Chemistry 431
Problem Set 13
Fall 2023
Solutions

1. For the cell

   Pt|H_2 (f=1 bar)|HCl|AgCl|Ag

   the measured *standard* EMF at 25.°C is $E^{\ominus}$=0.222 volts. If the measured EMF of the cell at 25.°C is 0.385 volts, what is the pH of the HCl solution? Using molalities, assume pH=-$\log_{10}(m_{H^+}/m_0)$.
   Answer:

$$\text{Right: } \text{AgCl}_{(s)} + e^- \longrightarrow \text{Ag}_{(s)} + \text{Cl}^-_{(aq)}$$

$$\text{Left: } \text{H}^+_{(aq)} + e^- \longrightarrow \frac{1}{2}\text{H}_{2(g)}$$

$$\text{Overall: } \text{AgCl}_{(s)} + \frac{1}{2}\text{H}_{2(g)} \longrightarrow \text{Ag}_{(s)} + \text{H}^+_{(aq)} + \text{Cl}^-_{(aq)}$$

$$E = E^{\ominus} - \frac{RT}{F}\ln\frac{(m_{H^+}/m_0)(m_{Cl^-}/m_0)}{f_{H_2}^{1/2}}$$

$$0.385\text{ V} = 0.222\text{ V} - \frac{(8.3144\text{ J mol}^{-1}\text{K}^{-1})(298\text{ K})}{96485\text{ C mol}^{-1}}\ln(m_{H^+}/m_0)^2$$

$$(m_{H^+}/m_0)^2 = 1.75\times10^{-3}$$

$$m_{H^+}/m_0 = 0.0418$$

$$\text{pH} = -\log_{10}(0.0418) = 1.38$$

2. Consider the cell

   $Ag_{(s)}|AgCl_{(s)}|HCl_{(aq)}|Cl_{2(g)}|Pt$

   (a) Use Table 11.1 to find the standard EMF for the cell at 25.°C.
   Answer:

$$\text{Right: } \text{Cl}_{2(g)} + 2e^- \longrightarrow 2\text{Cl}^-_{(aq)} \qquad E_R^{\ominus} = 1.35827\text{ V}$$

$$\text{Left: } 2\text{AgCl}_{(s)} + 2e^- \longrightarrow 2\text{Ag}_{(s)} + 2\text{Cl}^-_{(aq)} \qquad E_L^{\ominus} = 0.22233\text{ V}$$

$$E^{\ominus} = E_R^{\ominus} - E_L^{\ominus} = 1.13594\text{ V}$$

(b) Calculate ΔG at 25.°C when 1 Faraday of current passes through the cell.
Answer:

$$\Delta_{r,m}G^{\ominus} = -nFE^{\ominus}$$

For 1 Faraday, $n = 1$ and

$$\Delta_{r,m}G^{\ominus} = -(96485 \text{ C mol}^{-1})(1.13594 \text{ J C}^{-1}) = -109601 \text{ J}$$

(c) Show that the total reversible work attending the passage of 1 Faraday of current through the cell is

$$w_{rev} = -E^{\ominus}F + \frac{1}{2}RT.$$

Answer:

$$w_{rev} = w_{elec} + w_{PV}$$
$$= -E^{\ominus}F - P\Delta V$$
$$-E^{\ominus}F - \Delta(PV)$$
$$= -E^{\ominus}F - \Delta(nRT)$$
$$-E^{\ominus}F - RT\Delta n_{gas}$$
$$\Delta n_{gas} = -\frac{1}{2}$$
$$w_{rev} = -E^{\ominus}F + \frac{1}{2}RT$$

3. Show that

$$\left(\frac{\partial \dfrac{E^{\ominus}}{T}}{\partial T}\right)_P = \frac{\Delta_m H^{\ominus}}{nFT^2}$$

Answer:

$$\left(\frac{\partial E^{\ominus}/T}{\partial T}\right)_P = -\frac{1}{nF}\left(\frac{\partial \Delta_{r,m}G^{\ominus}/T}{\partial T}\right)_P$$
$$= \frac{\Delta_{r,m}H^{\ominus}}{nFT^2}$$

by the Gibbs-Helmholtz equation.

4. When the reaction

$$\frac{1}{2}H_{2(g)} + AgCl_{(s)} \longrightarrow Ag_{(s)} + HCl_{(aq)}$$

takes place at 25.°C in a cell, the reversible electrical work done by the reaction on the surroundings is 34476 Joules. When the same reaction takes place in a calorimeter doing only PV-work at a constant pressure of 1 bar at 25.°C, the heat transferred to the surroundings is 39292 Joules (the reaction is exothermic).

(a) What is the heat liberated by the reversible reaction to the surroundings in the electrochemical cell?
Answer:

$$\Delta U = q + w$$
$$= -39292 \text{ J} - P\Delta V$$
$$= -39292 \text{ J} - RT\Delta n_{gas}$$
$$= -39292 \text{ J} - (8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})(-0.5 \text{ mol}) = -38053 \text{ J}$$
$$-38053 \text{ J} = q_{rev} + \frac{1}{2}(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K}) - 34476 \text{ J}$$
$$q_{rev} = -4816 \text{ J}$$

(b) Calculate $\Delta_m S^{\ominus}, \Delta_m H^{\ominus}$ and $\Delta_m U^{\ominus}$ for the reaction. Assume ΔV for the reaction is just that associated with the disappearance of 1/2 mole of an ideal gas.
Answer:

$$\Delta_{r,m} U^{\ominus} = -38053 \text{ J mol}^{-1}$$
$$\Delta_{r,m} H^{\ominus} = q = -39292 \text{ J mol}^{-1}$$
$$\Delta_{r,m} G^{\ominus} = w_{elec} = -34476 \text{ J}$$
$$\Delta_{r,m} S^{\ominus} = \frac{\Delta_{r,m} H^{\ominus} - \Delta_{r,m} G^{\ominus}}{T}$$
$$= \frac{-39292 \text{ J mol}^{-1} + 34476 \text{ J mol}^{-1}}{298 \text{ K}} = -16.16 \text{ J mol}^{-1}\text{K}^{-1}$$

5. Use Table 11.1 to calculate the EMF of the cell

$\text{Ni}|\text{Ni}^{2+}_{(aq)}(a = 1.0\times\ 10^{-5})||\text{H}^{+}_{(aq)}\ (a = 1.0\times\ 10^{-6})|\text{H}_{2(g)}$ (f = 1 bar)|Pt

at 25.°C.
Answer:

$$\text{Right: } 2\text{H}^{+}_{(aq)} + 2e^{-} \longrightarrow \text{H}_{2(g)}$$
$$\text{Left: } \text{Ni}^{2+}_{2(aq)} + 2e^{-} \longrightarrow \text{Ni}_{(s)}$$
$$\text{Overall: } 2\text{H}^{+}_{(aq)} + \text{Ni}_{(s)} \longrightarrow \text{H}_{2(g)} + \text{Ni}^{2+}_{(aq)}$$
$$E^{\ominus} = E^{\ominus}_{R} - E^{\ominus}_{L} = 0 - (-0.257 \text{ V}) = 0.257 \text{ V}$$
$$E = E^{\ominus} - \frac{RT}{nF}\ln Q$$
$$E = E^{\ominus} - \frac{RT}{nF}\ln \frac{a_{Ni^{2+}} f(H_{2(g)})}{(a_{H^{+}})^2}$$
$$= 0.257 \text{ V} - \frac{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})}{2(96485 \text{ C mol}^{-1})}\ln\frac{10^{-5}\times 1}{(10^{-6})^2} = 0.050 \text{ V}$$

6. At 298 K, the EMF of the electrochemical cell

$$Cd_{(s)}|Cd(OH)_{2(s)}|OH^-_{(aq)}(a = 1.00{\times}10^{-4})||F^-_{(aq)}(a = 1.00{\times}10^{-5})|F_{2(g)}(P = 0.250 \text{ bar})|Pt_{(s)}$$

is 3.716 V. Given the standard half-cell reduction potentials $E^{\ominus}_{Cd^{2+}/Cd(OH)_2/Cd} = -0.809$ V and $E^{\ominus}_{F^-/F_2} = 2.866$ V, calculate the fugacity coefficient for the fluorine gas in the cell.

Answer:

$$\text{Right: } F_{2(g)} + 2e^- \longrightarrow 2F^-_{(aq)}$$

$$\text{Left : } \underline{Cd(OH)_{2(s)} + 2e^- \longrightarrow Cd_{(s)} + 2OH^-_{(aq)}}$$

$$\text{Overall: } F_{2(g)} + Cd_{(s)} + 2OH^-_{(aq)} \longrightarrow 2F^-_{(aq)} + Cd(OH)_{2(s)}$$

$$Q = \frac{(a_{F^-})^2}{(a_{OH^-})^2 P_{F_2}\gamma/P^{\ominus}}$$

$$E^{\ominus} = E^{\ominus}_R - E^{\ominus}_L = 3.675 \text{ V}$$

$$E = E^{\ominus} - \frac{RT}{nF}\ln Q = E^{\ominus} - \frac{RT}{nF}\ln\frac{(a_{F^-})^2}{(a_{OH^-})^2 P_{F_2}\gamma/P^{\ominus}}$$

$$3.716 \text{ V} = 3.675 \text{ V} - \frac{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})}{2(96485 \text{ C mol}^{-1})}\ln\frac{(1.00\times10^{-5})^2}{(1.00\times10^{-4})^2(0.250\gamma)}$$

$$\gamma = 0.975$$