Set 6 Solutions

(a)

The first stage it to lay out how you are going to solve the problem. To solve this problem we must first determine the ionic strength of the KNO_3 solution, and then determine the ionic strength of a solution of 2.73 g of $Ca(NO_3)_2$ dissolved in 500g of the KNO_3 solution. The sum of these two contributions to the ionic strength determines the ionic strength of the final solution (which should be 0.025). **[1]**

1 Find the ionic strength of the KNO_3 solution.

The ionic strength of a solution is given by:

$$I = \frac{1}{2}\sum_j z_j^2 b_j$$

The z_j are the charges on the ions (in units of the electronic charge), b is the molality of the solution expressed in terms of the standard - one mol kg^{-1}, and the sum is over all i ions in the solution. **[1]**

We know that b= 0.150, hence to determine $I(KNO_3)$ we must first determine the charges on the ions in solution.

KNO^3 (aq) → K^+(aq) + NO^{3-}(aq),

hence both zs are 1, and thus, I (KNO_3)= 0.150. **[1]**

2 Now calculate the ionic strength of the $Ca(NO_3)_2$ solution.

$Ca(NO_3)_2$ (aq) → Ca^{2+}(aq) + 2 NO_3^-(aq),

Thus, $z(Ca^{2+})$ = 2 and $z(NO_3^-)$ = -1.

b is the number of moles of solute per kg of solvent; **[1]**

We are told there is 0.500 kg of solvent, thus to determine b we must first determine the number of moles of $Ca(NO_3)_2$ in 2.73 g of it, then divide this by the mass of the solvent.

n = mass/molar mass = 2.73/164 = 0.0166 moles.

Hence b = 0.01665/0.500 = 0.033 mol kg-1. **[1]**

Substituting these values into the equation for the ionic strength gives
$I = ½ [2^2 + -1^2 + -1^2]$ 0.033 = 0.100
Hence the ionic strength increases from 0.150 to 0.250; as required. **[1]**

(b)

The activities of the solutions can be estimated by both the Debye Huckel limiting law and the Extended Debye-Huckel law **[0.5]**. However, in the present case, the concentrations of the solutions are so low that the Limiting law would provide acceptable estimates **[0.5]**.

[This part of the answer shows that I know what I need to answer the question. I then goes on to justify the use of the simpler limiting law based on the data. In doing so I also shows that I know the conditions under which the use of the limiting law is justified]

The Limiting law states that

$$\text{Log}\ \gamma_{\pm} = -A|z_{+}\ z_{-}|\ I^{½}$$

A is an empirical parameter with a value of 0.509 for aqueous solutions, the *z*s are the charge numbers on the positive and negative ions, and *I* is the ionic strength of the solution; as defined in the answer to Part (a) above. **[1 for the equation and defining the terms]**.

Therefore, to find the mean activity coefficients, we first need to find the ionic strength.

The reaction is $CaCl_2 + NaF \rightarrow Ca^{2+}(aq) + Na^{+}(aq) + 2\ Cl^{-}(aq) + F^{-}(aq)$

The molalities are: 0.010 mol kg^{-1} for $CaCl_2$ (aq), and 0.030 mol kg^{-1} for NaF (aq). **[0.5 for putting these given data in the context of answering the question]**

Thus, the ionic strength of the solution is: $I = ½\ [2^2 \text{ x } 0.010(Ca^{2+}) + 1^2 \text{ x } 0.030(Na^{+}) + 1^2 \text{ x } 0.010\ (Cl^{-})\ +\ 1^2 \text{ x } 0.010\ (Cl^{-}) + 1^2 \text{ x } 0.030(F^{-})] = 0.060$ **[1]**

$z^{+} = 1 \text{ x } 2\ z^{-} = -1 \text{ x } -1 \text{ x } -1$. Hence $|z_{+}z_{-}| = 2$ **[0.5]**

Hence, $\log \gamma_{\pm} = -\ 0.509 \times 2 \times 0.060^{½} = 0.2494 \Rightarrow \gamma_{\pm} = 0.56$ **[1]**

(You could also treat the two contributions separately and add them to find the total – as in the method in Question 1 above)

The activity is given by the product of the activity coefficient and the molality $a = \gamma_{\pm}b$ **[0.5]**

For $CaCl_2$, the activity = $a = \gamma_{\pm}b$ = 0.56 x 0.010 = 0.0056; and for NaF, the activity = $a = \gamma_{\pm}b$ = 0.56 x 0.030 = 0.017. The total activity is the sum of these components = 0.017 + 0.0056 = 0.023 **[1.5]**

(c) (i)

The extended Debye-Huckel law is:

$$\log \gamma_{\pm} = \frac{-A|z_{+}z_{-}|I^{\frac{1}{2}}}{1 + BI^{\frac{1}{2}}}$$

All terms are those defined for the limiting law except that *B* is a further empirical parameter. **[1]**

We are asked to determine *B* under the stated conditions; hence we should rearrange the equation in terms of *B*

$$B = \frac{-A|z_{+}z_{-}|}{\log \gamma_{\pm}} - \frac{1}{I^{\frac{1}{2}}}$$

[2]

The empirical parameter *A* has a value of 0.509, and we know the values for γ under the conditions (and hence can easily determine their respective log $\gamma_{\pm}$), therefore we only need to determine the values for the ionic strengths, *I*.

$$I = \frac{1}{2}\sum_{j} z_j^2 b_j$$

[**1** for putting the given data and the previously defined equation in terms of the question]

The reaction is HBr ⟶ H^{+} (aq) + Br^{-} (aq), hence all charge numbers are + 1 and – 1. **[1]**

For the 5.0 x 10^{-3} molal solution with $\gamma_{\pm}$ = 0.930:

I = ½[1^2 +(-1^2)] 5.0 x 10^{-3} = 5.0 x 10^{-3} **[1]**

Hence $B = \frac{-0.509}{-0.0315} - \frac{1}{0.07071} = 2.01$ **[1]**

For the 10.0 x 10^{-3} molal solution with $\gamma_{\pm}$ = 0.907:

I = ½[1^2 +(-1^2)] 10.0 x 10^{-3} = 10.0 x 10^{-3}

Hence $B = \frac{-0.509}{-0.0424} - \frac{1}{0.1000} = 2.01$ **[1]**

For the 10.0 x 10^{-3} molal solution with $\gamma_{\pm}$ = 0.879:

I = ½[1^2 +(-1^2)] 20.0 x 10^{-3} = 20.0 x 10^{-3}

Hence $B = \frac{-0.509}{-0.0560} - \frac{1}{0.1414} = 2.02$ **[1]**

Therefore, I estimate *B* to have a value of 2.01 **[1]**

(ii) Comment

The valued for the empirical parameter *B* is almost constant over a large range of concentrations **[1].** Therefore, in the present example the Extended Debye-Huckel law gives very accurate predictions. **[1]**