

10 Electrolyte Solutions

Problem numbers in italics indicate that the solution is included in the *Student Solutions Manual*.

Conceptual Problems

Q10.1 Discuss how the Debye–Hückel screening length changes as the (a) temperature, (b) dielectric constant, and (c) ionic strength of an electrolyte solution are increased.

- Increasing T increases the screening length. The random thermal motion spreads out the cloud of screening ions.
- Increasing ϵ_r increases the screening length. Increased ϵ_r makes the potential attracting the counter ion cloud weaker, causing it to spread out more.
- Increasing ionic strength decreases the screening length. More counter ions available leads to more effective screening, decreasing $1/\kappa$.

Q10.2 Why is it not possible to measure the Gibbs energy of solvation of Cl^- directly?

As discussed in Section 10.1, the sum of the Gibbs energies of solvation of $\text{H}^+(aq)$ and $\text{Cl}^-(aq)$ can be related to the Gibbs energy for the reaction $1/2\text{H}_2(g) + 1/2\text{Cl}_2(g) \rightarrow \text{H}^+(aq) + \text{Cl}^-(aq)$, which can be determined experimentally by the equation $\Delta G_R^\circ = \Delta G_{\text{solvation}}^\circ(\text{Cl}^-, aq) + \Delta G_{\text{solvation}}^\circ(\text{H}^+, aq) + 1272 \text{ kJ mol}^{-1}$.

However, the Gibbs energies of solvation of $\text{Cl}^-(aq)$ cannot be determined individually.

Q10.3 Why are activity coefficients calculated using the Debye–Hückel limiting law always less than one?

Activity coefficients calculated using the Debye–Hückel limiting law are always less than one because the net electrostatic interaction among ions surrounding an arbitrarily chosen central ion is attractive rather than repulsive.

Q10.4 How is the mean ionic chemical potential of a solute related to the chemical potentials of the anion and cation produced when the solute is dissolved in water?

$$\mu_{\pm} = \frac{\mu_{\text{solute}}}{\nu} = \frac{\nu_+ \mu_+ + \nu_- \mu_-}{\nu}$$

Q10.5 How is the chemical potential of a solute related to its activity?

$$\mu_+ = \mu_+^\circ + RT \ln a_+ \quad \text{and} \quad \mu_- = \mu_-^\circ + RT \ln a_-$$

Expressing the relations in terms of the mean ionic chemical potential gives

$$\mu_{\pm} = \mu_{\pm}^\circ + RT \ln a_{\pm}$$

Q10.6 Tabulated values of standard entropies of some aqueous ionic species are negative. Why is this statement not inconsistent with the third law of thermodynamics?

This is possible due to the choice of standard state as $S_f^\circ(\text{H}^+, aq) \equiv 0$. Although absolute entropies of neutral species can be determined, this is not possible for ionic species because the solution must be electrically neutral. Therefore, it is necessary to choose a reference value, but as generally only differences in entropies (and other thermodynamic quantities) are desired, it is not necessary to know the absolute value.

- Q10.7** Why is it not possible to measure the activity coefficient of $\text{Na}^+(aq)$?
It is impossible to create a solution of pure $\text{Na}^+(aq)$ in water. A counter ion is always required to give a solution that is electrically neutral, and this anion will always affect the measurement.
- Q10.8** Why is it possible to formulate a general theory for the activity coefficient for electrolyte solutions, but not for nonelectrolyte solutions?
The dissolved species in electrolyte solutions have a universal form for their dominant interaction with the solvent—the Coulomb interaction. Nonelectrolytes interact with much weaker, system specific potentials. The universality of the electrolyte–electrolyte interaction allows a general theory to be developed.
- Q10.9** Why does an increase in the ionic strength in the range where the Debye–Hückel law is valid lead to an increase in the solubility of a weakly soluble salt?
In this regime, $\ln \gamma_{\pm}$ decreases with increasing I (as \sqrt{I}). The chemical potential of the electrolyte in solution becomes lower with increasing ionic strength, thus increasing solubility. Physically, increasing I leads to increased screening of repulsion between like-charged solute ions.
- Q10.10** What is the correct order of the following inert electrolytes in their ability to increase the degree of dissociation of acetic acid?
a. 0.001*m* NaCl
b. 0.001*m* KBr
c. 0.10*m* CuCl_2
0.001*m* NaCl and 0.001*m* KBr will both increase dissociation of HOAc (salting in)—about the same (dilute solution, γ_{\pm} is the same according to Debye–Hückel). 0.1*m* CuCl_2 will decrease dissociation because the solution is concentrated, leading to salting out.
- Q10.11** How does salting in affect solubility?
At small values of the ionic strength, $\gamma_{\pm} < 1$, and the solubility increases as γ_{\pm} decreases with concentration until the minimum in a plot of γ_{\pm} versus I is reached.
- Q10.12** Why is it not appropriate to use ionic radii from crystal structures to calculate $\Delta G_{\text{solvation}}^{\circ}$ of ions using the Born model?
The effective cavity that the ion occupies in the solvent medium will not have the same radius as the lattice-based radius. Better results can be obtained using the ion–water distance (to the center of charge), a more realistic estimate of the cavity radius r in the Born model.
- Q10.13** Why do deviations from ideal behavior occur at lower concentrations for electrolyte solutions than for solutions in which the solute species are uncharged?
This is the case because the electrostatic interactions between ions in solution are long-range interactions, whereas the corresponding interactions for neutral species have a much shorter range.
- Q10.14** Why is the value for the dielectric constant for water in the solvation shell around ions less than that for bulk water?
Water molecules immediately around the ion are ordered more than those in the bulk because of the attractive forces between them and the ion. Thus, they are oriented in space around the ion and cannot respond to the electric field due to solvated ions. Therefore, they are less effective in screening the electric field due to solvated ions, leading to a smaller value of ϵ_r .
- Q10.15** What can you conclude about the interaction between ions in an electrolyte solution if the mean ionic activity coefficient is greater than one?
Overall repulsive interactions must more than compensate for any favorable attractive interactions between electrolyte solute and solvent.

Q10.16 Why is the inequality $\gamma_{\pm} < 1$ always satisfied in dilute electrolyte solutions?

The activity coefficients are less than one because the charge on an electrolyte lowers the chemical potential of the electrolyte when compared with an analogous solution of uncharged solute molecules. This occurs because the charges interact attractively with the solvent, lowering the energy. At high concentrations, repulsions between solvated ions become important and γ_{\pm} increases with concentration.

Q10.17 Under what conditions does $\gamma_{\pm} \rightarrow 1$ for electrolyte solutions?

This is the case as $m \rightarrow 0$.

Q10.18 How do you expect S_m° for an ion in solution to change as the ionic radius increases at constant charge?

It increases because the solvation shell is more tightly bound for the smaller ion.

Q10.19 How do you expect S_m° for an ion in solution to change as the charge increases at constant ionic radius?

It decreases because the solvation shell is more tightly bound for the ion with the greater charge.

Q10.20 It takes considerable energy to dissociate NaCl in the gas phase. Why does this process occur spontaneously in an aqueous solution? Why does it not occur spontaneously in CCl₄?

Dissociation takes place readily in water because the energy gain through formation of the solvation shell is greater than the energy needed to dissociate a formula unit of NaCl.

It does not occur in CCl₄ because CCl₄ is not an ionic solvent and is not capable of forming a tightly bound solvation shell.

Numerical Problems

P10.1 Calculate ΔS_R° for the reaction $\text{Ba}(\text{NO}_3)_2(aq) + 2\text{KCl}(aq) \rightarrow \text{BaCl}_2(s) + 2\text{KNO}_3(aq)$.

$$\Delta S_R^{\circ} = S^{\circ}(\text{BaCl}_2, s) - S^{\circ}(\text{Ba}^{2+}, aq) - 2 \times S^{\circ}(\text{Cl}^-, aq)$$

$$\Delta S_R^{\circ} = 123.7 \text{ JK}^{-1} \text{ mol}^{-1} - 9.6 \text{ JK}^{-1} \text{ mol}^{-1} - 2 \times 56.5 \text{ JK}^{-1} \text{ mol}^{-1} = 1.1 \text{ JK}^{-1} \text{ mol}^{-1}$$

P10.2 Calculate ΔS_R° for the reaction $\text{AgNO}_3(aq) + \text{KCl}(aq) \rightarrow \text{AgCl}(s) + \text{KNO}_3(aq)$.

$$\Delta S_R^{\circ} = S^{\circ}(\text{AgCl}, s) - S^{\circ}(\text{Ag}^+, aq) - S^{\circ}(\text{Cl}^-, aq)$$

$$\Delta S_R^{\circ} = 96.3 \text{ JK}^{-1} \text{ mol}^{-1} - 72.7 \text{ JK}^{-1} \text{ mol}^{-1} - 56.5 \text{ JK}^{-1} \text{ mol}^{-1} = -32.9 \text{ JK}^{-1} \text{ mol}^{-1}$$

P10.3 Using the Debye-Hückel limiting law, calculate the value of γ_{\pm} in (a) a $7.2 \times 10^{-3} m$ solution of NaBr, (b) a $7.50 \times 10^{-3} m$ solution of SrCl₂, and (c) a $2.25 \times 10^{-3} m$ solution of CaHPO₄. Assume complete dissociation.

(a) NaBr

$$I = \frac{m}{2}(v_+ z_+^2 + v_- z_-^2) = \frac{1}{2}(m_+ z_+^2 + m_- z_-^2)$$

$$I = \frac{1}{2}(0.0072 \text{ mol kg}^{-1} + 0.0072 \text{ mol kg}^{-1}) = 0.0072 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 |z_+ z_-| \sqrt{\frac{I}{\text{mol kg}^{-1}}} = -1.173 \times \sqrt{0.0072} = -0.09953$$

$$\gamma_{\pm} = 0.91$$

(b) $\text{Sr}(\text{Cl})_2$

$$I = \frac{m}{2}(v_+z_+^2 + v_-z_-^2) = \frac{1}{2}(m_+z_+^2 + m_-z_-^2)$$

$$I = \left(\frac{1}{2}\right)0.00750 \text{ mol/kg} (1 \times 2^2 + 2 \times 1^2) = 0.0225 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 |z_+z_-| \sqrt{\frac{I}{\text{mol kg}^{-1}}} = -1.173 \times 2 \times \sqrt{0.0225} = -0.3519$$

$$\gamma_{\pm} = 0.703$$

(c) CaHPO_4

$$I = \frac{m}{2}(v_+z_+^2 + v_-z_-^2) = \frac{1}{2}(m_+z_+^2 + m_-z_-^2)$$

$$I = \left(\frac{1}{2}\right)0.00225 \text{ mol/kg} (1 \times 2^2 + 1 \times 2^2) = 0.0090 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 |z_+z_-| \sqrt{\frac{I}{\text{mol kg}^{-1}}} = -1.173 \times 4 \times \sqrt{0.0090} = -0.4451$$

$$\gamma_{\pm} = 0.641$$

P10.4 Calculate the mean ionic molality, m_{\pm} , in 0.0750 *m* solutions of (a) $\text{Ca}(\text{NO}_3)_2$, (b) NaOH (c) MgSO_4 , and (d) AlCl_3 .

$$m_{\pm}^{\nu} = m_+^{\nu_+} m_-^{\nu_-}$$

(a) $\text{Ca}(\text{NO}_3)_2$ $\nu_+ = 1$, $\nu_- = 2$, $\nu = 3$

$$m_{\pm}^3 = (0.0750)(0.0750 \times 2)^2 \text{ (mol/kg)}^3$$

$$m_{\pm} = 0.119 \text{ mol kg}^{-1}$$

(b) NaOH $\nu_+ = 1$, $\nu_- = 1$, $\nu = 2$

$$m_{\pm}^2 = (0.0750)(0.0750) \text{ (mol/kg)}^2$$

$$m_{\pm} = 0.0750 \text{ mol kg}^{-1}$$

(c) MgSO_4 $\nu_+ = 1$, $\nu_- = 1$, $\nu = 2$

$$m_{\pm}^2 = (0.0750)(0.0750) \text{ (mol/kg)}^2$$

$$m_{\pm} = 0.0750 \text{ mol kg}^{-1}$$

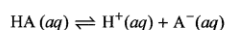
(d) AlCl_3 $\nu_+ = 1$, $\nu_- = 3$, $\nu = 4$

$$m_{\pm}^4 = (0.0750)(0.0750 \times 3)^3 \text{ (mol/kg)}^4$$

$$m_{\pm} = 0.171 \text{ mol kg}^{-1}$$

P10.5 A weak acid has a dissociation constant of $K_a = 2.50 \times 10^{-2}$. (a) Calculate the degree of dissociation for a 0.093 *m* solution of this acid using the Debye–Hückel limiting law. (b) Calculate the degree of dissociation for a 0.093 *m* solution of this acid that is also 0.200 *m* in KCl from the Debye–Hückel limiting law using an iterative calculation until the answer is constant in the second decimal place. (c) Repeat the calculation in (b) using the mean activity coefficient for KCl in Table 10.3. Is the use of the Debye–Hückel limiting law advisable at the given KCl concentration? Do you need to repeat the iterative calculation of (a) to solve (b) and (c)?

(a) A weak acid dissociates according to the following equilibrium reaction.



$$K_a = \frac{a_{\text{H}^+} a_{\text{A}^-}}{a_{\text{HA}}}$$

Because the undissociated acid is a neutral species, it is a good approximation to set its activity equal to its concentration. The activity of the ionic species produced upon dissociation are given by $a_{H^+} = \gamma_{\pm} c_{H^+}$ and $a_{A^-} = \gamma_{\pm} c_{A^-}$. The equilibrium expression becomes

$$K_a = \frac{\gamma_{\pm} c_{H^+} \gamma_{\pm} c_{A^-}}{c_{HA}} = \frac{(\gamma_{\pm})^2 \frac{m}{m^{\circ}}}{c^{\circ} - \frac{m}{m^{\circ}}}$$

This expression has two unknowns. We solve for m using an iterative method. We first assume that $\gamma_{\pm} = 1$ and solve for m . We use this value of m to calculate γ_{\pm} and using this value, recalculate m . We repeat this procedure until x is sufficiently constant.

$$\frac{\left(\frac{m}{m^{\circ}}\right)^2}{0.093 - \frac{m}{m^{\circ}}} = 2.50 \times 10^{-2}$$

$$m = 3.73 \times 10^{-2} \text{ mol kg}^{-1}$$

The ionic strength and γ_{\pm} are given by

$$I = \frac{m}{2}(2) = m = 0.0373 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{0.0373} = -0.2266$$

$$\gamma_{\pm} = 0.797$$

We use this value of γ_{\pm} to calculate a new value of m .

$$\frac{\left(\frac{m}{m^{\circ}}\right)^2 \times (0.787)^2}{0.093 - \frac{m}{m^{\circ}}} = 2.50 \times 10^{-2}$$

$$m = 4.39 \times 10^{-2} \text{ mol kg}^{-1}$$

The ionic strength and γ_{\pm} are given by

$$I = \frac{m}{2}(2) = m = 0.0439 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{0.0439} = -0.2459$$

$$\gamma_{\pm} = 0.782$$

We recalculate m and γ_{\pm} and iterate several times.

$$\frac{\left(\frac{m}{m^{\circ}}\right)^2 \gamma_{\pm}^2}{0.093 - \frac{m}{m^{\circ}}} = 2.50 \times 10^{-2} \text{ with } \gamma_{\pm} = 0.782$$

$$m = 4.45 \times 10^{-2} \text{ mol kg}^{-1}$$

$$I = \frac{m}{2}(2) = m = 4.45 \times 10^{-2} \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{4.45 \times 10^{-2}} = -0.2475$$

$$\gamma_{\pm} = 0.781$$

When $\gamma_{\pm} = 0.781$,

$$\frac{\left(\frac{m}{m^{\circ}}\right)^2 \gamma_{\pm}^2}{0.093 - \frac{m}{m^{\circ}}} = 2.50 \times 10^{-2}$$

$$m = 4.46 \times 10^{-2} \text{ mol kg}^{-1}$$

This is a sufficiently good result, and we calculate the degree of dissociation to be

$$\frac{0.0446 \text{ mol kg}^{-1}}{0.093 \text{ mol kg}^{-1}} \times 100\% = 48\%$$

- (b) We first calculate the degree of dissociation using the limiting law and neglecting the increase in ionic strength produced by the acid dissociation.

$$I = \frac{m}{2}(2) = m = 0.200 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{0.200} = -0.5246$$

$$\gamma_{\pm} = 0.592$$

$$\frac{\left(\frac{m}{m^{\circ}}\right)^2 \gamma_{\pm}^2}{0.093 - \frac{m}{m^{\circ}}} = 2.50 \times 10^{-2} \text{ with } \gamma_{\pm} = 0.592$$

$$m = 5.33 \times 10^{-2} \text{ mol kg}^{-1}$$

We next calculate the additional concentration of the ions produced through the dissociation of the acid in the solution when $\gamma_{\pm} = 0.592$.

$$I = 0.200 \text{ mol kg}^{-1} + \frac{m}{2}(2) = 0.253 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{0.253} = -0.5903$$

$$\gamma_{\pm} = 0.554$$

We next calculate the total concentration of the ions in the solution when $\gamma_{\pm} = 0.554$.

$$\frac{\left(\frac{m}{m^{\circ}}\right)^2 \gamma_{\pm}^2}{0.0930 - \frac{m}{m^{\circ}}} = 2.50 \times 10^{-2}$$

$$m = 5.54 \times 10^{-2} \text{ mol kg}^{-1}$$

We recalculate m and γ_{\pm} and iterate.

$$I = \frac{m}{2}(2) + 0.200 \text{ mol/kg} = m + 0.200 \text{ mol/kg} = 0.2554 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{0.2554} = -0.5928$$

$$\gamma_{\pm} = 0.553$$

$$\frac{\left(\frac{m}{m^{\circ}}\right)^2 \gamma_{\pm}^2}{0.093 - \frac{m}{m^{\circ}}} = 2.50 \times 10^{-2} \text{ with } \gamma_{\pm} = 0.553$$

$$m = 5.54 \times 10^{-2} \text{ mol kg}^{-1}$$

This is a sufficiently good result, and we calculate the degree of dissociation to be

$$\frac{0.0554}{0.093} = 60.0\%$$

(c) We use the value of $\gamma_{\pm} = 0.718$ from Table 10.3.

$$\frac{\left(\frac{m}{m^{\circ}}\right)^2 \gamma_{\pm}^2}{0.093 - \frac{m}{m^{\circ}}} = 2.50 \times 10^{-2}$$

$$m = 4.71 \times 10^{-2} \text{ mol kg}^{-1}$$

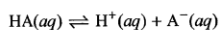
The degree of dissociation is $\frac{0.0471}{0.093} = 51\%$.

P10.6 Calculate the mean ionic activity of a 0.0350 *m* Na₃PO₄ solution for which the mean activity coefficient is 0.685.

$$a_{\pm} = \left(\frac{(v_+^{v_+} v_-^{v_-})^{1/2} m}{m^{\circ}} \right) \gamma_{\pm} = (3^3 1^1)^{1/4} 0.0350 \times 0.685 = 0.0547$$

P10.7 At 25°C, the equilibrium constant for the dissociation of acetic acid, K_a , is 1.75×10^{-5} . Using the Debye-Hückel limiting law, calculate the degree of dissociation in 0.150 *m* and 1.50 *m* solutions using an iterative calculation until the answer is constant in the second decimal place. Compare these values with what you would obtain if the ionic interactions had been ignored. Compare your results with the degree of dissociation of the acid assuming $\gamma_{\pm} = 1$.

A weak acid dissociates according to the following equilibrium reaction.

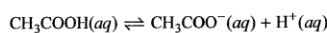


$$K_a = \frac{a_{\text{H}^+} a_{\text{A}^-}}{a_{\text{HA}}}$$

Because the undissociated acid is a neutral species, it is a good approximation to set its activity equal to its concentration. The activity of the ionic species produced upon dissociation are given by $a_{\text{H}^+} = \gamma_{\pm} c_{\text{H}^+}$ and $a_{\text{A}^-} = \gamma_{\pm} c_{\text{A}^-}$. The equilibrium expression becomes

$$K_a = \frac{\gamma_{\pm} c_{\text{H}^+} \gamma_{\pm} c_{\text{A}^-}}{c_{\text{HA}}} = \frac{(\gamma_{\pm})^2 \frac{m}{m^{\circ}}}{c^{\circ} - \frac{m}{m^{\circ}}}$$

This expression has two unknowns. We solve for *m* using an iterative method. We first assume that $\gamma_{\pm} = 1$ and solve for *m*. We use this value of *m* to calculate γ_{\pm} and using this value, recalculate *m*. We repeat this procedure until *x* is sufficiently constant.



For 0.150 *m*

$$\frac{m^2 \gamma_{\pm}^2}{0.150 \text{ mol kg}^{-1} - m} = 1.75 \times 10^{-5}$$

When $\gamma_{\pm} = 1$

$$m = 1.611 \times 10^{-3} \text{ mol kg}^{-1}$$

$$I = \frac{m}{2}(2) = m = 1.611 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} - 1.173 \times 1 \times \sqrt{1.611 \times 10^{-3}} = -0.04709$$

$$\gamma_{\pm} = 0.954$$

When $\gamma_{\pm} = 0.954$

$$\frac{\left(\frac{m}{m^{\circ}}\right)^2 \gamma_{\pm}^2}{0.150 - \frac{m}{m^{\circ}}} = 1.75 \times 10^{-5}$$

$$m = 1.689 \times 10^{-3} \text{ mol kg}^{-1}$$

We iterate several times.

When $m = 1.689 \times 10^{-3} \text{ mol kg}^{-1}$

$$I = \frac{m}{2}(2) = m = 1.689 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} - 1.173 \times 1 \times \sqrt{1.689 \times 10^{-3}} = -0.04820$$

$$\gamma_{\pm} = 0.953$$

When $\gamma_{\pm} = 0.953$

$$\frac{\left(\frac{m}{m^{\circ}}\right)^2 \gamma_{\pm}^2}{0.150 - \frac{m}{m^{\circ}}} = 1.75 \times 10^{-5}$$

$$m = 1.691 \times 10^{-3} \text{ mol kg}^{-1}$$

This result has converged sufficiently to calculate the degree of dissociation.

$$m = 1.691 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\frac{1.691 \times 10^{-3} \text{ mol kg}^{-1}}{0.150 \text{ mol kg}^{-1}} \times 100\% = 1.13\%$$

For 1.50 m

$$\frac{\left(\frac{m}{m^{\circ}}\right)^2 \gamma_{\pm}^2}{1.50 - \frac{m}{m^{\circ}}} = 1.75 \times 10^{-5}$$

When $\gamma_{\pm} = 1$

$$m = 5.115 \times 10^{-3} \text{ mol kg}^{-1}$$

$$I = m = 5.115 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -0.08389$$

$$\gamma_{\pm} = 0.920$$

When $\gamma_{\pm} = 0.920$

$$\frac{\left(\frac{m}{m^{\circ}}\right)^2 \gamma_{\pm}^2}{1.50 - \frac{m}{m^{\circ}}} = 1.75 \times 10^{-5}$$

$$m = 5.561 \times 10^{-3} \text{ mol kg}^{-1}$$

We iterate several times.

When $m = 5.561 \times 10^{-3} \text{ mol kg}^{-1}$

$$I = \frac{m}{2}(2) = m = 5.561 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{5.561 \times 10^{-3}} = -0.08748$$

$$\gamma_{\pm} = 0.916$$

When $\gamma_{\pm} = 0.916$

$$\frac{\left(\frac{m}{m^{\circ}}\right)^2 \gamma_{\pm}^2}{1.50 - \frac{m}{m^{\circ}}} = 1.75 \times 10^{-5}$$

$$m = 5.581 \times 10^{-3} \text{ mol kg}^{-1} \rightarrow 5.58 \times 10^{-3} \text{ mol kg}^{-1}$$

This result has converged sufficiently to calculate the degree of dissociation.

$$m = 5.58 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\frac{5.58 \times 10^{-3} \text{ mol kg}^{-1}}{1.50 \text{ mol kg}^{-1}} \times 100\% = 0.372\%$$

If ionic interactions are ignored:

For 0.150 m

$$\frac{\left(\frac{m}{m^{\circ}}\right)^2}{0.150 - \frac{m}{m^{\circ}}} = 1.75 \times 10^{-5}$$

$$m = 1.61 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\frac{1.61 \times 10^{-3}}{0.150} \times 100\% = 1.07\%$$

For 1.50 m

$$\frac{\left(\frac{m}{m^{\circ}}\right)^2}{1.50 - \frac{m}{m^{\circ}}} = 1.75 \times 10^{-5}$$

$$m = 5.11 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\frac{5.11 \times 10^{-3}}{1.50} \times 100\% = 0.341\%$$

P10.8 From the data in Table 10.3 (see Appendix B, Data Tables), calculate the activity of the electrolyte in 0.200 *m* solutions assuming complete dissociation of

- a. KCl b. Na₂SO₄ c. MgCl₂

(a) KCl 0.200 *m* $\gamma_{\pm} = 0.718$

$$a_{\pm} = \left(\frac{m_{\pm}}{m^{\circ}}\right)\gamma_{\pm}; \quad m_{\pm}^{\nu} = m_{+}^{\nu} m_{-}^{\nu}$$

$$m_{\pm}^2 = (0.200)(0.200); \quad m_{\pm} = 0.200 \text{ mol kg}^{-1}$$

$$a_{\pm} = (0.200)(0.718) = 0.144$$

(b) Na₂SO₄ 0.200 *m* $\gamma_{\pm} = 0.209$

$$m_{\pm}^3 = (2 \times 0.200)^2 (0.200)^1$$

$$m_{\pm} = 0.317 \text{ mol kg}^{-1}$$

$$a_{\pm} = (0.317) \times (0.209) = 0.0663$$

(c) MgCl₂ 0.200 *m* $\gamma_{\pm} = 0.489$

$$m_{\pm}^3 = (0.200)(2 \times 0.200)^2$$

$$m_{\pm} = 0.317 \text{ mol kg}^{-1}$$

$$a_{\pm} = (0.317) \times (0.489) = 0.155$$

P10.9 Estimate the degree of dissociation of a 0.200 *m* solution of nitrous acid ($K_a = 4.00 \times 10^{-4}$) that is also 0.500 *m* in the strong electrolyte given in parts (a)–(c). Use the data tables to obtain γ_{\pm} , as the electrolyte concentration is too high to use the Debye–Hückel limiting law.

- a. BaCl₂ b. KOH c. AgNO₃

Compare your results with the degree of dissociation of the acid assuming $\gamma_{\pm} = 1$.

In each case, the activity of the ions produced in the dissociation of acetic acid is determined by the strong electrolyte.

(a) BaCl₂

From Table 10.3, $\gamma_{\pm} = 0.397$

$$4.00 \times 10^{-4} = \frac{\gamma_{\pm}^2 \left(\frac{m}{m^{\circ}}\right)^2}{0.200 - \frac{m}{m^{\circ}}} = \frac{(0.397)^2 \left(\frac{m}{m^{\circ}}\right)^2}{0.200 - \frac{m}{m^{\circ}}}$$

$$m = 0.0213 \text{ mol kg}^{-1}$$

$$\frac{0.0213 \text{ mol kg}^{-1}}{0.200 \text{ mol kg}^{-1}} \times 100\% = 10.6\%$$

(b) KOH

From Table 10.3, $\gamma_{\pm} = 0.732$

$$4.00 \times 10^{-4} = \frac{(0.732)^2 \left(\frac{m}{m^{\circ}}\right)^2}{0.200 \text{ mol kg}^{-1} - \frac{m}{m^{\circ}}}$$

$$m = 1.19 \times 10^{-2} \text{ mol kg}^{-1}$$

$$\frac{1.19 \times 10^{-2} \text{ mol kg}^{-1}}{0.200 \text{ mol kg}^{-1}} \times 100\% = 5.92\%$$

(c) AgNO_3 From Table 10.3, $\gamma_{\pm} = 0.536$

$$1.75 \times 10^{-5} = \frac{\gamma_{\pm}^2 \left(\frac{m}{m^{\circ}}\right)^2}{0.200 - \frac{m}{m^{\circ}}} = \frac{(0.536)^2 \left(\frac{m}{m^{\circ}}\right)^2}{0.200 - \frac{m}{m^{\circ}}}$$

$$m = 1.60 \times 10^{-2} \text{ mol kg}^{-1}$$

$$\frac{1.60 \times 10^{-2} \text{ mol kg}^{-1}}{0.200 \text{ mol kg}^{-1}} \times 100\% = 8.00\%$$

Assuming $\gamma_{\pm} = 1$,

$$4.00 \times 10^{-4} = \frac{\gamma_{\pm}^2 \left(\frac{m}{m^{\circ}}\right)^2}{0.200 \text{ mol kg}^{-1} - \frac{m}{m^{\circ}}} = \frac{\left(\frac{m}{m^{\circ}}\right)^2}{0.200 - \frac{m}{m^{\circ}}}$$

$$m = 8.75 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\frac{8.75 \times 10^{-3} \text{ mol kg}^{-1}}{0.200 \text{ mol kg}^{-1}} \times 100\% = 4.37\%$$

P10.10 Calculate ΔH_R° and ΔG_R° for the reaction $\text{Ba}(\text{NO}_3)_2(aq) + 2\text{KCl}(aq) \rightarrow \text{BaCl}_2(s) + 2\text{KNO}_3(aq)$.

$$\Delta G_R^{\circ} = \Delta G_f^{\circ}(\text{BaCl}_2, s) + 2\Delta G_f^{\circ}(\text{K}^+, aq) + 2\Delta G_f^{\circ}(\text{NO}_3^-, aq) - \Delta G_f^{\circ}(\text{Ba}^{2+}, aq) - 2\Delta G_f^{\circ}(\text{NO}_3^-, aq) - 2\Delta G_f^{\circ}(\text{K}^+, aq) - 2\Delta G_f^{\circ}(\text{Cl}^-, aq)$$

$$\Delta G_R^{\circ} = \Delta G_f^{\circ}(\text{BaCl}_2, s) - \Delta G_f^{\circ}(\text{Ba}^{2+}, aq) - 2\Delta G_f^{\circ}(\text{Cl}^-, aq)$$

$$\Delta G_R^{\circ} = -806.7 \text{ kJ mol}^{-1} + 560.8 \text{ kJ mol}^{-1} + 2 \times 131.2 \text{ kJ mol}^{-1} = 16.5 \text{ kJ mol}^{-1}$$

$$\Delta H_R^{\circ} = \Delta H_f^{\circ}(\text{BaCl}_2, s) - \Delta H_f^{\circ}(\text{Ba}^{2+}, aq) - 2\Delta H_f^{\circ}(\text{Cl}^-, aq)$$

$$\Delta H_R^{\circ} = -855.0 \text{ kJ mol}^{-1} + 537.6 \text{ kJ mol}^{-1} + 2 \times 167.2 \text{ kJ mol}^{-1} = 17.0 \text{ kJ mol}^{-1}$$

P10.11 Express a_{\pm} in terms of a_+ and a_- for (a) Li_2CO_3 , (b) CaCl_2 , (c) Na_3PO_4 , and (d) $\text{K}_4\text{Fe}(\text{CN})_6$. Assume complete dissociation.

$$(a) \quad \text{Li}_2\text{CO}_3: a_{\pm} = (a_+^2 a_-^2)^{\frac{1}{3}} = (a_+^2 a_-)^{\frac{1}{3}}$$

$$(b) \quad \text{CaCl}_2: a_{\pm} = (a_+^2 a_-^2)^{\frac{1}{3}} = (a_+ a_-^2)^{\frac{1}{3}}$$

$$(c) \quad \text{Na}_3\text{PO}_4: a_{\pm} = (a_+^3 a_-^4)^{\frac{1}{7}} = (a_+^3 a_-)^{\frac{1}{7}}$$

$$(d) \quad \text{K}_4\text{Fe}(\text{CN})_6: a_{\pm} = (a_+^4 a_-^6)^{\frac{1}{10}} = (a_+^4 a_-)^{\frac{1}{5}}$$

P10.12 Calculate $\Delta G_{\text{solvation}}^{\circ}$ in an aqueous solution for $\text{Rb}^+(aq)$ using the Born model. The radius of the Rb^+ ion is 161 pm.

$$\Delta G_{\text{solvation}}^{\circ} = \frac{Z^2 e^2 N_A}{8\pi\epsilon_0 r} \left(\frac{1}{\epsilon_r} - 1 \right)$$

$$= \frac{1^2 \times (1.602 \times 10^{-19} \text{ C})^2 \times N_A}{8\pi \times 8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ mol}^{-1} \times 1.61 \times 10^{-10} \text{ m}} \times \left(\frac{1}{78.5} - 1 \right)$$

$$= -426 \text{ kJ}$$

Copyright © 2013 Pearson Education, Inc.

P10.13 Calculate the ionic strength in a solution that is 0.0750 *m* in K_2SO_4 , 0.0085 *m* in Na_3PO_4 , and 0.0150 *m* in $MgCl_2$.

$$I_{K_2SO_4} = \frac{m}{2}(v_+z_+^2 + v_-z_-^2) \\ = \frac{0.0750}{2}(2 + 4) = 0.225 \text{ mol kg}^{-1}$$

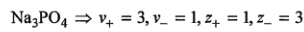
$$I_{Na_3PO_4} = \frac{m}{2}(v_+z_+^2 + v_-z_-^2) \\ = \frac{0.0085}{2}(3 + 9) = 0.051 \text{ mol kg}^{-1}$$

$$I_{MgCl_2} = \frac{m}{2}(v_+z_+^2 + v_-z_-^2) \\ = \frac{0.0150}{2}(4 + 2) = 0.0450 \text{ mol kg}^{-1}$$

Total ionic strength

$$I = (0.225 + 0.0510 + 0.0450) \text{ mol kg}^{-1} \\ = 0.321 \text{ mol kg}^{-1}$$

P10.14 Calculate I , γ_{\pm} , and a_{\pm} for a 0.0120 *m* solution of Na_3PO_4 at 298 K. Assume complete dissociation.



$$I = \frac{m}{2}(v_+z_+^2 + v_-z_-^2)$$

$$I = \frac{0.0120}{2}(3 + 9) = 0.0720 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 |z_+z_-| \sqrt{\frac{I}{\text{mol kg}^{-1}}} = -1.173 \times 2 \times \sqrt{0.0720} = -0.9442$$

$$\gamma_{\pm} = 0.389$$

$$m_{\pm}^{(v_+ + v_-)} = m_+^{v_+} m_-^{v_-}$$

$$m_{\pm}^3 = (0.015)^2 (0.0075)^1 = 5.60 \times 10^{-7}$$

$$m_{\pm} = 0.0273 \text{ mol kg}^{-1}$$

$$a_{\pm} = \left(\frac{m_{\pm}}{m^{\circ}}\right) \gamma_{\pm}$$

$$a_{\pm} = 0.0273 \times 0.389 = 0.0106$$

P10.15 Express μ_{\pm} in terms of μ_+ and μ_- for (a) $NaCl$, (b) $MgBr_2$, (c) Li_3PO_4 , and (d) $Ca(NO_3)_2$. Assume complete dissociation.

$$(a) \quad NaCl: \mu_{\pm} = \frac{\mu_{\text{solute}}}{\nu} = \frac{v_+\mu_+ + v_-\mu_-}{\nu} = \frac{\mu_+ + \mu_-}{2}$$

$$(b) \quad MgBr_2: \mu_{\pm} = \frac{\mu_{\text{solute}}}{\nu} = \frac{v_+\mu_+ + v_-\mu_-}{\nu} = \frac{\mu_+ + 2\mu_-}{3}$$

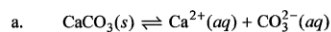
$$(c) \quad Li_3PO_4: \mu_{\pm} = \frac{\mu_{\text{solute}}}{\nu} = \frac{v_+\mu_+ + v_-\mu_-}{\nu} = \frac{3\mu_+ + \mu_-}{4}$$

$$(d) \quad Ca(NO_3)_2: \mu_{\pm} = \frac{\mu_{\text{solute}}}{\nu} = \frac{v_+\mu_+ + v_-\mu_-}{\nu} = \frac{\mu_+ + 2\mu_-}{3}$$

- P10.16** In the Debye-Hückel theory, the counter charge in a spherical shell of radius r and thickness dr around the central ion of charge $+Q$ is given by $-Q\kappa^2 r e^{-\kappa r} dr$. Calculate the radius at which the counter charge has its maximum value, r_{\max} , from this expression. Evaluate r_{\max} for a 0.090 *m* aqueous solution of Na_3PO_4 at 298 K.

$$\begin{aligned} \frac{d(-Q\kappa^2 r e^{-\kappa r})}{dr} &= -Q\kappa^2 e^{-\kappa r_{\max}} + Q\kappa^3 r_{\max} e^{-\kappa r_{\max}} = 0 \\ -1 + \kappa r_{\max} &= 0; \quad r_{\max} = \frac{1}{\kappa} \\ \frac{1}{r_{\max}} &= 3.29 \times 10^9 \sqrt{I} \text{ m}^{-1} = 3.29 \times 10^9 \times \sqrt{\frac{m}{2}(v_+ z_+^2 + v_- z_-^2)} \\ 3.29 \times 10^9 \times \sqrt{\frac{0.090}{2}(2 \times 1^1 + 1 \times 2^2)} &= 3.29 \times 10^9 \times \sqrt{0.540} \text{ m}^{-1} = 2.41 \times 10^9 \text{ m}^{-1} \\ r_{\max} &= 4.1 \times 10^{-10} \text{ m} = 0.41 \text{ nm} \end{aligned}$$

- P10.17** Calculate the solubility of CaCO_3 ($K_{sp} = 3.4 \times 10^{-9}$) (a) in pure H_2O and (b) in an aqueous solution with $I = 0.0250 \text{ mol kg}^{-1}$. For part (a), do an iterative calculation of γ_{\pm} and the solubility until the answer is constant in the second decimal place. Do you need to repeat this procedure in part (b)?



$$\begin{aligned} v_+ &= 1, & v_- &= 1 \\ z_+ &= 2, & z_- &= 2 \\ K_{sp} &= \left(\frac{c_{\text{Ca}^{2+}}}{c^\circ} \right) \left(\frac{c_{\text{CO}_3^{2-}}}{c^\circ} \right) \gamma_{\pm}^2 = 3.4 \times 10^{-9} \\ c_{\text{Ca}^{2+}} &= c_{\text{CO}_3^{2-}} \\ K_{sp} &= \left(\frac{c_{\text{Ca}^{2+}}}{c^\circ} \right)^2 \gamma_{\pm}^2 = 3.4 \times 10^{-9} \end{aligned}$$

When $\gamma_{\pm} = 1$ $c_{\text{Ca}^{2+}} = 5.8 \times 10^{-5} \text{ mol L}^{-1}$

$$\begin{aligned} I &= \frac{m}{2} \sum (v_+ z_+^2 + v_- z_-^2) \\ &= \frac{5.8 \times 10^{-5}}{2} \times (4 + 4) = 2.33 \times 10^{-4} \text{ mol kg}^{-1} \\ \ln \gamma_{\pm} &= -1.173 \times 4 \times \sqrt{2.33 \times 10^{-4}} = -0.07166 \\ \gamma_{\pm} &= 0.9309 \end{aligned}$$

When $\gamma_{\pm} = 0.9309$ $c_{\text{Ca}^{2+}} = 6.26 \times 10^{-5} \text{ mol L}^{-1}$

$$\begin{aligned} I &= \frac{6.26 \times 10^{-5}}{2} \times (8) = 2.51 \times 10^{-4} \text{ mol kg}^{-1} \\ \ln \gamma_{\pm} &= -1.173 \times 4 \times \sqrt{2.51 \times 10^{-4}} = -0.07427 \\ \gamma_{\pm} &= 0.928 \end{aligned}$$

When $\gamma_{\pm} = 0.928$ $c_{\text{Ca}^{2+}} = 6.28 \times 10^{-5} \text{ mol L}^{-1}$

$$\begin{aligned}
 \text{b. } I &= 0.0250 \text{ mol kg}^{-1} \\
 \ln \gamma_{\pm} &= 1.173 \times 4 \times \sqrt{0.0250} = -0.74187 \\
 \gamma_{\pm} &= 0.476 \\
 K_{sp} &= \left(\frac{c_{\text{Ca}^{2+}}}{c^{\circ}} \right)^2 \times (0.476)^2 = 3.4 \times 10^{-9} \\
 c_{\text{Ca}^{2+}} &= 1.22 \times 10^{-4} \text{ mol L}^{-1}
 \end{aligned}$$

There is no need to repeat the calculation because the ionic strength in the solution is not influenced by the dissociation of the BaSO_4 .

P10.18 Calculate the probability of finding an ion at a distance greater than $1/\kappa$ from the central ion.

$$\begin{aligned}
 \int u \, dv &= uv - \int v \, du \\
 \text{Let } u &= -q\kappa^2 r; \quad dv = e^{-\kappa r} dr \quad v = -\frac{1}{\kappa} e^{-\kappa r} \quad du = -q\kappa^2 dr \\
 -\int q\kappa^2 r e^{-\kappa r} dr &= q\kappa r e^{-\kappa r} - q\kappa \int e^{-\kappa r} dr = q\kappa r e^{-\kappa r} + qe^{-\kappa r} \\
 P\left(r > \frac{1}{\kappa}\right) &= \frac{\int_{\frac{1}{\kappa}}^{\infty} q\kappa^2 r e^{-\kappa r} dr}{\int_0^{\infty} q\kappa^2 r e^{-\kappa r} dr} = \frac{\left[q\kappa r e^{-\kappa r} + qe^{-\kappa r} \right]_{\frac{1}{\kappa}}^{\infty}}{\left[q\kappa r e^{-\kappa r} + qe^{-\kappa r} \right]_0^{\infty}} = \frac{0 - 2qe^{-1}}{0 - q} = \frac{2}{e} = 0.736
 \end{aligned}$$

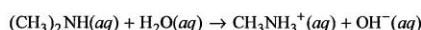
P10.19 Express γ_{\pm} in terms of γ_+ and γ_- for (a) SrSO_4 , (b) MgBr_2 , (c) K_3PO_4 , and (d) $\text{Ca}(\text{NO}_3)_2$. Assume complete dissociation.

$$\begin{aligned}
 \text{(a) } \text{SrSO}_4: \gamma_{\pm} &= (\gamma_+ \gamma_-)^{\frac{1}{2}} \\
 \text{(b) } \text{MgBr}_2: \gamma_{\pm} &= (\gamma_+ \gamma_-^2)^{\frac{1}{3}} \\
 \text{(c) } \text{K}_3\text{PO}_4: \gamma_{\pm} &= (\gamma_+^3 \gamma_-)^{\frac{1}{4}} \\
 \text{(d) } \text{Ca}(\text{NO}_3)_2: \gamma_{\pm} &= (\gamma_+ \gamma_-^2)^{\frac{1}{3}}
 \end{aligned}$$

P10.20 Calculate the mean ionic molality and mean ionic activity of a 0.105 *m* K_3PO_4 solution for which the mean ionic activity coefficient is 0.225.

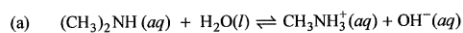
$$\begin{aligned}
 m_{\pm} &= (v_+^{\nu_+} v_-^{\nu_-})^{\frac{1}{\nu}} m = (3^3 1^1)^{\frac{1}{4}} 0.105 \text{ mol kg}^{-1} = 0.239 \text{ mol kg}^{-1} \\
 a_{\pm} &= \left(\frac{m_{\pm}}{m^{\circ}} \right) \gamma_{\pm} = 0.239 \times 0.225 = 0.0539
 \end{aligned}$$

P10.21 The equilibrium constant for the hydrolysis of dimethylamine,



is 5.12×10^{-4} . Calculate the extent of hydrolysis for (a) a 0.210 *m* solution of $(\text{CH}_3)_2\text{NH}$ in water using an iterative calculation until the answer is constant in the second decimal place. (b) Repeat the calculation for a solution that is also 0.500 *m* in NaNO_3 . Do you need to use an iterative calculation in this case?

We use an iterative method as explained in the solution to P10.5.



$$K = \frac{\left(\frac{m}{m^\circ}\right)^2 \gamma_{\pm}^2}{0.210 - \frac{m}{m^\circ}} = 5.12 \times 10^{-4}$$

If $\gamma_{\pm} = 1$, $m = 1.01 \times 10^{-2} \text{ mol kg}^{-1}$.

When $m = 1.01 \times 10^{-2} \text{ mol kg}^{-1}$

$$I = \frac{m}{2}(2) = m = 1.01 \times 10^{-2} \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{1.01 \times 10^{-2}} = -0.1180$$

$$\gamma_{\pm} = 0.889$$

When $\gamma_{\pm} = 0.889$

$$\frac{\left(\frac{m}{m^\circ}\right)^2 \gamma_{\pm}^2}{0.210 - \left(\frac{m}{m^\circ}\right)} = 5.12 \times 10^{-4}$$

$$m = 1.13 \times 10^{-2} \text{ mol kg}^{-1}$$

We iterate several times.

When $m = 1.13 \times 10^{-2} \text{ mol kg}^{-1}$

$$I = \frac{m}{2}(2) = m = 1.13 \times 10^{-2} \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{1.13 \times 10^{-2}} = -0.1250$$

$$\gamma_{\pm} = 0.883$$

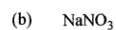
When $\gamma_{\pm} = 0.883$

$$\frac{\left(\frac{m}{m^\circ}\right)^2 \gamma_{\pm}^2}{0.210 - \frac{m}{m^\circ}} = 5.12 \times 10^{-4}$$

$$m = 1.14 \times 10^{-2} \text{ mol kg}^{-1}$$

The degree of hydrolysis is

$$\frac{0.0114}{0.210} \times 100\% = 5.44\%$$



$$\text{Na}^+ \quad \text{NO}_3^- \quad \nu_+ = 1 \quad \nu_- = 1$$

$$0.500 \quad 0.500 \quad z_+ = 1 \quad z_- = 1$$

$$I = \frac{500}{2}(1+1) = 0.500 \text{ mol kg}^{-1}$$

Add to this the ionic strength from the last iteration of part (a).

$$\begin{aligned}
 I_{total} &= 0.500 + 0.0114 = 0.511 \text{ mol kg}^{-1} \\
 \ln \gamma_{\pm} &= -1.173 \times 1 \times \sqrt{0.511} = -0.8389 \\
 \gamma_{\pm} &= 0.432 \\
 K &= \frac{\left(\frac{m}{m^{\circ}}\right)^2 (\gamma_{\pm})^2}{0.210 - \left(\frac{m}{m^{\circ}}\right)} = \frac{\left(\frac{m}{m^{\circ}}\right)^2 (0.432)^2}{0.210 - \left(\frac{m}{m^{\circ}}\right)} = 5.12 \times 10^{-4} \\
 m &= 0.0227 \text{ mol kg}^{-1}
 \end{aligned}$$

Carrying out another iteration,

$$\begin{aligned}
 I_{total} &= 0.500 + 0.0227 = 0.523 \text{ mol kg}^{-1} \\
 \ln \gamma_{\pm} &= -1.173 \times 1 \times \sqrt{0.523} = -0.8480 \\
 \gamma_{\pm} &= 0.428 \\
 K &= \frac{\left(\frac{m}{m^{\circ}}\right)^2 (\gamma_{\pm})^2}{0.210 - \left(\frac{m}{m^{\circ}}\right)} = \frac{\left(\frac{m}{m^{\circ}}\right)^2 (0.428)^2}{0.125 - \left(\frac{m}{m^{\circ}}\right)} = 5.12 \times 10^{-4} \\
 m &= 0.0229 \text{ mol kg}^{-1}
 \end{aligned}$$

The degree of hydrolysis is

$$\frac{0.0229}{0.210} \times 100\% = 10.9\%$$

P10.22 Dichloroacetic acid has a dissociation constant of $K_a = 3.32 \times 10^{-2}$. Calculate the degree of dissociation for a 0.105 m solution of this acid (a) using the Debye-Hückel limiting law using an iterative calculation until the answer is constant to within ± 2 in the second decimal place. (b) Repeat the calculation assuming that the mean ionic activity coefficient is one.

We use an iterative method as explained in the solution to P10.5.

(a) We first consider the case when γ is given by the Debye-Hückel limiting law. The concentration of the ionic species is given by

$$\begin{aligned}
 \frac{\left(\frac{m}{m^{\circ}}\right)^2}{0.105 - \frac{m}{m^{\circ}}} &= 3.32 \times 10^{-2} \\
 m &= 4.47 \times 10^{-2} \text{ mol kg}^{-1}
 \end{aligned}$$

The ionic strength and γ_{\pm} are given by

$$\begin{aligned}
 I &= \frac{m}{2} (2) = m = 0.0447 \text{ mol kg}^{-1} \\
 \ln \gamma_{\pm} &= -1.173 \times 1 \times \sqrt{0.0447} = -0.2481 \\
 \gamma_{\pm} &= 0.780
 \end{aligned}$$

We recalculate m and γ_{\pm} and iterate several times.

$$\begin{aligned}
 \frac{\left(\frac{m}{m^{\circ}}\right)^2 \gamma_{\pm}^2}{0.105 - \frac{m}{m^{\circ}}} &= 3.32 \times 10^{-2} \text{ with } \gamma_{\pm} = 0.780 \\
 m &= 5.31 \times 10^{-2} \text{ mol kg}^{-1}
 \end{aligned}$$

$$I = \frac{m}{2}(2) = m = 5.31 \times 10^{-2} \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{5.31 \times 10^{-2}} = -0.2705$$

$$\gamma_{\pm} = 0.763$$

When $\gamma_{\pm} = 0.763$

$$\frac{\left(\frac{m}{m^{\circ}}\right)^2 \gamma_{\pm}^2}{0.105 - \frac{m}{m^{\circ}}} = 3.32 \times 10^{-2}$$

$$m = 5.40 \times 10^{-2} \text{ mol kg}^{-1}$$

$$I = \frac{m}{2}(2) = m = 5.40 \times 10^{-2} \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{5.40 \times 10^{-2}} = -0.27246$$

$$\gamma_{\pm} = 0.762$$

When $\gamma_{\pm} = 0.762$

$$\frac{\left(\frac{m}{m^{\circ}}\right)^2 \gamma_{\pm}^2}{0.105 - \left(\frac{m}{m^{\circ}}\right)} = 3.32 \times 10^{-2}$$

$$m = 5.40 \times 10^{-2} \text{ mol kg}^{-1}$$

This is a sufficiently good result, and we calculate the degree of dissociation to be

$$\frac{0.0540 \text{ mol kg}^{-1}}{0.105 \text{ mol kg}^{-1}} \times 100\% = 51.5\%$$

(b) $\gamma_{\pm} = 1$

$$\frac{\left(\frac{m}{m^{\circ}}\right)^2}{0.105 - \frac{m}{m^{\circ}}} = 3.32 \times 10^{-2}$$

$$m = 4.47 \times 10^{-2} \text{ mol kg}^{-1}$$

$$\frac{0.0447 \text{ mol kg}^{-1}}{0.105 \text{ mol kg}^{-1}} \times 100\% = 42.5\%$$

This result is 9% smaller than that calculated using the Debye-Hückel limiting law.

P10.23 Calculate the Debye-Hückel screening length $1/\kappa$ at 298 K in a 0.0075 *m* solution of K_3PO_4 .

$$\kappa = 3.29 \times 10^9 \sqrt{I} \text{ m}^{-1}$$

$$I = \frac{m}{2}(v_+ z_+^2 + v_- z_-^2) = \frac{0.0075}{2}(3 \times 1^1 + 3^2) = 0.045 \text{ mol kg}^{-1}$$

$$\kappa = 3.29 \times 10^9 \sqrt{0.045} \text{ m}^{-1} = 6.98 \times 10^8 \text{ m}^{-1}$$

$$\frac{1}{\kappa} = 1.4 \times 10^{-9} \text{ m} = 1.4 \text{ nm}$$

P10.24 Calculate I , γ_{\pm} , and a_{\pm} for a 0.0215 *m* solution of K_2SO_4 at 298 K. How confident are you that your calculated results will agree with experimental results?

$$I = \frac{m}{2}(v_+z_+^2 + v_-z_-^2) = \frac{1}{2}(m_+z_+^2 + m_-z_-^2)$$

$$I = \frac{1}{2}(2 \times 0.0215 \text{ mol kg}^{-1} + 2^2 \times 0.0215 \text{ mol kg}^{-1}) = 0.0645 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 |z_+z_-| \sqrt{\frac{I}{\text{mol kg}^{-1}}} = -1.173 \times 2 \times \sqrt{0.0645} = -0.5958$$

$$\gamma_{\pm} = 0.551$$

$$m_{\pm} = (v_+^{\nu} v_-^{\nu})^{\frac{1}{\nu}} m = (2^2)^{\frac{1}{3}} \times 0.0215 \text{ mol kg}^{-1} = 0.1024 \text{ mol kg}^{-1}$$

$$a_{\pm} = \left(\frac{m_{\pm}}{m^{\circ}}\right) \gamma_{\pm} = 0.1024 \times 0.551 = 0.0564$$

Not very confident. Figures 10.6 and 10.7 show significant deviations from predicted behavior for $I > 0.01 \text{ mol kg}^{-1}$.

P10.25 Calculate I , γ_{\pm} , and a_{\pm} for a 0.0175 m solution of Na_3PO_4 at 298 K . Assume complete dissociation. How confident are you that your calculated results will agree with experimental results?

$$\text{Na}_3\text{PO}_4 \Rightarrow v_+ = 3, z_+ = 1, v_- = 1, z_- = 3$$

$$I = \frac{m}{2}(v_+z_+^2 + v_-z_-^2) = \frac{0.0175}{2}(3 + 9) = 0.105 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 3 \times \sqrt{0.105} = -1.1403$$

$$\gamma_{\pm} = 0.320$$

$$a_{\pm} = \left(\frac{m_{\pm}}{m^{\circ}}\right) \gamma_{\pm}$$

$$m_{\pm} = (v_+^{\nu} v_-^{\nu})^{\frac{1}{\nu}} m = (3^3 \cdot 1)^{\frac{1}{4}} 0.0175 \text{ mol kg}^{-1} = 0.0399 \text{ mol kg}^{-1}$$

$$a_{\pm} = \left(\frac{m_{\pm}}{m^{\circ}}\right) \gamma_{\pm} = 0.0399 \times 0.320 = 0.0128$$

Not very confident. Figures 10.6 and 10.7 show significant deviations from predicted behavior for $I > 0.01 \text{ mol kg}^{-1}$.

P10.26 Calculate the ionic strength of each of the solutions in Problem P10.4.

$$I = \frac{m}{2}(v_+z_+^2 + v_-z_-^2)$$

For $\text{Ca}(\text{NO}_3)_2$

$$I = \frac{0.0750}{2}(1 \times 2^2 + 2 \times 1^2) = 0.225 \text{ mol kg}^{-1}$$

For NaOH

$$I = \frac{0.0750}{2}(1 + 1) = 0.0750 \text{ mol kg}^{-1}$$

For MgSO_4

$$I = \frac{0.0750}{2}(1 \times 2^2 + 1 \times 2^2) = 0.300 \text{ mol kg}^{-1}$$

For AlCl_3

$$I = \frac{0.0750}{2}(1 \times 3^2 + 3 \times 1^2) = 0.450 \text{ mol kg}^{-1}$$

P10.27 Calculate the value of m_{\pm} in 5.5×10^{-3} molal solutions of (a) KCl, (b) $\text{Ca}(\text{NO}_3)_2$, and (c) ZnSO_4 . Assume complete dissociation.

(a) KCl

$$m_{\pm} = (v_+^{\nu} v_-^{\nu})^{\frac{1}{\nu}} m$$

$$m_{\pm} = (1^1 1^1)^{\frac{1}{2}} m = 5.5 \times 10^{-3} \text{ mol kg}^{-1}$$

(b) $\text{Ca}(\text{NO}_3)_2$

$$m_{\pm} = (v_+^{\nu} v_-^{\nu})^{\frac{1}{\nu}} m$$

$$m_{\pm} = (1^1 2^2)^{\frac{1}{3}} m = (4)^{\frac{1}{3}} \times 5.5 \times 10^{-3} \text{ mol kg}^{-1} = 8.7 \times 10^{-3} \text{ mol kg}^{-1}$$

(c) ZnSO_4

$$m_{\pm} = (v_+^{\nu} v_-^{\nu})^{\frac{1}{\nu}} m$$

$$m_{\pm} = (1^1 1^1)^{\frac{1}{2}} m = 5.5 \times 10^{-3} \text{ mol kg}^{-1}$$

P10.28 Calculate ΔH_R and ΔG_R for the reaction $\text{AgNO}_3(aq) + \text{KCl}(aq) \rightarrow \text{AgCl}(s) + \text{KNO}_3(aq)$.

$$\Delta G_R^{\circ} = \Delta G_f^{\circ}(\text{AgCl}, s) + \Delta G_f^{\circ}(\text{K}^+, aq) + \Delta G_f^{\circ}(\text{NO}_3^-, aq) - \Delta G_f^{\circ}(\text{Ag}^+, aq) - \Delta G_f^{\circ}(\text{NO}_3^-, aq) - \Delta G_f^{\circ}(\text{K}^+, aq) - \Delta G_f^{\circ}(\text{Cl}^-, aq)$$

$$\Delta G_R^{\circ} = \Delta G_f^{\circ}(\text{AgCl}, s) - \Delta G_f^{\circ}(\text{Ag}^+, aq) - \Delta G_f^{\circ}(\text{Cl}^-, aq) = -109.8 \text{ kJ mol}^{-1} - 77.1 \text{ kJ mol}^{-1} + 131.2 \text{ kJ mol}^{-1} = -55.7 \text{ kJ mol}^{-1}$$

$$\Delta H_R^{\circ} = \Delta H_f^{\circ}(\text{AgCl}, s) - \Delta H_f^{\circ}(\text{Ag}^+, aq) - \Delta H_f^{\circ}(\text{Cl}^-, aq)$$

$$\Delta H_R^{\circ} = -127.0 \text{ kJ mol}^{-1} - 105.6 \text{ kJ mol}^{-1} + 167.2 \text{ kJ mol}^{-1} = -65.4 \text{ kJ mol}^{-1}$$

P10.29 Calculate the pH of a buffer solution that is 0.200 molal in CH_3COOH and 0.15 molal in CH_3COONa using the Davies equation to calculate γ_{\pm} . What pH value would you have calculated if you had assumed that $\gamma_{\pm} = 1$?

We write the equilibrium constant in the form

$$K = \frac{\gamma_+ m(\text{H}_3\text{O}^+) \gamma_- m(\text{CH}_3\text{COO}^-)}{m(\text{CH}_3\text{COOH})}$$

$$1.75 \times 10^{-5} = \frac{(\gamma_{\pm})^2 x \times (0.150 + x)}{(0.200 - x)} \approx \frac{0.150}{0.200} (\gamma_{\pm})^2 x$$

$$m(\text{H}_3\text{O}^+) = \frac{0.200}{0.150} \times \frac{1.75 \times 10^{-5}}{(\gamma_{\pm})^2}$$

$$\text{pH} = \log\{m(\text{H}_3\text{O}^+)\}$$

To calculate γ_{\pm} from the Davies equation, we must first calculate the ionic strength of the solution. The small value of K tells us that the degree of ionization of the acetic acid is small so that the ionic strength can be calculated from the concentration of CH_3COONa alone.

$$I = \frac{m}{2} (v_+ z_+^2 + v_- z_-^2) = \frac{0.150 \text{ mol kg}^{-1}}{2} \times (1 + 1) = 0.150 \text{ mol kg}^{-1}$$

Using the Davies equation

$$\begin{aligned}\log_{10} \gamma_{\pm} &= -0.51 |z_+ z_-| \left[\frac{\left(\frac{I}{m^\circ}\right)^{1/2}}{1 + \left(\frac{I}{m^\circ}\right)^{1/2}} - 0.30 \left(\frac{I}{m^\circ}\right) \right] \\ &= -0.51 \left[\frac{(0.150)^{1/2}}{1 + (0.150)^{1/2}} - 0.30 \times 0.150 \right] = -0.1194 \\ \gamma_{\pm} &= 0.760\end{aligned}$$

$$m(\text{H}_3\text{O}^+) = \frac{0.200}{0.150} \times \frac{1.75 \times 10^{-5}}{(0.760)^2} = 4.04 \times 10^{-5} \text{ mol kg}^{-1}$$

$$\text{pH} = -\log\{4.04 \times 10^{-5}\} = 4.39$$

If we had assumed $\gamma_{\pm} = 1$

$$m(\text{H}_3\text{O}^+) = \frac{0.200}{0.150} \times \frac{1.75 \times 10^{-5}}{(\gamma_{\pm})^2} = 2.33 \times 10^{-5}$$

$$\text{pH} = -\log\{2.33 \times 10^{-5}\} = 4.63$$

P10.30 Use the Davies equation to calculate γ_{\pm} for a 1.00 molar solution of KOH. Compare your answer with the values in Table 10.3.

$$\begin{aligned}\log_{10} \gamma_{\pm} &= -0.51 |z_+ z_-| \left[\frac{\left(\frac{I}{m^\circ}\right)^{1/2}}{1 + \left(\frac{I}{m^\circ}\right)^{1/2}} - 0.30 \left(\frac{I}{m^\circ}\right) \right] \\ &= -0.51 \left[\frac{(1.00)^{1/2}}{1 + (1.00)^{1/2}} - 0.30 \times 1.00 \right] = -0.1020 \\ \gamma_{\pm} &= 0.791\end{aligned}$$

This answer is reasonably close to the tabulated value of 0.0756.