

KEY

For full credit show all work and put correct units on final answers. Note that information that is not needed may be present in some problems.

Please Read: If you get a quantitative answer that is many powers of 10 from what you think it should be and cannot find the error, you will be rewarded for pointing out approximately what you expected and why. You will be penalized by 25% on a problem for sign and unit errors that lead to unreasonable results if you do not say why it is unreasonable.

SET UP calculations for all the problems first, and obtain the numbers last in case time is short.

(15 pts) 1. (a) Using Table A.5 provided, calculate the equilibrium constant at 298 K for the reaction:



$$\Delta G^\circ = -371.22 - (300.19 + 0)$$

$$K_{eq} = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-(-71.03 \times 10^3)}{(8.3145) 298}} = 2.8 \times 10^{12}$$

(b) What will the equilibrium constant be at $T = 400\text{K}$?

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\Delta H^\circ = -395.72 - (-296.83 - 0) = -98.89 \text{ kJ/mol}$$

$$= -\left(\frac{-98890}{8.3145}\right) \left(\frac{1}{400} - \frac{1}{298}\right) = -10.18$$

$$\frac{K_2}{K_1} = e^{-10.18} = 3.80 \times 10^{-5}$$

$$K_{400} = (3.8 \times 10^{-5}) 2.8 \times 10^{12} = 1.06 \times 10^8$$

(10 pts) 2. If the Third Law absolute entropy of a system is $83.145 \text{ JK}^{-1}\text{mol}^{-1}$, calculate the number of microstates available to the system.

$$S = R \ln W$$

$$\ln W = \frac{S}{R} = \frac{83.145}{8.3145} = 10.00$$

$$W = e^{10} = 2.2 \times 10^4$$

(15 pts) 3. Consider a fertilized hen's egg, kept at constant temperature by the mother hen (sitting continually on the nest). Consider the egg as a constant-volume, open system (egg shells are porous), but that pV work on atmosphere = 0.

Tell whether the following are positive, zero, or negative. Give a brief justification for each of your answers. If it is not possible to unequivocally know the answer for some of these, indicate this and say why.

← *const temp is given*

$$q \text{ — } w \text{ 0 } \Delta T \text{ 0 } \Delta U \text{ — } \Delta H \text{ — } \Delta S \text{ — } \Delta G \text{ — } \Delta S_{\text{surr}} \text{ + } \Delta S_{\text{univ}} \text{ + }$$

$$\Delta S = - \text{ ordering}$$

$$\Delta S_{\text{univ}} = + \text{ happened}$$

$$\Delta S_{\text{surr}} = + = \Delta S_{\text{univ}} - \Delta S$$

$$q = -T\Delta S_{\text{surr}} = -$$

$$\Delta H = \Delta U + \Delta pV = \Delta U = q + 0 = -$$

$$\Delta G = - \text{ spontaneous and } p = p_{\text{ext}} = \text{const}, T_{\text{ons}}, w_{\text{useful}} = 0$$

(10 pts) 4. (a) If ΔG for the reaction in a system = -3000 J/mol and $w_{\text{useful}} = +3000$ J/mol (work is put into the system) at 300 K, what is $\Delta S_{\text{universe}}$? Assume $p = p_{\text{ext}} = \text{constant}$ and T is constant.

$$\Delta G = -T\Delta S_{\text{univ}} + w_{\text{useful}}$$

$$T\Delta S_{\text{univ}} = -\Delta G + w_{\text{useful}} = +3000 + 3000 = 6000$$

$$\Delta S_{\text{univ}} = \frac{6000}{300}$$

$$\Delta S_{\text{univ}} = 20 \text{ J/K}$$

(b) Is the process spontaneous, non-spontaneous, or at equilibrium? What is your reasoning?

SPONTANEOUS because $\Delta S_{\text{univ}} > 0$

Note: ΔG is not guaranteed to be negative
 $\nexists w_{\text{useful}} \neq 0$

(10 pts) 5. Given that: $dT = (-1/S)dG + (V/S)dp$

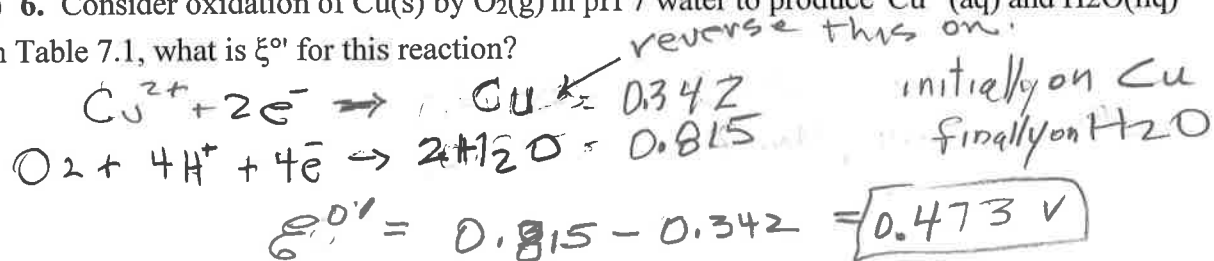
(a) $\left(\frac{\partial T}{\partial p}\right)_G = ? \quad \frac{V}{S}$

(b) $\left(\frac{\partial T}{\partial G}\right)_p = ? \quad -\frac{1}{S}$

(c) $\left(\frac{\partial(V/S)}{\partial G}\right)_p = ? \quad \left(\frac{\partial(-1/S)}{\partial p}\right)_G$

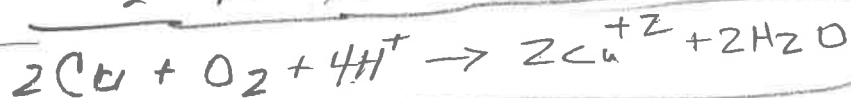
(15 pts) 6. Consider oxidation of Cu(s) by O₂(g) in pH 7 water to produce Cu²⁺(aq) and H₂O(l)

(a) From Table 7.1, what is $\xi^{\circ'}$ for this reaction?



(b) Balance this equation so that there is 1 mole of O₂ in the equation.

Need to mult Cu²⁺... by 2



(c) Calculate $\Delta G^{\circ'}$ for the reaction as balanced in (b).

$n = 4$ from (b)

$$\Delta G^{\circ'} = -nF\xi^{\circ'} = -4(96500)(0.473)$$

$$= -1.825 \times 10^5 \text{ J/mol}$$

- (10 pts) 7. Using the Boltzmann distribution, what is the ratio of the number of gases water molecules to liquid molecules at equilibrium in a closed container at 100° C, assuming that ΔU for vaporization = 40 kJ/mol if we assume the degeneracies in the liquid and vapor states are the same.

$$\frac{N_{\text{gas}}}{N_{\text{liq}}} = e^{-\frac{40000}{(8.3145)373}} = 2.50 \times 10^{-6}$$

- (15 pts) 8. (a) For the reaction of the acid $\text{HA}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{A}^-(\text{aq})$, $K_a = 1 \times 10^{-4}$. What is the pH when the acid is 50% dissociated, assuming ideal behavior.

$$K = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{1[\text{HA}]} = 10^{-4} \text{ M} \quad \text{pH} = 4$$

- (b) Write Q for this reaction, assuming non-ideal behavior of **all** reactants and products.

$$Q = \frac{(\gamma_{\text{H}_3\text{O}^+} [\text{H}_3\text{O}^+])(\gamma_{\text{A}^-} [\text{A}^-])}{X_{\text{H}_2\text{O}(\text{l})} \gamma_{\text{HA}} [\text{HA}]}$$

- (c) The addition of salt ions can make the activity coefficient for $\text{H}_3\text{O}^+(\text{aq})$ and $\text{A}^-(\text{aq})$ both equal to 0.5. Calculate the $[\text{H}_3\text{O}^+(\text{aq})]$ concentration under this condition if HA is 20M and ideal, and the mole fraction of water = 0.5 but behaving **ideally**. (There is no other source for the $\text{H}_3\text{O}^+(\text{aq})$ and $\text{A}^-(\text{aq})$ so $[\text{H}_3\text{O}^+] = [\text{A}^-]$).

$$K = 1 \times 10^{-4} = \frac{(0.5 [\text{H}_3\text{O}^+])^2}{(0.5)(20)} = \frac{0.25 [\text{H}_3\text{O}^+]^2}{10} = 1 \times 10^{-4}$$

$$[\text{H}_3\text{O}^+]^2 = 40 \times 10^{-4} = 4 \times 10^{-3}$$

$$[\text{H}_3\text{O}^+] = (4 \times 10^{-3})^{1/2} = 6.3 \times 10^{-2} \text{ M}$$

TABLE A.5 Inorganic Compounds* (cont.)

	$\Delta_f H^\circ$ (kJ mol ⁻¹)	S° (J K ⁻¹ mol ⁻¹)	$\Delta_f G^\circ$ (kJ mol ⁻¹)
HCO ₃ ⁻ (aq)	-691.99	91.2	-586.77
CO ₃ ²⁻ (aq)	-677.14	-56.9	-527.81
Fe(s)	0	27.28	0
Fe ₂ O ₃ (s)	-824.2	87.40	-742.2
H ₂ (g)	0	130.79	0
H ₂ O(g)	-241.82	188.93	-228.73
H ₂ O(l)	-285.83	69.91	-237.13
H ⁺ (aq)	0	0	0
OH ⁻ (aq)	-229.99	-10.75	-157.244
H ₂ O ₂ (aq)	-191.17	143.9	-134.03
H ₂ S(g)	-20.63	205.90	-33.56
H ₂ SO ₄ (g)	-735.13	298.8	-653.37
N ₂ (g)	0	191.72	0
NH ₃ (g)	-46.11	192.56	-16.78
NH ₃ (aq)	-80.29	111.3	-26.50
NH ₄ ⁺ (aq)	-132.51	113.4	-79.31
NO(g)	90.25	210.87	86.55
NO ₂ (g)	33.18	240.17	51.47
NO ₃ ⁻ (aq)	-205.0	146.40	-108.74
Na ⁺ (aq)	-240.12	59.0	-261.90
NaCl(s)	-411.15	72.13	-384.14
NaCl(aq)	-407.27	115.5	-393.13
NaOH(s)	-425.61	64.46	-379.49
O ₂ (g)	0	205.25	0
O ₃ (g)	142.7	239.04	163.4
S(rhombic)	0	31.80	0
SO ₂ (g)	-296.83	248.33	-300.19
SO ₃ (g)	-395.72	256.87	-371.22

* Standard thermodynamic values at 25°C (298.15 K) and 1 bar pressure. Values for ions refer to an aqueous solution at unit activity on the molarity scale. Standard enthalpy of formation, $\Delta_f H^\circ$, third-law entropies, S° , and standard Gibbs free energy of formation, $\Delta_f G^\circ$, are given.

† The standard state for all ions and for species labeled (aq) is that of a solute on the molarity scale.

(Data from *The NBS Tables of Thermodynamic Properties*, D. D. Wagman et al., eds., *J. Phys. Chem. Ref. Data*, 11, Suppl. 2 (1982), corrected to 1 bar pressure.)

TABLE 7.1 Standard Reduction Electrode Potentials at 25°C (cont.)

Oxidant/Reductant	Electrode reaction	E° (V)	E° (V) (pH 7)
Cu^{2+}/Cu	$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	+0.342	
I_2/I^-	$\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$	+0.535	
Ag^+/Ag	$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	+0.800	
$\text{O}_2/\text{H}_2\text{O}$	$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$	+1.229	+0.815
$\text{NO}_3^-/\text{NO}_2^-$	$\text{NO}_3^- + 3\text{H}^+ + 2e^- \rightarrow \text{HNO}_2 + \text{H}_2\text{O}$	+0.934	
$\text{Br}_2(\text{aq})/\text{Br}^-$	$\text{Br}_2 + 2e^- \rightarrow 2\text{Br}^-$	+1.087	
$\text{Cl}_2(\text{g})/\text{Cl}^-$	$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$	+1.358	
$\text{Mn}^{3+}/\text{Mn}^{2+}$	$\text{Mn}^{3+} + e^- \rightarrow \text{Mn}^{2+}$	+1.541	
$\text{F}_2(\text{g})/\text{F}^-$	$\text{F}_2 + 2e^- \rightarrow 2\text{F}^-$	+2.866	