

# Chemistry 210

# Exam 4

Be sure to put your name on each page. This page can be removed from your exam so that you will have a Periodic Table handy throughout the exam, it does not need to be turned in. Show all your work for problems which require any sort of calculation, no credit will be given for answers without work shown. If you have shown a significant amount of work or multiple drawings for a problem, draw a box around what you consider your final answer.

Avogadro's Number =  $6.022 \times 10^{23}$  units/mol

$32.00^\circ\text{F} = 0.000^\circ\text{C} = 273.15\text{K}$

Density of Water =  $1.000 \text{ g/mL}$

$R = 0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K} = 8.314 \text{ J}/\text{mol}\cdot\text{K}$

$1\text{atm} = 760\text{torr} = 760\text{mmHg} = 101.325\text{kPa}$

$PV = nRT$

$\Delta T_{\text{fp/bp}} = k_{\text{fp/bp}} \cdot m \cdot i$

For water:  $k_{\text{fp}} = -1.86^\circ\text{C}/m$   
 $k_{\text{bp}} = 0.512^\circ\text{C}/m$

$P_1 = X_1 P_1^\circ$

$\Pi = MRTi$

$C_1 V_1 = C_2 V_2$

Integrated Rate Laws:

0<sup>th</sup>  $[A]_t = -kt + [A]_o$

1<sup>st</sup>  $\ln[A]_t = -kt + \ln[A]_o$

2<sup>nd</sup>  $1/[A]_t = kt + 1/[A]_o$

$k = Ae^{-E_a/RT}$

$\ln(k) = \left( \frac{-E_a}{R} \right) \left( \frac{1}{T} \right) + \ln(A)$

$\ln\left( \frac{k_1}{k_2} \right) = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$

$\text{pH} = \text{pK}_a + \log\left( \frac{[\text{conjugate base}]}{[\text{conjugate acid}]} \right)$

$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q$

$E_{\text{cell}}^\circ = \frac{RT}{nF} \ln K^\circ$

$K^\circ = e^{(nF/RT) E_{\text{cell}}^\circ}$

$F = 96485 \text{ J}/\text{V}\cdot\text{mol of electrons}$

$\Delta G^\circ = \Delta H^\circ_{\text{system}} - T\Delta S^\circ_{\text{system}}$

$\Delta G^\circ = -nFE_{\text{cell}}^\circ = -RT \ln K^\circ$

$\Delta G = \Delta G^\circ + RT \ln Q$

$F = 96485 \text{ C}/\text{mol electrons}$

$1A = 1 \text{ C} / \text{sec}$

Quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

1 <b>H</b> 1.0079																	2 <b>He</b> 4.0026				
3 <b>Li</b> 6.941	4 <b>Be</b> 9.0122															5 <b>B</b> 10.811	6 <b>C</b> 12.011	7 <b>N</b> 14.007	8 <b>O</b> 15.999	9 <b>F</b> 18.998	10 <b>Ne</b> 20.180
11 <b>Na</b> 22.990	12 <b>Mg</b> 24.305															13 <b>Al</b> 26.982	14 <b>Si</b> 28.086	15 <b>P</b> 30.974	16 <b>S</b> 32.066	17 <b>Cl</b> 35.453	18 <b>Ar</b> 39.948
19 <b>K</b> 39.098	20 <b>Ca</b> 40.078	21 <b>Sc</b> 44.956	22 <b>Ti</b> 47.88	23 <b>V</b> 50.942	24 <b>Cr</b> 51.996	25 <b>Mn</b> 54.938	26 <b>Fe</b> 55.847	27 <b>Co</b> 58.933	28 <b>Ni</b> 58.69	29 <b>Cu</b> 63.546	30 <b>Zn</b> 65.39	31 <b>Ga</b> 69.723	32 <b>Ge</b> 72.61	33 <b>As</b> 74.922	34 <b>Se</b> 78.96	35 <b>Br</b> 79.904	36 <b>Kr</b> 83.80				
37 <b>Rb</b> 85.468	38 <b>Sr</b> 87.62	39 <b>Y</b> 88.906	40 <b>Zr</b> 91.224	41 <b>Nb</b> 92.906	42 <b>Mo</b> 95.94	43 <b>Tc</b> (98)	44 <b>Ru</b> 101.07	45 <b>Rh</b> 102.91	46 <b>Pd</b> 106.42	47 <b>Ag</b> 107.87	48 <b>Cd</b> 112.41	49 <b>In</b> 114.82	50 <b>Sn</b> 118.71	51 <b>Sb</b> 121.76	52 <b>Te</b> 127.60	53 <b>I</b> 126.90	54 <b>Xe</b> 131.29				
55 <b>Cs</b> 132.91	56 <b>Ba</b> 137.33	71 <b>Lu</b> 174.97	72 <b>Hf</b> 178.49	73 <b>Ta</b> 180.95	74 <b>W</b> 183.84	75 <b>Re</b> 186.21	76 <b>Os</b> 190.23	77 <b>Ir</b> 192.22	78 <b>Pt</b> 195.08	79 <b>Au</b> 196.97	80 <b>Hg</b> 200.59	81 <b>Tl</b> 204.38	82 <b>Pb</b> 207.2	83 <b>Bi</b> 208.98	84 <b>Po</b> (209)	85 <b>At</b> (210)	86 <b>Rn</b> (222)				
87 <b>Fr</b> (223)	88 <b>Ra</b> 226.03	103 <b>Lr</b> (260)	104 <b>Rf</b> (261)	105 <b>Db</b> (262)	106 <b>Sg</b> (263)	107 <b>Bh</b> (262)	108 <b>Hs</b> (265)	109 <b>Mt</b> (266)	110 <b>(269)</b>	111 <b>(272)</b>	112 <b>(277)</b>			114			116				

57 <b>La</b> 138.91	58 <b>Ce</b> 140.12	59 <b>Pr</b> 140.91	60 <b>Nd</b> 144.24	61 <b>Pm</b> (145)	62 <b>Sm</b> 150.36	63 <b>Eu</b> 151.97	64 <b>Gd</b> 157.25	65 <b>Tb</b> 158.93	66 <b>Dy</b> 162.50	67 <b>Ho</b> 164.93	68 <b>Er</b> 167.26	69 <b>Tm</b> 168.94	70 <b>Yb</b> 173.04
89 <b>Ac</b> 227.03	90 <b>Th</b> 232.04	91 <b>Pa</b> 231.04	92 <b>U</b> 238.03	93 <b>Np</b> 237.05	94 <b>Pu</b> (244)	95 <b>Am</b> (243)	96 <b>Cm</b> (247)	97 <b>Bk</b> (247)	98 <b>Cf</b> (251)	99 <b>Es</b> (252)	100 <b>Fm</b> (258)	101 <b>Md</b> (258)	102 <b>No</b> (259)

**Multiple Choice (5pts each):** Circle the letter of the most correct response.

- A large negative change in free energy means:
  - The reaction is very slow
  - The system is becoming more disordered
  - The reaction is spontaneous**
  - The reaction is exothermic
  - The reaction is not spontaneous
- A reaction will be spontaneous at relatively high temperature and non-spontaneous at relatively low temperature if:
  - $\Delta H^\circ_{\text{system}} > 0$  and  $\Delta S^\circ_{\text{system}} > 0$**
  - $\Delta H^\circ_{\text{system}} > 0$  and  $\Delta S^\circ_{\text{system}} < 0$
  - $\Delta H^\circ_{\text{system}} < 0$  and  $\Delta S^\circ_{\text{system}} < 0$
  - $\Delta H^\circ_{\text{system}} < 0$  and  $\Delta S^\circ_{\text{system}} > 0$
  - $\Delta H^\circ_{\text{system}} > 0$  and  $\Delta S^\circ_{\text{system}} = 0$
- For a reaction with a small negative  $\Delta S$ :
  - Heat is liberated by the reaction
  - The disorder of the system is increasing
  - The reaction proceeds very quickly
  - The system is becoming more ordered**
  - The reaction is not spontaneous
- If the change in enthalpy for a reaction is positive and the change in entropy is negative:
  - The system is becoming more disordered
  - The reaction will be non-spontaneous at all temperatures**
  - The reaction will be spontaneous only at low temperatures
  - The reaction releases heat
  - The reaction will be spontaneous at all temperatures
- A reaction will be product-favored/spontaneous if:
  - $\Delta G^\circ < 0$**
  - $\Delta S^\circ < 0$
  - $E^\circ_{\text{cell}} < 0$
  - $K_{\text{eq}} < 1$
  - $\Delta H > 0$
- How are the change in Gibbs Free Energy and the equilibrium constant for a reaction related?
  - As  $K$  approaches zero,  $\Delta G$  approaches zero
  - They're not.
  - As  $\Delta G$  gets more negative,  $K$  gets very large**
  - The value of  $\Delta G$  is equal to  $(-\log K)$
  - As  $\Delta G$  gets more positive,  $K$  approaches 1
- In a spontaneous electrochemical voltaic cell, which of the following is **true**?
  - The cell potential is zero
  - Cations flow through the salt bridge from the cathode to the anode
  - The metal cathode gains mass as the cell reaction proceeds**
  - Oxidation occurs at the cathode
  - Electrons flow from the cathode to the anode

8. For a spontaneous redox reaction, which of the following is *false*?
- Oxidation is the process of losing electrons
  - Water molecules are added to balance any extra oxygen atoms
  - $\Delta G$  is negative.
  - Gaining electrons is reduction
  - Electrons appear on the left side of the oxidation half reaction**

9. Give the oxidation number for each atom in the following formulas. (15pts)



Li → +1  
Br → +5  
O → -2

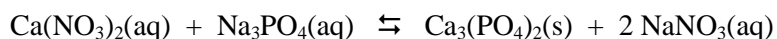


P → +5  
O → -2

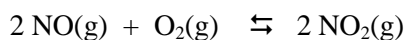


P → -3  
H → +1

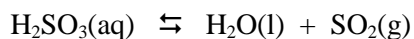
10. For each of the following reactions, predict whether the sign if  $\Delta S^\circ$  will be positive or negative and explain your answer. (15pts)



Forming a solid from aqueous solutions, the system is becoming more ordered.  
 $\Delta S^\circ$  should be negative



All reactants and products are gases... 3 particles becoming 2 particles, the system is becoming more ordered.  
 $\Delta S^\circ$  should be negative



An aqueous solution is forming a gas, the system is becoming more disordered  
 $\Delta S^\circ$  should be positive

11. Why is the standard reduction potential for  $\text{Ca}^{+2}|\text{Ca}$  ( $E^\circ_{\text{red}} = -2.868\text{V}$ ) more negative than the standard reduction potential for  $\text{Mg}^{+2}|\text{Mg}$  ( $E^\circ_{\text{red}} = -2.371\text{V}$ )? (5pts)

It might be easier to visualize this as the reverse reaction, the oxidation...  
Oxidation of Ca to  $\text{Ca}^{+2}$  is more spontaneous ( $E^\circ_{\text{ox}}$  is more positive) because calcium atoms are bigger. A bigger atom has its outer electrons farther from the nucleus, so it is easier to remove those electrons (easier to oxidize).

12. You are studying a process for which  $\Delta H^\circ = +41.63 \text{ kJ/mol}$  and  $\Delta S^\circ = +318.7 \text{ J/mol}\cdot\text{K}$ . What is  $\Delta G^\circ$  for this process at  $25.00^\circ\text{C}$ ? Will the reaction be more or less spontaneous at  $20.00^\circ\text{C}$ ? (10pts)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (+41.63 \text{ kJ/mol}) - (298.15\text{K})(0.3187 \text{ kJ/mol}\cdot\text{K}) = -53.39 \text{ kJ/mol}$$

Since  $\Delta H$  and  $\Delta S$  are both positive, this rxn is spontaneous at relatively high T and non-spontaneous at relatively low T, so lowering the T will make this rxn *less* spontaneous.

Alternatively, we could just plug in the new T...

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (+41.63 \text{ kJ/mol}) - (293.15\text{K})(0.3187 \text{ kJ/mol}\cdot\text{K}) = -52.07 \text{ kJ/mol}$$

$-52 \text{ kJ/mol}$  is less spontaneous than  $-53 \text{ kJ/mol}$ .

13. Ethane  $\{\text{C}_2\text{H}_6(\text{g})\}$  can burn in oxygen to form carbon dioxide and water. How much {Gibb's Free} energy can be liberated by burning 39.618g of ethane in an unlimited supply of oxygen? (10pts)

$$2 \text{ C}_2\text{H}_6(\text{g}) + 7 \text{ O}_2(\text{g}) \rightarrow 4 \text{ CO}_2(\text{g}) + 6 \text{ H}_2\text{O}(\text{g})$$

$$\Delta G^\circ_{\text{rxn}} = 2(+32.9 \text{ kJ/mol}) + 7(-0 \text{ kJ/mol}) + 4(-394.4 \text{ kJ/mol}) + 6(-228.6 \text{ kJ/mol}) = -2883.4 \text{ kJ/mol}$$

$$(39.618 \text{ g C}_2\text{H}_6) \left( \frac{1 \text{ mol C}_2\text{H}_6}{30.0694 \text{ g C}_2\text{H}_6} \right) \left( \frac{1 \text{ mol rxn}}{2 \text{ mol C}_2\text{H}_6} \right) \left( \frac{2883.4 \text{ kJ}}{1 \text{ mol rxn}} \right) = 1899.5 \text{ kJ}$$

14. You are studying the reaction of acetic acid  $\{\text{CH}_3\text{CO}_2\text{H}(\text{l})\}$  with methyl amine  $\{\text{CH}_3\text{NH}_2(\text{l})\}$  to produce N-methylacetamide  $\{\text{C}_3\text{H}_7\text{NO}(\text{l})\}$  and water. When you run the reaction at  $23.61^\circ\text{C}$ , you find that  $\Delta G$  for this reaction is  $+51.03 \text{ kJ/mol}$  and  $\Delta S = +61.37 \text{ J/mol}\cdot\text{K}$  (10pts)

- Is the reaction endothermic or exothermic? (*Explain your answer with explicit calculations.*)
- Over what temperature range is this reaction spontaneous?

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

$$+51.03 \text{ kJ/mol} = \Delta H - (296.76\text{K})(0.06137 \text{ kJ/mol}\cdot\text{K})$$

$$\Delta H = +69.24 \text{ kJ/mol} \rightarrow \text{endothermic}$$

Plugging back in to find the transition temperature:

$$0 \text{ kJ/mol} = (69.24 \text{ kJ/mol}) - T(0.06137 \text{ kJ/mol}\cdot\text{K})$$

$T = 1128\text{K}$ . Since  $\Delta H$  and  $\Delta S$  are both positive, the rxn is spontaneous above this T. (Yikes, that's warm!)

15. You have burned 72.612g of ethene  $\{\text{C}_2\text{H}_4(\text{g})\}$  in oxygen to form carbon dioxide and water. If all of the Gibb's Free Energy liberated by this reaction is used to decompose calcium fluoride to calcium metal and fluorine gas, how many grams of calcium metal will be formed? (15pts)

$$\text{C}_2\text{H}_4(\text{g}) + 3 \text{ O}_2(\text{g}) \rightarrow 2 \text{ CO}_2(\text{g}) + 2 \text{ H}_2\text{O}(\text{g})$$

$$\Delta G^\circ_{\text{rxn}} = 1(-68.1 \text{ kJ/mol}) + 3(-0 \text{ kJ/mol}) + 2(-394.4 \text{ kJ/mol}) + 2(-228.6 \text{ kJ/mol}) = -1314.1 \text{ kJ/mol}$$

$$(72.612 \text{ g C}_2\text{H}_4) \left( \frac{1 \text{ mol C}_2\text{H}_4}{28.0536 \text{ g C}_2\text{H}_4} \right) \left( \frac{1 \text{ mol rxn}}{1 \text{ mol C}_2\text{H}_4} \right) \left( \frac{1314.1 \text{ kJ}}{1 \text{ mol rxn}} \right) = 3401.326 \text{ kJ}$$

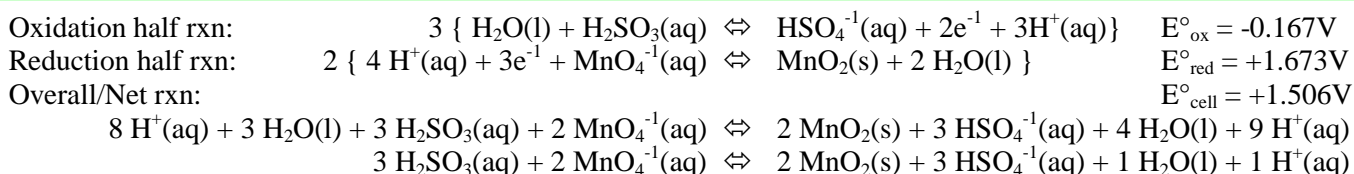
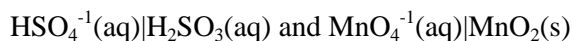
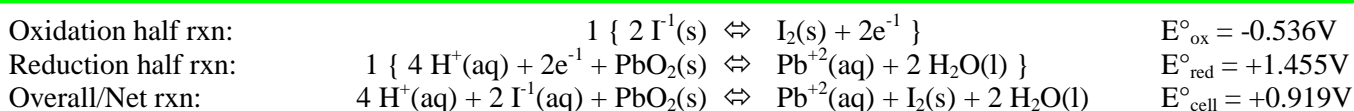
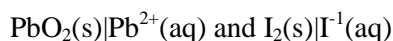
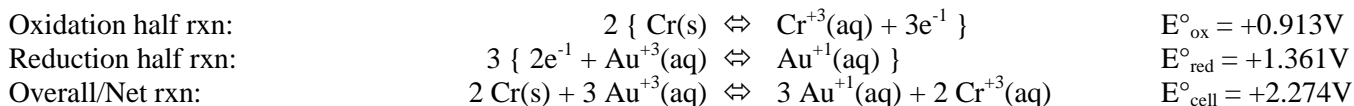
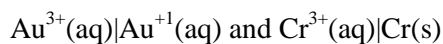
This is supplying energy to the next part of the process...

$$\text{CaF}_2(\text{s}) \rightarrow \text{Ca}(\text{s}) + \text{F}_2(\text{g})$$

$$\Delta G^\circ_{\text{rxn}} = 1(+1175.6 \text{ kJ/mol}) + 1(0 \text{ kJ/mol}) + 1(0 \text{ kJ/mol}) = 1175.6 \text{ kJ/mol}$$

$$(3401.326 \text{ kJ}) \left( \frac{1 \text{ mol rxn}}{1175.6 \text{ kJ}} \right) \left( \frac{1 \text{ mol Ca}(\text{s})}{1 \text{ mol rxn}} \right) \left( \frac{40.078 \text{ g Ca}(\text{s})}{1 \text{ mol Ca}(\text{s})} \right) = 115.96 \text{ g Ca}(\text{s})$$

16. For each of the following pairs of half-reactions/half-cells, determine the voltage of the spontaneous reaction/cell and write a balanced equation for the spontaneous reaction, identifying the oxidation and reduction half-reactions. (10pts each)



**Thermodynamic Values at 25°C:**

Substance	$\Delta H^{\circ}_{\text{f}}$ (kJ/mol)	$S^{\circ}$ (J/mol·K)	$\Delta G^{\circ}_{\text{f}}$ (kJ/mol)
$\text{C}_2\text{H}_6(\text{g})$	-84.69	+229.5	-32.9
$\text{O}_2(\text{g})$	0	+205.138	0
$\text{CO}_2(\text{g})$	-393.5	+213.8	-394.4
$\text{H}_2\text{O}(\text{g})$	-241.8	+188.8	-228.6
$\text{H}_2\text{O}(\text{l})$	-285.8	+69.91	-237.2
$\text{C}_2\text{H}_4(\text{g})$	+52.3	+219.5	+68.1
$\text{CaF}_2(\text{s})$	-1228.0	+68.5	-1175.6
$\text{Ca}(\text{s})$	0	+41.6	0
$\text{F}_2(\text{g})$	0	+202.8	0

**Standard Reduction Potentials at 25°C:**

Half cell	$E^{\circ}_{\text{red}}$ (volts)	Half cell	$E^{\circ}_{\text{red}}$ (volts)
$\text{Au}^{3+}(\text{aq}) \text{Au}^{+}(\text{aq})$	+1.361	$\text{I}_2(\text{g}) \text{I}^{-}(\text{aq})$	+0.536
$\text{Cr}^{3+}(\text{aq}) \text{Cr}(\text{s})$	-0.913	$\text{HSO}_4^{-}(\text{aq}) \text{H}_2\text{SO}_3(\text{aq})$	+0.167
$\text{PbO}_2(\text{s}) \text{Pb}^{2+}(\text{aq})$	+1.455	$\text{MnO}_4^{-}(\text{aq}) \text{MnO}_2(\text{s})$	+1.673