

page 1 (25) _____

2 (25) _____

total (150)

3 (25) _____

4 (30) _____

chk

5 (25) _____

6 (25) _____

The Management will appreciate your not writing in this space.

1. (13 points) (a) If we were to combine 10 mol of water at 0°C with 20 mol of water at 60°C, assuming no heat loss to the surroundings, we would obviously end up with all the water at 40°C. If we began instead with 10 mol of ice at 0°C and added 20 mol of liquid water at 60°C, would you expect the final temperature to be higher or lower than 40°C? Why (*briefly*)?

3 Some heat from the warm water must go toward melting the ice, so the final temp will be lower than 40°C

(b) Calculate the final temperature of the water. The heat capacity of H₂O (l) is 75.3 J/molK (i.e. J mol⁻¹ K⁻¹), and its "enthalpy of fusion" is 6.01 kJ/mol.

10

heat m: to melt ice + to raise T of cold water = heat lost by warm water

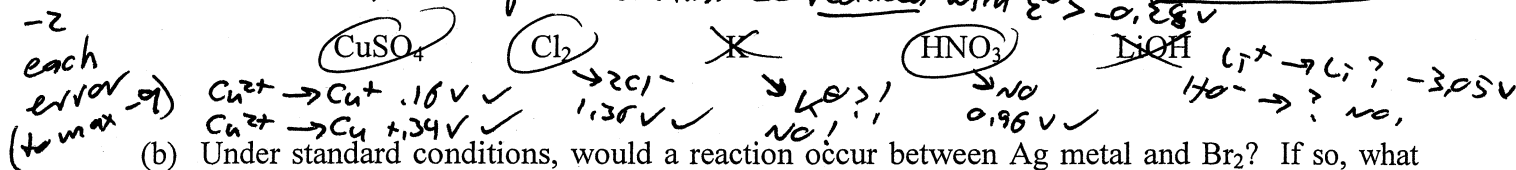
$$(10 \text{ mol})(6010 \text{ J/mol}) + (10 \text{ mol})(75.3 \text{ J/molK})(T_f - 0^\circ\text{C}) = (20 \text{ mol})(75.3 \text{ J/molK})(60^\circ\text{C} - T_f)$$

$$60100 \text{ J} + 753 \text{ J/degree} \cdot T_f = 90360 \text{ J} - 1506 \text{ J/degree} \cdot T_f$$

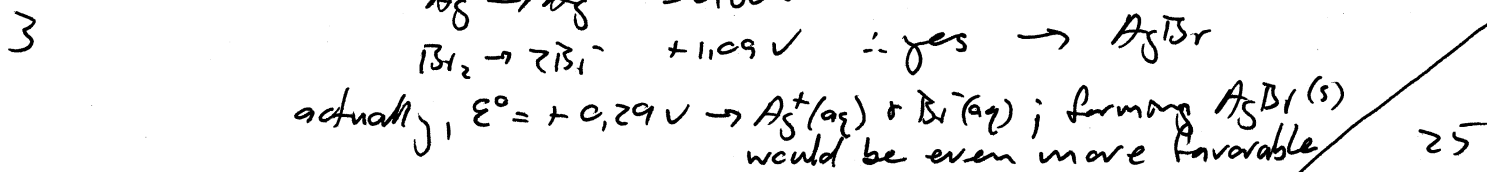
$$(2259 \text{ J/degree}) \cdot T_f = 30260 \text{ J}$$

$$T_f = 13.4^\circ\text{C}$$

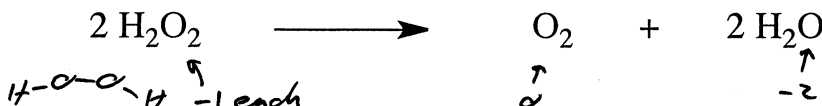
2. (12 points) The standard reduction potential for Co²⁺(aq) → Co(metal) is -0.28V. (a) Under standard conditions, which of the following is/are capable of oxidizing metallic Co? (circle one or more choices). these species must be reduced with E° > -0.28V



(b) Under standard conditions, would a reaction occur between Ag metal and Br₂? If so, what would be produced?



3. (25 points) Hydrogen peroxide decomposes to oxygen and water in a redox process, as shown below.



- 2 (a) What is oxidized and what is reduced?
one O of H₂O₂ is oxidized (to O₂); other is reduced
- (b) According to the NIST database, H₂O₂ (gas) has ΔH_f[°] = -136.1 kJ/mol and S[°] = 233 J/molK. Use these and other relevant data from the attached tables to calculate ΔH[°] and ΔS[°] for the reaction in the gas phase, per mol of H₂O₂.

7

$$\Delta H^\circ = 2(-242) + 0 - 2(-136.1) = -212 \text{ kJ/mol of H}_2\text{O}_2$$

$$= -106 \text{ kJ/mol}$$

$$\Delta S^\circ = 2(189) + 205 - 2(233) = 117 \text{ J/k}\cdot\text{mol}$$

$$= 58.5 \text{ J/mol}\cdot\text{K}$$

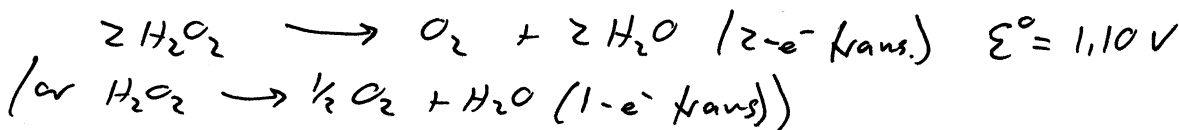
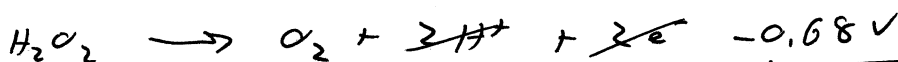
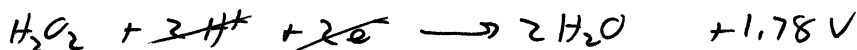
or just divide the eqns by 2 (H₂O₂ → 1/2 O₂ + H₂O)!

- 5 (c) Use your values from part b to calculate ΔG[°] at 25°C.

$$\Delta G^\circ = -106 \text{ kJ/mol} - 298\text{K}(58.5 \text{ J/mol}\cdot\text{K}) \quad \text{watch the units!}$$

$$= -173 \text{ kJ/mol}$$

- (d) You will find two half-cell reactions in the table of standard reduction potentials that involve H₂O₂. Use these to calculate the E[°] value for the reaction above (at 25°C).



- (e) Use your E[°] to calculate ΔG[°] for the reaction, per mol of H₂O₂.

4

$$\Delta G^\circ = -nF E^\circ \quad \text{use } n=2, \text{ then divide } \Delta G^\circ \text{ by } 2$$

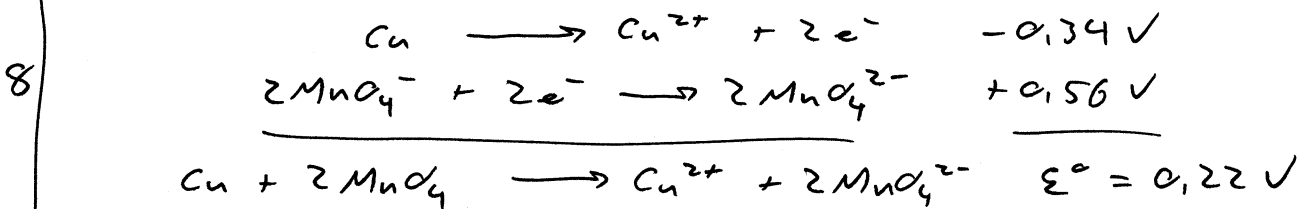
$$= -(1\text{e}^-)(96485 \text{ J/V}\cdot\text{mol})(1.10 \text{ V}) = -106 \text{ kJ/mol} \quad \text{or use } n=1 \text{ to get } \Delta G^\circ \text{ per mol of } 1/2 \text{ H}_2\text{O}_2$$

- (f) Briefly explain any difference between your ΔG[°] values from parts c and e.

2 This must be mainly due to the fact that the part-c value is for the gas phase + the electrochemical measurements were in solution.

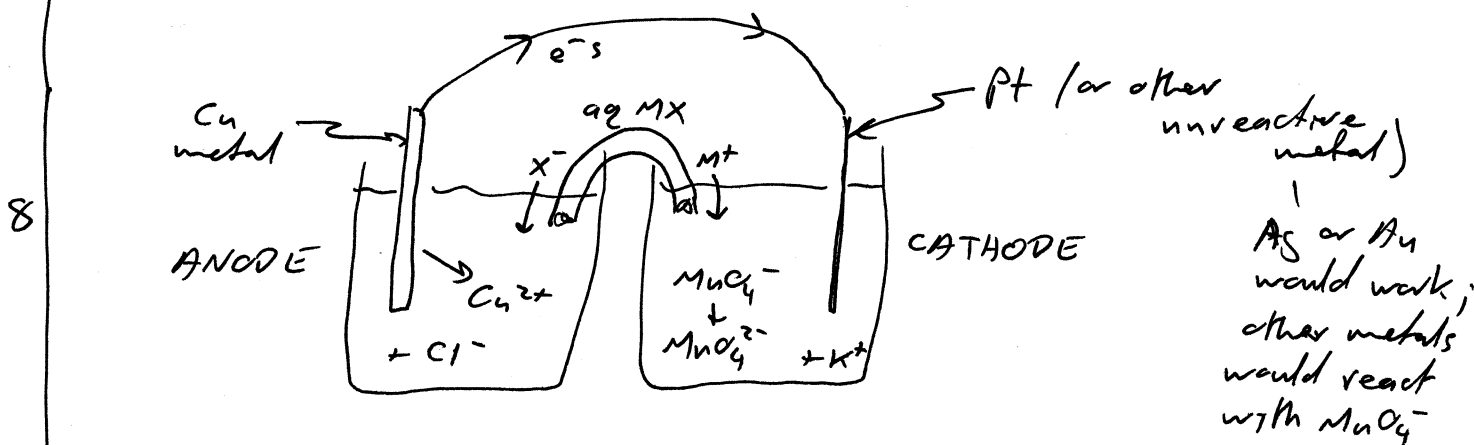
4. (25 points) A Galvanic cell is constructed with Cu metal and aqueous CuCl₂ in one beaker and aqueous KMnO₄ and K₂MnO₄ in the other. The salts are all water-soluble.

(a) Write the relevant half-cell equations and the balanced overall reaction, in the direction for which the reaction is spontaneous.



(b) What is ϵ° for your battery (at 25°C)? $+0.22 \text{ V}$

(c) Sketch the battery, showing the electrode materials, the direction of electron flow through the wire connecting them, and the salt bridge, if one is necessary.



(d) On your diagram above, label the anode and cathode, and indicate which way cations and anions would flow out of the salt bridge into the separate solutions.

(e) What would the voltage of your battery be if the two solutions were prepared by dissolving 0.15 moles of CuCl₂ 1.00L of water, and by dissolving 0.40 moles of KMnO₄ and 0.010 moles of K₂MnO₄ in 1.00 L of water?

6

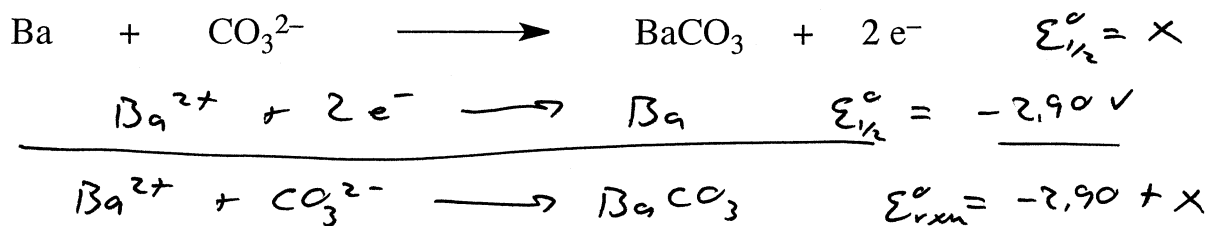
$$\begin{aligned}
 \epsilon &= +0.22 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \left(\frac{[\text{Cu}^{2+}][\text{MnO}_4^{2-}]^2}{[\text{MnO}_4^{-}]^2} \right) \\
 &= +0.34 \text{ V} \quad \frac{(0.15)(0.010)^2}{(0.40)^2}
 \end{aligned}$$

(f) What will happen if you remove the electrodes from the solutions, still connected, and switch them?

3

Cu will react directly with MnO₄⁻. (No current will flow.)

5. (15 points) Barium carbonate is a very slightly water-soluble solid. Oxidation of barium metal in the presence of carbonate produces BaCO_3 directly, rather than aqueous Ba^{2+} . The solubility product, K_{sp} , for BaCO_3 , is 1.6×10^{-9} at 25°C . Calculate the value of \mathcal{E}° for the reaction below.



$$K_{sp} = 1.6 \times 10^{-9} \text{ for } \text{BaCO}_3 \rightleftharpoons \text{Ba}^{2+} + \text{CO}_3^{2-}$$

$$\Delta G^\circ = -RT \ln K_{sp}$$

$$\Delta G^\circ = +50.2 \text{ kJ/mol}$$

$$\mathcal{E}_{\text{rxn}}^\circ = -\Delta G^\circ / nF$$

$$\mathcal{E}_{\text{rxn}}^\circ = -0.26 \text{ V} \quad \mathcal{E}_{\text{rxn}}^\circ \text{ for } \text{Ba}^{2+} + \text{CO}_3^{2-} \rightarrow \text{BaCO}_3 \text{ is } +0.26 \text{ V}$$

thus is for solid \rightarrow ions!

$$+0.26 \text{ V} = -2.90 \text{ V} + X$$

$$X = +3.16 \text{ V}$$

6. (15 points) 0.05 mol of solid ammonium nitrate, NH_4NO_3 , is dissolved in 100g of water in a double-coffee-cup calorimeter. The final mass of the solution is 104g, and its specific heat capacity is 4.184 J/gK (i.e. $\text{J g}^{-1} \text{ K}^{-1}$). The temperature is observed to decrease by 3.06°C .

$$(\Delta T = 3.06 \text{ K})$$

(a) Is the enthalpy change for solid ammonium nitrate dissolving in water positive or negative?

2 ΔH must be positive - heat is absorbed from the solution

(b) Calculate the ΔH for dissolution of NH_4NO_3 (in kJ/mol).

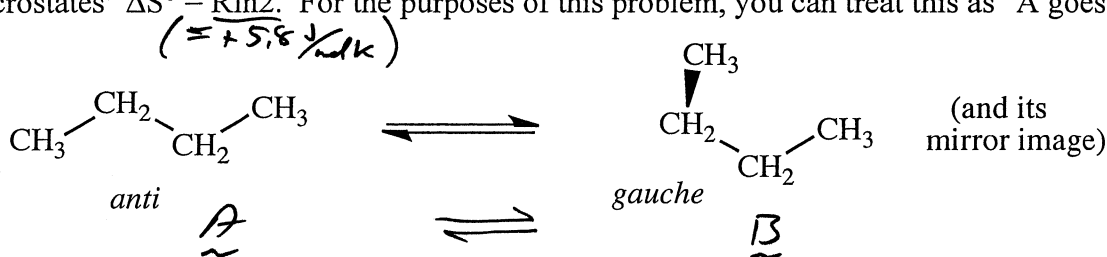
10 heat flow: $q = (4.184 \text{ J/gK})(3.06 \text{ K})(104 \text{ g}) = 1332 \text{ J}$
 $(\Delta T \text{ in } ^\circ\text{C} \sim \text{K})$

$$\frac{1332 \text{ J}}{0.05 \text{ mol of } \text{NH}_4^+ \text{NO}_3^-} = 26.6 \text{ kJ/mol}$$

(c) Obviously, the solid dissolves spontaneously, so what can you say about ΔS for this process?

3 $\Delta G = \Delta H - T\Delta S$
 spontaneous \Rightarrow neg ΔG \Rightarrow ΔH pos \Rightarrow ΔS must be positive \Rightarrow increase in disorder when NH_4NO_3 dissolves.
 (Always!) ΔS must be positive \Rightarrow increase in disorder when NH_4NO_3 dissolves.

7. (25 points) The conformational change shown below for butane has $\Delta H^\circ = +3.8 \text{ kJ/mol}$ and $\Delta S^\circ = +5.8 \text{ J/molK}$, i.e. $+5.8 \text{ J mol}^{-1} \text{ K}^{-1}$. (You need not be concerned with the fact that the conformation on the right can exist in two mirror image forms, though because there two "microstates" $\Delta S^\circ = R \ln 2$. For the purposes of this problem, you can treat this as "A goes to B".)



(a) What is ΔG° (in kJ/mol) for the process as written above, at 25°C ?

7

$$\Delta G^\circ = +3.8 \text{ kJ/mol} - (298 \text{ K})(+5.8 \text{ J/molK})$$

$$= +2.1 \text{ kJ/mol}$$

watch the units!

(b) What is the equilibrium constant, K_{eq} ?

7

$$K = e^{-\frac{(2100 \text{ J/mol})}{(8.314 \text{ J/molK})(298 \text{ K})}}$$

$$= 0.43$$

(c) What is ΔG when the system is at equilibrium?

3

0

(d) As the temperature is raised, would you expect the equilibrium to shift more toward product or toward reactant?

3 ΔH° is positive, so K should increase, i.e. rxn will "shift" toward product side.

(e) Calculate ΔG° and K_{eq} at 500°C . Assume that ΔH° and ΔS° are temperature-independent.

10

$$\Delta G^\circ = 3.8 \text{ kJ/mol} - (773 \text{ K})(5.8 \text{ J/molK})$$

$$= -0.68 \text{ kJ/mol}$$

$$K = e^{-\frac{(-680 \text{ J/mol})}{(8.314 \text{ J/molK})(773 \text{ K})}} = 1.1$$

B is favored !!!

(f) Calculate ΔG° and K_{eq} at 77K (the boiling point of liquid nitrogen).

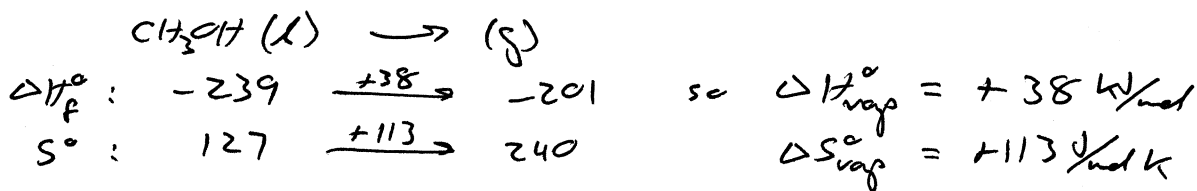
as above:

$$\Delta G^\circ = 3.4 \text{ kJ/mol}$$

$$K = 0.0053 \text{ (using calc'd } \Delta G^\circ \text{ of } 3.35 \text{ or } 0.0049 \text{ using rounded } \Delta G^\circ \text{ of } 3.4)$$

only $\frac{1}{2}\%$ of B at this temp!

8. (10 points) The tables attached include ΔH_f° and S° values for both liquid and gaseous methanol, CH_3OH . Use these values to calculate methanol's boiling point (in $^\circ\text{C}$).

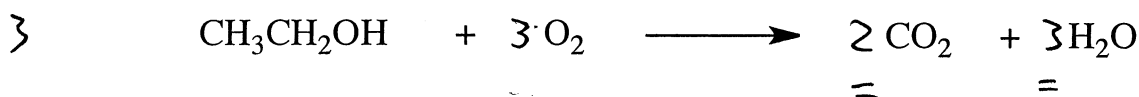


$$\Delta H_{\text{vap}}^\circ = T \Delta S_{\text{vap}}^\circ$$

$$T = \frac{\Delta H_{\text{vap}}^\circ}{\Delta S_{\text{vap}}^\circ} = \frac{38000 \text{ J/mol}}{113 \text{ J/mol K}} = 336 \text{ K}$$

(actual bp = 65°C) = 63°C

9. (15 points) Combustion of ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ produces CO_2 and water and releases lots of heat. (a) Start by balancing the combustion reaction below.



(b) Use the data in the tables attached to calculate ΔH° for the reaction with all reactants and products in the gas phase (note that the only ΔH_f° value in the table for ethanol is for the liquid. But according to NIST, $\Delta H_{\text{vaporization}}^\circ$ of ethanol is 42.0 kJ/mol , and its boiling point is 78°C .)

12 ethanol: $\Delta H_f^\circ(\text{gas}) = \Delta H_f^\circ(\text{liquid}) + \Delta H_{\text{vap}}^\circ$ ↑ we're not calculating S° , so we don't need T_b

"EtOH" $= -278 + 42$

$= -236 \text{ kJ/mol}$

$$\Delta H_{\text{rxn}}^\circ = 3 \overset{\text{H}_2\text{O(g)}}{(-242)} + 2 \overset{\text{CO}_2(\text{g})}{(-393.5)} - 3(0) - (-236) \quad \text{all kJ/mol}$$

$$= -1277 \text{ kJ/mol} \quad \text{yes, that's kJ, not J.}$$

(15 free points!)