Third Hour Exam **5.111**

Write your name below. This is a closed book exam. Solve all 6 problems. Read all problems thoroughly and read all parts of a problem. Many of the latter parts of a problem can be solved without having solved earlier parts. Show all work to receive full credit. Physical constants, formulas, standard reduction potentials, and a periodic table are given on the last two pages of the exam. You may detach the last 2 pages after the exam has started.

1. THERMODYNAMICS (12 points)___________

2. CHEMICAL EQUILIBRIUM (12 points)___________

3. ACID-BASE EQUILIBRIUM (12 points)___________

4. ACID-BASE TITRATION (22 points)______________

5. OXIDATION/REDUCTION (30 points)_____________

6. OXIDATION/REDUCTION (12 points)_____________

Total (100 points)_____________

Name____ANSWER KEY__________________

1. THERMODYNAMICS (14 points total)

Consider the formation of MgO (s). Assume that $\Delta H_r°$ and $\Delta S_r°$ are independent of temperature.

$Mg\ (s) + 1/2\ O_2\ (g) \rightarrow MgO\ (s)$ $\Delta H_r° = -602$ kJ/mol
$\Delta S_r° = -108\ JK^{-1}mol^{-1}$.

(a) (6 points) Calculate $\Delta G_r°$ for the formation of MgO (s) at 0 °C (273 K). Is the reaction spontaneous or non-spontaneous at 0 °C?

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -602\ \text{kJ/mol}\ \underbrace{-\ 273(-0.108\ \text{kJmol}^{-1}\text{K}^{-1})}_{+\ 29.\underline{4}8}$$

$$\Delta G = -57\underline{2}.52$$

- 573 kJ/mol **spontaneous**

(b) (6 points) Is there a temperature at which the formation of MgO switches from spontaneous to non-spontaneous or vice versa? If no, explain briefly why not. If yes, calculate the temperature (T*) at which the spontaneity of the reaction switches.

Yes.

$$0 = \Delta H - T^*\Delta S$$

$$T^* = \Delta H / \Delta S \qquad T^* = \frac{-60\underline{2}\ \text{kJ/mol}}{-\ 0.108\ \text{kJ/mol} \bullet \text{K}}$$

$$T^* = 55\underline{7}4\ \text{K}$$

T* = 5570 K

2. CHEMICAL EQUILIBRIUM (12 points total)

Explain the effect of each of the following stresses on the position of the following equilibrium:

$$3\ NO\ (g) \rightleftharpoons N_2O\ (g) + NO_2\ (g)$$

The reaction as written is exothermic.

(a) (4 points) The equilibrium mixture is cooled. Explain your answer.

$\longrightarrow$ shift toward products

Heat is produced in the forward direction. As heat is removed, the reaction will shift to produce more heat.

(**b**) (4 points) The volume of the equilibrium mixture is reduced at constant temperature. Explain your answer.

$\longrightarrow$ shift toward products

If volume decreases, then the total pressure (and each partial pressure) increases.

3 mol of g to 2 mol of g
reaction shifts to 2 mol of gas.

(**c**) (4 points) Gaseous argon (which does not react) is added to the equilibrium mixture while both the total gas pressure and the temperature are kept constant. Explain your answer.

$\longleftarrow$ shift toward reactants

If total pressure is the same, volume must have increased. If volume increased, the partial pressure of each gas decreased, so shift to side with more mol of gas to compensate

3 mol g $\leftarrow$ 2 mol g

3. ACID-BASE EQUILIBRIUM (12 points total)

(**a**) (6 points) Calculate the pH in a solution prepared by dissolving 0.050 mol of acetic acid (CH_3COOH) and 0.20 mol of sodium acetate ($NaCH_3COO$) in water and adjusting the volume to 500. mL. The pKa for acetic acid (CH_3COOH) is 4.75.

buffer problem

$$pH \cong pKa - \log\left(\frac{[HA]}{[A^-]}\right)$$

$$pH \cong 4.75 - \log\left(\frac{0.050\ mol}{0.20\ mol}\right)$$ ok to use mol b/c volume is the same

$$pH \cong 4.75 \underbrace{- \log 0.2\underline{5}}_{+\,0.6\underline{0}2}$$

$$pH = 4.75 + 0.6\underline{0}2$$

pH ≅ 5.35

(b) (6 points) Suppose 0.010 mol of NaOH is added to the buffer from part (a). Calculate the pH of the solution that results.

mol of HA = $0.05\underline{0}$ mol – $0.01\underline{0}$ mol = $0.04\underline{0}$ mol
mol of A^- = $0.2\underline{0}$ mol + $0.01\underline{0}$ mol = $0.2\underline{1}$ mol

$$pH \cong pKa - \log\left(\frac{[HA]}{[A^-]}\right)$$

$$pH \cong 4.75 - \log\left(\frac{0.04\underline{0}\ mol}{0.2\underline{1}\ mol}\right)$$ ok to use mol b/c volume is the same

$$pH = 4.75 \underbrace{- \log 0.1\underline{9}}_{+\,0.7\underline{2}1}$$

$$pH = 4.75 + 0.7\underline{2}1$$

pH = 5.47

4. ACID-BASE TITRATION (22 points total)
A 10.0 mL sample of 0.20 M HNO_2 (aq) solution is titrated with 0.10 M NaOH (aq).
(K_a of HNO_2 is 4.3 x 10^{-4}).

(a) (5 points) Calculate the volume of NaOH needed to reach the equivalence point.

$$0.0100\text{ L} \times \frac{0.20\text{ mol}}{\text{L}} = 0.002\underline{0}\text{ mol of NaOH needed}$$

$$0.0020\text{ mol NaOH} \times \frac{\text{L}}{0.10\text{ mol}} = 0.02\underline{0}\text{ L or } \mathbf{20.\ mL}$$

(b) (12 points) Calculate the pH at the equivalence point. Check assumptions for full credit.

This is a weak base problem. All of the HNO_2 is converted to NO_2^-.

$$\text{initial mol of } NO_2^- = \frac{0.0020\text{ mol}}{0.030\text{ L}} = 0.06\underline{6}7\text{ M}$$

	NO_2^-	+ H_2O ⇆	HNO_2	+ ^-OH
I	$0.06\underline{6}7$		0	0
C	-x		+ x	+ x
E	$0.06\underline{6}7$ – x		+ x	+ x

$K_w = K_aK_b$

$$K_b = \frac{1.00 \times 10^{-14}}{4.3 \times 10^{-4}} = 0.2\underline{3}3 \times 10^{-10} \text{ or } 2.\underline{3}3 \times 10^{-11}$$

$$K_b = \frac{x^2}{0.06\underline{6}7 - x} \approx \frac{x^2}{0.06\underline{6}7} = 2.\underline{3}3 \times 10^{-11}$$

$x = 1.\underline{2}47 \times 10^{-6} = [^-OH]$

pOH = - log ($1.\underline{2}47 \times 10^{-6}$)

pOH = $5.9\underline{0}$

pH = 14.00 – 5.90 = **8.10** (accept 8.08, 8.09, or 8.10)

Check assumption:

$$\frac{1.\underline{2}47 \times 10^{-6}}{0.0667} \times 100\ \%$$

= 0.00186%

(c) (5 points) Calculate the pH with 2.00 mL of NaOH added past the equivalence point.

$$0.0020\ \text{L} \times \frac{0.10\ \text{mol}}{\text{L}} = 0.0002\underline{0}\ \text{mol NaOH}$$

$$[^{-}\text{OH}] = \frac{0.0002\underline{0}\ \text{mol}}{\underbrace{10.0\ \text{mL} + 20.\ \text{mL} + 2.00\ \text{mL}}_{\text{new volume} = 0.03\underline{2}\ \text{L}}} = 0.006\underline{2}5\ \text{M}$$

$$\text{pOH} = -\log[^{-}\text{OH}] = -\log(0.006\underline{2}5)$$

$$= 2.2\underline{0}4$$

$$\text{pH} = 14.00 - 2.2\underline{0}4 = \mathbf{11.80}$$

5. OXIDATION/REDUCTION REACTIONS (30 points total)

For a cell constructed with a Cu (s) | Cu^{2+} (aq) anode and Ag^{+} (aq) | Ag (s) cathode at 25.0°C.

(**a**) (5 points) Write the overall balanced equation under acidic conditions.

$$\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^{-}$$

$$2\,(\text{Ag}^{+} + e^{-} \rightarrow \text{Ag})$$

$$\text{Cu (s)} + 2\text{Ag}^{+}\text{(aq)} + \cancel{2e^{-}} \rightarrow \text{Cu}^{2+}\text{(aq)} + 2\text{Ag (s)} + \cancel{2e^{-}}$$

$$\mathbf{Cu\ (s) + 2Ag^{+}\ (aq) \rightarrow Cu^{2+}\ (aq) + 2Ag\ (s)}$$

(**b**) (13 points) Calculate the cell potential at 25.0°C under non-standard conditions:
$[Cu^{2+}]$ = 0.300 M and $[Ag^{+}]$ = 0.0500 M

$E°_{cell} = E°\text{ (cathode)} – E°\text{ (anode)}$

$E°_{cell} = 0.80 – 0.34 = 0.4\underline{6}$ V

n = 2

$Q = \frac{(0.300)}{(0.0500)^2}$

$E_{cell} = E°_{cell} – (1/n)(RT/\mathfrak{F})\ln Q$

$$= E°_{cell} – \frac{0.025693\text{ V}}{2} \underbrace{\ln 120}_{4.78\underline{7}}$$

$= 0.4\underline{6}$ V – $0.0615\underline{0}$ V

= **0.40 V**

(**c**) (6 points) Is the above cell a galvanic or electrolytic cell under standard conditions? Explain your choice of answer.

galvanic

ΔE° is positive, so ΔG° is negative

(**d**) (6 points) Of the following, list <u>all</u> of the atoms or ions that will oxidize Ag (s):
Au^{+} (aq), Pb^{2+}(aq), Zn (s), Cr^{3+}(aq), Ni (s), Au (s).

Au^{+} only

higher redox potential than Ag^{+}

6. OXIDATION-REDUCTION (12 points total)
The following reaction has an $\Delta E°$(cell) of 2.27 V and a K = 10^{383} at 25°C:

$2\ MnO_4^-\ (aq) + 5\ Zn\ (s) + 16\ H_3O^+\ (aq) \rightarrow 2Mn^{2+}\ (aq) + 5\ Zn^{2+}\ (aq) + 24\ H_2O\ (l)$

(**a**) (4 points) What is the oxidation number for Mn in MnO_4^-?

MnO_4^- ← total charge on the molecule is -1

↑ (Mn) ↑ 4(-2) (O)

+7

(**b**) (4 points) How many electrons are transferred in this reaction (in other words, what is "n")?

Consider either: $2\left[MnO_4^- + 5e^- \rightarrow Mn^{2+} \right]$

MnO_4^-: ↑ +7 Mn^{2+}: ↑ +2

or

$5\left[Zn \rightarrow Zn^{2+} + 2e^- \right]$

Zn: ↑ 0 Zn^{2+}: ↑ +2

10 electrons n = 10

(**c**) (4 points) Would you expect a large quantity of MnO_4^- ions at equilibrium at 25°C? Why or why not?

No.

Expect a small quantity of MnO_4^- ions because K is huge.

Equations and constants for Exam 3

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$pK_a = -\log [K_a]$

$pOH = -\log [OH^-]$

$R = 8.315\ J\ K^{-1} mol^{-1}$

$\Im$ (Faraday's constant) = 96,485 C mol^{-1}

$pH = -\log [H_3O^+]$

1V = 1 J/C

$$pH \cong pK_a - \log\left(\frac{[HA]}{[A^-]}\right)$$

1A = 1C/s

$K_w = 1.00 \times 10^{-14}$ at 25°C

$\Delta E°(cell) = E°(cathode) - E°(anode)$

$RT/\Im = 0.025693$ V at 25.00 °C

14.00 = pH + pOH at 25°C

$\Im/RT = 38.921\ V^{-1}$ at 25.00 °C

$\Delta G° = - RT \ln K$

$\Delta E_{cell} = E°_{cell} - (RT/\Im\, n) \ln Q$

$\Delta G = \Delta G° + RT \ln Q$

$\ln K = (n\Im/RT)\, \Delta E°$

$\Delta G° = \Delta H° - T\Delta S°$

$E_3° = [n_1 E_1°(reduction) - n_2 E_2°(oxidation)]/n_3$

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

$\Delta G°_{cell} = -(n)(\Im)\, \Delta E°_{cell}$

$K_w = K_a K_b$

Q = It

Standard Reduction Potentials at 25°C

Half-Reactions	E°(volts)
Au^+ (*aq*)+ e^- $\Rightarrow$ Au (s)	1.69
MnO_4^- (aq) + $8H^+$ (aq) + $5e^-$ $\rightarrow$ Mn^{2+} (aq) + $4H_2O$ (l)	1.51
Ag^+ (aq) + $1e^-$ $\rightarrow$ Ag (s)	0.80
Cu^{2+} (*aq*) + $2e^-$ $\Rightarrow$ Cu(*s*)	0.34
AgCl (s) + $1e^-$ $\rightarrow$ Ag (s) + Cl^- (aq)	0.22
Sn^{4+} (aq) + $2e^-$ $\rightarrow$ Sn^{2+} (aq)	0.15
$2H^+$ (*aq*) + $2e^-$ $\Rightarrow$ H_2	0
Pb^{2+}(*aq*) + 2 e^- $\Rightarrow$ Pb (s)	-0.13
Sn^{2+}(*aq*) + 2 e^- $\Rightarrow$ Sn (s)	-0.14
Ni^{2+}(*aq*) + 2 e^- $\Rightarrow$ Ni (s)	-0.23
Fe^{2+} (*aq*) + $2e^-$ $\rightarrow$ Fe (*s*)	-0.44
Cr^{3+} (*aq*) + $3e^-$ $\Rightarrow$ Cr (*s*)	-0.74
Zn^{2+}(*aq*) + $2e^-$ $\Rightarrow$ Zn (s)	-0.76

1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18[a] VIIIA b
The Active Metals																	Noble Gases
1 H 1.008												The Nonmetals					2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179
11 Na 22.990	12 Mg 24.305	Transition Elements										13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.41	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.29
55 Cs 132.905	56 Ba 137.33	57 La 138.905	* 72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.966	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.025	89 Ac 227.028	† 104 Unq (261)	105 Unp (262)	106 Unh (263)												

Inner Transition Metals

* Lanthanides	58 Ce 140.12	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
† Actinides	90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

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