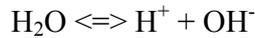
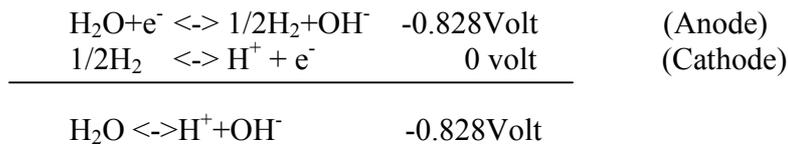


Homework IV Solution

1. For an overall reaction of



(a) Use the Table 4.1 in the Lecture Note – Electrochemical Energy Conversion and Storage to define two half cell reactions for the above reaction and calculate the electrochemical potential of the reaction under standard conditions.



(b) Calculate the molalities of H^+ and OH^- in deionized water at 298K. Show calculation step by step and state all assumptions made.

Note that ε is related to mole fractions of H^+ and OH^- by the following equations assuming that the activity coefficients of the species are 1:

$$\text{Eq. 1 } \frac{a_{\text{H}^+} a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}} = \frac{\gamma_{\text{H}^+} m_{\text{H}^+} \gamma_{\text{OH}^-} m_{\text{OH}^-}}{1} = K_p(T, P) = \exp\left(-\frac{\Delta G_r^\circ}{RT}\right)$$

Assuming $\gamma_{\text{H}^+} = \gamma_{\text{OH}^-} = 1$,

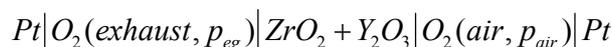
$$\frac{m_{\text{H}^+} m_{\text{OH}^-}}{1} = K_p(T, P) = \exp\left(-\frac{\Delta G_r^\circ}{RT}\right)$$

$$\text{Eq. 2 } -nF\varepsilon = \Delta G_r^\circ$$

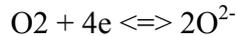
From Eqs. 1 and 2, one can get $K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ at 298K. If $\text{pH} = 7$, then $[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7}$. Then, the molalities (m_{H^+} and m_{OH^-}) and molarities ($[\text{H}^+]$ and $[\text{OH}^-]$) of H^+ and OH^- are identical, which is equal to 1.0×10^{-7} mole per 1000g water.

The molality is the number of moles of solute present in 1000 grams of water while molarity is the number of moles of solute present in one liter of water. Note that 1000 grams is equivalent to one liter of water.

2. An exhaust gas analyzer uses an electrochemical solid state cell (sensor) to measure oxygen concentrations in the exhaust. This cell consists of a solid-state electrolyte zirconium dioxide (ZrO_2) with yttria (Y_2O_3) that provides oxygen ion conduction in the cell, and Pt electrodes used for anode and cathode, depicted as,



The electrode reaction that occurs at high temperature at both the anode-electrolyte and cathode-electrolyte interfaces is



- (a) Please write the governing equation for the cell potential as a function of pressures, P_{eg} and P_{air} .

If one assumes that $P_{\text{eg}} > P_{\text{air}}$ and P_{eg} and P_{air} are the partial pressure of O_2 in the exhaust and the air, respectively, the potential generated by partial pressure difference is as follow:

$$\varepsilon = -\frac{RT}{nF} \log\left(\frac{P_{\text{eg}}}{P_{\text{air}}}\right)$$

Note that Pt electrodes in the air acts as a cathode due to higher partial pressure of O_2 . Also, it is assumed that the activity coefficients are 1.

- (b) What would the cell voltage be when the partial pressure of oxygen in the exhaust gas is 0.02atm?

State all assumptions made in answering (a) -(b)

If we assume $T=300\text{K}$, $P_{\text{air}}=0.21\text{atm}$, then we get

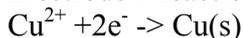
$$\varepsilon = -8.314 \cdot 300 / (4 \cdot 96485) \cdot \log(0.02 / 0.21) = 15.2\text{mV}$$

3. Consider an electrochemical cell with different concentration of aqueous CuCl_2 solutions in each 1/2 cell. 3.5 molal CuCl_2 on one side and 1 molal CuCl_2 solution on the other side separated by a ion conducting membrane permeable only to Cu^{+2} and Cl^{-1} ions. The electrodes are Pt coated with a thin film of copper metal.

- (a) Initially will the cell produce a current against a resistive load? Explain.

A concentration cell produces a voltage as it attempts to reach equilibrium, which will occur when the concentration in both cells are equal. To reach this point, Cu^{2+} ions in the concentrated solution (3.5molal solution) are reduced while oxidation increases Cu^{2+} in the dilute solution. However, oxidation of Cl^{-1} cannot occur since the standard potential of Cl^{-1} is higher than that of Cu^{2+} . Hence, released electrons from the anode by Cu^{2+} oxidation can produce current passing through a resistive circuit. To satisfy the local electroneutrality, Cl^{-} should migrate from the concentration cell through the membrane to the dilute cell. These reactions are represented as follow:

Electrode 1 reaction (Cathode, 3.5molal solution)



$$\varepsilon_{\text{cathode}} = 0.337\text{V} - RT / (nF) \log(1 / \gamma_{\text{Cu}^{2+}} m_{\text{Cu}^{2+}}) \text{ where activity coefficient is equal to 1.}$$

Note that $\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^{-}$ is not available and hence reduction of Cu^{2+} only occurs in the cathode.

Electrode 2 reaction (Anode, 1molal solution)



$$\varepsilon_{\text{anode}} = 0.337\text{V} - \frac{RT}{nF} \log(\gamma_{\text{Cu}^{2+}} m_{\text{Cu}^{2+}})$$

Potential in the resistive load can be calculated as

$$\varepsilon = \varepsilon_{\text{cathode}} - \varepsilon_{\text{anode}} = -\frac{RT}{nF} \log \frac{[\gamma_{\text{Cu}^{2+}} m_{\text{Cu}^{2+}}]_{\text{Dilute}}}{[\gamma_{\text{Cu}^{2+}} m_{\text{Cu}^{2+}}]_{\text{Conc}}} = -\frac{RT}{nF} \log \frac{[m_{\text{Cu}^{2+}}]_{\text{Dilute}}}{[m_{\text{Cu}^{2+}}]_{\text{Conc}}} \text{ assuming the}$$

activity coefficients of Cu^{2+} ions in the dilute and concentrated solutions are the same.

Note that $[m_{\text{Cu}^{2+}}]_{\text{concentrated}} > [m_{\text{Cu}^{2+}}]_{\text{Dilute}}$ and hence $\varepsilon > 0$.

(b) What is the maximum amount of work that such a cell would produce?

Note that concentration of Cu^{2+} changes from 3.5 to $(3.5+1)/2=2.25$ in the concentration cell and from 1 to 2.25 in the dilute cell.

If we define X is the change in the molal values in the concentrated solution and assume that the activity coefficient of Cu^{2+} is 1 or does not change within the range between 1 to 3.5 molal, we get

$$\varepsilon = -\frac{RT}{nF} \log \left(\frac{[m_{\text{Cu}^{2+}}]_{\text{Dilute}}}{[m_{\text{Cu}^{2+}}]_{\text{Conc}}} \right)$$

Since X changes from 0 to 1.25.

$$\text{Work} = -\Delta G = nF\varepsilon = -RT \int_0^{1.25} \log \left(\frac{1+X}{3.5-X} \right) dX$$

Assuming $T=300\text{K}$, we get $\text{Work}=1.47\text{kJ}/(\text{mole of CuCl}_2)$

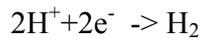
(c) What happens to the concentrations of ions in the cell after a period of time?

Over a long period of time the potential will drop to zero when the concentrations of Cu^{2+} become 1.25 molal in both cells. Also, Cl^- ions will move to the dilute solution to satisfy local electroneutrality (1.25 molal in both cells).

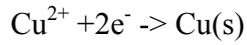
(d) Is there a way that you could modify this cell to determine the mean ionic activity of CuCl_2 as a function of concentration? (hint- Consider coupling the cell to a standard hydrogen electrode via a salt bridge. State all assumptions made in answering (a)-(d))

If the cathode of the cell is connected to the hydrogen electrode, we get the following reaction:

Hydrogen electrode (Anode)



Electrode 2 reaction (Cathode, 3.5 molal solution)



Potential between two electrodes can be calculated as

$$\varepsilon = \varepsilon^o - \frac{RT}{nF} \ln \left(\frac{[a_{\text{H}^+}]^2 [a_{\text{Cu(s)}}]}{[P_{\text{H}_2}] [a_{\text{Cu}^{2+}}]} \right) = 0.337\text{V} - \frac{8.314\text{J}/(\text{mol} \cdot \text{K}) \cdot 300\text{K}}{2 \cdot 96485\text{C/mol}} \ln(1/\gamma[\text{Cu}^{2+}])$$

Hence, one can get γ value by measuring ε .