

# 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 =  $1.000 \text{ g/mL}$

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

$PV = nRT$

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

For water,  $k_{\text{fp}} = -1.86^\circ\text{C}/m$ ;  $k_{\text{bp}} = 0.52^\circ\text{C}/m$

$P_1 = X_1 P_1^\circ$

$P = cRTi$

$C_1 V_1 = C_2 V_2$

Quadratic formula:

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

Integrated Rate Laws:

$\ln[A]_t = -kt + \ln[A]_0$

$1/[A]_t = kt + 1/[A]_0$

$[A]_t = -kt + [A]_0$

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

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

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

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

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

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

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

$F = 96500 \text{ J}/\text{V}\cdot\text{mol of electrons}$

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

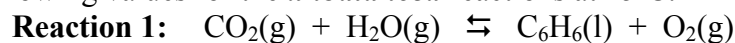
$\Delta G^\circ = -nFE_{\text{cell}}^\circ = -RT \ln K^\circ$

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

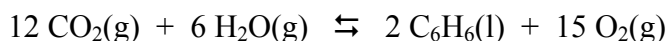
1 <b>H</b> 1.0079																	2 <b>He</b> 4.0026				
3 <b>Li</b> 6.941	4 <b>Be</b> 9.0122															5 <b>B</b> 10.811	6 <b>C</b> 12.011	7 <b>N</b> 14.007	8 <b>O</b> 15.999	9 <b>F</b> 18.998	10 <b>Ne</b> 20.180
11 <b>Na</b> 22.990	12 <b>Mg</b> 24.305															13 <b>Al</b> 26.982	14 <b>Si</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	57 <b>La</b> 138.91	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	89 <b>Ac</b> 227.03	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							

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	71 <b>Lu</b> 174.97
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)	103 <b>Lr</b> (260)

1. Calculate the following values for the **unbalanced** reactions at 25°C.



**Balanced Equation:**



$\Delta H_{\text{rxn}}^\circ$  (6pts)

$$\Delta H_{\text{rxn}}^\circ = 12(393.509 \text{ kJ/mol}) + 6(241.818 \text{ kJ/mol}) + 2(49.028 \text{ kJ/mol}) + 15(0 \text{ kJ/mol}) = 6271.07 \text{ kJ/mol}$$

$\Delta S_{\text{rxn}}^\circ$  (6pts)

$$\begin{aligned} \Delta S_{\text{rxn}}^\circ &= 12(-213.74 \text{ J/mol}\cdot\text{K}) + 6(-188.25 \text{ J/mol}\cdot\text{K}) + 2(172.8 \text{ J/mol}\cdot\text{K}) + 15(205.138 \text{ J/mol}\cdot\text{K}) \\ &= -271.7 \text{ J/mol}\cdot\text{K} \end{aligned}$$

$\Delta G_{\text{rxn}}^\circ$  (6pts)

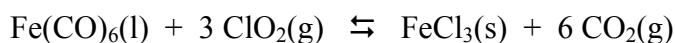
$$\begin{aligned} \Delta G_{\text{rxn}}^\circ &= 12(394.359 \text{ kJ/mol}) + 6(228.572 \text{ kJ/mol}) + 2(124.50 \text{ kJ/mol}) + 15(0 \text{ kJ/mol}) = 6352.74 \text{ kJ/mol} \\ \Delta G_{\text{rxn}}^\circ &= \Delta H_{\text{rxn}}^\circ - T \Delta S_{\text{rxn}}^\circ = 6271.07 \text{ kJ/mol} - (298 \text{ K})(-271.7 \text{ J/mol}\cdot\text{K}) = 6352.0 \text{ kJ/mol} \end{aligned}$$

Is the reaction spontaneous? (4pts) Yes

No



**Balanced Equation:**



$\Delta H_{\text{rxn}}^\circ$  (6pts)

$$\Delta H_{\text{rxn}}^\circ = (783.5 \text{ kJ/mol}) + 3(-102.5 \text{ kJ/mol}) + (-399.49 \text{ kJ/mol}) + 6(-393.509 \text{ kJ/mol}) = -2284.5 \text{ kJ/mol}$$

$\Delta S_{\text{rxn}}^\circ$  (6pts)

$$\Delta S_{\text{rxn}}^\circ = (-363.8 \text{ J/mol}\cdot\text{K}) + 3(-256.84 \text{ J/mol}\cdot\text{K}) + (142.3 \text{ J/mol}\cdot\text{K}) + 6(213.74 \text{ J/mol}\cdot\text{K}) = 290.4 \text{ J/mol}\cdot\text{K}$$

$\Delta G_{\text{rxn}}^\circ$  (6pts)

$$\begin{aligned} \Delta G_{\text{rxn}}^\circ &= (711.3 \text{ kJ/mol}) + 3(-120.5 \text{ kJ/mol}) + (-334.00 \text{ kJ/mol}) + 6(-394.359 \text{ kJ/mol}) = -2350.4 \text{ kJ/mol} \\ \Delta G_{\text{rxn}}^\circ &= \Delta H_{\text{rxn}}^\circ - T \Delta S_{\text{rxn}}^\circ = (-2284.5 \text{ kJ/mol}) - (298 \text{ K})(290.4 \text{ J/mol}\cdot\text{K}) = -2371.0 \text{ kJ/mol} \end{aligned}$$

Is the reaction spontaneous? (4pts) Yes

No

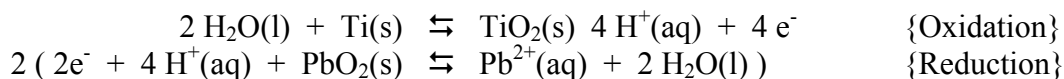
2. For each of the following pairs of half-reactions/half-cells, determine the voltage of the spontaneous reaction/cell and write a balanced equation for the reaction that occurs, identifying the oxidation and reduction half-reactions. (14pts each)

PbO<sub>2</sub>|Pb<sup>2+</sup> and TiO<sub>2</sub>|Ti

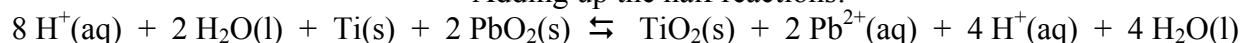
$$E^{\circ}_{\text{red}}(\text{PbO}_2|\text{Pb}^{2+}) = +1.467 \text{ V}; E^{\circ}_{\text{red}}(\text{TiO}_2|\text{Ti}) = -0.872 \text{ V}$$

For a spontaneous rxn, the {TiO<sub>2</sub>|Ti} half rxn should be oxidative, so:

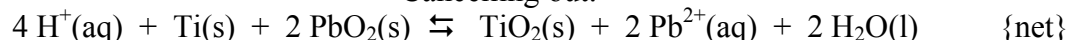
$$E^{\circ}_{\text{cell}} = (+1.467 \text{ V}) + (+0.872 \text{ V}) = +2.339 \text{ V}$$



Adding up the half reactions:



Cancelling out:

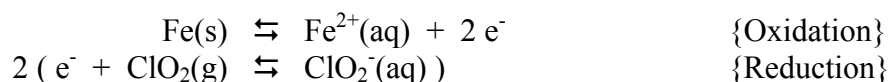


Fe<sup>2+</sup>|Fe and ClO<sub>2</sub>|ClO<sub>2</sub><sup>-</sup>

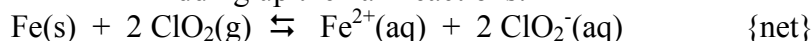
$$E^{\circ}_{\text{red}}(\text{Fe}^{2+}|\text{Fe}) = -0.409 \text{ V}; E^{\circ}_{\text{red}}(\text{ClO}_2|\text{ClO}_2^-) = +0.953 \text{ V}$$

For a spontaneous rxn, the { Fe<sup>2+</sup>|Fe } half rxn should be oxidative, so:

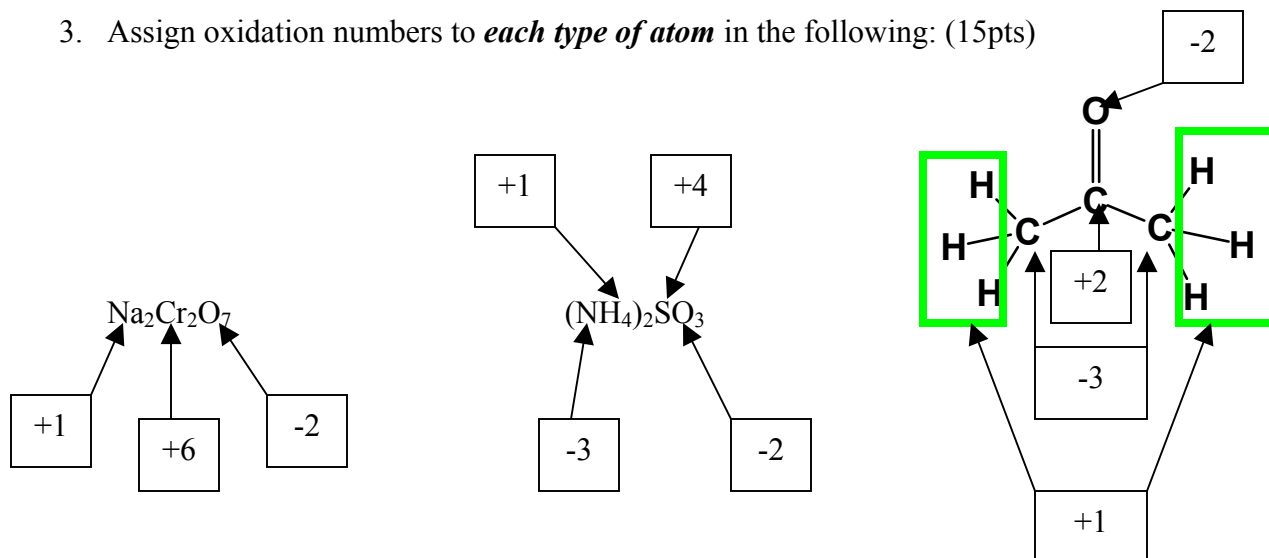
$$E^{\circ}_{\text{cell}} = (+0.409 \text{ V}) + (+0.953 \text{ V}) = +1.362 \text{ V}$$



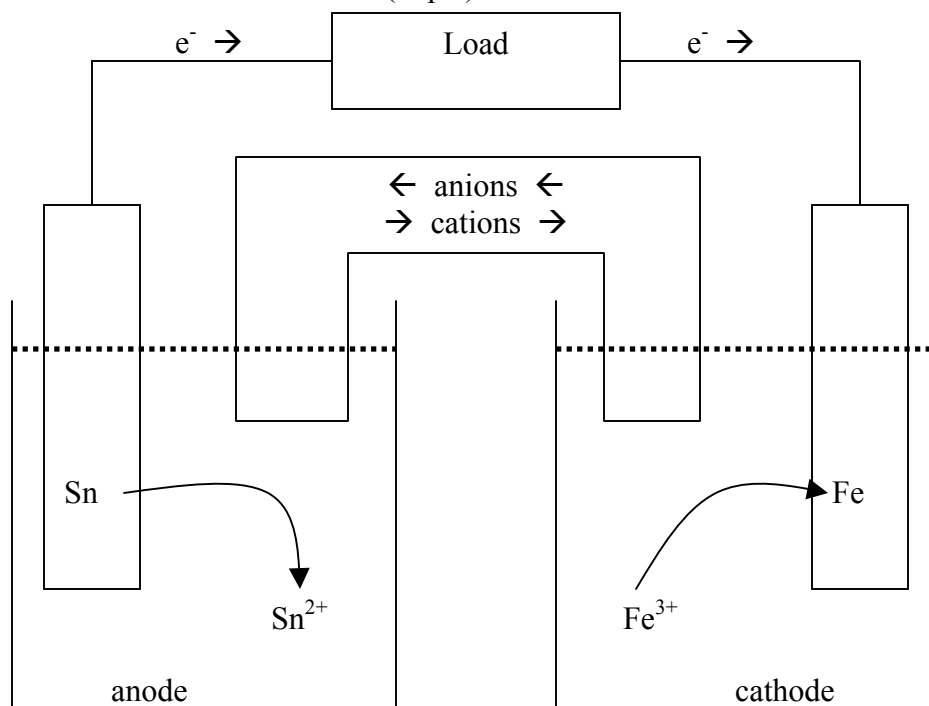
Adding up the half reactions:



3. Assign oxidation numbers to *each type of atom* in the following: (15pts)



4. Draw the spontaneous voltaic cell you would make from a  $\text{Sn}^{2+}|\text{Sn}$  and a  $\text{Fe}^{3+}|\text{Fe}$  half-cell. Be sure to indicate the direction of electron and counterion flow, and specify which half-cell is the cathode and which is the anode. (21pts)



5. You react Compounds A and B to yield Compound C. The temperature in your laboratory is  $21^\circ\text{C}$  and you find that  $\Delta G$  for this reaction is  $31.996 \text{ kJ/mol}$ . You have also calculated that for this reaction  $\Delta S = 169.284 \text{ J/mol}\cdot\text{K}$ . (21pts)
- Is this reaction endothermic or exothermic?
  - Is the reaction spontaneous in boiling water?

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

$$31.996 \text{ kJ/mol} = \Delta H^\circ_{\text{rxn}} - (294\text{K})(0.169284 \text{ kJ/mol}\cdot\text{K})$$

$$\Delta H^\circ_{\text{rxn}} = +81.77 \text{ kJ/mol}$$

Endothermic

$$\Delta G^\circ_{\text{rxn}} = (81.77 \text{ kJ/mol}) - (373\text{K})(0.169284 \text{ kJ/mol}\cdot\text{K})$$

$$\Delta G^\circ_{\text{rxn}} = +18.60 \text{ kJ/mol}$$

Not spontaneous in boiling water

6. When iron filings and oxygen gas are sealed in a vessel, reactions occur that generate  $\text{Fe}_2\text{O}_3(\text{s})$  and  $\text{Fe}_3\text{O}_4(\text{s})$ . If these are the only products, and  $\Delta G^\circ$  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.*) (21pts)

Looking at the two reactions involved:

$$4 \text{Fe}(\text{s}) + 3 \text{O}_2(\text{g}) \rightleftharpoons 2 \text{Fe}_2\text{O}_3(\text{s})$$

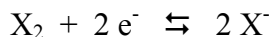
$$\Delta G^\circ_{\text{rxn}} = 4(0 \text{ kJ/mol}) + 3(0 \text{ kJ/mol}) + 2(-742.2 \text{ kJ/mol}) = -1484.4 \text{ kJ/mol}$$

$$3 \text{Fe}(\text{s}) + 2 \text{O}_2(\text{g}) \rightleftharpoons \text{Fe}_3\text{O}_4(\text{s})$$

$$\Delta G^\circ_{\text{rxn}} = 3(0 \text{ kJ/mol}) + 2(0 \text{ kJ/mol}) + (-1015.4 \text{ kJ/mol}) = -1015.4 \text{ kJ/mol}$$

Since the first reaction is *more* spontaneous, when the reaction is complete there will be more  $\text{Fe}_2\text{O}_3(\text{s})$  present than  $\text{Fe}_3\text{O}_4(\text{s})$ .

Bonus: The halogens ( $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ,  $\text{At}_2$ ) all appear in Standard Reduction Potential tables in half-cells of the following type with the listed reduction potentials:



Halogen	$E^\circ_{\text{red}}$ (volts)
$\text{F}_2$	3.03
$\text{Cl}_2$	1.36
$\text{Br}_2$	1.07
$\text{I}_2$	0.54
$\text{At}_2$	0.2

Explain this trend in  $E^\circ_{\text{red}}$ . (+8 pts)

The more positive a reduction potential is, the more easily the species is reduced. In this series of molecules, fluorine is very easy to reduce while astatine is not. Since fluorine is (relatively) small, the electron that is added during reduction is quite close to the nucleus, meaning that it is strongly attracted and tightly held. As the halogens get larger (moving down the column), the added electron is farther and farther from the nucleus and the corresponding electrostatic attraction is lower and lower. This is the same rationale and explanation of the trend in electron affinity within a column of the Periodic Table.

**Thermodynamic Values at 25°C:**

Substance	$\Delta H_f^\circ$ (kJ/mol)	$S^\circ$ (J/mol·K)	$\Delta G_f^\circ$ (kJ/mol)
CO <sub>2</sub> (g)	-393.509	213.74	-394.359
H <sub>2</sub> O(g)	-241.818	188.25	-228.572
C <sub>6</sub> H <sub>6</sub> (l)	49.028	172.8	124.50
O <sub>2</sub> (g)	0	205.138	0
Fe(CO) <sub>5</sub> (l)	-783.5	363.8	-711.3
ClO <sub>2</sub> (g)	102.5	256.84	120.5
FeCl <sub>3</sub> (s)	-399.49	142.3	-334.00
Fe <sub>2</sub> O <sub>3</sub> (s)	-824.2	87.40	-742.2
Fe <sub>3</sub> O <sub>4</sub> (s)	-1118.4	146.4	-1015.4

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

Half cell	$E^\circ_{\text{red}}$ (volts)	Half cell	$E^\circ_{\text{red}}$ (volts)
PbO <sub>2</sub>  Pb <sup>2+</sup>	+1.467	Fe <sup>2+</sup>  Fe	-0.409
TiO <sub>2</sub>  Ti	-0.872	ClO <sub>2</sub>  ClO <sub>2</sub> <sup>-</sup>	+0.953
Sn <sup>2+</sup>  Sn	-0.14	Fe <sup>3+</sup>  Fe	-0.04