Chemistry 342

Problem Set 11

1. The reversible emf that is measured for a cell gives the reversible work associated with the cell reaction. Since this is reversible work at constant temperature and pressure, it is therefore the free energy change. The maximum electrical work that a system (the cell) can do is given by the value of $\Delta_{\rm rxn}\boldsymbol{G}$ for the cell reaction,

$$\Delta_{\rm rxn}\boldsymbol{G} = -\nu\mathcal{F}\mathcal{E}$$

Starting from this equation, <u>write the counterparts of the following relationships</u> (a)- (h) (that we had derived previously) <u>in terms of $\mathcal{E}$</u>.

•when $(\partial \boldsymbol{G}/\partial T)_p = -\boldsymbol{S}$ is applied to each reactant and product of a chemical equation,

(a) $(\partial\Delta_{\rm rxn}\boldsymbol{G}/\partial T)_p = -\Delta_{\rm rxn}\boldsymbol{S}$

•when applied to each reactant and product of a chemical equation, in their standard states,

(b) $(\partial\Delta_{\rm rxn}\boldsymbol{G}^{\ominus}/\partial T)_p = -\Delta_{\rm rxn}\boldsymbol{S}^{\ominus}$

•when $\boldsymbol{G} = \boldsymbol{H} - T\boldsymbol{S}$ is applied to each reactant and product of a chemical equation at constant temperature,

(c) $\Delta_{\rm rxn}\boldsymbol{H} = \Delta_{\rm rxn}\boldsymbol{G}_T + T\Delta_{\rm rxn}\boldsymbol{S}$

•when applied to each reactant and product of a chemical equation, in their standard states,

(d) $\Delta_{\rm rxn}\boldsymbol{H}^{\ominus} = \Delta_{\rm rxn}\boldsymbol{G}^{\ominus}{}_T + T\Delta_{\rm rxn}\boldsymbol{S}^{\ominus}$

•when the Gibbs-Helmholtz relation $(\partial(\boldsymbol{G}/T)/\partial T)_p = -\boldsymbol{H}/T^2$ is applied to each reactant and product of a chemical equation, in their standard states,

(e) $(\partial(\Delta_{\rm rxn}\boldsymbol{G}^{\ominus}/T)/\partial T)_p = -\Delta_{\rm rxn}\boldsymbol{H}^{\ominus}/T^2$

•when applied to the equilibrium state of the chemically reacting system

(f) $d(\ln K_p)/dT = -\Delta_{\rm rxn}\boldsymbol{H}^{\ominus}/T^2$

•when $\mu(T) = \mu^{\ominus}(T) + RT\ln \boldsymbol{a}$ is applied to each reactant and product of a chemical equation,

(g) $\Delta_{\rm rxn}\boldsymbol{G}_T = \Delta_{\rm rxn}\boldsymbol{G}^{\ominus}{}_T + RT\ln \boldsymbol{Q}$ where $\boldsymbol{Q}$ is in the same form as the true equilibrium constant K for the reaction $bB + cC \rightarrow pP + rR$

•when applied to the equilibrium state of the chemically reacting system,

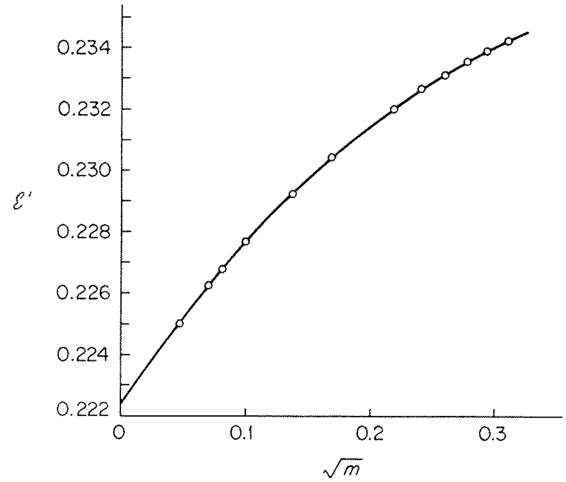
(h) $\Delta_{\rm rxn}\boldsymbol{G}^{\ominus} = -RT\ln K$

Now apply the equations that you have found in problem **1** to the following problems:

2. For the cell

$$Pt|H_2(1\ \text{atm})|HCl(m)|AgCl|Ag$$

the emf $\mathcal{E}$ of the cell has been measured at 25°C and the quantity $\mathcal{E}' = \mathcal{E} + 0.1183 \log_{10} m$ has been plotted as a function of the molality $m^{1/2}$:



From the plot, determine the value of $\mathcal{E}^{\ominus}$. Rationalize the choice of the function $\mathcal{E}'$ for this purpose. Rationalize the choice of the function $m^{1/2}$ for this plot. Determine the equilibrium constant for the reaction

$$\tfrac{1}{2}H_2(g) + AgCl = Ag + H^+ + Cl^-$$

Write the reaction at the anode. Write the reaction at the cathode.

3. The emf of the cell

$$Cd|\text{solution saturated with } CdCl_2{\cdot}2.5H_2O|AgCl|Ag$$

is 0.6753 volt at 25°C, and $d\mathcal{E}/dT = -0.00065$ volt K^{-1}. If we write the cell reaction as

$$Cd + 2AgCl = CdCl_2(\text{satd. soln.}) + 2Ag$$

then calculate $\Delta \boldsymbol{S}$, $\Delta \boldsymbol{H}$, $\Delta \boldsymbol{G}$, for this reaction. Note that q for a reversibly operating cell is q_{REV} , is given by $T\Delta \boldsymbol{S}$, which is what value in this example? The measured q when the reaction occurs directly, that is,

$$Cd + 2AgCl = CdCl_2(\text{satd. soln.}) + 2Ag \quad \text{not in a cell}$$

is given by q_p which is $\Delta \boldsymbol{H}$. How much heat would be released in the direct reaction?

Put the numerical values into the appropriate brackets in the following:

(total energy change) = (energy available to do work) + (energy not available to do work)

or enthalpy change or change in free energy

$$\Delta H = \Delta G + T\Delta S$$

4. Given that the $\mathcal{E}^{\ominus}$ for the $Cu^{+}|Cu^{2+}$ half-cell is -0.153 volt. What is the equilibrium concentration (neglecting the activity coefficients) of Cu^{+} in a 0.01 molal Cu^{2+} solution at pH 3 and saturated with respect to $H_2(g)$ at 1 atm and 25°C?
[Hint: First write the chemical equation for the reaction. Then find the $\mathcal{E}^{\ominus}$ for the reaction. Then find the equilibrium constant. Then find the Cu^{+} concentration.]
Would the H_2 further reduce the Cu^{+} to Cu^{0}? Is this feasible?
[Hint: First write the equation for the chemical reaction in which H_2 reduces Cu^{+} to Cu^{0}. Then look up the $\mathcal{E}^{\ominus}$ for the reaction. Then find the equilibrium constant. Then find the Cu^{+} concentration.]

5. To what extent should 0.01 molal Hg_2^{2+} disproportionate into Hg and Hg^{2+} at 25°C?
[Hint: First write the equation for the chemical reaction which is the disproportionation. Then find the two half-cell reactions that make up the net reaction. Look up the $\mathcal{E}^{\ominus}$ for these half cell reactions to find the net $\mathcal{E}^{\ominus}$. Then find the equilibrium constant. Then find the Hg^{2+} concentration under the conditions that some Hg(liq) is formed or is present.]

6. Calculate the solubility product constant at 25°C for Ag_2SO_4.
Given that $\mathcal{E}^{\ominus} = -0.627$ volt for the cell

$$Ag|Ag_2SO_4|H_2SO_4(m)|H_2|Pt$$

[Hint: You will need to look up the $\mathcal{E}^{\ominus}$ for the Ag,Ag^{+} half cell.]

7. Consider the concentration cell,

$$Pt|H_2(1\text{ atm})|\ m\ Ba(OH)_2|Ba(\text{amalgam})|\ 0.1200\text{ m } Ba(OH)_2|H_2(1\text{ atm})|Pt$$

At 25°C, the measured $\mathcal{E}$ for the above cell for various values of m are as follows:

$1000m$	2.45	7.93	15.09	49.70	199.60
$\mathcal{E}$ (volt)	-0.1245	-0.0840	-0.0630	-0.0254	+0.0144

(a) Write the cell reaction (each electrode separately, then the net reaction).
(b) By means of an appropriate plot and extrapolation procedure, calculate the mean activity coefficient for 0.1000 molal $Ba(OH)_2$.