Problem 7-03 Two simultaneous reactions in solution, calculation of equilibrium composition

Substance A decomposes in two possible ways

$$A = R + S \qquad (1)$$

$$A = B + D \qquad (2)$$

The equilibrium constants have the following values for the standard state infinite dilution, $c^{st} = 1$ mol dm^{-3}: $K_1 = 0.32$ and $K_2 = 1.28$. The equilibrium solution contains all components, A, B, D, R, and S. What is its composition (in mol. %)? The initial solution contained only the substance A in concentration $c_{A0} = 0.1$ mol dm^{-3}. Assume that activity coefficients are equal to one.

[1.652 mol. % A; 16.391 mol. % R; 16.391 mol. % S; 32.783 mol. % B; 32.783 mol. % D]

Solution:

Balance:

$$c_A = c_{A0} - x_1 - x_2$$
$$c_R = x_1$$
$$c_S = x_1$$
$$c_B = x_2$$
$$c_D = x_2$$
$$\Sigma c = c_{A0} + x_1 + x_2$$

Ideal behaviour: $a_i = c_i / c^{st}$ $(\gamma_i = 1)$

$$K_1 = \frac{c_R \cdot c_S}{c_A} \cdot \frac{1}{c^{st}} = \frac{x_1^2}{c_{A0} - x_1 - x_2} \quad (c^{st} = 1 \text{ mol dm}^{-3})$$

$$K_2 = \frac{c_B \cdot c_D}{c_A} \cdot \frac{1}{c^{st}} = \frac{x_2^2}{c_{A0} - x_1 - x_2} \quad (c^{st} = 1 \text{ mol dm}^{-3})$$

$$\Big\} \quad \frac{x_2}{x_1} = \left(\frac{K_2}{K_1}\right)^{1/2} = \left(\frac{1.28}{0.32}\right)^{1/2} = 2$$

$x_2 = 2\, x_1$

$$K_2 = 1.28 = \frac{4\, x_1^2}{0{,}1 - x_1 - 2\, x_1}$$

$$4\, x_1^2 + 3.84\, x_1 - 0.128 = 0$$

$$x_1 = \frac{-3.84 \pm (3.84^2 + 4 \cdot 4 \cdot 0.128)^{1/2}}{2 \cdot 4} = 0.03225$$

$x_2 = 2 \cdot 0.03225 = 0.0645$

$c_A = 0.1 - 0.03225 - 0.0645 = 0.00325$..... 1.652 mol.% A

$c_R = 0.03225$ .....16.391 mol % R

$c_S = 0.03225$ .....16.391 mol % S

$c_B = 0.0645$ .....32.783 mol % B

$c_D = 0.0645$ .....32.783 mol % D

$\Sigma c = 0.1 + 0.03225 + 0.0645 = 0.19675$