Thermodynamics: Examples for chapter 7.

1. How much work (in kJ/mol) can in principle be obtained when an electron is brought to 0.5000 nm distance from a proton?

Solution:

The work is obtained by integrating the work differential:

$$\int_{0}^{w} dw = \int_{0}^{Q_{1}} \underbrace{\frac{Q_{2}}{4\pi\epsilon_{0}\epsilon_{r}r}}_{=\phi} dQ_{1}$$
$$\Rightarrow w = \frac{1}{4\pi\epsilon_{0}\epsilon_{r}} \times \frac{Q_{1}Q_{2}}{r} = (0.8988 \times 10^{10} \text{ N m}^{2} \text{ C}^{-2}) \times \frac{(1.602 \times 10^{-19} \text{ C})^{2}}{5.000 \times 10^{-10} \text{ m}}$$
$$= 4.613 \times 10^{-19} \text{ J}$$

To get this in units $kJ \mod^{-1}$, we have to multiply by the Avogadro constant:

$$w = (6.022 \times 10^{23} \text{ mol}^{-1}) \times (4.613 \times 10^{-19} \text{ J}) = 277.8 \text{ kJ mol}^{-1}$$

2. (a) The mean ionic activity coefficient of 0.1 molal HCl(aq) at 25 °C is 0.796. What is the activity of HCl in this solution? (b) The mean activity coefficient of 0.1 molal $H_2SO_4(aq)$ is 0.265. What is the activity of H_2SO_4 in this solution?

Solution:

The mean activity coefficients can be calculated as follows: (a) $a(\text{HCl}) = (0.796)^2 \times (0.1)^2 = 0.00634$. Here $v_{\pm} = v_{+} + v_{-} = 1 + 1 = 2$. (b) $a(\text{H}_2\text{SO}_4) = (0.265)^3 \times (0.1)^3 \times 1^1 \times 2^2 = 7.44 \times 10^{-5}$. Here $v_{+} = 2$ and $v_{-} = 1$. 3. Estimate the cell EMF: $Zn(s)|ZnCl_2(aq, 0.02 \text{ mol } kg^{-1})|AgCl(s)|Ag(s)$ at 25 °C by using the Debye-Hückel equation.

Solution:

First we need to write down the electrode reactions (E° 's from table):

 $\begin{array}{l} \mbox{Right electrode: } \mbox{AgCl}(s) + e^- = \mbox{Ag}(s) + \mbox{Cl}^- \ (E^\circ = 0.222 \ \mbox{V}). \\ \mbox{Left electrode: } \frac{1}{2} \mbox{Zn}^{2+} + e^- = \frac{1}{2} \mbox{Zn}(s) \ (E^\circ = -0.763 \ \mbox{V}). \end{array}$

The total reaction is then:

$$\operatorname{AgCl}(s) + \frac{1}{2}\operatorname{Zn}(s) = \operatorname{Ag}(s) + \underbrace{\frac{1}{2}\operatorname{Zn}^{2+} + \operatorname{Cl}^{-}}_{=\frac{1}{2}\operatorname{Zn}\operatorname{Cl}_{2}(aq)}$$

From the half-reactions we get $E^{\circ} = 0.985$ V.To get the actual cell potential (EMF), we must use the Nernst equation (solids have activities of 1 below):

$$E = E^{\circ} - \frac{RT}{\underbrace{|v_e|}_{=1}F} \ln\left(a(\operatorname{ZnCl}_2)^{1/2}\right) = E^{\circ} - \frac{RT}{2F} \ln\left(a(\operatorname{ZnCl}_2)\right)$$

The activity of ZnCl_2 can be calculated using the Debye-Hückel equation:

$$I = \frac{1}{2} \left(m \times 2^2 + 2m \times 1^1 \right) = \frac{6m}{2} = 0.06 \text{ mol kg}^{-1}$$
$$A = \frac{1}{2.303} \left(\frac{2\pi (6.022 \times 10^{23} \text{ mol}^{-1})(997 \text{ kg})}{1.000 \text{ m}^3} \right)^{1/2}$$
$$\times \left(\frac{(1.602 \times 10^{-19} \text{ C})^2 (0.8988 \times 10^{10} \text{ N m}^2 \text{ C}^{-2})}{(78.54)(1.3807 \times 10^{-23} \text{ J K}^{-1})(298.15 \text{ K})} \right)^{3/2}$$
$$= 0.509 \text{ kg}^{1/2} \text{ mol}^{-1/2}$$
$$\gamma_{\pm} = 10^{Az_{\pm}z_{-}\sqrt{I}} = 0.563$$

The activity of the electrolyte is then given by:

$$a(\text{ZnCl}_2) = (0.563)^{2+1} (m/m^\circ)^{2+1} \times 2^2 \times 1^2 = 0.714 \times m^3 = 5.71 \times 10^{-6}$$

where $m^{\circ} = 1, v_{-} = 2, v_{+} = 1$. The Nernst equation then gives:

$$E = (0.985 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{2(96485 \text{ C mol}^{-1})} \ln (5.71 \times 10^{-6}) = 1.140 \text{ V}$$

4. For the galvanic cell: $H_2(g)|HCl(aq)|Cl_2(g)$, where both gas pressures are 1 bar, the standard EMF at 298.15 K is 1.3604 V and $(\partial E^{\circ}/\partial T)_P =$ -1.247×10^{-3} V K⁻¹. Note that HCl is a strong acid and fully ionized.(a) What are the values of $\Delta_r G^{\circ}$, $\Delta_r H^{\circ}$, and $\Delta_r \bar{S}^{\circ}$ for the cell reaction? (b) What are the values of $\Delta_f G^{\circ}$, $\Delta_f H^{\circ}$, and S° for Cl⁻ ion? The following data is known (see the Chemistry Webbook): $\Delta_f G^{\circ}(H^+) =$ $\Delta_f H^{\circ}(H^+) = \Delta_f S^{\circ}(H^+) = 0, \bar{S}^{\circ}(H_2(g)) = 130.684$ J K⁻¹ mol⁻¹, and $\bar{S}^{\circ}(Cl_2(g)) = 223.066$ J K⁻¹ mol⁻¹. Note that $\Delta_f G^{\circ}(HCl) = \Delta_f G^{\circ}(Cl_2) =$ 0.

Solution:

(a) First the cell half-reactions must be written: Right electrode: $\frac{1}{2}Cl_2(g) + e^- = Cl^-(aq)$. Left electrode: $H^+(aq) + e^- = \frac{1}{2}H_2(g)$. Total: $\frac{1}{2}Cl_2(g) + \frac{1}{2}H_2(g) = H^+(aq) + Cl^-(aq)$.

The standard reaction Gibbs energy is then given by $(v_e = 1)$:

$$\Delta_r G^{\circ} = -|v_e| F E^{\circ} = -(96485 \text{ C mol}^{-1})(1.3604 \text{ V}) = -131.260 \text{ kJ mol}^{-1}$$

and the remaining thermodynamic quantities are given by (see lecture notes):

$$\Delta_r H^{\circ} = -|v_e| F E^{\circ} + |v_e| F T \left(\frac{\partial E^{\circ}}{\partial T}\right)_P$$

= -131.2604 kJ mol⁻¹ + (9.6485 C mol⁻¹) × (298.15 K)
×(-1.247 × 10⁻³ V K⁻¹) = -167.13 kJ mol⁻¹

$$\Delta_r S^\circ = |v_e| F\left(\frac{\partial E^\circ}{\partial T}\right)_P = -120.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

(b) By definition: $\Delta_f G^{\circ}(\mathrm{H}^+) = \Delta_f H^{\circ}(\mathrm{H}^+) = \Delta_f S^{\circ}(\mathrm{H}^+) = 0$. From the above we also have $\Delta_f G^{\circ}(\mathrm{Cl}^-) = -131.260 \text{ kJ mol}^{-1} \text{ and } \Delta_f H^{\circ}(\mathrm{Cl}^-) = -167.13 \text{ kJ mol}^{-1}$. The only missing quantity is $\bar{S}^{\circ}(\mathrm{Cl}^-(aq))$ (i.e. the entropy of $\mathrm{Cl}^-(aq)$. By definition, we have:

$$\underbrace{\Delta_r S^{\circ}}_{=-120 \text{ J K}^{-1} \text{ mol}^{-1}} = \underbrace{\bar{S}^{\circ}(\mathrm{H}^+)}_{=0} + \underbrace{\bar{S}^{\circ}(\mathrm{Cl}^-(aq))}_{=?} - \frac{1}{2} \underbrace{\bar{S}^{\circ}(\mathrm{H}_2(g))}_{=130.684 \text{ J K}^{-1} \text{ mol}^{-1}} - \frac{1}{2} \underbrace{\bar{S}^{\circ}(\mathrm{Cl}_2(g))}_{=223.066 \text{ J K}^{-1} \text{ mol}^{-1}}$$

Solving for $\bar{S}^{\circ}(\mathrm{Cl}^-(aq))$ gives 56.6 J K⁻¹ mol⁻¹.

- 5. What are the values of $\Delta_r G^{\circ}$ and K for the following reactions:
 - (a) $Cu(s) + Zn^{2+}(aq) = Cu^{2+}(aq) + Zn(s)$
 - (b) $H_2(g) + Cl_2(g) = 2HCl(aq)$
 - (c) $Ca^{2+}(aq) + CO_3^{2-}(aq) = CaCO_3(s)$
 - (d) $\frac{1}{2}Cl_2(g) + Br^{-}(aq) = \frac{1}{2}Br_2(aq) + Cl^{-}(aq)$
 - (e) $Ag^+(aq) + Fe^{2+}(aq) = Fe^{3+}(aq) + Ag(s)$

The following values are known (see the Chemistry Webbook): $\Delta_f G^{\circ}(\operatorname{Cu}^{2+}(aq)) = 65.49 \text{ kJ mol}^{-1}, \Delta_f G^{\circ}(\operatorname{Zn}(s)) = 0, \Delta_f G^{\circ}(\operatorname{Zn}^{2+}(aq)) = -147.06 \text{ kJ mol}^{-1}, \Delta_f G^{\circ}(\operatorname{Cu}(s)) = 0, \Delta_f G^{\circ}(\operatorname{HCl}(aq)) = -131.228 \text{ kJ mol}^{-1}, \text{ and } \Delta_f G^{\circ}(\operatorname{Cl}_2(g)) = 0, \Delta_f G^{\circ}(\operatorname{H}_2(g)) = 0.$

Solution:

(a)

$$\Delta_r G^{\circ} = \underbrace{\Delta_f G^{\circ}(\operatorname{Cu}^{2+}(aq))}_{=65.49 \text{ kJ mol}^{-1}} + \underbrace{\Delta_f G^{\circ}(\operatorname{Zn}(s))}_{=0} - \underbrace{\Delta_f G^{\circ}(\operatorname{Zn}^{2+}(aq))}_{=-147.06 \text{ kJ mol}^{-1}} - \underbrace{\Delta_f G^{\circ}(\operatorname{Cu}(s))}_{=0} = 212.55 \text{ kJ mol}^{-1}$$
$$= 212.55 \text{ kJ mol}^{-1}$$
$$K = \exp\left(-\frac{\Delta_r G^{\circ}}{RT}\right) = 5.79 \times 10^{-38}$$

(b)

$$\Delta_r G^{\circ} = 2 \underbrace{\Delta_f G^{\circ}(\text{HCl}(aq))}_{=-131.228 \text{ kJ mol}^{-1}} - \underbrace{\Delta_f G^{\circ}(\text{Cl}_2(g))}_{=0} - \underbrace{\Delta_f G^{\circ}(\text{H}_2(g))}_{=0} = -262.46 \text{ kJ mol}^{-1}$$
$$K = 9.56 \times 10^{45}$$

(c) Continuing the same way: $\Delta_r G^\circ = -47.40 \text{ kJ mol}^{-1}$ and $K = 2.01 \times 10^8$. (d) Continuing the same way: $\Delta_r G^\circ = -25.71 \text{ kJ mol}^{-1}$ and $K = 3.20 \times 10^4$.

(e) Continuing the same way: $\Delta_r G^\circ = -2.9 \text{ kJ mol}^{-1}$ and K = 3.23.

- 6. (a) Write the reaction that occurs when the cell Zn|ZnCl₂|AgCl|Ag, where $m(\text{ZnCl}_2) = 0.555 \text{ mol kg}^{-1}$, delivers current at 25 °C. At this temperature, E = 1.015 V and $(\partial E/\partial T)_P = -4.02 \times 10^{-4} \text{ V}$ K⁻¹.
 - (b) What is $\Delta_r G$?
 - (c) What is $\Delta_r S$?
 - (d) What is $\Delta_r H$?

Solution:

(a)

Right electrode: $AgCl + e^- = Ag + Cl^- (E^\circ = +0.222V)$ Left electrode: $\frac{1}{2}Zn^{2+} + e^- = \frac{1}{2}Zn (E^\circ = -0.763 V)$ Total: $AgCl + \frac{1}{2}Zn = \frac{1}{2}Zn^{2+} + Ag + Cl^- (E^\circ = +0.985 V)$ (b) $\Delta_r G = -|v_e| FE = -(1)(96485 C mol^{-1})(1.015 V) = -97.93 kJ mol^{-1}$ Note that if we had written the total reaction as $2AgCl + Zn = Zn^{2+} + 2Ag + 2Cl^-$, $\Delta_r G^\circ$ would be twice as much as above.

(c) For a non-standard state we can write:

$$\Delta_r S = |v_e| F\left(\frac{\partial E}{\partial T}\right)_P = (1)(96485 \text{ C mol}^{-1})(-4.02 \times 10^{-4} \text{ V K}^{-1})$$
$$= -38.79 \text{ J K}^{-1} \text{ mol}^{-1}$$

(d) Using $\Delta_r H = \Delta_r G + T \Delta_r S$, we can get

$$\Delta_r H = (-97930 \text{ J mol}^{-1}) + (298.15 \text{ K})(-38.79 \text{ J K}^{-1} \text{ mol}^{-1}) = 109.5 \text{ kJ mol}^{-1}$$

Note that this would have been twice as much if the reaction was written as discussed above.

7. Consider a cell that has the following cell reaction:

$$AgBr(s) = Ag^{+} + Br^{-}$$

Calculate the equilibrium constant (usually called the solubility product) for this reaction at 25°C.

Solution:

The half-cell reactions are:

Right: Ag|Ag⁺ with Ag⁺ + e^- = Ag ($E^\circ = 0.7992$ V) Left: Br⁻|AgBr(s)|Ag with AgBr + e^- = Ag + Br⁻ ($E^\circ = 0.0732$ V) Total: Ag|AgBr(s)|Br⁻|Ag⁺|Ag with Ag⁺+Br⁻ = AgBr ($E^\circ = 0.7260$ V)

The equilibrium constant is then given by:

$$K = \exp\left(-\frac{|v_e|FE^\circ}{RT}\right) = 5.35 \times 10^{-13}$$

This means that the balance is on the left side in the reaction. Note that the cell chemical equation came out in the opposite order as given in the problem and this introduces a sign difference.

8. For 0.002 mol kg⁻¹ CaCl₂ at 25 °C use the Debye-Hückel limiting law to calculate the activity coefficients of Ca²⁺ and Cl⁻. What are the ion activity coefficients (γ_+ and γ_-) and the mean activity coefficient for the electrolyte (γ_{\pm})?

Solution:

Use the equations given in the lecture notes:

$$m_{\rm Ca^{2+}} = 0.002 \text{ mol kg}^{-1}$$

$$m_{\rm Cl^-} = 2 \times 0.002 \text{ mol } \text{kg}^{-1} = 0.004 \text{ mol } \text{kg}^{-1}$$
$$z_{\rm Cl^-} = -1.0 \text{ and } z_{\rm Ca^{2+}} = +2.0$$
$$I = \frac{1}{2} \left(m_{\rm Ca^{2+}} z_{\rm Ca^{2+}}^2 + m_{\rm Cl^-} z_{\rm Cl^-}^2 \right) = 6.0 \times 10^{-3} \text{ mol } \text{kg}^{-1}$$
$$A = 0.509 \text{ kg}^{1/2} \text{ mol}^{-1/2} \text{ (from problem 3)}$$
$$\gamma \left(\text{Ca}^{2+} \right) = 10^{-Az_{\rm Ca^{2+}}^2 \sqrt{I}} = 0.85$$
$$\gamma \left(\text{Cl}^- \right) = 10^{-Az_{\rm Cl^-}^2 \sqrt{I}} = 0.96$$
$$\gamma_{\pm} = 10^{-Az_{+}z_{-}\sqrt{I}} = 0.83$$