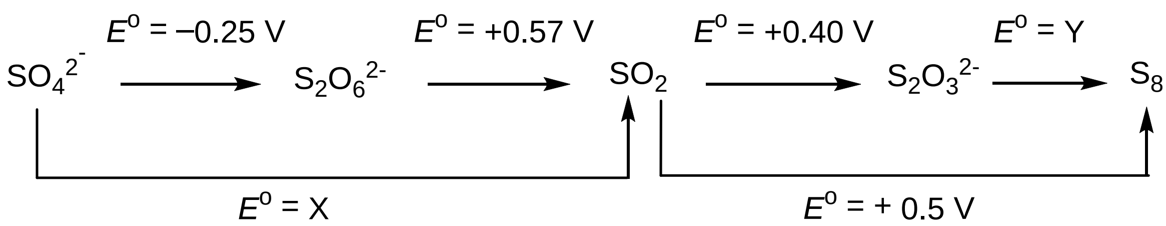
CM 1111 Tutorial 8

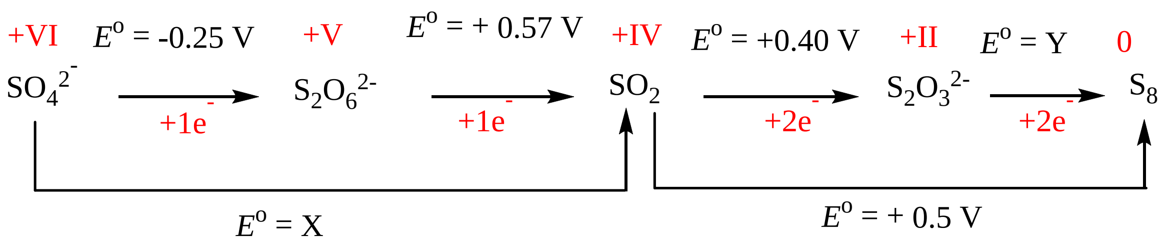
Question 1

Shown below is a Latimer diagram for sulfur oxoanions determined at pH = 0.



a) Find the standard reduction potentials X and Y.

First, find the oxidation states of the sulfur atoms in the molecules, because it will tell you the number of electrons involved in each reduction step:



X = [1 x (-0.25) + 1 x (+0.57)] / 2 = +0.16 V

0.5 = [2 x (0.4) + 2(Y)] / 4;   Y = 0.6 V

b) Is the disproportionation of $S_2O_6^{2-}$ (reaction 1) thermodynamically favorable? Briefly explain your answer (hint: protons are needed to balance the half-reactions involved in the overall disproportionation).

$$S_2O_6^{2-} \rightleftharpoons SO_4^{2-} + SO_2 \qquad \text{(reaction 1)}$$

To evaluate if the disproportionation is favorable or not, one needs to find the ΔE of the following half reactions:

$$S_2O_6^{2-} + 4\,H^+ + 2e^- \rightleftharpoons 2\,SO_2 + 2\,H_2O \quad E1 = 0.57\ V$$

$$2\,SO_4^{2-} + 4\,H^+ + 2e^- \rightleftharpoons S_2O_6^{2-} + 2\,H_2O \quad E2 = -0.25\ V$$

$$2\,S_2O_6^{2-} \rightleftharpoons 2\,SO_4^{2-} + 2\,SO_2 \quad \Delta E = +0.82\ V$$

ΔE for the disproportionation = E1 – E2 = +0.82 V

Since $\Delta G = -nF\Delta E$, the ΔG is negative, hence the disproportionation is thermodynamically favorable.

(c) Combustion of sulfur-containing coal and petroleum produces sulfur dioxide SO_2. It is believed that SO_2 is responsible for 'acid rain" which contains H_2SO_4. Explain why the formation of H_2SO_4 form SO_2 is thermodynamically favorable. (Hint: look up the reduction potential of oxygen).

The formation of H_2SO_4 from SO_2 involves oxidation of sulfur from oxidation state +IV in SO_2 to oxidation state +VI in H_2SO_4. Oxygen is the only oxidizing agent in air. To prove that oxidation SO_2 by O_2 is thermodynamic favorable, one needs to calculate the ΔE of the following reaction:

$$O_2 + 4\,H^+ + 4e^- \rightleftharpoons 2\,H_2O \quad E1$$

$$2\,H_2SO_4 + 4\,H^+ + 4e^- \rightleftharpoons 2\,SO_2 + 4\,H_2O \quad E2$$

Overall reaction: $O_2 + 2\,SO_2 + 2\,H_2O \rightleftharpoons 2\,H_2SO_4 \quad \Delta E = E1 - E2$

From part (a) of the question, you know E2 = 0.16 V

From lecture notes or other sources, you know E1 = 1.23 V

So ΔE = 1.23 - 0.16 = 1.07 V

Since $\Delta G = -nF\Delta E$, the ΔG is negative and hence the oxidation is thermodynamically favorable.

Question 2

a) Plot a Frost diagram for copper using the reduction potentials given below.

$$Cu^{2+} + 1e^{-} \rightleftharpoons Cu^{+} \qquad E^{o} = +0.15 \text{ V vs NHE}$$

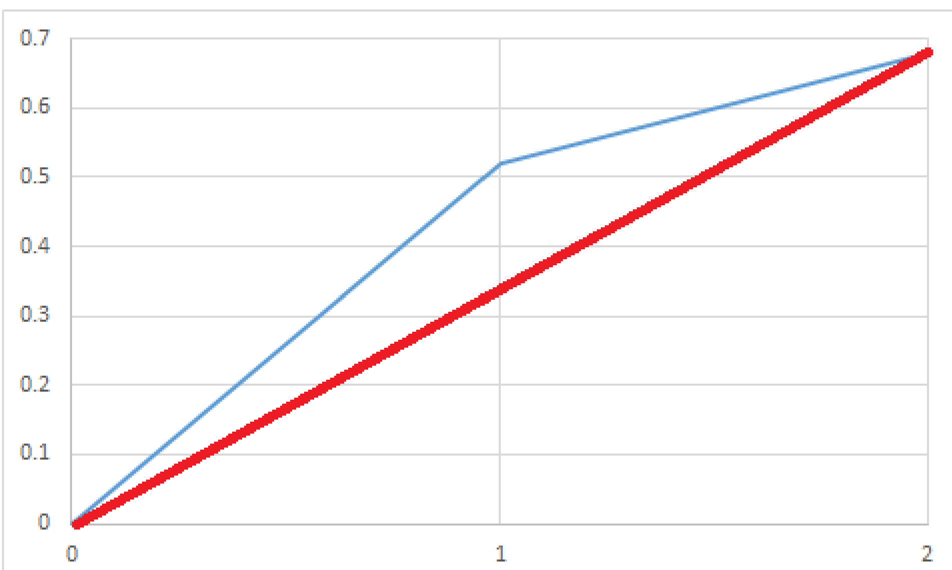
$$Cu^{+} + 1e^{-} \rightleftharpoons Cu \qquad E^{o} = +0.52 \text{ V vs NHE}$$

What is the most stable oxidation state of Cu? Which oxidation state of copper will tend to undergo disproportionation? Calculate the equilibrium constant K of the disproportionation.

To plot the Frost diagram, one needs to calculate the energy difference between Cu^{+} and Cu and the energy difference between Cu^{2+} and Cu.

Oxidation state N	E^{o}	Free energy in $N \times E^{o}$ (V)
0	0	0
+I	0.52 V	1 x 0.52 = 0.52 V
+II	(1 x 0.52 + 1 x 0.15)/2 = 0.34 V	2 x 0.34 = 0.68 V

Plot the energy against the oxidation state and you will get a Frost diagram as follows:



Copper(0) is the most stable oxidation state, since it is the “lowest” in the diagram!

The point for Cu^{I} is convex point which lies above the line (the red line) joining Cu^{0} and Cu^{II}. Accordingly Cu^{I} has a tendency to undergo disproportionation to form Cu^{II} and Cu^{0}.

Disproportionation of Cu^{I}: $2\,Cu^{I} \rightleftharpoons Cu^{II} + Cu^{0}$ ΔE

To find the equilibrium constant of above reaction, one needs to find the difference in the reduction potentials ΔE of the reaction, which is equal to E1 - E2:

$$Cu^{+} + 1\,e^{-} \rightarrow Cu \qquad E1$$

$$Cu^{2+} + 1\,e^{-} \rightarrow Cu^{+} \qquad E2$$

E1 = 0.52 V, E2 = 0.15 V, so ΔE = 0.37 V

To find the equilibrium constant for the disproportionation, one needs to find ΔG from the following equation;

$\Delta G = -nF\,\Delta E$ (n = 1 as it is an one-electron redox-reaction); F = 96,485 C/mol; V = J/C

$\Delta G = -35.7\ kJ\cdot mol^{-1}$ (convert back to $J\ mol^{-1}$ in calculating the equilibrium constant as the gas constant R is in unit of $J\cdot mol^{-1}\cdot K^{-1}$)

$$\Delta G = -RT\ln K \qquad R = 8.3144598(48)\ J\cdot mol^{-1}\cdot K^{-1}$$

So at room temperature (T = 298 K), the equilibrium constant K for the disproportionation is $K = 1.8 \times 10^{6}$

b) Explain why copper metal cannot dissolve in diluted HCl but in diluted HNO_3 (hint: look up the reduction potential of NO_3^{-})

Copper does not dissolve in diluted HCl, because the oxidation of copper(0) to copper(II) by protons is thermodynamically unfavorable:

$Cu^{0} + 2\,H^{+} \rightarrow Cu^{2+} + H_2$ thermodynamically unfavorable.

Oxidation to Cu+ is not considered, because it is unstable and disproportionates to Cu/Cu^{2+} !

Reason:

$2\ H^+ + 2e^- \rightarrow H_2$ E1 = 0 V

$Cu^{2+} + 2\ e^- \rightarrow Cu^0$ E2 = 0.34 V (see Q2a: E2 = (0.15 + 0.52) V /2 = 0.34 V)

ΔE = E1 – E2 gives the potential difference for $Cu^0 + 2\ H^+ \rightarrow Cu^{2+} + H_2$

ΔE for the reaction is –0.34 V, thus ΔG is positive, so the reaction is thermodynamically unfavorable.

The reason why copper can dissolve in HNO_3 is because the NO_3^- ion can oxidize Cu^0 to Cu^{II}.

The NO_3^- ion is reduced in oxidizing Cu^0 to Cu^{II}. It is possible for NO_3^- to form several lower oxidation state compounds such as HNO_2 and NO_2. It does not matter for this question, which species is formed, because the reduction potential for any couple is higher than the reduction potentials for $Cu^{2+} + 2e^- \rightarrow Cu^0$.

For example: reduction of NO_3^- gives NO_2.

$2\ NO_3^- + 2e^- + 4\ H^+ \rightarrow 2\ NO_2 + 2\ H_2O$	E1 = +0.8 V vs NHE
$Cu^{2+} + 2e^- \rightarrow Cu$	E2 = +0.34 V vs NHE
$2\ NO_3^- + Cu^0 + 4\ H^+ \rightarrow 2\ NO_2 + Cu^{2+} + 2\ H_2O$	ΔE = E1 – E2 = +0.46 V

ΔE for the reaction is +0.46 V. ΔG is negative, so the reaction is thermodynamically favorable. That is why copper can dissolve in diluted nitric acid.