## Problem 7-01 Two simultaneous reactions in solution, calculation of equilibrium constants

Two simultaneous reactions, which can be schematically written as

$$\mathrm{A\ (aq) = R\ (aq) + 2S\ (aq)} \qquad (1)$$

$$\mathrm{A\ (aq) = B\ (aq)} \qquad (2)$$

are taking place in a solution initially containing only A in concentration $c_{A0} = 0.15$ mol dm$^{-3}$. Equilibrium mixture of A, B, R, and S contained 28.57 mol. % S and 35.71 mol. % B. Calculate equilibrium constants of both reactions assuming that all activity coefficients are equal to one. Standard state: infinite dilution, $c^{st} = 1$ mol dm$^{-3}$.

[$K_1 = 2.4\cdot10^{-3}$; $K_2 = 1.667$]

Solution:

Balance:

$$c_A = c_{A0} - x_1 - x_2$$
$$c_R = x_1$$
$$c_S = 2\,x_1$$
$$c_B = x_2$$
$$\Sigma c = c_{A0} + 2\,x_1$$

$c_{A0} = 0.15$ mol dm$^{-3}$

$c^{st} = 1$ mol dm$^{-3}$

$$\frac{c_S}{\Sigma c} = \frac{2\,x_1}{c_{A0} + 2\,x_1} = 0.2857 \quad \Rightarrow \quad x_1 = \frac{0.2857\cdot 0.15}{2\cdot(1-0.2857)} = 0.03$$

$$\frac{c_B}{\Sigma c} = \frac{x_2}{c_{A0} + 2\,x_1} = 0.3571 \quad \Rightarrow \quad x_2 = 0.3571\cdot(0.15 + 2\cdot 0.03) = 0.075$$

$$K_1 = \frac{a_R\cdot a_S^2}{a_A} = \frac{c_R\cdot c_S^2}{c_A}\cdot\frac{1}{(c^{st})^2} = \frac{x_1\cdot(2\,x_1)^2}{c_{A0} - x_1 - x_2} = \frac{4\cdot 0.03^3}{0.15 - 0.03 - 0.075} = 2.4\cdot10^{-3}$$

$$K_2 = \frac{a_B}{a_A} = \frac{c_B}{c_A} = \frac{x_2}{c_{A0} - x_1 - x_2} = \frac{0.075}{0.15 - 0.03 - 0.075} = 1.667$$