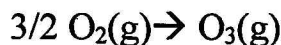


For full credit show all work and put correct units on final answers. Note that information that is not needed may be present in some problems.

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.

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



$$K = e^{-\Delta G^\circ / RT}$$

$$\Delta G^\circ = 163.4 \text{ kJ/mol} = 163,400 \text{ J/mol}$$

$$K_{298} = e^{-\frac{163400}{(8.3145)(298)}} = 2.39 \times 10^{-29}$$

(b) What will the equilibrium constant be at $T = 350\text{K}$?

$$\Delta H^\circ = 142.7 \text{ kJ/mol}$$

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

$$\ln \left(\frac{K_2}{K_1} \right) = -\frac{142,700}{8.3145} \left(\frac{1}{350} - \frac{1}{298} \right) = 8.56$$

$$K_{350} = K_{298} e^{8.56} = 2.39 \times 10^{-29} \times 5200 = 1.24 \times 10^{-25}$$

(10 pts) 2. If the number of microstates available to a system = 10^{30} , compute the Third Law absolute entropy in $\text{J K}^{-1} \text{mol}^{-1}$. (To do this recall the algebra involving logarithms of a number raised to a power.)

$$S = R \ln 10^{30} = 30(8.3145) \ln 10$$

$$\text{(or } S = k_B \ln 10^{30} \text{)} \\ \text{J K}^{-1} \text{ molecule}^{-1}$$

$$= 574.3 \text{ J/K mol}$$

(15 pts) 3. An isolated, constant volume initially containing water and crystals of an unknown salt eventually comes to an equilibrium state in which all of the crystals have dissolved. 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. (Assume that for practical purposes the pressure in the system is constant, although it would change very slightly.)

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

$$\Delta S_{\text{surr}}, q, w, \Delta U = 0 \quad (\text{1st Law isolated}) \quad \Delta S = \Delta S_{\text{univ}}$$

$$\Delta H = \Delta U + \Delta(PV) = 0 + 0 \quad P \& V \text{ const.}$$

$$\Delta G = \Delta H - \Delta(TS) \quad \text{Cannot be sure of } T_2 - T_1$$

We know $S_2 > S_1$ but do not know if $T_2 > T_1$

(Some salts have endothermic heats of dissolving.)

(10 pts) 4. (a) If ΔG for the reaction in a system $A \rightarrow B = +2000 \text{ J/mol}$ and $w_{\text{other}} = +5000 \text{ J/mol}$ (work in put into the system) at 300 K, what is $\Delta S_{\text{universe}}$? Assume $p = p_{\text{ext}} = \text{constant}$ and T is constant.

Under these conditions $\Delta G = -T \Delta S_{\text{univ}} + w_{\text{other}}$

$$T \Delta S_{\text{univ}} = w_{\text{other}} - \Delta G = 3000 \text{ J/mol}$$

$$\Delta S_{\text{univ}} = \frac{3000}{300} = \boxed{10 \text{ J/K}}$$

(b) Is the process spontaneous? What is your reasoning?

YES, $\Delta S_{\text{univ}} > 0$

EVEN THOUGH $\Delta G = +$ the LARGE INPUT OF WORK FORCES THE REACTION "UPHILL"

B \rightarrow A

Common
EXAMPLE:

A \rightarrow B

The discharging of your cell phone battery (system) has $\Delta G = \text{NEG.}$
The charging of your cell phone battery (") has $\Delta G = \text{POS.}$
The Volts \times charge from the charger = positive w_{other}

The charging process (fortunately) is SPONTANEOUS



(10 pts) 5. Given that: $dG = -SdT + VdP$

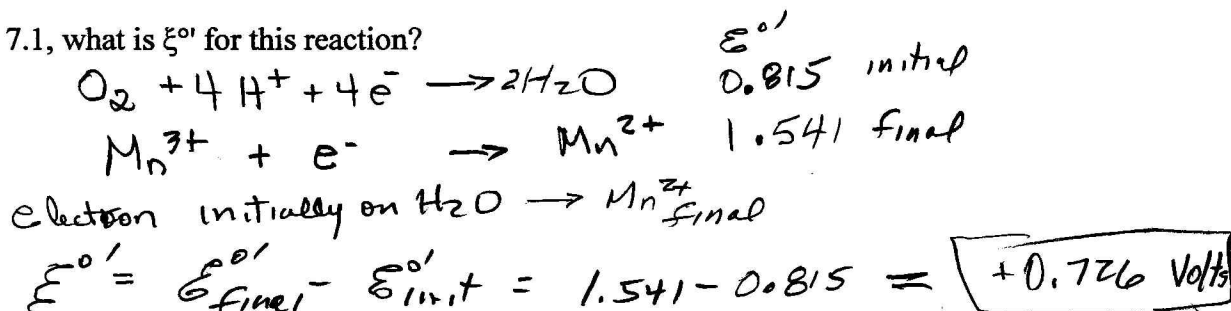
(a) $\left(\frac{\partial G}{\partial T}\right)_P = ?$ $\nearrow -S$

(b) $\left(\frac{\partial G}{\partial P}\right)_T = ?$ $\nearrow V$

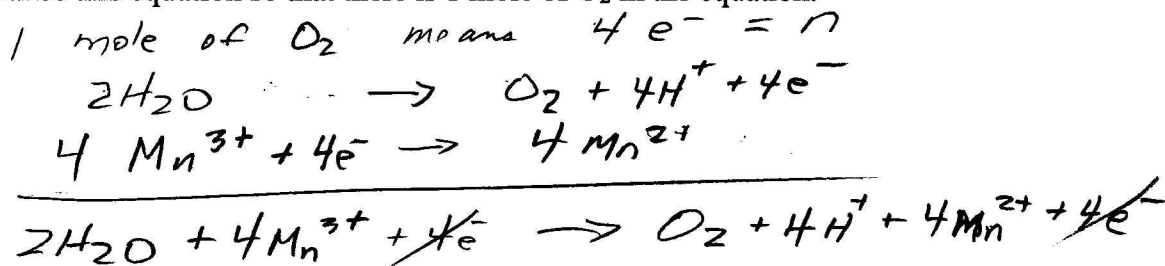
(c) $\left(\frac{\partial S}{\partial P}\right)_T = ? -\left(\frac{\partial V}{\partial T}\right)_P$

(15 pts) 6. Consider oxidation of H_2O by Mn^{3+} to produce O_2 and Mn^{2+} (as happens in photosynthesis). $H_2O + Mn^{3+} \rightarrow O_2 + Mn^{2+}$ unbalanced.

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



(b) Balance this equation so that there is 1 mole of O_2 in the equation.



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

$$\begin{aligned} \Delta G^{\circ'} &= -n F \xi^{\circ'} = -4(96500)(0.726) \\ &= \boxed{-280,236 \text{ J/mol}} \end{aligned}$$

- (10 pts) 7. Using the Boltzmann distribution, what is the ratio of the number of H atoms in the 2p energy level to those in the 1s level at 6000 K (the temperature of the Sun's surface), given that the 2p energy is 656 kJ above the 1s level. (remember, the degeneracy of the 2p level = 3, i.e., 2px, 2py, and 2pz).

$$\frac{N_{2p}}{N_{1s}} = \frac{g_2}{g_1} e^{-\frac{\Delta E}{RT}} = \frac{3}{1} e^{-\frac{656000}{(8.3145)(6000)}} = 5.84 \times 10^{-6}$$

because
$$= \frac{g_2}{g_1} e^{-\frac{\Delta E}{RT}}$$

- (15 pts) 8. (a) For the reaction of the acid $\text{HA(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{A}^-(\text{aq})$, $K_a = 1 \times 10^{-6}$.

What is the pH when the acid is 50% dissociated, assuming ideal behavior.

$$[A^-] = [HA] \quad K = \frac{[H_3O^+][A^-]}{[HA] \cdot 1} = 1 \times 10^{-6} \quad \text{pH} = 6$$

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

$$Q = \frac{\gamma_{H_3O^+} [H_3O^+] \gamma_{A^-} [A^-]}{\gamma_{HA} [HA] \gamma_{H_2O} X_{H_2O}}$$

- (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 1 M and *ideal*. (There is no other source for the $\text{H}_3\text{O}^+(\text{aq})$ and $\text{A}^-(\text{aq})$ so $[\text{H}_3\text{O}^+] = [\text{A}^-]$).

$$\text{H}_2\text{O(l)} \text{ also ideal} \quad [H_3O^+] = [A^-] = C$$

$$\frac{((0.5)C)^2}{1 \cdot 1} = 1 \times 10^{-6}$$

$$0.5 C = 1 \times 10^{-3}$$

$$[H_3O^+] = C = \frac{1 \times 10^{-3}}{0.5} = 2 \times 10^{-3} \text{ M}$$

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	