

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 g/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:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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							

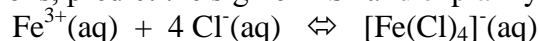
58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.94	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)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

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Multiple Choice (5pts each)

- The symbol ΔS represents:
 - Change in entropy**
 - Change in solubility
 - Change in enthalpy
 - Change in free energy
 - Change in time
- A small 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 negative 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
- A reaction will be product-favored/spontaneous/naturally occurring if:
 - $\Delta G^\circ < 0$**
 - $K_{eq} < 1$
 - $\Delta H > 0$
 - $\Delta S^\circ < 0$
 - $K_{eq} < 0$
- A reaction will be spontaneous at all 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 $\Delta S^\circ_{system} < 0$
- If the change in enthalpy for a reaction is positive and the change in entropy is negative:
 - The reaction releases heat
 - The reaction will never be spontaneous**
 - The system is becoming more disordered
 - The reaction will always be spontaneous
 - The reaction will be spontaneous only at low temperatures
- 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**

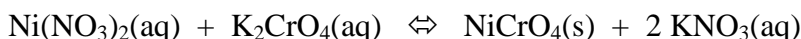
8. For each of the following reactions, predict the sign of ΔS° and explain your answer (6pts each):



Negative. Four aqueous particles are becoming 1 aqueous particle making the system much more ordered.



Positive. A solid is much more ordered than an aqueous solution, so this system is becoming more disordered.



Negative. A solid is forming from aqueous solutions, so this system is becoming more ordered even though the coefficients in the equation make it look like 2 particles becoming 3 particles. If you really want to use a particles-to-particles argument, think of the ionic equation (or the net ionic equation) and you'll see that ~~six~~ reactant particles are forming 5 product particles, but the fact that a solid is forming will have a MUCH larger impact on the disorder/order of the system than the change in number of particles.

9. You are studying the reaction of aspirin $\{\text{C}_9\text{H}_8\text{O}_4(\text{s})\}$ with caffeine $\{\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2(\text{s})\}$ to produce aspeine $\{\text{C}_9\text{H}_{10}\text{N}_2\text{O}_3(\text{s})\}$ and caffirin $\{\text{C}_8\text{H}_8\text{N}_2\text{O}_3(\text{s})\}$. The temperature in your laboratory is 22.63°C and you find that ΔG for this reaction is -11.18 kJ/mol . You have also determined that for this reaction $\Delta S = +94.85 \text{ J/mol}\cdot\text{K}$ (20pts)

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

$$\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T\Delta S_{\text{rxn}}$$

Plugging in:

$$\begin{aligned} -11.18 \text{ kJ/mol} &= \Delta H_{\text{rxn}} - (295.78\text{K})(0.09485 \text{ kJ/mol}\cdot\text{K}) \\ \Delta H_{\text{rxn}} &= 16.87 \text{ kJ/mol} \end{aligned}$$

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

b. Over what temperature range is this reaction spontaneous?

Since ΔH_{rxn} and ΔS_{rxn} are both positive, there will be a temperature where the reaction changes from spontaneous to non-spontaneous. At that temperature, ΔG_{rxn} will be zero.

Plugging in:

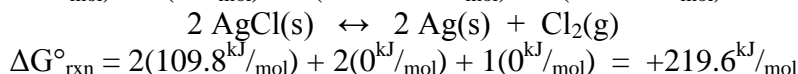
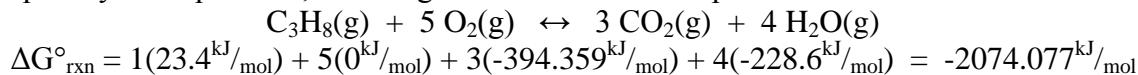
$$\begin{aligned} 0 \text{ kJ/mol} &= (16.87 \text{ kJ/mol}) - (T)(0.09485 \text{ kJ/mol}\cdot\text{K}) \\ T &= 177.9\text{K} \end{aligned}$$

Since the reaction is spontaneous at 295.78K , the reaction will be spontaneous at all temperatures above 177.9K .

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10. Propane {C₃H₈(g)} reacts with oxygen gas in gas grills to produce carbon dioxide gas, water gas and heat. How much energy is released by burning 58.371g of propane in an unlimited supply of oxygen? If all of this energy is used to decompose silver chloride solid to chlorine gas and silver metal, how many grams of silver metal can be produced? (25pts)

This is a coupled systems problem, so let's get both reactions set up first.



A couple notes: I pulled the ΔG°_f values from the table at the end of the exam. The $\Delta G^\circ_{\text{rxn}}$ value for the propane combustion has too many sig figs, but I'm just using that in the middle of a calculation so I'll carry extra sig figs. If I were reporting that as a final answer, I'd round to $-2074.1^{\text{kJ/mol}}$.

OK, let's burn that propane:

$$(58.371\text{g propane}) \left(\frac{1\text{mol propane}}{44.096\text{g propane}} \right) \left(\frac{1\text{mol rxn}}{1\text{mol propane}} \right) \left(\frac{2074.077\text{kJ}}{1\text{mol rxn}} \right) = 2745.5\text{kJ released}$$

{“Released” implies the negative sign that I dropped}

Now we want to dump all that energy into the silver reaction to make some money...

$$(2745.5\text{kJ}) \left(\frac{1\text{mol rxn}}{219.6\text{kJ}} \right) \left(\frac{2\text{mols Ag}}{1\text{mol rxn}} \right) \left(\frac{107.87\text{g Ag}}{1\text{mol Ag}} \right) = 2697\text{g Ag}$$

At current market prices, that's not a bad little lump of silver...

11. You would like to plate 2.46g of platinum (atomic # = 78) using an electrolytic cell containing a solution of platinum(II) nitrate and operating at 5.81A. How long will you have to run the cell? (15pts)

Work with your units and this problem will largely set itself up as long as you remember that an amp (A) is a coulomb per second.

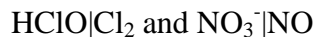
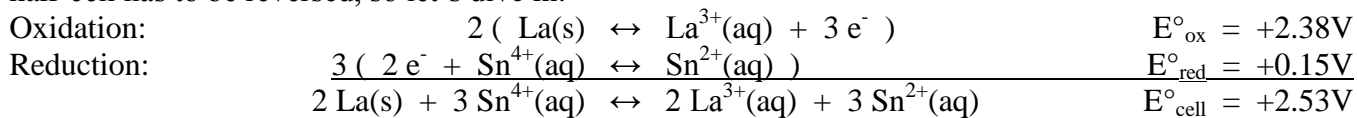
$$(2.46\text{g Pt}) \left(\frac{1\text{mol Pt}}{195.08\text{g Pt}} \right) \left(\frac{2\text{mol e}^-}{1\text{mol Pt}} \right) \left(\frac{96485\text{C}}{1\text{mol e}^-} \right) \left(\frac{1\text{sec}}{5.81\text{C}} \right) = 419\text{sec}$$

If you prefer to convert this to minutes, go for it, 6.98min.

12. 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. (20pts each)



First we need to determine the spontaneous direction. Looking at the standard reduction potentials, the La half-cell has to be reversed, so let's dive in:



This one's a little more challenging, so let's start with assigning oxidation numbers.

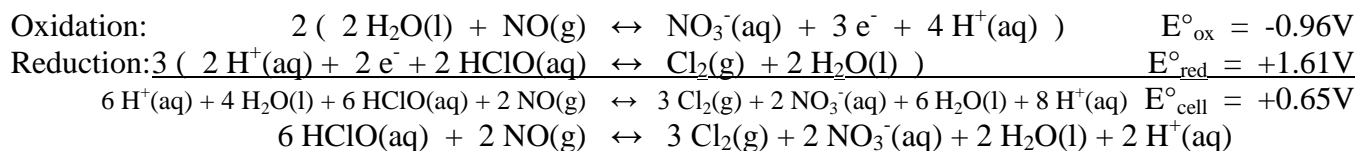
$\text{HClO} \rightarrow$ If the H is +1 and the O is -2, then the Cl must be +1. (sum of ox#'s = charge)

$\text{Cl}_2 \rightarrow$ An uncombined element in its natural/standard state, ox# = 0

$\text{NO}_3^- \rightarrow$ Assume the three O's are each -2, that makes the N +5. (sum of ox#'s = charge)

$\text{NO} \rightarrow$ Assume O = -2, then N = +2.

OK, now to determine the spontaneous direction. Looking at the standard reduction potentials, the nitrate half-cell has to be reversed.



Notes: There are *two* chlorines each going from +1 to 0, so they each need an electron. Add electrons to compensate for the change in oxidation state, not necessarily the charge.

Thermodynamic Values at 25°C:

Substance	ΔH°_f (kJ/mol)	S° (J/mol·K)	ΔG°_f (kJ/mol)
$\text{C}_3\text{H}_8(g)$	-103.85	270.3	-23.4
$\text{O}_2(g)$	0	205.138	0
$\text{CO}_2(g)$	-393.509	213.74	-394.359
$\text{H}_2\text{O}(g)$	-241.8	188.8	-228.6
$\text{AgCl}(s)$	-127.0	96.3	-109.8
$\text{Cl}_2(g)$	0	223.1	0
$\text{Ag}(s)$	0	42.6	0

Standard Reduction Potentials at 25°C:

Half cell	E°_{red} (volts)	Half cell	E°_{red} (volts)
$\text{Pt}^{2+}(\text{aq}) \text{Pt}(s)$	+0.76	$\text{HClO}(\text{aq}) \text{Cl}_2(g)$	+1.61
$\text{La}^{3+}(\text{aq}) \text{La}(s)$	-2.38	$\text{NO}_3^-(\text{aq}) \text{NO}(g)$	+0.96
$\text{Sn}^{4+}(\text{aq}) \text{Sn}^{2+}(\text{aq})$	+0.15		