

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 = 6.022×10^{23} units/mol

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

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

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

$PV = nRT$

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

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

$P_1 = X_1 P_1^\circ$

$\Pi = MRTi$

$C_1 V_1 = C_2 V_2$

Quadratic formula:

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

Integrated Rate Laws:

0th order $[A]_t = -kt + [A]_o$

1st order $\ln[A]_t = -kt + \ln[A]_o$

2nd order $1/[A]_t = kt + 1/[A]_o$

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

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

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

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

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

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

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

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

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

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

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

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

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

1 H 1.0079																	2 He 4.0026				
3 Li 6.941	4 Be 9.0122															5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305															13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.066	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80				
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29				
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)				
87 Fr (223)	88 Ra 226.03	89 Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)	114		116							

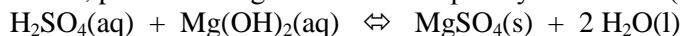
58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.94	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (258)	101 Md (258)	102 No (259)	103 Lr (260)

Multiple Choice (4pts each): Circle the letter of the most correct response.

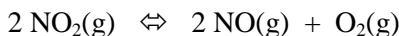
- A large negative change in free energy means:
 - The reaction is very slow
 - The reaction is exothermic
 - The reaction is not spontaneous
 - The system is becoming more disordered
 - The reaction is spontaneous**
- For a reaction with a small negative ΔS :
 - Heat is liberated by the reaction
 - The system is becoming more ordered**
 - The reaction is not spontaneous
 - The temperature of the system is increasing
 - The reaction proceeds very quickly
- A reaction will be product-favored/spontaneous if:
 - $\Delta G^\circ < 0$**
 - $K_{eq} < 1$
 - $\Delta H > 0$
 - $\Delta S^\circ < 0$
 - $E^\circ_{cell} < 0$
- A reaction will be spontaneous at relatively high temperature and non-spontaneous at relatively low temperature if:
 - $\Delta H^\circ_{system} > 0$ and $\Delta S^\circ_{system} > 0$**
 - $\Delta H^\circ_{system} < 0$ and $\Delta S^\circ_{system} > 0$
 - $\Delta H^\circ_{system} > 0$ and $\Delta S^\circ_{system} = 0$
 - $\Delta H^\circ_{system} > 0$ and $\Delta S^\circ_{system} < 0$
 - $\Delta H^\circ_{system} < 0$ and $\Delta S^\circ_{system} < 0$
- In a spontaneous electrochemical voltaic cell, which of the following is *true*?
 - The cell potential is zero
 - Oxidation occurs at the cathode
 - Electrons flow from the cathode to the anode
 - Cations flow through the salt bridge from the cathode to the anode
 - The metal cathode gains mass as the cell reaction proceeds**
- For a spontaneous redox reaction, which of the following is *false*?
 - Oxidation is the process of losing electrons
 - Gaining electrons is reduction
 - Electrons appear on the left side of the oxidation half reaction**
 - Water molecules are added to balance any extra oxygen atoms
 - ΔG is negative.
- How are the change in Gibb's Free Energy and the equilibrium constant for a reaction related?
 - As K approaches zero, ΔG approaches zero
 - They're not.
 - The value of ΔG is equal to $(-\log K)$
 - As ΔG gets more positive, K approaches 1
 - As ΔG gets more negative, K gets very large**

Problems:

8. For each of the following reactions, predict the sign of ΔS° and explain your answer (5pts each):



Forming a solid from solutions, rxn is getting more ordered, ΔS° should be negative.

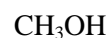


All gases, 2 particles forming 3 particles, rxn is becoming more disordered, ΔS° should be positive.

9. Give the oxidation number for each atom in the following formulas. (5pts each formula)



K = +1
S = +4
O = -2



H = +1
C = -2
O = -2

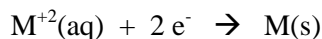
10. You are studying the reaction of acetic acid $\{\text{CH}_3\text{CO}_2\text{H}(\text{l})\}$ with iso-propanol $\{\text{C}_3\text{H}_8\text{O}(\text{l})\}$ to produce isopropylacetate $\{\text{C}_5\text{H}_{10}\text{O}_2(\text{l})\}$ and water. When you run the reaction at 22.67°C , you find that ΔG for this reaction is -35.19 kJ/mol and $\Delta S = +79.18 \text{ J/mol}\cdot\text{K}$ (10pts)

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

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ -35.19 \text{ kJ/mol} &= \Delta H^\circ - (22.67 + 273.15 \text{ K})(0.07918 \text{ kJ/mol}\cdot\text{K}) \\ \Delta H^\circ &= -11.77 \text{ kJ/mol} \text{ exothermic} \end{aligned}$$

Since ΔH° is negative and ΔS° is positive, this rxn will be spontaneous at all temperatures.

11. The alkaline earth metals (Be, Mg, Ca, Sr, Ba) all appear in your Standard Reduction Potential tables in half-cells of the type:



Explain the trend in E°_{red} for these metals. (10 pts)

No real calculations here... As we move down the P.T., the E°_{red} tends to get more negative. This means that it is harder and harder to reduce the metal cation (or conversely, easier to oxidize the metal atom). Because the $\text{M}^{+2}(\text{aq})$ cations get larger going down the P.T., they become less able to attract the electrons required/responsible for the reduction; lower charge density/effective nuclear charge means weaker coulombic interaction between the positively charge nucleus and the electrons in the outermost shells.

12. You are studying a process for which $\Delta H^\circ = +30.71 \text{ kJ/mol}$ and $\Delta S^\circ = +192.44 \text{ J/mol}\cdot\text{K}$. What is ΔG° for this process at 25.00°C ? Will the reaction be more or less spontaneous at 20.00°C ? (8pts)

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

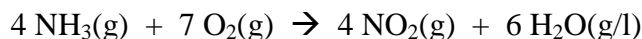
$$\Delta G^\circ = +30.71 \text{ kJ/mol} - (25.00 + 273.15 \text{ K})(0.19244 \text{ kJ/mol}\cdot\text{K}) = -26.67 \text{ kJ/mol}$$

For the second part, either calculate ΔG at 20.00°C or describe the change

$$\Delta G^\circ = +30.71 \text{ kJ/mol} - (20.00 + 273.15 \text{ K})(0.19244 \text{ kJ/mol}\cdot\text{K}) = -25.70 \text{ kJ/mol} \rightarrow \text{less negative, less spontaneous}$$

Since $\Delta H^\circ > 0$ and $\Delta S^\circ > 0$, rxn is more spontaneous @ higher T, 20.00°C is lower temp so rxn is less spont

13. Ammonia $\{\text{NH}_3(\text{g})\}$ can burn in oxygen to form nitrogen dioxide and water. How much {Gibb's Free} energy can be liberated by burning 15.772g of ammonia in an unlimited supply of oxygen? (10pts)



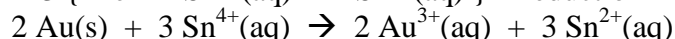
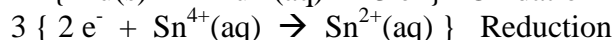
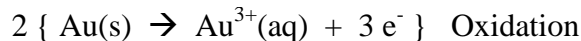
$$\Delta G^\circ = 4(+16.45 \text{ kJ/mol}) + 7(-0 \text{ kJ/mol}) + 4(+51.31 \text{ kJ/mol}) + 6(-228.6 \text{ kJ/mol}) = -1100.56 \text{ kJ/mol} \text{ \{if H}_2\text{O}(\text{g})\}}$$

$$\Delta G^\circ = 4(+16.45 \text{ kJ/mol}) + 7(-0 \text{ kJ/mol}) + 4(+51.31 \text{ kJ/mol}) + 6(-237.2 \text{ kJ/mol}) = -1152.16 \text{ kJ/mol} \text{ \{if H}_2\text{O}(\text{l})\}}$$

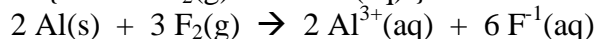
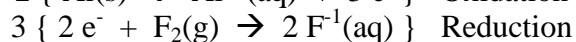
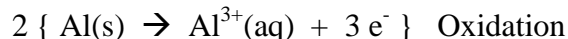
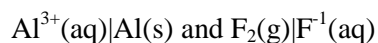
$$(15.772 \text{ g NH}_3(\text{g})) (1 \text{ mol NH}_3 / 17.031 \text{ g NH}_3) (1 \text{ mol rxn} / 4 \text{ mol NH}_3) (1100.56 \text{ kJ} / \text{mol rxn}) = 254.80 \text{ kJ} \text{ \{if H}_2\text{O}(\text{g})\}}$$

$$(15.772 \text{ g NH}_3(\text{g})) (1 \text{ mol NH}_3 / 17.031 \text{ g NH}_3) (1 \text{ mol rxn} / 4 \text{ mol NH}_3) (1152.16 \text{ kJ} / \text{mol rxn}) = 266.75 \text{ kJ} \text{ \{if H}_2\text{O}(\text{l})\}}$$

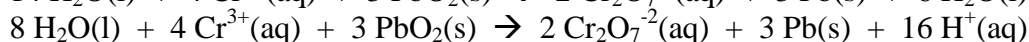
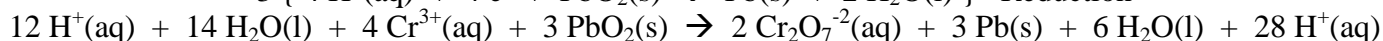
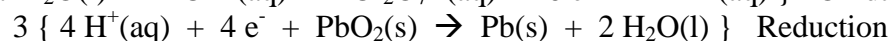
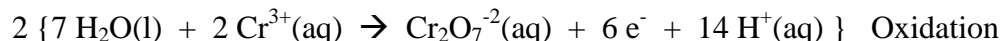
14. For each of the following pairs of half-reactions/half-cells, determine the voltage of the spontaneous reaction/cell and write a balanced equation for the spontaneous reaction, identifying the oxidation and reduction half-reactions. (10pts each)



$$E^\circ_{\text{cell}} = +1.50 \text{ V} + 0.15 \text{ V} = +1.65 \text{ V}$$



$$E^\circ_{\text{cell}} = +1.676 \text{ V} + 2.87 \text{ V} = +4.55 \text{ V}$$

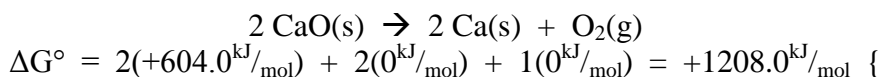
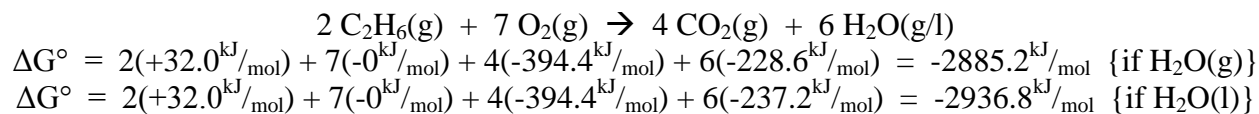


$$E^\circ_{\text{cell}} = -1.33 \text{ V} + 1.93 \text{ V} = +0.60 \text{ V}$$

15. After a strong storm, you are without electricity and would like to construct a flashlight from some materials you have found in your garage. You have a lightbulb that will produce light if you apply a voltage greater than 0.80 V. You have found the following materials: a box of iron (Fe) nails, a silver (Ag) necklace, Fe(NO₃)₃, FeSO₄, and AgNO₃. What cell(s) can you construct to power your flashlight? Explain your choices. (12 pts)

The half cells that can be constructed are: Fe³⁺(aq)|Fe(s) {E°_{red} = -0.04V}; Fe²⁺(aq)|Fe(s) {E°_{red} = -0.44V};
 Ag⁺(aq)|Ag(s) {E°_{red} = +0.799V}
 The cells that can make 0.80V would be
 Fe(s)|Fe³⁺(aq)||Ag⁺(aq)|Ag(s) {E°_{red} = +0.84V}
 Fe(s)|Fe²⁺(aq)||Ag⁺(aq)|Ag(s) {E°_{red} = +1.24V}

16. How many grams of ethane {C₂H₆(g)} would you have to burn to liberate enough Gibb's Free Energy to break 14.227g of CaO(s) into Ca(s) and O₂(g)? (Assume 100% efficiency.) (12 pts)

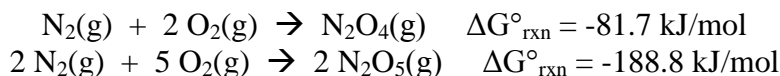


$$(14.227 \text{g CaO}(\text{s})) (1 \text{mol CaO} / 56.077 \text{g CaO}) (1 \text{mol rxn} / 2 \text{mol CaO}) (1208.0 \text{kJ} / \text{mol rxn}) = 153.24 \text{kJ}$$

$$(153.24 \text{kJ}) (1 \text{mol rxn} / 2885.2 \text{kJ}) (2 \text{mol C}_2\text{H}_6(\text{g}) / 1 \text{mol rxn}) (30.069 \text{g C}_2\text{H}_6 / \text{mol C}_2\text{H}_6) = 3.194 \text{g C}_2\text{H}_6 \quad \{\text{if H}_2\text{O}(\text{g})\}$$

$$(153.24 \text{kJ}) (1 \text{mol rxn} / 2936.8 \text{kJ}) (2 \text{mol C}_2\text{H}_6(\text{g}) / 1 \text{mol rxn}) (30.069 \text{g C}_2\text{H}_6 / \text{mol C}_2\text{H}_6) = 3.138 \text{g C}_2\text{H}_6 \quad \{\text{if H}_2\text{O}(\text{l})\}$$

17. When nitrogen gas and oxygen gas are sealed in a vessel, reactions occur that generate N₂O₄(g) and N₂O₅(g). If these are the only products, and ΔG° is the only factor that affects the composition of this mixture, which of these products would you expect to be present in higher quantity at the end of the reaction? (Explain your answer with explicit calculations/numbers.) (10 pts)



Since the rxn to form N₂O₅ has a more negative/more spontaneous ΔG°, it will have the higher concentration when the rxn "ends".

The same argument can be made just using the ΔG°_f values for N₂O₄(g) and N₂O₅(g).

Thermodynamic Values at 25°C:

Substance	ΔH_f° (kJ/mol)	S° (J/mol·K)	ΔG_f° (kJ/mol)
NH ₃ (g)	-46.11	+192.45	-16.45
O ₂ (g)	0	+205.138	0
NO ₂ (g)	+33.18	+240.06	+51.31
H ₂ O(g)	-241.8	+188.8	-228.6
H ₂ O(l)	-285.8	+69.91	-237.2
C ₂ H ₆ (g)	-84.68	+229.2	-32.0
CO ₂ (g)	-393.5	+213.6	-394.4
CaO(s)	-635.1	+39.75	-604.0
Ca(s)	0	+41.4	0
N ₂ O ₄ (g)	+9.16	+304.2	-81.7
N ₂ O ₅ (g)	+11.3	+355.6	-94.4

Standard Reduction Potentials at 25°C:

Half cell	E°_{red} (volts)
Au ³⁺ (aq) Au(s)	-1.50
Sn ⁴⁺ (aq) Sn ²⁺ (aq)	+0.15
Al ³⁺ (aq) Al(s)	-1.676
F ₂ (g) F ⁻ (aq)	+2.87
PbO ₂ (s) Pb(s)	+1.93
Cr ₂ O ₇ ⁻² (aq) Cr ³⁺ (aq)	+1.33
Fe ³⁺ (aq) Fe(s)	-0.04

Half cell	E°_{red} (volts)
Be ⁺² (aq) Be(s)	-1.97
Mg ⁺² (aq) Mg(s)	-2.36
Ca ⁺² (aq) Ca(s)	-2.84
Sr ⁺² (aq) Sr(s)	-2.89
Ba ⁺² (aq) Ba(s)	-2.92
Fe ²⁺ (aq) Fe(s)	-0.44
Ag ⁺ (aq) Ag(s)	+0.799