm^{-3} , $c_{AB} = 0.002963$ mol dm^{-3}, (c) $T_2 = 315$ K]

Solution:

(a) $T_1 = 298.15$ K

$c_{AB,0} = 0.4$ mol dm^{-3}
$c_{A,0} = 0.1$ mol dm^{-3}

$c_{AB} = c_{AB,0} - x = 0.4 - 0.0224 = 0.3776$ mol dm^{-3}
$c_A = x = 0.0224$ mol dm^{-3}
$c_B = c_{B0} + x = 0.1 + 0.0224 = 0.1224$ mol dm^{-3}
$c^{st} = 1$ mol dm^{-3}

$$K_1 = \frac{a_A \cdot a_B}{a_{AB}} = \frac{\frac{c_A}{c^{st}} \cdot \frac{c_B}{c^{st}}}{\frac{c_{AB}}{c^{st}}} = \frac{0.0224 \cdot 0.1224}{0.3776} = 7.261 \cdot 10^{-3}$$

(b) $c_{AB,0} = 0.0076$ mol dm^{-3}
$c_{AB} = c_{AB,0} - x$
$c_A = c_B = x$

$$K_1 = 7.261 \cdot 10^{-3} = \frac{x^2}{c_{AB,0} - x} = \frac{x^2}{0.0076 - x}$$

$$x^2 + 7.261 \cdot 10^{-3}\ x - 5.5183 \cdot 10^{-5} = 0$$

$$x = -3.6305 \cdot 10^{-3} \pm (1.318053 \cdot 10^{-5} + 5.5183 \cdot 10^{-5})^{1/2}$$
$$= -3.6305 \cdot 10^{-3} \pm 8.26826 \cdot 10^{-3}$$

$x = c_A = c_B = 0.0046377$ mol dm^{-3}
$c_{AB} = 0.0076 - 0.0046377 = 0.0029627$ mol dm^{-3}

(c) $T_2 = ?$, $\Delta_r H^\ominus = 42800$ J mol^{-1}
$c_{AB,0} = 0.4$ mol dm^{-3}
$c_{A,0} = 0.1$ mol dm^{-3}

$c_{AB} = c_{AB,0} - x = 0.4 - 0.0448 = 0.3552$ mol dm^{-3}
$c_A = x = 2 \cdot 0.0224 = 0.0448$ mol dm^{-3}
$c_B = c_{B0} + x = 0.1 + 0.0448 = 0.1448$ mol dm^{-3}

$$K_2 = \frac{c_{\mathrm{A}} \cdot c_{\mathrm{B}}}{c_{\mathrm{AB}}} = \frac{0.0448 \cdot 0.1448}{0.3552} = 1.8263 \cdot 10^{-2}$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta_{\mathrm{r}} H^{\ominus}}{\boldsymbol{R}} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\frac{1}{T_2} = \frac{1}{T_1} - \frac{\boldsymbol{R}}{\Delta_{\mathrm{r}} H^{\ominus}} \cdot \ln \frac{K_2}{K_1} = \frac{1}{298.15} - \frac{8.314}{4280} \cdot \ln \frac{1.8263 \cdot 10^{-2}}{7.261 \cdot 10^{-3}} = 0.003354 - 0.00017917$$

$$= 3.17483 \cdot 10^{-3}$$

$T_2 = 315$ K