

CHMY 361 Exam 2

Friday, Oct. 12, 2012, 7:55-8:55 AM

Name _____

4 x 6 note card

Last,

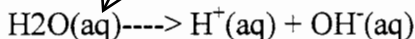
First

100 points in 8 problems on 6 pages including tables 4.1 and A.5

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 problem

should have been
H₂O(l)

(13 pts) 1. (a) Using data from Table A.5, calculate the equilibrium constant for the autoionization of water at 298 K



$$\Delta G^\circ = -237.129 \quad 0 \quad -157.244 \quad \Delta G^\circ = -157.2 - (-237.1) \text{ kJ/mol} = 79.9 = 79,900 \text{ J}$$

$$K = e^{-\frac{\Delta G^\circ}{RT}} = e^{-\frac{79900}{8.3145(298)}} = 9.9 \times 10^{-15}$$

(b) Calculate K for this reaction at 373 K.

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

$$\Delta H^\circ = -229.99 - (-285.83) = +55.84 \text{ kJ/mol}$$

$$\ln \left(\frac{K_{373}}{9.9 \times 10^{-15}} \right) = \frac{-55,840}{8.3145} \left(-6.747 \times 10^{-4} \right)$$

$$K_{373} = 9.9 \times 10^{-15} \times e^{4.53} = 8.5 \times 10^{-13}$$

(12 pts) 2. For the reaction : $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$, calculate ΔS° 298 K. using the data in Table A.5

$$\Delta S^\circ = 2(210.76) - (191.61) - (205.14) = +24.77 \text{ J/K}$$

- (12 pts) 3. A supersaturated solution of sugar at room temperature (made by adding sugar to hot water and cooling to room temperature) will eventually precipitate crystals of sugar. If the process is done isothermally and at constant pressure, tell whether the following are positive, zero, or negative. Give a brief justification for each of your answers.

q — ΔT 0 ΔH — ΔS — ΔG —

$$\Delta G = \Delta H - T \Delta S = \text{neg.}$$

ΔH must be neg.

$$q = \Delta H$$

ordering spontaneous

- (13 pts) 4. (a) If during an isothermal process at 300 K and constant pressure, the system is said to give off 600 kJ of heat and does 200 kJ of non-PV work and $\Delta S = -10 \text{ J/K}$, what is ΔG ?

$$q = -600,000 \text{ J} \quad w^* = -200,000 \text{ J}$$

$$\Delta S_{\text{sur}} = -\frac{q}{T} = \frac{+600,000}{300} = 2000 \text{ J/K}^{\circ}$$

$$\Delta S_{\text{univ}} = \Delta S + \Delta S_{\text{sur}} = (-10 + 2000) = +1990 \text{ J/K}^{\circ}$$

$$\Delta G = -T \Delta S_{\text{univ}} + w^* = (-300)(1990) - 200,000 = -597000 - 200000 = -797000 \text{ J/K}^{\circ}$$

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

Spontaneous

$$\Delta S_{\text{univ}} = +1990$$

allowed by 2nd Law

Not because ΔG is negative

- (10 pts) 5. Given that: $dA = -PdV - SdT$

- (a) what is the partial derivative of A with respect to V at constant T?

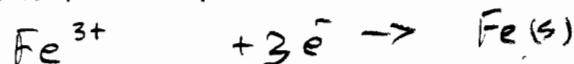
$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

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

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \text{so} \quad \left(\frac{\partial S}{\partial V}\right)_T = \frac{\partial^2 A}{\partial T \partial V}$$

(15 pts) 6. For the oxidation of NADPH(aq) by $\text{Fe}^{3+}(\text{aq})$ to give $\text{NADP}^+(\text{aq})$, $\text{H}^+(\text{aq})$ and $\text{Fe}(\text{s})$:

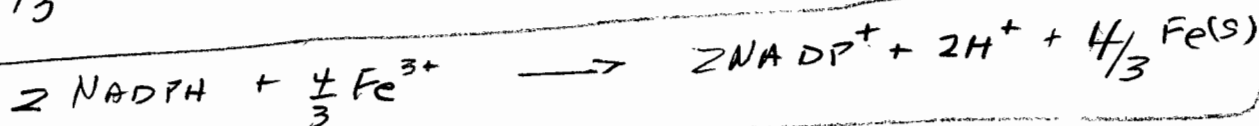
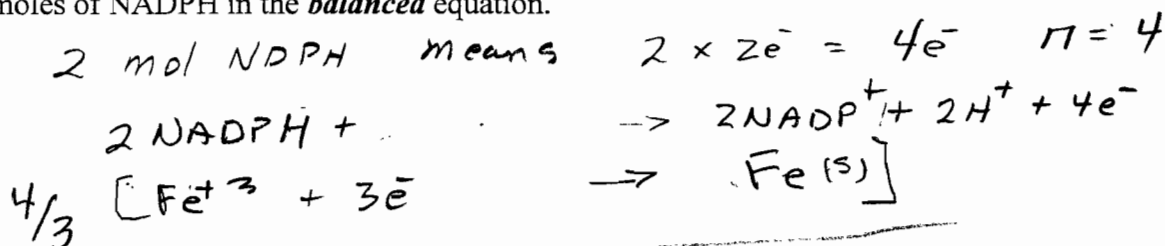
(a) From Table 4.1, what is $\xi^{\circ'}$ for this reaction?



$\xi^{\circ'}$
-0.324 initial
-0.036 final

$$\xi_{\text{reaction}}^{\circ'} = \xi_{\text{final}}^{\circ'} - \xi_{\text{init}}^{\circ'} = -0.036 - (-0.324) = \boxed{+0.288 \text{ Volts}}$$

(b) Write the balanced equation for this reaction and the expression for Q so that there are 2 moles of NADPH in the **balanced** equation.



(c) SET UP the equation that gives ξ for this reaction when balanced as in (b) when the pH is 5, and the activity of each of the aqueous species = 0.1M, and $\text{Fe}(\text{s})$ is pure.

$$\xi = \xi^{\circ'} - \frac{0.0592}{4} \log \left[\frac{\gamma_{\text{NADP}^+} [\text{NADP}^+]^2 \gamma_{\text{H}^+}^2 \gamma_{\text{Fe}}^{4/3}}{\gamma_{\text{NADPH}}^2 \gamma_{\text{Fe}^{3+}} [\text{Fe}^{3+}]^{4/3}} \right]$$

$$\xi = 0.288 - \frac{0.0592}{4} \log \left[\frac{(0.1)^2 (10^{-5})^2 (1)^{4/3}}{(0.1)^2 (0.1)^{4/3}} \right]$$

$$\frac{1 \cdot 1 \cdot 1}{1 \cdot 1 \cdot 10^{-7}}$$

- (10 pts) 7. If a system is known to have 10^N microstates, where N is 6×10^{23} , calculate the absolute entropy using Boltzmann's equation for absolute entropy.

$$S = k_B \ln 10^{6 \times 10^{23}} = (6 \times 10^{23}) k_B \ln 10$$

$$= R \times 2.303 = 8.3145 \times 2.303 =$$

$$= \boxed{19.14 \text{ J/K}}$$

- (15 pts) 8. For the acid ionization, $\text{HA(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{H}^+(\text{aq}) + \text{A}^-(\text{aq})$, $K = 1 \times 10^{-4}$ at 298 K and $\Delta H^\circ = +20 \text{ kJ/mol}$.

- (a) Calculate ΔG° for this reaction at 298 K.

$$\Delta G^\circ = -RT \ln K = -8.3145 (298) \ln 10^{-4}$$

$$= \boxed{+22.82 \text{ kJ/mol}}$$

- (b) Write Q for this reaction, assuming non-ideal behavior and recognizing that the water is not 100% pure.

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

- (c) If the activity coefficients for $\text{H}^+(\text{aq})$ and $\text{A}^-(\text{aq})$ are both 0.7 (because of added salt), and that of water is 0.8, what will be the pH? $[\text{HA}] = 1$ $X_{\text{H}_2\text{O}} \approx 1$ $\gamma_{\text{H}_2\text{O}} = 0.8$
 $\gamma_{\text{HA}} = 0.8$

$$K = \frac{(0.7) [\text{H}^+] 0.7 [\text{A}^-]}{0.8 [\text{HA}] 0.8 X_{\text{H}_2\text{O}}} = 10^{-4}$$

$$X_{\text{H}_2\text{O}} \approx 1$$

$$[\text{H}^+] = [\text{A}^-]$$

$$[\text{H}^+]^2 = \frac{10^{-4} \times (0.8)^2}{(0.7)^2}$$

$$[\text{H}^+] = \frac{10^{-2} \cdot 0.8}{0.7} = 0.01142 \text{ M}$$

$$\text{pH} = -\log 0.01142 = 1.94$$

TABLE 4.1 Standard reduction electrode potentials at 25°C

Oxidant/Reductant	Electrode reaction	\mathcal{E}^0 (V)*	$\mathcal{E}^{0'}$ (V) [†] (pH 7)
Li ⁺ /Li	Li ⁺ + e ⁻ → Li	-3.045	
Na ⁺ /Na	Na ⁺ + e ⁻ → Na	-2.714	
Mg ²⁺ /Mg	Mg ²⁺ + 2e ⁻ → Mg	-2.363	
OH ⁻ /H ₂ /Pt	2H ₂ O + 2e ⁻ → H ₂ + 2OH ⁻	-0.8281	
Zn ²⁺ /Zn	Zn ²⁺ + 2e ⁻ → Zn	-0.7628	
Acetate/acetaldehyde	OAc ⁻ + 3H ⁺ + 2e ⁻ → CH ₃ CHO + H ₂ O		-0.581
Fe ²⁺ /Fe	Fe ²⁺ + 2e ⁻ → Fe	-0.4402	
Glucanate/glucose	C ₆ H ₁₁ O ₇ ⁻ + 3H ⁺ + 2e ⁻ → C ₆ H ₁₂ O ₆ + H ₂ O		-0.44
Spinach ferredoxin	Fd[Fe(III)] + e ⁻ → Fd[Fe(II)]		-0.432
CO ₂ /formate	CO ₂ + 2H ⁺ + 2e ⁻ → HCO ₂ ⁻ + H ⁺	-0.20	-0.42
NAD ⁺ /NADH [†]	NAD ⁺ + H ⁺ + 2e ⁻ → NADH	-0.105	-0.320
Fe ³⁺ /Fe	Fe ³⁺ + 3e ⁻ → Fe	-0.036	
H ⁺ /H ₂ /Pt	2H ⁺ + 2e ⁻ → H ₂	0	-0.421
Acetoacetate/ β-hydroxybutyrate	CH ₃ COCH ₂ CO ₂ ⁻ + 2H ⁺ + 2e ⁻ → CH ₃ CHOHCH ₂ CO ₂ ⁻		-0.346
Mn hematoporphyrin IX	He[Mn(III)] + e ⁻ → He[Mn(II)]		-0.342
NADP ⁺ /NADPH	NADP ⁺ + H ⁺ + 2e ⁻ → NADPH		-0.324
Horseradish peroxidase	HRP[Fe(III)] + e ⁻ → HRP[Fe(II)]		-0.271
FAD/FADH ₂ [‡]	FAD + 2H ⁺ + 2e ⁻ → FADH ₂		-0.219
Acetaldehyde/ethanol	CH ₃ CHO + 2H ⁺ + 2e ⁻ → CH ₃ CH ₂ OH		-0.197
Pyruvate/lactate	CH ₃ COCO ₂ ⁻ + 2H ⁺ + 2e ⁻ → CH ₃ CHOHCO ₂ ⁻		-0.18
Oxaloacetate/malate	O ₂ CCOCH ₂ CO ₂ ⁻ + 2H ⁺ + 2e ⁻ → O ₂ CCHOHCH ₂ CO ₂ ⁻		-0.166
Fumarate/succinate	O ₂ CCH=CHCO ₂ ⁻ + 2H ⁺ + 2e ⁻ → O ₂ CCH ₂ CH ₂ CO ₂ ⁻		+0.031
Myoglobin	Mb[Fe(III)] + e ⁻ → Mb[Fe(II)]		+0.046

TABLE A.5 Inorganic Compounds*

	$\Delta H_f^\circ \equiv \bar{H}^\circ$ (kJ mol ⁻¹)	S° (J K ⁻¹ mol ⁻¹)	$\Delta G_f^\circ \equiv \bar{G}^\circ$ (kJ mol ⁻¹)
Ag(s)	0	42.55	0
Ag ⁺ (aq) [†]	105.579	72.68	77.107
AgCl(s)	-127.068	96.2	-109.789
C(g)	716.682	158.096	671.257
C(s, graphite)	0	5.740	0
C(s, diamond)	1.895	2.377	2.900
Ca(s)	0	41.42	0
CaCO ₃ (s, calcite)	-1206.92	92.9	-1128.79
Cl ₂ (g)	0	223.066	0
Cl ⁻ (aq)	-167.159	56.5	-131.228
CO(g)	-110.525	197.674	-137.168
CO ₂ (g)	-393.509	213.74	-394.359
CO ₂ (aq)	-413.80	117.6	-385.98
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	130.684	0
H ₂ O(g)	-241.818	188.825	-228.572
- H ₂ O(l)	-285.830	69.91	-237.129
- H ⁺ (aq)	0	0	0
- OH ⁻ (aq)	-229.994	-10.75	-157.244
H ₂ O ₂ (aq)	-191.17	143.9	-134.03
H ₂ S(g)	-20.63	205.79	-33.56
N ₂ (g)	0	191.61	0
NH ₃ (g)	-46.11	192.45	-16.45
NH ₃ (aq)	-80.29	111.3	-26.50
NH ₄ ⁺ (aq)	-132.51	113.4	-79.31
NO(g)	90.25	210.761	86.55
NO ₂ (g)	33.18	240.06	51.31
NO ₃ ⁻ (aq)	-205.0	146.4	-108.74
Na ⁺ (aq)	-240.12	59.0	-261.905
NaCl(s)	-411.153	72.13	-384.138
NaCl(aq)	-407.27	115.5	-393.133
NaOH(s)	-425.609	64.455	-379.494
O ₂ (g)	0	205.138	0
O ₃ (g)	142.7	238.93	163.2
S(rhombic)	0	31.80	0
SO ₂ (g)	-296.830	248.22	-300.194
SO ₃ (g)	-395.72	256.76	-371.06

* Standard thermodynamic values at 25°C (298 K) and 1 atm pressure. Values for ions refer to an aqueous solution at unit activity on the molarity scale. Standard enthalpy of formation, ΔH_f° , third-law entropies, S° , and standard Gibbs free energy of formation, ΔG_f° , are given.

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

SOURCE: Data from *The NBS Tables of Thermodynamic Properties*, D. D. Wagman et al., eds., J. Phys. Chem. Ref. Data, 11, Suppl. 2 (1982).