Problem 7-02 Two simultaneous reactions in solution, calculation of equilibrium constants

In a solution initially containing the components A and R in concentrations $c_{A0} = 0.07$ mol dm^{-3} and $c_{R0} = 0.25$ mol dm^{-3} two simultaneous reactions are taking place:

$$\text{R (aq)} = \text{D (aq)} + \text{S (aq)} \qquad (1)$$

$$\text{A (aq)} + \text{R (aq)} = 2\ \text{B (aq)} \qquad (2)$$

Equilibrium mixture of A, R, B, D, and S contained 20 mol. % D and 22 mol. % B. Calculate the equilibrium constants for the standard states infinite dilution, $c^{st} = 1$ mol dm^{-3}. Activity coefficients can be considered as equal to one.

[$K_1 = 0.0508$; $K_2 = 2.3639$]

Solution:

$c_{A0} = 0.07$ mol dm^{-3}
$c_{R0} = 0.25$ mol dm^{-3}
$c^{st} = 1$ mol dm^{-3}

Balance:

$c_R = c_{R0} - x_1 - x_2$
$c_A = c_{A0} - x_2$
$c_D = x_1$
$c_S = x_1$
$c_B = 2\ x_2$
$\Sigma c = c_{A0} + c_{R0} + x_1$

$$\frac{c_D}{\Sigma c} = \frac{x_1}{c_{A0} + c_{R0} + x_1} = 0.2 \quad \Rightarrow \quad x_1 = \frac{0.32 \cdot 0.2}{1 - 0.2} = 0.08$$

$$\frac{c_B}{\Sigma c} = \frac{2\ x_2}{c_{A0} + c_{R0} + x_1} = 0.22 \quad \Rightarrow \quad x_2 = ½ \cdot 0.22 \cdot (0.07 + 0.25 + 0.08) = 0.044$$

$$K_1 = \frac{a_D \cdot a_S}{a_R} = \frac{c_D \cdot c_S}{c_R} \cdot \frac{1}{c^{st}} = \frac{x_1 \cdot x_1}{c_{R0} - x_1 - x_2} = \frac{0.08^2}{0.25 - 0.08 - 0.044}$$

$K_1 = 0.050794$

$$K_2 = \frac{a_B^2}{a_A \cdot a_R} = \frac{c_B^2}{c_A \cdot c_R} = \frac{(2\ x_2)^2}{(c_{A0} - x_2) \cdot (c_{R0} - x_1 - x_2)} = \frac{4 \cdot 0.044^2}{(0.07 - 0.044) \cdot (0.25 - 0.08 - 0.044)}$$

$K_2 = 2.3639$