

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 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/ t

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

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

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

$PV = nRT$

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

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

$0.52^\circ\text{C}/m$

$P_1 = X_1 P_1^\circ$

$P = cRT$

$C_1 V_1 = C_2 V_2$

Quadratic formula:

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

Integrated Rate Laws:

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

$$1/[A]_t = kt + 1/[A]_o$$

$$[A]_t = -kt + [A]_o$$

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

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

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

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

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

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

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

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

$$\Delta G^\circ = \Delta H_{\text{system}}^\circ - T\Delta S_{\text{system}}^\circ$$

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

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

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

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

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)										

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 (5pts each)

- A reaction will likely be reactant-favored/non-spontaneous/not naturally occurring if:
 - $\Delta G^\circ > 0$**
 - $K_{\text{eq}} > 1$
 - $\Delta H < 0$
 - $\Delta S^\circ > 0$
 - $K_{\text{eq}} < 0$
- For which of the following reactions would you expect $\Delta S^\circ_{\text{system}}$ to be negative?
 - $\text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$
 - $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$**
 - $\text{BaSO}_4(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$
 - $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$
 - $\text{C}_2\text{H}_4(\text{l}) + 3 \text{O}_2(\text{g}) \rightleftharpoons 2 \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$
- A reaction will be non-spontaneous at all 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 $\Delta S^\circ_{\text{system}} < 0$
- The symbol ΔH represents:
 - Change in entropy
 - Change in height
 - Change in enthalpy**
 - Change in free energy
 - Change in time
- A large positive change in free energy means:
 - The reaction is very slow
 - The reaction is endothermic
 - The reaction is not spontaneous**
 - The system is becoming more disordered
 - The reaction is spontaneous
- For a reaction with a large positive ΔS :
 - Heat is required to make the reaction proceed
 - The system is becoming much more ordered
 - The reaction is not spontaneous
 - The disorder of the system is increasing**
 - The reaction proceeds very slowly

7. If the change in enthalpy for a reaction is negative and the change in entropy is positive:
- The reaction requires heat
 - The reaction will never be spontaneous
 - The system is becoming more ordered
 - The reaction will always be spontaneous**
 - The reaction will be spontaneous only at high temperatures
8. 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**
9. Predict the sign of the change in entropy for each of the following reactions (3pts each):

Reaction	Sign of $\Delta S^\circ_{\text{rxn}}$
$2 \text{CH}_3\text{OH}(\text{l}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{g})$	+ or -
$\text{Mg}(\text{s}) + \text{F}_2(\text{g}) \rightarrow \text{MgF}_2(\text{s})$	+ or -
$\text{H}_2(\text{g}) + \text{Br}_2(\text{l}) \rightarrow 2 \text{HBr}(\text{g})$	+ or -

10. You react Compounds A and B to yield Compounds C and D. The temperature in your laboratory is 20.36°C and you find that ΔG for this reaction is -6.394 kJ/mol . You have also determined that for this reaction $\Delta S = 186.9 \text{ J/mol}\cdot\text{K}$ (12pts)

- a. Is the reaction endothermic or exothermic? (*Explain your answer with explicit calculations*)

$$\begin{aligned} \Delta G_{\text{rxn}} &= \Delta H_{\text{rxn}} - T\Delta S_{\text{rxn}} \\ -6.394 \text{ kJ/mol} &= \Delta H_{\text{rxn}} - (293.51\text{K})(0.1869 \text{ kJ/mol}\cdot\text{K}) \\ \Delta H_{\text{rxn}} &= +48.46 \text{ kJ/mol} \end{aligned}$$

Since ΔH_{rxn} is positive, this reaction is endothermic

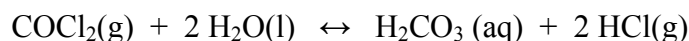
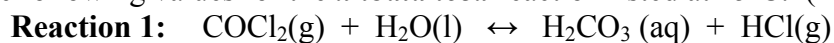
- b. Over what temperature range is this reaction spontaneous?

In essence, we're looking for the temperature at which $\Delta G = 0$. Plugging in:

$$\begin{aligned} 0 \text{ kJ/mol} &= (48.46 \text{ kJ/mol}) - (x)(0.1869 \text{ kJ/mol}\cdot\text{K}) \\ x &= 259.30\text{K} \end{aligned}$$

The reaction will be spontaneous at all temperatures above 259.30K

11. Calculate the following values for the **unbalanced** reaction listed at 25°C. (16pts)



$\Delta H^\circ_{\text{rxn}}$

$$219.1 \text{ kJ/mol} + 2(285.8 \text{ kJ/mol}) + (-699.7 \text{ kJ/mol}) + 2(-92.3 \text{ kJ/mol}) = -93.6 \text{ kJ/mol}$$

$\Delta S^\circ_{\text{rxn}}$

$$-283.5 \text{ J/mol}\cdot\text{K} + 2(-70.0 \text{ J/mol}\cdot\text{K}) + (187.4 \text{ J/mol}\cdot\text{K}) + 2(186.9 \text{ J/mol}\cdot\text{K}) = +137.7 \text{ J/mol}\cdot\text{K}$$

$\Delta G^\circ_{\text{rxn}}$

$$204.9 \text{ kJ/mol} + 2(237.1 \text{ kJ/mol}) + (-623.2 \text{ kJ/mol}) + 2(-95.3 \text{ kJ/mol}) = -134.7 \text{ kJ/mol}$$

or

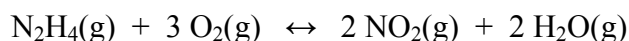
$$\Delta G^\circ_{\text{rxn}} = (-93.6 \text{ kJ/mol}) - (298.15 \text{ K})(0.1337 \text{ kJ/mol}\cdot\text{K}) = -134.7 \text{ kJ/mol}$$

Is the reaction spontaneous?

Yes

No

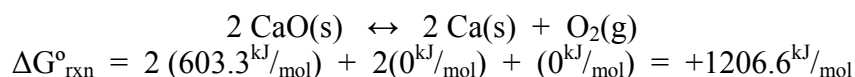
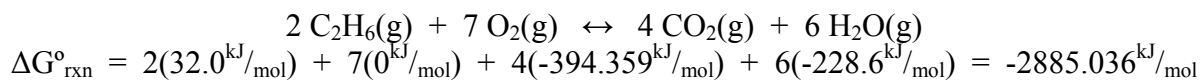
12. Hydrazine $\{\text{N}_2\text{H}_4(\text{g})\}$ can be used as a rocket fuel by burning with oxygen to form nitrogen dioxide and water. How much energy can be liberated by burning 21.964g of hydrazine in an unlimited supply of oxygen? (14pts)



$$\Delta G^\circ_{\text{rxn}} = (-159.4 \text{ kJ/mol}) + 3(0 \text{ kJ/mol}) + 2(51.31 \text{ kJ/mol}) + 2(-228.6 \text{ kJ/mol}) = -513.98 \text{ kJ/mol}$$

$$\left(513.98 \frac{\text{kJ}}{\text{mol rxn}}\right) \left(\frac{1 \text{ mol rxn}}{1 \text{ mol N}_2\text{H}_4}\right) \left(\frac{1 \text{ mol N}_2\text{H}_4}{32.046 \text{ g N}_2\text{H}_4}\right) (21.964 \text{ g N}_2\text{H}_4) = 352.28 \text{ kJ}$$

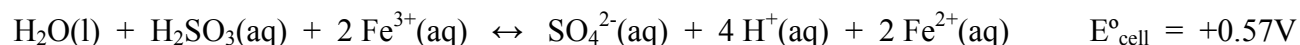
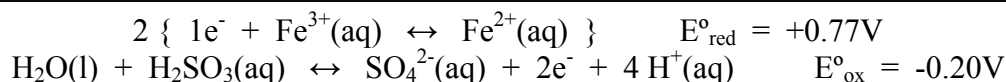
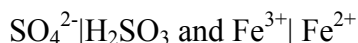
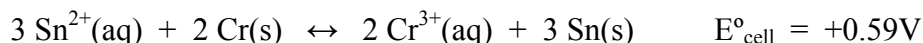
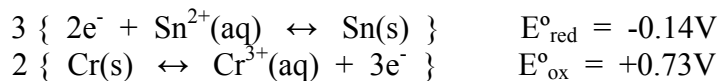
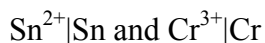
13. How many grams of ethane {C₂H₆(g)} would you have to burn to liberate enough Gibb's Free Energy to break 14.227g of CaO(s) into Ca(s) and O₂(g)? (Assume 100% efficiency.) (16pts)



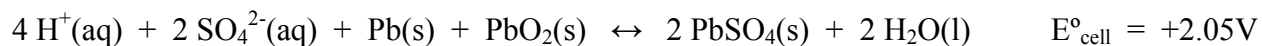
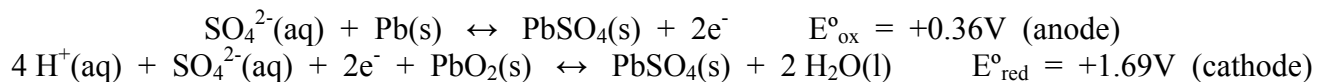
$$\left(1206.6 \frac{\text{kJ}}{\text{mol rxn}}\right) \left(\frac{1 \text{mol rxn}}{2 \text{mol CaO}}\right) \left(\frac{1 \text{mol CaO}}{56.077 \text{g CaO}}\right) (14.227 \text{g CaO}) = 153.06 \text{kJ needed}$$

$$(153.06 \text{kJ}) \left(\frac{1 \text{mol rxn}}{2885.036 \text{kJ}}\right) \left(\frac{2 \text{mol C}_2\text{H}_6}{1 \text{mol rxn}}\right) \left(\frac{30.069 \text{g C}_2\text{H}_6}{1 \text{mol C}_2\text{H}_6}\right) = 3.1905 \text{g C}_2\text{H}_6 \text{ needed}$$

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 reaction that occurs, identifying the oxidation and reduction half-reactions. (12pts each)



15. A lead-acid battery consists of a lead electrode {Pb(s)} and a lead(IV) oxide electrode in a sulfuric acid liquid phase, meaning that the half cell reactions are PbO₂|PbSO₄ and PbSO₄|Pb. Write the balanced chemical equation for the spontaneous cell constructed from these cells and calculate the cell voltage. Identify the anode and the cathode of the spontaneous cell. After the battery has been discharged, it can be recharged by passing 4.28amps of electricity backwards through the cell for 73.63minutes. How many grams of anode material are formed during this recharging process? (20pts)



Recharging will generate Pb(s)

$$\left(4.28 \frac{\text{C}}{\text{sec}}\right)(73.63\text{min}) \left(\frac{60\text{sec}}{1\text{min}}\right) \left(\frac{1\text{mol electrons}}{96485\text{C}}\right) \left(\frac{1\text{mol Pb}(\text{s})}{2\text{mol electrons}}\right) \left(\frac{207.2\text{g Pb}(\text{s})}{1\text{mol Pb}(\text{s})}\right) = 20.3\text{g Pb}(\text{s})$$

Thermodynamic Values at 25°C:

Substance	ΔH°_f (kJ/mol)	S° (J/mol·K)	ΔG°_f (kJ/mol)
COCl ₂ (g)	-219.1	283.5	-204.9
H ₂ O(l)	-285.8	70.0	-237.1
H ₂ CO ₃ (aq)	-699.7	187.4	-623.2
HCl(g)	-92.3	186.9	-95.3
N ₂ H ₄ (g)	95.4	238.5	159.4
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
CO ₂ (g)	-393.509	213.74	-394.359
C ₂ H ₆ (g)	-84.68	229.2	-32.0
Ca(s)	0	41.6	0
CaO(s)	-634.9	38.1	-603.3

Standard Reduction Potentials at 25°C:

Half cell	E°_{red} (volts)	Half cell	E°_{red} (volts)
Sn ²⁺ (aq) Sn(s)	-0.14	Fe ³⁺ (aq) Fe ²⁺ (aq)	+0.77
Cr ³⁺ (aq) Cr(s)	-0.73	PbO ₂ (s) PbSO ₄ (s)	+1.69
SO ₄ ²⁻ (aq) H ₂ SO ₃ (aq)	+0.20	PbSO ₄ (s) Pb(s)	-0.36

