

### CHM 152 Exam 4 Review – Ch. 18 19 KEY

1. Predict whether the entropy change will be positive or negative for the following:

- |  |                      |
|--|----------------------|
| a. $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$   | $\Delta S$ ___ - ___ |
| b. $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) \rightarrow 2\text{C}_2\text{H}_5\text{OH}(\text{l}) + 2\text{CO}_2(\text{g})$     | $\Delta S$ ___ + ___ |
| c. $2\text{NH}_3(\text{g}) + \text{CO}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{NH}_2\text{CONH}_2(\text{aq})$ | $\Delta S$ ___ - ___ |
| d. $\text{NaCl}(\text{s}) \rightarrow \text{NaCl}(\text{aq})$  | $\Delta S$ ___ + ___ |
| e. $\text{Cu}(\text{s}) (100^\circ\text{C}) \rightarrow \text{Cu}(\text{s}) (25^\circ\text{C})$                                    | $\Delta S$ ___ - ___ |
| f. $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$  | $\Delta S$ ___ + ___ |

2. Calculate  $\Delta H^\circ_{\text{rxn}}$  for  $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) \rightarrow 2\text{C}_2\text{H}_5\text{OH}(\text{l}) + 2\text{CO}_2(\text{g})$  using  $\Delta H^\circ_f$  values.

$$\Delta H^\circ_{\text{rxn}} = [(2 \text{ mol})(-277.7 \text{ kJ/mol}) + (2 \text{ mol})(-393.5 \text{ kJ/mol})] - (1 \text{ mol})(-1273.02 \text{ kJ/mol}) = \mathbf{-69.38 \text{ kJ}}$$

	$\Delta H_f^\circ$ (kJ/mol)	$S^\circ$ (J/mol·K)
$\text{C}_6\text{H}_{12}\text{O}_6$	-1273.02	212.1
$\text{C}_2\text{H}_5\text{OH}$	-277.7	160.7
$\text{CO}_2$	-393.5	213.6

3. Calculate  $\Delta S^\circ_{\text{rxn}}$  and  $\Delta S^\circ_{\text{surr}}$ .

$$\Delta S^\circ_{\text{rxn}} = [(2 \text{ mol})(160.7 \text{ J/molK}) + (2 \text{ mol})(213.6 \text{ J/molK})] - (1 \text{ mol})(212.1 \text{ J/molK}) = \mathbf{536.5 \text{ J/K}}$$

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} \quad \Delta S_{\text{surr}} = \frac{-(-69380 \text{ J})}{298.15 \text{ K}} = \mathbf{232.7 \text{ J/K}}$$

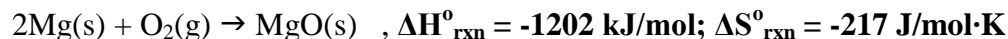
4. Based on your values for  $\Delta S^\circ_{\text{rxn}}$  and  $\Delta S^\circ_{\text{surr}}$ , is the reaction spontaneous under standard thermodynamic conditions?

*Yes,  $\Delta S^\circ_{\text{rxn/sys}} + \Delta S^\circ_{\text{surr}} = 536.5 \text{ J/K} + 232.7 \text{ J/K} = 769.2 \text{ J/K}$ . Since this value is  $>0$ , it is spontaneous.*

5. Is this reaction always spontaneous? If not, determine at what temperatures it changes from spontaneous to non-spontaneous.

***With a  $-\Delta H^\circ$ , and  $+\Delta S^\circ$ , this reaction will be spontaneous under all conditions.***

6. For the following reaction:



- Calculate  $\Delta G^\circ$  using  $\Delta G = \Delta H - T\Delta S$

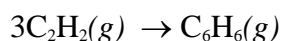
$$\Delta G = -1202 \text{ kJ/mol} - (298.15 \text{ K})(-0.217 \text{ kJ/mol K}) = \mathbf{-1137 \text{ kJ/mol}}$$

- Is the reaction spontaneous under standard conditions? Yes, since  $\Delta H$  and  $\Delta S$  (along with 298.15K) are all under standard conditions (the “°” tells us standard conditions).
- Based on the signs of  $\Delta H$  and  $\Delta S$ , comment on the spontaneity of this reaction at different temperatures. **Spontaneous at “low” temperatures, non-spontaneous at “high” temps.**
- At what temperature does the reaction become spontaneous/non-spontaneous?

$$0 = -1202 \text{ kJ/mol} - T(-0.212 \text{ kJ/mol K})$$

$$\frac{1202 \text{ kJ/mol}}{0.217 \text{ kJ/mol K}} = \mathbf{5540 \text{ K}} \text{ At this temp and } \mathbf{higher}, \text{ the reaction is non-spontaneous.}$$

7. a) Calculate  $\Delta G^\circ_{\text{rxn}}$  using  $\Delta G = \Delta H - T\Delta S$  (assuming 298.15K)



	$\Delta H^\circ_f$ (kJ/mol)	$\Delta G^\circ_f$ (kJ/mol)	$S^\circ$ (J/mol K)
$\text{C}_2\text{H}_2(\text{g})$	227.4	209.9	200.9
$\text{C}_6\text{H}_6(\text{g})$	82.9	129.7	269.2

$$\Delta H^\circ_{\text{rxn}} = (1 \text{ mol C}_6\text{H}_6)(82.9 \text{ kJ/mol}) - (3 \text{ mol C}_2\text{H}_2)(227.4 \text{ kJ/mol}) = \mathbf{-599.3 \text{ kJ}}$$

$$\Delta S^\circ_{\text{rxn}} = (1 \text{ mol C}_6\text{H}_6)(269.2 \text{ J/mol}) - (3 \text{ mol C}_2\text{H}_2)(200.9 \text{ J/mol}) = \mathbf{-333.5 \text{ J}}$$

$$\Delta G = \Delta H - T\Delta S \quad \Delta G^\circ_{\text{rxn}} = -599.3 \text{ kJ} - (298.15 \text{ K})(-0.3335 \text{ kJ}) = \mathbf{-499.9 \text{ kJ}}$$

- b) Calculate  $\Delta G^\circ_{\text{rxn}}$  for the following reaction using  $\Delta G^\circ_f$  only.

$$\Delta G^\circ_{\text{rxn}} = (1 \text{ mol C}_6\text{H}_6)(129.7 \text{ kJ/mol}) - (3 \text{ mol})(209.9 \text{ kJ/mol}) = \mathbf{-500.0 \text{ kJ}}$$

- Are the values similar? Should they be? Yes they are. And they should be. You are calculating the same thing,  $\Delta G^\circ_{\text{rxn}}$ .
- What is the value of the equilibrium constant at 298 K?

$$\Delta G = -RT \ln K \quad - \frac{-500.0 \times 10^3 \text{ J}}{-(8.314 \text{ J/molK})(298.15 \text{ K})} = \ln K \quad e^{201.7} = e^{\ln K} \quad \mathbf{K = 3.955 \times 10^{87}}$$

Is this reaction spontaneous at 298 K? **Yes, because  $\Delta G_{\text{rxn}} < 0$ . We could also look at  $K$ , which is very large. Each of these shows spontaneity of the reaction at standard conditions.**

Calculate  $\Delta G_{\text{rxn}}$  with the product and reactant both starting at 35 atm and 501 K. (Hint, what is the value of  $Q$ ?).

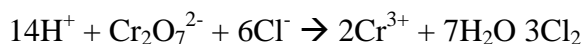
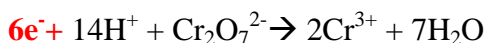
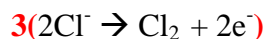
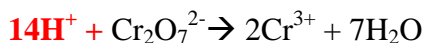
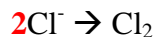
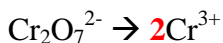
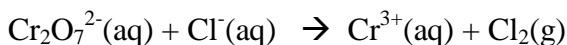
$$Q = \frac{35}{(35)^3} = 8.16 \times 10^{-4} \quad \Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G = -500.0 \times 10^3 \text{ J} + (8.314 \text{ J/mol K})(501 \text{ K}) \ln(8.16 \times 10^{-4}) = \mathbf{-529.6 \times 10^3 \text{ J or } -529.6 \text{ kJ}}$$

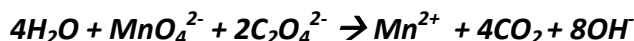
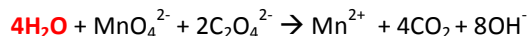
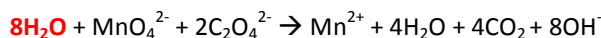
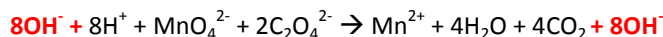
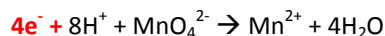
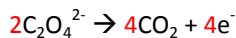
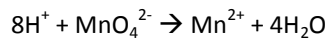
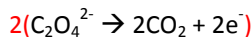
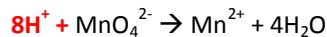
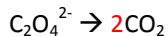
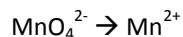
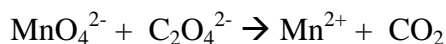
It is "more spontaneous" under the new conditions.

8. Balance the following equations:

Assume acidic media:



Assume basic media:



9. Assign oxidation numbers of all elements in the following reaction:

- $\text{Al(s)} + \text{O}_2\text{(g)} \rightarrow \text{Al}_2\text{O}_3\text{(s)}$
- $\text{MnO}_2\text{(s)} + 4\text{HCl(aq)} \rightarrow \text{MnCl}_2\text{(aq)} + \text{Cl}_2\text{(g)} + 2\text{H}_2\text{O(l)}$
- $\text{HNO}_3\text{(aq)} + \text{NaOH(aq)} \rightarrow \text{H}_2\text{O(l)} + \text{NaNO}_3\text{(aq)}$

Reactants: Al = 0, O = 0 Products: Al = +3, O = -2

Reactants: Mn = +4, O = -2, H = +1, Cl = -1 Products: Mn = +2, Cl in  $\text{MnCl}_2$  = -1 Cl in  $\text{Cl}_2$  = 0, H = +1, O = -2

Reactants: H in both reactants = +1, N = +5, Na = +1, O in both reactants = -2, Products: H = +1, O in both products = -2, Na = +1, N = +5

- For each reaction determine what is reduced and what is oxidized.

***O: 0 → -2, reduced; Al: 0 → +3, oxidized***

***Mn: +4 → +2, reduced; Cl: -1 → 0, oxidized***

***Oxidation numbers for last reaction unchanged; no a REDOX reaction***

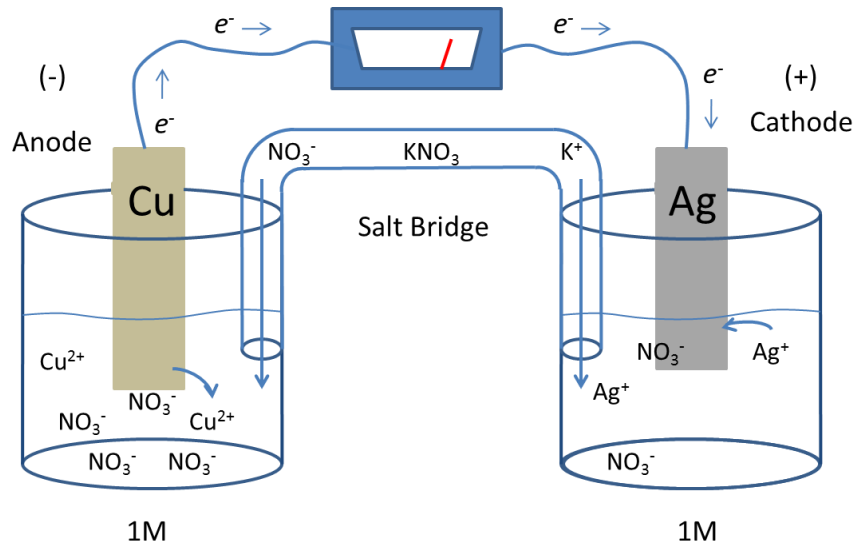
- For each reaction determine the oxidizing agent and reducing agent.

***Oxidizing agent:  $\text{O}_2\text{(g)}$  Reducing agent:  $\text{Al(s)}$***

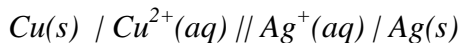
***Oxidizing agent:  $\text{MnO}_2\text{(s)}$  Reducing agent:  $\text{HCl}$***

When naming "agents", chemists customarily give the entire formula not just the element
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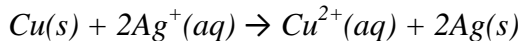
10. Draw a voltaic cell diagram using silver and copper (assume the  $\text{Cu}^{2+}$  ion). Place the anode on the left hand side. Also show the following: salt bridge; direction of electron travel; Indicate which electrode is being dissolved into solution and which electrode is being "plated" (show what the ions are doing at each electrode).



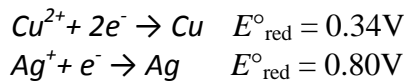
- a. Give the short-hand notation for the copper/silver cell.



- b. Would  $\text{CuCl}_2$  make a good salt for the salt bridge in this cell? Explain.  
*No. The  $\text{Ag}^+$  ion will react with  $\text{Cl}^-$  from the salt bridge forming a precipitate. Also,  $\text{Cu}^{2+}$  is part of the chemical reaction, this might also complicate matters (Usually we use  $\text{NaNO}_3$ ,  $\text{KNO}_3$ , etc....).*
- c. Write the balanced chemical reaction for the cell.

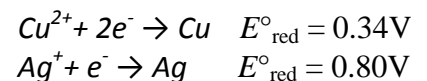


- d. What is the  $E^\circ_{\text{cell}}$  for the cell above?



Since copper is oxidized,  $E^\circ_{\text{ox}} = -0.34\text{V}$ . Thus  $E^\circ_{\text{cell}} = 0.80\text{V} + (-0.34\text{V}) = 0.46\text{V}$

- e. Based on your value and sign of  $E^\circ_{\text{cell}}$  is it spontaneous? Explain.



*Yes. Since the  $E^\circ_{\text{cell}}$  is positive, it means the reaction will be spontaneous ( $\Delta G^\circ < 0$ )*

f. Calculate the equilibrium constant (K) for the cell.

$$\boxed{E^\circ_{cell} = \frac{RT}{nF} \ln K} \quad 0.46V = \frac{\left(8.314 \frac{J}{mol K}\right)(289.15K)}{(2mol e^-)\left(96,500 \frac{J}{V mol}\right)} \ln K \quad 35.82 = \ln K$$

$$e^{35.82} = e^{(\ln K)} \quad K = 3.6 \times 10^{15}$$

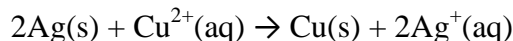
g. Based on your value and sign of K, is the reaction spontaneous? Explain.

**Yes.  $K \gg 1$  is spontaneous and "product favored".**

h. Which species is the oxidizing agent in the cell? Cu(s) Cu<sup>2+</sup>(aq) Ag(s) Ag<sup>+</sup>(aq)

i. Which species loses electrons? Cu(s) Cu<sup>2+</sup>(aq) Ag(s) Ag<sup>+</sup>(aq)

j. Based on your answers from c, g and h, determine if the following reaction is spontaneous. Explain.



*No, the reaction as written above is not spontaneous. Based on the spontaneous reaction written in part c, Cu(s) is more likely to give up electrons and Ag<sup>+</sup>(aq) is more likely to accept electrons. The reaction as written in part "j", is in the reverse direction of the spontaneous reaction. Thus, it is non-spontaneous.*

k. Calculate  $\Delta G^\circ$  for the voltaic cell.

$$\boxed{\Delta G^\circ = -nFE^\circ_{cell}} \quad \Delta G^\circ = -(2mol e^-)\left(96,500 \frac{J}{V mol}\right)(0.46V) \quad \Delta G^\circ = -89,000J \text{ or } -89kJ$$

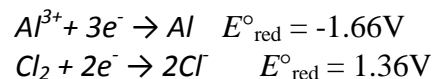
l. Calculate the  $E_{cell}$  if the [Cu<sup>2+</sup>] = 2.00M and [Ag<sup>+</sup>] = 0.0111M

$$\boxed{E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln Q} \quad Q = \frac{[Cu^{2+}]}{[Ag^+]^2} = \frac{[2.00]}{[0.0111]^2} = 16000$$

$$E_{cell} = 0.46V - \frac{\left(8.314 \frac{J}{mol K}\right)(289.15K)}{(2mol e^-)\left(96,500 \frac{J}{V mol}\right)} \ln(16,232) \quad E_{cell} = 0.45V$$

11. Based on reduction potentials, which of the following reactions should be spontaneous? Explain.

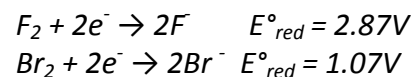
- $2Al(s) + 3Cl_2(g) \rightarrow 2Al^{3+}(aq) + 6Cl^{-}(aq)$
- $2Al^{3+}(aq) + 6Cl^{-}(aq) \rightarrow 2Al(s) + 3Cl_2(g)$



Since Aluminum has the largest negative reduction potential, we know that it will be the reducing agent (Al(s) is being oxidized). If we were calculating cell potential, we would “flip” this half-reaction to show oxidation potential. When we “flip” the Al half-reaction, Al(s) is on the reactants side. Thus, the reaction with Al(s) on the reactant side is the spontaneous reaction.

Another way to think about this is if to compare Al(s) vs. Al<sup>3+</sup>(aq). The **Al(s)** form is more likely to give up electrons as the reducing agent (being oxidized), since you can think of Al<sup>3+</sup> as already oxidized. (oxidation number for Al(s) = 0, Al<sup>3+</sup> = +3)

12. Based on reduction potentials, which of the following reactants should give a spontaneous reaction? (HINT: Pay attend to states of matter...which should give up electrons which should accept electrons) Explain.



- a.  $F_2(g) + Br_2(l)$
- b.  $F_2(g) + 2Br^{-}(aq)$
- c.  $2F^{-}(aq) + 2Br^{-}(aq)$
- d.  $2F^{-}(aq) + Br_2(l)$

*Based on reduction potentials, since Bromine has the smallest positive reduction potential, it will be the reducing agent (becoming oxidized) and the half-reaction that will be “flipped”. Once the bromine half-reaction is flipped, **Br<sup>-</sup>(aq) is on the reactant side.** The reaction with fluorine will not be flipped, and has **F<sub>2</sub>(g) on the reactant side.** Thus, those forms of Bromine and Fluorine will react spontaneously, F<sub>2</sub>(g) and Br<sup>-</sup>(aq).*

Another way to think about this is to compare the Br<sub>2</sub>(l) and Br<sup>-</sup>(aq) forms. Br<sup>-</sup> is more likely to give up electrons as the reducing agent (it becomes oxidized), since you can think of the Br<sub>2</sub>(l) form as already oxidized (oxidation number for Br<sup>-</sup> = -1, Br<sub>2</sub> = 0). For Fluorine, the opposite is true: The F<sub>2</sub>(g) is more likely to accept electrons than the F<sup>-</sup>(aq), F<sup>-</sup>(aq) is already reduced.