6. Table 7.1
7. ratio K

CHMY 361 Exam 2
Friday, Oct. 11, 2013, 7:55-8:55 AM
4 x 6 note card
100 points in 8 problems on 6 pages including tables A.5 and 7.1

Name KEY
Last First

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.** Calculate the equilibrium constant for the reaction $NH_3(aq) \rightarrow NH_3(g)$ at 298 K and at 373K using the data from Table A.5.

$\Delta_f G^\circ$ $NH_3(g) = -16.78$ kJ/mol
" $NH_3(aq) = -26.50$ "
$\Delta G^\circ = -16.78 - 26.50 = +9.72$

$K_{298} = e^{-\frac{\Delta G^\circ}{RT}} = e^{\frac{-9720}{(8.3145)298}} = 0.0198 \frac{bar}{mol\ L^{-1}}$

Need ΔH° for K_{373}; $\Delta H^\circ = -46.11 - (-80.29)$
$= +34.18$ kJ mol^{-1}

$\ln \frac{K_{373}}{K_{298}} = -\frac{\Delta H^\circ}{R}\left(T_{373}^{-1} - T_{298}^{-1}\right) = -\frac{34180}{8.3145}\left(373^{-1} - 298^{-1}\right)$
$= 2.77$

$K_{373} = K_{298} \times e^{2.77} = 0.0198 \times 16.02 = 0.317 \frac{bar}{mol\ L^{-1}}$
as it should be according to Le Chatelier.

(10 pts) **2.** Calculate $\Delta_f S^0$ for H_2O gas at 298 K using the data in Table A.5.

Reaction is $H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(g)$
absolute S: 130.79 205.25 188.93

$\Delta_f S^\circ = 188.93 - 130.79 - 1/2(205.25)$
$= -44.49$ J K^{-1}

Constant V

(10 pts) 3. A liquid evaporates into a space that was initially a vacuum, all in an ***isolated*** system, and eventually comes to equilibrium. 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 any of these, indicate this and say why.

q 0 w 0 ΔT − ΔU 0 ΔH + ΔS + ΔG ? ΔS_{surr} 0 ΔS_{univ} +

Isolated means q, w, ΔU = 0, and $\Delta S_{surr} = 0$

ΔH = ΔU + Δ(PV) = + (P increases)

ΔT evaporation requires energy from liq: ↓ T

ΔS: = + gas more disordered

ΔS_{UNIV} = + : it happens

ΔG = ΔH − TΔS Cannot tell if neg or pos
+ − +

(15 pts) 4. (a) If during an isothermal process at 300 K and $p_{ext} = p$ = constant, the system is said to have ΔS = -40 J/K, q = -10 kJ and w_{other} = +400 kJ of non-PV work. **What is ΔG?**

$\Delta G = -T\Delta S_{UNIV} + W_{other}$

$\Delta S_{surr} = -q/T = -\frac{-10000}{300} = +33\ J\ K^{-1}$

$\Delta S_{UNIV} = -40\ J K^{-1} + 33\ J K^{-1} = \boxed{-7\ JK}$

$\Delta G = -(300)(-7) + 400\,000\ J =$
$= +2100 + 400{,}000 = \boxed{402100\ J}$

(b) Is this process spontaneous or is it fictitious? Explain your answer.

Fictitious: $\Delta S_{UNIV} < 0$ Not possible

(That ΔG > 0 is irrelevant under these conditions)

(10 pts) **5.** Given that: $dU = -PdV + TdS$ $\qquad dU = \left(\frac{\partial U}{\partial V}\right)_S dV + \left(\frac{\partial U}{\partial S}\right)_V dS$

(a) What is the partial derivative of U with respect to S at constant V?

$$\left(\frac{\partial U}{\partial S}\right)_V = T$$

(b) What is the partial derivative of U with respect to V at constant S?

$$\left(\frac{\partial U}{\partial V}\right)_S = -P$$

(c) what is the partial derivative of T with respect to V at constant S?

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

(15 pts) **6.** For the oxidation of NADH to NAD^+ by $O_2(g)$ to give $H2O(l)$:

(a) From Table ~~4~~ 7.1, what is $\xi^{o\prime}$ for this reaction?

$NAD^+ + H^+ + 2e^- \rightarrow NADH$ $\qquad -0.324$ initial

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $\qquad +0.815$ final

$\mathcal{E}^{o\prime} = \mathcal{E}^{o\prime}_{final} - \mathcal{E}^{o\prime}_{init} = 0.815 - (-0.324) = \boxed{1.139\ V}$

(b) Balance this equation any way you like (as long as it is balanced).

reverse the first × mult by 2

$2NADH \rightarrow 2NAD^+ + 2H^+ + 4e^-$

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

$2NADH + O_2 + \cancel{4}\,2H^+ \rightarrow 2NAD^+ + 2H_2O + \cancel{2H^+}$

$n = 4$

(c) Calculate $\Delta G^{0'}$ for ***your*** balanced equation.

$n = 4$

$\Delta G^0 = -nF\mathcal{E}^{o\prime} = (-4\ \text{mol})\,96{,}500\ \frac{\text{coul}}{\text{mol}} \times 1.139\ \frac{J}{\text{coul}} = \boxed{-439{,}600\ J}$

$= -439.6\ kJ$

for 2 mol NADH

or half that for 1 mol "

etc.

$100\ mi = 100\ mi \times 5280\ ft/mile \times \frac{1\ m}{3.28\ ft} = 1.61 \times 10^5\ m$

(10 pts) 7. One can read that the edge of the atmosphere of Earth is at an elevation of 100 miles above sea level. According to the Boltzmann distribution what is the ratio of pressures at 100 miles to that at sea level. Assume that the gravitational constant is constant out to that distance and the average temperature is 250 K. Use a ratio of degeneracies that is g(100 mi)/g(sea level) = 1.05 (there is 5% more space 100 miles up)

$$\frac{P_{100}}{P_0} = \frac{g_{100}}{g_0} e^{-\frac{Mgh}{RT}} = \frac{1.05}{1} e^{-\frac{0.029\ kg/mol \cdot 9.8\ m s^{-2} \cdot 1.61 \times 10^5\ m}{8.3145\ J/mol K \cdot 250}}$$

$$= \boxed{2.9 \times 10^{-10}\ atm\ (or\ bar.)}$$

(15 pts) **8.** For the reaction, $NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l)$

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

$$Q = \frac{\gamma_{NH_3} P_{NH_3}\ \gamma_{H_2O} X_{H_2O}}{\gamma_{NH_4^+}[NH_4^+]\ \gamma_{OH^-}[OH^-]}$$

(b) If *at equilibrium* the concentrations of $NH_4^+(aq)$ and $OH^-(aq)$ are both 0.1 M, and their activity coefficients are both 0.8, the partial pressure of NH_3 is 0.2 bar and ideal, and the activity of water is 0.95, **what is ΔG^0**?

$$K = \frac{(0.2)(0.95)}{[(0.8)(0.1)]^2} = 29.69$$

$$\Delta G^0 = -RT \ln K$$

$$= -(8.3145\ \frac{J}{mol\ K})(298\ K) \ln 29.69$$

$$= \boxed{-8401\ J} = \boxed{-8.401\ kJ}$$

TABLE A.5 Inorganic Compounds* *(cont.)*

	$\Delta_f H$ (kJ mol^{-1})	S (J K^{-1} mol^{-1})	$\Delta_f G$ (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
$Fe_2O_3(s)$	−824.2	87.40	−742.2
$H_2(g)$	0	130.79	0
$H_2O(g)$	−241.82	188.93	−228.73
$H_2O(l)$	−285.83	69.91	−237.13
$H^+(aq)$	0	0	0
$OH^-(aq)$	−229.99	−10.75	−157.244
$H_2O_2(aq)$	−191.17	143.9	−134.03
$H_2S(g)$	−20.63	205.90	−33.56
$H_2SO_4(g)$	−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, $\Delta_f H°$, third-law entropies, $S°$, and standard Gibbs free energy of formation, $\Delta_f G°$, 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

Oxidant/Reductant	Electrode reaction	$\mathcal{E}°$(V)	$\mathcal{E}°'$(V) (pH 7)
K^+/K	$K^+ + e^- \rightarrow K$	−2.931	
Ca^{2+}/Ca	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.868	
Na^+/Na	$Na^+ + e^- \rightarrow Na$	−2.71	
Mg^{2+}/Mg	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.372	
Mn^{2+}/Mn	$Mn^{2+} + 2e \rightarrow Mn$	−1.185	
Zn^{2+}/Zn	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.7618	
Acetate/acetaldehyde	$CH_3COO^- + 2e^- + 3H^+ \rightarrow CH_3CHO + H_2O$	−0.105	−0.586
Fe^{2+}/Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.447	
$H^+/H_2/Pt$	$2H^+ + 2e^- \rightarrow H_2$	0	−0.414
CO_2/formate	$CO_2(aq) + H^+ + 2e^- \rightarrow HCOO^-$	−0.181	−0.409
Ferredoxin	$Fd[Fe^{3+}] \rightarrow Fd[Fe^{2+}]$		−0.395
FMN(Mitochondrial complex I)	$FMN + 2H^+ + 2e^- \rightarrow FMNH_2$		−0.380
Gluconolactone/glucose	$C_6H_{10}O_6 + 2H^+ + 2e^- \rightarrow C_6H_{12}O_6$		−0.345
L-cystine/L-cysteine	L-cystine + $2H^+ + 2e^- \rightarrow$ 2 L-cysteine		−0.355
Fe^{3+}/Fe	$Fe^{3+} + 2e^- \rightarrow Fe$	−0.037	
Acetoacetate/ β-hydroxybutyrate	$CH_3COCH_2COO^- + 2H^+ + 2e^- \rightarrow CH_3CHOHCH_2COO^-$		−0.346
$NADP^+/NADPH$	$NADP^+ + H^+ + 2e^- \rightarrow NADPH$		−0.339
$NAD^+/NADH$	$NAD^+ + H^+ + 2e \rightarrow NADH$		−0.324
Glutathione(S-S)/ GlutathioneSH	$GSSG + 2H^+ + 2e^- \rightarrow 2\,GSH$		−0.240
$FMN/FMNH_2$	$FMN + 2H^+ + 2e^- \rightarrow FMNH_2$		−0.213
$FAD/FADH_2$	$FAD + 2H^+ + 2e^- \rightarrow FADH_2$		−0.212
Acetaldehyde/ethanol	$CH_3CHO + 2e^- + 2H^+ \rightarrow CH_3CH_2OH$	+0.221	−0.193
Pyruvate/lactate	$CH_3COCOO^- + 2H^+ + 2e \rightarrow CH_3CHOHCOO^-$		−0.184
Oxaloacetate/malate	$^-OOCCOCH_2COO^- + 2H^+ + 2e^- \rightarrow {}^-OOCCHOHCH_2COO^-$		−0.158
$FAD/FADH_2$(Complex II)	$FAD^+ + 2H^+ + 2e^- \rightarrow FADH_2$		−0.05
Fumarate/succinate	$^-OOCCH{=}CHCOO^- + 2H^+ + 2e^- \rightarrow {}^-OOCCH_2CH_2COO^-$		+0.045
Myoglobin	$Mb[Fe^{3+}] + e^- \rightarrow Mb[Fe^{2+}]$		+0.046
Ubiquinone	$UQ + 2H^+ + 2e^- \rightarrow UQH_2$		+0.052
Dehydroascorbate/ ascorbate	$DHA + H^+ + 2e^- \rightarrow Asc^-$		+0.080
$AgCl/Ag/Cl^-$	$AgCl + e^- \rightarrow Ag + Cl^-$	+0.222	
Cytochrome *c*	$Cyt\text{-}c[Fe^{3+}] + e^- \rightarrow Cyt\text{-}c[Fe^{2+}]$		+0.254
Calomel	$\frac{1}{2} Hg_2Cl_2 + e^- \rightarrow Hg + Cl^-$	+0.268	
O_2/H_2O_2	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	+0.695	+0.281
also O_2/H_2O	$O_2 + 4H^+ + 4e^- - 2H_2O$	+1.229	+0.815

(continues)