Chemistry 112, Fall 2006, Section 1 (Garman and Heuck)
Exam 3a (100 points)
12 Dec 2006

Name: KEY 3A

YOU MUST:
Put your **name** and **student ID** on the bubble sheet correctly.
Put the exam version on the bubble sheet on the upper left side above the word "NAME". **This is exam 3A.**
Put **all** your answers on the bubble sheet.
Sign the statement on the last page of the exam at the completion of the exam

Please make sure your exam has 7 pages (plus this cover sheet and 2 reference pages at the back).
Please keep your eyes on your own paper and your answers covered.
Use the exam as scratch paper. We will not grade anything on the exam itself.
Turn in both the exam and bubble sheet when you are done. **Good luck!**

Chem 112, Fall 06, Section 1
Exam 3a

Name: KEY 3A

1) (4 points) Calculate the pH of a buffer that has $[CH_3COOH] = 0.550$ M and $[CH_3COO^-] = 0.350$ M. $K_a = 1.8 \times 10^{-5}$

a) 9.46
b) 4.54
c) 4.74
d) 9.26
e) 4.94

$pH = pK_a + \log \frac{[\text{Conj. Base}]}{[\text{Acid}]} = -\log(1.8\times10^{-5}) + \log\left(\frac{0.350}{0.550}\right)$

2) (3 points) If you want to prepare a buffer at pH 7.0, which of the following acid/conjugate base pairs is the best choice?

a) $HAcO/AcO^-$ $pK_a = 4.7$
b) HSO_4^-/SO_4^{2-} $pK_a = 1.9$
c) HCO_3^-/CO_3^{2-} $pK_a = 10.3$
d) $H_2PO_4^-/HPO_4^{2-}$ $pK_a = 7.2$
e) All of them

$pH = \pm pK_a$

3) (6 points) What volume of a 0.154 M potassium hydroxide (KOH) solution is required to neutralize 13.7 mL of a 0.275 M perchloric acid ($HClO_4$) solution?

a) 13.7 ml
b) 3.77 ml
c) 12.2 ml
d) 24.5 ml
e) none of the above

for $HClO_4$ $\frac{13.7\text{ mL}}{1000\text{ mL/L}} \times 0.275\text{ mol/L} = 3.77\cdot10^{-3}$ mol

for KOH $\frac{3.77\cdot10^{-3}\text{ mol}}{0.154\text{ mol/L}} = 0.0245\text{ L} = 24.5\text{ ml}$

4) (3 points) When a titration of a weak acid is half complete:

a) the titration is at the equivalence point No. This is a complete titration
b) the pH = pK_a
c) the pH is higher than 7 For acetic acid pH = 4.74 < 7. Not always valid.
c) the pH depends on the initial concentration of the acid. No.
d) none of the above

5) (3 points) At the equivalence point for a titration of a monoprotic weak acid:

a) the pH = pK_a No. This is half point.
b) the moles of NaOH added equals the initial amount of moles of acid
c) the pH is lower than the initial pH. Not possible if adding NaOH
d) none of the above

Name: KEY 3A

6) (3 points) Given the concentration of a salt in pure water, if $Q_{sp} > K_{sp}$

a) all of the salt is soluble No.
b) some of the salt will precipitate
c) the salt will precipitate only if $K_{sp} > 1$
d) the salt will precipitate only if $K_{sp} < 1$
e) none of the above

No. If $Q_{sp} > K_{sp}$ ⇒ precipitate independently of the value of K_{sp}

7) (6 points) A student measures the molar solubility of silver iodide (AgI) in a water solution to be 1.18×10^{-8} M. Based on her data, the solubility product constant for this compound is

a) 1.18×10^{-8}
b) 1.39×10^{-16}
c) 2.30×10^{-8}
d) 7.93
e) none of the above

$AgI(s) \rightleftharpoons Ag^+ + I^-$

$K_{sp} = [Ag^+][I^-] = 1.18 \times 10^{-8} \cdot 1.18 \cdot 10^{-8}$

$= 1.39 \times 10^{-16}$

8) (3 points) The equilibrium constant expression for the solubility of $PbCl_2$ is:

a) $K_{sp} = [Pb^{2+}] \cdot 2 \cdot [Cl^-]$
b) $K_{sp} = [Pb^{2+}] \cdot [Cl^-]^2$
c) $K_{sp} = [Pb^{2+}] \cdot [Cl^-]$
d) $K_{sp} = [Pb^{2+}] \cdot [Cl^-]/[AgCl]$
e) none of the above

$PbCl_2(s) \rightleftharpoons Pb^{2+} + 2Cl^-$

$K_{ps} = [Pb^{2+}][Cl^-]^2$

9) (3 points) The entropy for a mol of water at 25 °C in the liquid state is :

a) higher than the entropy for a mol of water in the gas state
b) equal to the entropy for a mol of water in the gas state
c) higher than the entropy for a mol of water in the solid state
d) lower than the entropy for a mol of water in the solid state
e) none of the above

More disorder in liquid than in solid ⇒ higher entropy

10) (3 points) - A reaction will be spontaneous if:

a) $\Delta S^0_{univ} > 0$
b) $\Delta G > 0$ No. If $\Delta G < 0$ will be spontaneous
c) $\Delta S^0_{surr} > 0$ No. Depends also on ΔS°_{sys}.
d) $\Delta H^0 > 0$ No. Depends also on $(-T\Delta S^\circ)$
e) none of the above

Name: KEY 3A

11) (6 points) For the reaction

$2HBr(g) \longrightarrow H_2(g) + Br_2(l)$

$\Delta G^o = 111.2$ kJ and $\Delta H^o = 72.6$ kJ at 337 K and 1 atm. The entropy change for the reaction of 1.3 moles of HBr(g) at this temperature would be:

a) -114.5 J/K
b) 114.5 J/K
c) 74.4 J/K
d) -74.4 J/K
e) none of the above

$\Delta G^o = \Delta H^o - T\Delta S^o \Rightarrow \Delta S^o = \frac{\Delta H^o - \Delta G^o}{T}$

$\Delta S^o = \frac{72,6\,kJ - 111,2\,kJ}{337\,K} = -0,1145\ kJ/K$

for 1,3 mol of HBr $\Rightarrow \frac{-114,5\ J/K}{2} \cdot 1,3 = -74,4\ J/K$

12) (3 points) At the equilibrium, the ΔG for a reaction is:

a) equal to the $\Delta H/T$
b) higher than ΔG^0
c) equal to zero
d) equal to ΔG^0
e) none of the above

$\Delta G = \Delta G^o + RT \ln Q$

at eq. $\Delta G = 0 \Rightarrow \Delta G^o = -RT \ln K_{eq}$.

13) (6 points) Using standard thermodynamic data at 298K, calculate the free energy change (ΔG^0) for the following reaction when 3.4 moles of H_2S (g) react at standard conditions.

$2H_2S\ (g) + 3O_2\ (g) \longrightarrow 2H_2O\ (l) + 2SO_2\ (g)$

a) -856.32 kJ
b) -1712.6 kJ
c) -1007.4 kJ
d) -503.72 kJ
e) none of the above

$\Delta G^o_{rxn} = \sum \Delta G_f^{prod} - \sum \Delta G_f^{react} =$

$= 2mol(-300,13)kJ/mol + 2mol(-237,15)kJ/mol -$

$- 2mol(-33,56)kJ/mol - 3.0 =$

$= -1007,4\ kJ$

for 3,4 mol H_2S $\frac{-1007,4\ kJ}{2\,mol} \times 3,4\,mol = -1712,6\ kJ$

The next **4 questions** refer to the following reaction:

$2N_2(g) + O_2(g) \longrightarrow 2N_2O(g)$

Without doing any calculations, match the following thermodynamic properties with their appropriate numerical sign for the following endothermic reaction.

$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn}$

14) (2 points) ΔH_{rxn} a) endothermic $\rightarrow \Delta H_{rxn} > 0$
15) (2 points) ΔS_{rxn} b) 3 moles convert to 2 moles
16) (2 points) ΔG_{rxn} a) $\Delta H > 0$ and $\Delta S < 0 \Rightarrow \Delta G > 0$
17) (2 points) ΔS_{univ} b) if $\Delta G > 0 \Rightarrow \Delta S_{univ} < 0$ not spontaneous

a) > 0
b) < 0
c) = 0
d) > 0 low T, < 0 high T
e) < 0 low T, > 0 high T

Name: KEY 3A

The next **3 questions** refer to the following reaction:

$Mg\ (s) + Br_2\ (l) \leftrightarrows Mg^{2+}\ (aq) + 2Br^-\ (aq)$

The standard reduction potentials of the half-reactions are

$Br_2\ (l) + 2e^- \rightarrow 2Br^-\ (aq)$ $E° = +1.08$ V

$Mg^{2+}\ (aq) + 2e^- \rightarrow Mg\ (s)$ $E° = -2.37$ V

18) (2 points) Which species is oxidized?

a) Mg
b) Br_2

19) (2 points) Which species is the oxidizing agent?

a) Mg
b) Br_2

20) (4 points) Calculate E° for the reaction

a) -3.45 V
b) -1.29 V
c) 1.29 V
d) 3.45 V
e) None of the above

$E°_{cell} = E°_{cathode} - E°_{anode}$
$= 1.08\ V - (-2.37\ V)$
$= 3.45\ V$

21) (5 points) For the reaction

$2Au^{3+}\ (aq) + 3Sn^{2+}\ (aq) \leftrightarrows 2Au\ (s) + 3Sn^{4+}\ (aq)$, $\rightarrow$ 6 e^- transferred

E° for the reaction is +1.35 V. Calculate ΔG° for the reaction.

a) -782 kJ
b) -130 kJ
c) 130 kJ
d) 782 kJ
e) None of the above

$\Delta G° = -nFE°$
$= (-6)(96{,}485\ \frac{J}{V\,mole})(1.35\ V)$
$= -782{,}000\ J$
$= -782\ kJ$

Name: KEY 3A

22) (6 points) Balance the following redox reaction in acidic conditions:

$$VO_2^+ + Fe^{2+} \leftrightarrows V^{2+} + Fe^{3+}$$

a) $VO_2^+ + 3Fe^{2+} + 2H_2O \leftrightarrows V^{2+} + 3Fe^{3+} + 4OH^-$
b) $VO_2^+ + 3Fe^{2+} + 4H^+ \leftrightarrows V^{2+} + 3Fe^{3+} + 2H_2O$
c) $VO_2^+ + Fe^{2+} + 4H^+ \leftrightarrows V^{2+} + Fe^{3+} + 2H_2O$
d) $VO_2^+ + Fe^{2+} + 2H_2O \leftrightarrows V^{2+} + Fe^{3+} + 4OH^-$
e) None of the above

Red: $4H^+ + VO_2^+ + 3e^- \rightarrow V^{2+} + 2H_2O$

Ox $3Fe^{2+} \rightarrow 3Fe^{3+} + 3e^-$

$$4H^+ + VO_2^+ + 3Fe^{2+} \rightleftharpoons V^{2+} + 3Fe^{3+} + 2H_2O$$

23) (6 points) Balance the following redox reaction in acidic conditions:

$$MnO_4^-\,(aq) + HSO_3^-\,(aq) \leftrightarrows Mn^{2+}\,(aq) + SO_4^{2-}\,(aq)$$

a) $MnO_4^- + HSO_3^-\,(aq) + 5H^+ \leftrightarrows Mn^{2+}\,(aq) + SO_4^{2-}\,(aq) + 3H_2O$
b) $MnO_4^- + 5HSO_3^-\,(aq) + H_2O \leftrightarrows Mn^{2+}\,(aq) + 5SO_4^{2-}\,(aq) + 2H^+$
c) $2MnO_4^- + 5HSO_3^-\,(aq) + H^+ \leftrightarrows 2Mn^{2+}\,(aq) + 5SO_4^{2-}\,(aq) + 3H_2O$
d) $2MnO_4^- + 3HSO_3^-\,(aq) + 7H^+ \leftrightarrows 2Mn^{2+}\,(aq) + 3SO_4^{2-}\,(aq) + 5H_2O$
e) None of the above

Red: $8H^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Ox: $H_2O + HSO_3^- \rightarrow SO_4^{2-} + 3H^+ + 2e^-$

$\Downarrow$ balance electrons

$16H^+ + 2MnO_4^- + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$

$5H_2O + 5HSO_3^- \rightarrow 5SO_4^{2-} + 15H^+ + 10e^-$

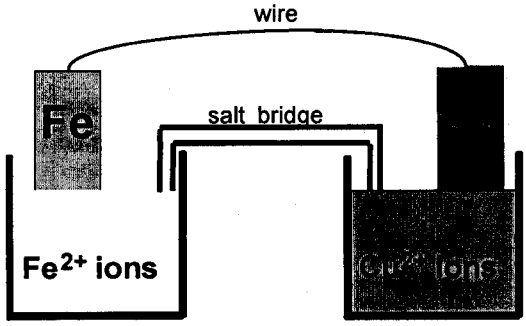
$$16H^+ + 5H_2O + 2MnO_4^- + 5HSO_3^- \rightleftharpoons 2Mn^{2+} + 5SO_4^{2-} + 8H_2O + 15H^+$$

$$H^+ + 2MnO_4^- + 5HSO_3^- \rightleftharpoons 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

Name: KEY 3A

The next **6 questions** refer to the electrochemical cell shown:
The standard reduction potentials are

Cu^{2+} (aq) + $2e^-$ → Cu (s) E° = +0.34 V
Fe^{2+} (aq) + $2e^-$ → Fe (s) E° = -0.44 V



24) (2 points) Which reaction occurs at the anode?
a) Cu^{2+} (aq) + $2e^-$ → Cu (s)
b) Cu (s) → Cu^{2+} (aq) + $2e^-$
c) Fe^{2+} (aq) + $2e^-$ → Fe (s)
d) Fe (s) → Fe^{2+} (aq) + $2e^-$

25) (2 points) Which reaction occurs at the cathode?
a) Cu^{2+} (aq) + $2e^-$ → Cu (s)
b) Cu (s) → Cu^{2+} (aq) + $2e^-$
c) Fe^{2+} (aq) + $2e^-$ → Fe (s)
d) Fe (s) → Fe^{2+} (aq) + $2e^-$

26) (2 points) Where do the electrons flow?
a) From the left to the right along the wire
b) From the right to the left along the wire
c) From the left to the right through the salt bridge
d) From the right to the left through the salt bridge
e) None of these

27) (2 points) Where do the negatively charged ions flow?
a) From the left to the right along the wire
b) From the right to the left along the wire
c) From the left to the right through the salt bridge
d) From the right to the left through the salt bridge
e) None of these

28) (3 points) What is the overall reaction that occurs in this electrochemical cell?
a) Cu^{2+} (aq) + Fe (s) ⇆ Fe^{2+} (aq) + Cu (s)
b) Fe^{2+} (aq) + Cu (s) ⇆ Cu^{2+} (aq) + Fe (s)
c) Fe (s) + Cu (s) ⇆ Cu^{2+} (aq) + Fe^{2+} (aq)
d) Fe^{2+} (aq) + Cu^{2+} (aq) ⇆ Cu (s) + Fe (s)
e) None of the above

29) (4 points) Calculate E° for this electrochemical cell
a) -0.78 V
b) -0.10 V
c) +0.10 V
d) +0.78 V
e) None of the above

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$
$= (0.34\,V) - (-0.44\,V)$
$= 0.78\,V$

Name: KEY 3A

Extra Credit:

30) (5 points) A buffer solution contains 0.276 M NH_4Cl and 0.452 M NH_3 (ammonia). Determine the pH of the solution after the addition of 0.131 mol HI to 1.00 L of the buffer. $K_a(NH_4^+) = 5.6 \times 10^{-10}$

a) 9.46
b) 9.15
c) 4.74
d) 4.64
e) none of the above

$NH_3 + HI \rightarrow NH_4^+ + I^-$

0,452 M — 0,276 M

+0,131

(0,452-0,131) — (0,276+0,131)

0,321 — 0,407

$pH = pka + \log \frac{[Conj. base]}{[Acid]} = 9,25 + \log \frac{0,321}{0,407}$

$= 9,25 + (-0,103) = 9,15$

31) (5 points) For the reaction

$3Cl_2 (g) + 2Al (s) \leftrightarrows 2Al^{3+} (aq) + 6Cl^- (aq)$, $E° = 3.020$ V.

Calculate E at 25°C when the concentrations and pressures of the reagents are:

$[Al^{3+}] = 0.1000$ M
$[Cl^-] = 0.1000$ M
$P_{Cl_2} = 0.2000$ atm

$E^0 = 3.020$ V
$n = 6\ e^-$

a) 2.962 V
b) 3.020 V
c) 3.033 V
d) 3.078 V
e) None of the above

$E = E^0 - \frac{.0257}{n} \ln Q$

$Q = \frac{[Al^{3+}]^2 [Cl^-]^6}{[Cl_2]^3}$

$= \frac{(0.100\ M)^2 (0.100\ M)^6}{(0.200\ atm)^3}$

$= 1.25 \times 10^{-6}$

$\ln Q = -13.592$

$E = E^0 - \frac{.0257}{n} \ln Q$

$= 3.020 - \left(\frac{.0257}{6}\right)(-13.592)$

$= 3.078$

Please sign the following statement at the completion of the exam:
I did not cheat on this exam. _____(name)

_____(signature)

PERIODIC TABLE OF THE ELEMENTS

1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A	8A
1 H 1.008																	2 He 4.003
3 Li 6.939	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.71	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (99)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 181.0	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.0	89 Ac 227.0	104 Unq (261)	105 Unp (262)	106 Unh (263)	107 Uns (262)	108 Uno (265)	109 Une (266)									

USEFUL INFORMATION:

Constants

$K_w = 1 \times 10^{-14}$, 25 °C	1 atm = 760 mm Hg	T (°C) + 273 = T (K)
F = 96,485 coulombs/mole e^- = 96,485 J/(V•mole)	R = 0.0821 (L atm)/(mol K) = 8.31×10^{-3} kJ/(mol K)	Room Temperature = 25°C = 298K

Formulae:

$a.x^2+b.x+c = 0$	$x = [-b \pm sqrt(b^2-4.a.c)]/(2.a)$	$P.V = n.R.T$
$pX = -\log X$	$pK_w = pK_a + pK_b$; $pK_w = pH + pOH$	
pH = pKa + log ([Conjugate Base]/[Acid])	pOH = pKb + log ([Conjugate Acid]/[Base])	
$\Delta G^0_{rxn} = \Delta H^0_{rxn} - T\Delta S^0_{rxn}$	$\Delta S = q_{rev}/T$	$\Delta S_{sys} = \Delta S_{fus} = \Delta H_{fus}/T_{fus}$
$\Delta S_{surr} = -\Delta H_{sys}/T = -\Delta H_{rxn}/T$	$\Delta S_{sys} = \Delta S_{vap} = \Delta H_{vap}/T_{vap}$	$\Delta S_{uni} = \Delta S_{sys} + S_{sur}$
$\Delta G = \Delta H - T\Delta S$	$\Delta G = -RT \ln K$	$\Delta G = \Delta G^0 + RT \ln Q$
$E°_{cell} = E°_{cathode} - E°_{anode}$	$E = E° - (0.0257/n) \ln Q$ (at 25°C)	$\Delta G° = -nFE°$
$\ln K_{eq} = nE°/0.0257$ (at 25°C)	Current I (Amperes, A) = electric charge (coulombs, C) / time (sec)	

Compound	ΔG_f^0 (kJ/mol)	ΔH_f^0 (kJ/mol)	S^0 (J/(K.mol)
$SO_2(g)$	-300.13	-296.84	248.21
$H_2S(g)$	-33.56	-20.63	205.79
$O_2(g)$	0	0	205.07
$H_2O(l)$	-237.15	-285.83	69.95
$H_2O(g)$	-228.59	-241.83	188.84