Name Key
(Please Print)

Chem 104 - Section 1
Sample Final Examination

This test consists of eleven (11) pages, including this cover page. Be sure your copy is complete before beginning your work. If this test packet is defective, ask for another one.

The following tables, which may be used for any problem, will be distributed separately: periodic table; conjugate acid-base pairs and K_a's; oxidizing and reducing agents and $E°$ values.

Give all numerical answers to the proper number of significant figures.

You must show work leading to your numeric answers, except in question 1.

R = 0.0821 L·atm/K·mol = 8.134 J/K·mol
1 Faraday = 9.65 x 10^4 Coulombs
$E_{cell} = E°_{cell} - (0.0592/n)\log Q$ at 25°C

K = °C + 273
K_w = 1.00 x 10^{-14} at 25°C
1.00 mol ideal gas = 22.4 L at STP

DO NOT WRITE BELOW THIS LINE

This is a copy of a typical final exam given in Chem 104. Your test will be different. This test is being posted to give you a sense of the format, style, scope, and level of a typical final exam in this course. This test may have questions on topics that will not be covered on the test you take. Moreover, your test may have questions on topics that are not covered on this test. Posting this test in no way limits the format, style, scope, or level of the test that you will take. **Do not limit your preparation to the material on this sample test.**

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1. (100 points; 4 points each) Circle the correct answers.

a. Has dipole-dipole intermolecular forces

$NaCl$ C_6H_6 NH_3 I_2 SiO_2

b. Would make an acidic solution in water

$NaHCO_3$ $(CH_3)_3N$ KNO_3 $Fe(NO_3)_3$ $NaC_6H_5CO_2$

c. Does not have hydrogen bonding

H_2O NH_3 CH_4 C_6H_5OH HF

d. "At constant pressure, the volume of a gas sample is proportional to its absolute temperature" is a statement of

Boyle's Law Gay-Lussac's Law Amonton's Law Dalton's Law Charles' Law

e. A 0.100 *m* solution of sugar in water has a freezing point of –0.186°C. Ideally, a 0.100 *m* solution of Na_3PO_4 should have a freezing point of

–0.186 °C –0.372 °C –0.558 °C –0.744 °C –0.062 °C

f. A 4.00-L sample of an ideal gas in a piston chamber at 200 K and 1.00 atm is heated to 300 K and the pressure is raised to 1.50 atm. The new volume will be

4.00 L 6.00 L 9.00 L 0.750 L 1.50 L

g. Consider the equilibrium $C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g)$ in a container of fixed volume. Increasing the total pressure by introducing some inert He(*g*) will cause

K_p to increase K_p to decrease more C_2H_6 (*g*) to form

more $C_2H_4(g) + H_2(g)$ to form no change

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h. The equilibrium $A_2(g) \rightleftharpoons 2A(g)$ is a single-step reaction in both directions. For the forward reaction $A_2(g) \rightarrow 2A(g)$ the activation energy E_a^f is 289 kJ and ΔH is +125 kJ. Therefore, E_a^r, the activation energy for the reverse reaction $2A(g) \rightarrow A_2(g)$ is

– 125 kJ –289 kJ +164 kJ +414 kJ +125 kJ

i. For the equilibrium $A_2(g) \rightleftharpoons 2A(g)$, described in part h, if the temperature were increased

[A] would increase, [A_2] would decrease, and K_c would remain unchanged.

[A_2] would increase, [A] would decrease, and K_c would remain unchanged.

[A] would increase, [A_2] would decrease, and K_c would increase.

[A_2] would increase, [A] would decrease, and K_c would decrease.

[A_2], [A], and K_c would remain unchanged.

j. Consider the equilibrium $A_2(g) \rightleftharpoons 2A(g)$, described in part h, for which K_c = 44.2 mol/L at 200 °C. If an equilibrium mixture at 200 °C is found to contain 0.100 mol/L of A(g), what is the concentration of $A_2(g)$ in mol/L?

0.442 5.00×10^{-2} 1.00×10^{-2} 9.05×10^{-4} 2.26×10^{-4}

k. As the mechanism in part h indicates, the forward reaction $A_2(g) \rightarrow 2A(g)$ should obey the differential rate law $rate_f = k_f[A_2]$. Therefore, a plot of ln [A_2] versus time should give a straight line whose slope is

$-E_a/R$ ln [A] $t_{½}$ $-k_f$ ln $[A_2]_o$

l. The half-life of the forward reaction $A_2(g) \rightarrow 2A(g)$ described in part h is $t_{½}$ = 2.5 s. If 1.6 mol $A_2(g)$ is introduced into an empty one-liter vessel at 200 °C, what will be the concentration of $A_2(g)$ in mol/L after the reaction has run for 10.0 s? [Assume the reverse reaction $2A(g) \rightarrow A_2(g)$ has been suppressed by removing product as it is formed.]

1.6 0.80 0.40 0.20 0.10

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m. What is the *molality* (*m*) of a solution prepared by dissolving 36.04 g of glucose (m.w. = 180.2 u) in 275 g of water?

0.727   0.655   0.200 7.25×10^{-4} 312

n. What is the expected osmotic pressure in atmospheres (atm) at 298 K of a 0.250 M solution of $CaCl_2(aq)$? $CaCl_2 \rightarrow Ca^{2+} + 2Cl^- \Rightarrow M_{ions} = 0.750\ M$

6.12   12.2   18.3 6.05×10^2 1.82×10^3

o. Consider a 0.10 M solution of the weak base B, for which $K_b = 1.0 \times 10^{-2}$. Which of the following expressions could be used to obtain a reasonably accurate value of the hydroxide concentration, $[OH^-]$, for this solution without carrying out unnecessary calculations?

$[OH^-] = \sqrt{C_B K_b}$ $[OH^-] = C_B$ $K_b = \dfrac{[OH^-]^2}{C_B - [OH^-]}$

$K_b = K_w/K_a$ $pOH = pK_b + \log\left(\dfrac{C_{BH^+}}{C_B}\right)$

p. Which among the following is the strongest base in water?

$F_3CCO_2^-$ C_2H_5OH ClO_4^- $CH_3CO_2^-$ HSO_4^-

q. Nitrogen gas comprises 78% of air by volume and has a Henry's Law constant of 6.8×10^{-4} mol/L·atm for dissolving in water at 25 °C. What is the solubility at 25 °C in mol/L of nitrogen when the air pressure is 690 torr?

7.5×10^{-4} 6.8×10^{-4} 6.2×10^{-4} 5.3×10^{-4} 4.8×10^{-4}

r. In $KHSO_3$, the oxidation number for the S atom is

+6   +5   +4   −1   −2

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[Consult the Table of Oxidizing and Reducing Agents for the following three questions.]

s. Consider the reaction,

$$Al(s) + NO_3^-(aq) + 4H^+(aq) \rightleftharpoons Al^{3+}(aq) + NO(g) + 2H_2O(l)$$

Under standard conditions this reaction is $E^\circ_{cell} = +2.64V$

spontaneous nonspontaneous at equilibrium

t. Among the following, the strongest *oxidizing agent* is

$MnO_4^-(aq)$ $Sn^{2+}(aq)$ $Hg(l)$ $Fe^{3+}(aq)$ $Cd^{2+}(aq)$

u. Among the following, which one could be used to reduce Pb^{2+} to Pb° ($E^\circ = -0.126$ v) under standard conditions?

$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$ $Co(s) \rightarrow Co^{2+}(aq) + 2e^-$ $H_2(g) \rightarrow 2H^+(aq) + 2e^-$

$Cu(s) \rightarrow Cu^{2+} + 2e^-$ $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$

v. The reaction $X_2(g) + Y_2(g) \rightarrow 2XY(g)$ has the experimental rate law $Rate = k[X_2]$. Which one of the following four proposed mechanisms is consistent with this observed rate law?

Mechanism I: $X_2 + Y_2 \rightarrow 2XY$

Mechanism II:
$X_2 \rightarrow 2X$ slow
$2X + Y_2 \rightarrow 2XY$ fast

Mechanism III:
$X_2 \rightleftharpoons 2X$ fast equilibrium
$X + Y_2 \rightarrow XY + Y$ slow
$X + Y \rightarrow XY$ fast

Mechanism IV:
$Y_2 \rightarrow 2Y$ slow
$Y + X_2 \rightarrow XY + X$ fast
$X + Y \rightarrow XY$ fast

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The next three questions pertain to following rate data for the reaction $A_2 + B_2 \rightarrow 2AB$. (All concentrations are in mol/liter.)

	$[A_2]$	$[B_2]$	Initial rate $(mol/L) \cdot s^{-1}$
Experiment 1	0.15	0.15	2.0×10^{-4}
Experiment 2	0.15	0.60	8.0×10^{-4}
Experiment 3	0.60	0.15	4.0×10^{-4}

w. In the differential rate law for this reaction, the dependence of rate on $[A_2]$ would be expressed as *Rate* $\propto$

$[A_2]^0$ $\quad$ $[A_2]$ $\quad$ $[A_2]^2$ $\quad$ $[A_2]^{1/2}$ $\quad$ $[A_2]^{3/2}$

x. In the differential rate law for this reaction, the dependence of rate on $[B_2]$ would be expressed as *Rate* $\propto$

$[B_2]^0$ $\quad$ $[B_2]$ $\quad$ $[B_2]^2$ $\quad$ $[B_2]^{1/2}$ $\quad$ $[B_2]^{3/2}$

y. The units on the rate constant, *k*, are

s^{-1} $\quad$ $(mol/L) \cdot s^{-1}$ $\quad$ $(mol/L)^{-1} \cdot s^{-1}$ $\quad$ $(mol/L)^{-2} \cdot s^{-1}$ $\quad$ $(mol/L)^{-1/2} \cdot s^{-1}$

[End of multiple choice questions.]

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2. (28 points) Given the following two couples and their corresponding standard reduction potentials:

$\longrightarrow$ $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $\quad E^\circ = +0.337$ v
$\longleftarrow$ $Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$ $\quad E^\circ = -0.126$ v

Part I (20 points; 2 points each) Fill in the blanks below regarding the following galvanic cell under standard conditions.

cathode $Cu|Cu^{2+}||Pb^{2+}|Pb$ anode

☞ *Do not assume that the cell is shown in the proper order (i.e., anode and cathode placed on the correct sides). You must determine whether or not it is properly shown.*

a. The oxidation half-reaction is

$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$

b. The reduction half-reaction is

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

c. The overall net ionic reaction for the cell is

$Cu^{2+} + Pb \longrightarrow Cu + Pb^{2+}$

d. E°_{cell} = +0.463 volts

e. The oxidizing agent is Cu^{2+}

f. The reducing agent is Pb

g. In the cell diagram *as shown above*, the anode is shown on the right (right/left).

h. Is the cell diagram *as shown above* in conventional order? no (yes/no)

i. In the cell diagram *as shown above*, the direction of electron flow in the circuit wire is

right to left (left to right/right to left).

j. As the cell runs, E_{cell} will decrease (increase/decrease/stay the same).

[Part II on the following page]

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2. Part II (8 points) Calculate E_{cell} for the galvanic cell described in Part I (previous page) when $[Cu^{2+}] = 0.360$ M and $[Pb^{2+}] = 1.00 \times 10^{-3}$ M.

$$E = E^\circ - \frac{0.0592}{2} \log \frac{[Pb^{2+}]}{[Cu^{2+}]} = +0.463 - 0.0296 \log \frac{1.00 \times 10^{-3}}{0.360}$$

$$= +0.463 - 0.0296 \log (2.77_8 \times 10^{-3}) = +0.463 - (0.0296)(-2.55_6)$$

$$= +0.463 + 0.0756_6 = +0.538_{65} V = +0.539 V$$

3. (16 points) Balance the following skeletal redox equation in *acidic solution* using the ion-electron (half-reaction) method:

$$HClO_2(aq) + As(s) \rightarrow Cl^-(aq) + HAsO_2(aq)$$

In answering this question, you must show the following:

(1) A balanced half-reaction for $HClO_2(aq) \rightarrow Cl^-(aq)$ in *acidic solution* (6 points);
(2) A balanced half-reaction for $As(s) \rightarrow HAsO_2(aq)$ in *acidic solution* (6 points);
(3) The balanced overall redox reaction, with lowest whole-number coefficients (4 points).

Don't bother writing the state designations (*aq*) and (*s*), **but be sure that charges on all species are properly shown.**

$$3\,(4e^- + 3H^+ + HClO_2 \longrightarrow Cl^- + 2H_2O)$$

$$4\,(2H_2O + As \longrightarrow HAsO_2 + 3H^+ + 3e^-)$$

$$2H_2O + 3HClO_2 + 4As \longrightarrow 3Cl^- + 4HAsO_2 + 3H^+$$

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4. (10 points) How many grams of nickel metal (at. wt. 58.71 u) will be produced at the electrode in the electrolysis of a $Ni(NO_3)_2$ solution for 8.00 amp for a period of 96.0 minutes? The half-reaction at the electrode is $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$.

$$Q = It = (8.00\,A)(96.0\,min)\left(\frac{60\,s}{min}\right) = 4.60_8 \times 10^4\,A \cdot s$$

$$g\,Ni = (4.60_8 \times 10^4\,C)\left(\frac{mol\ e's}{9.65 \times 10^4\,C}\right)\left(\frac{mol\ Ni}{2\,mol\ e's}\right)\left(\frac{58.71\,g\,Ni}{mol\ Ni}\right)$$

$$= 14.0\,g\,Ni$$

5. (10 points) Consider the following equilibrium for which $K_c = 7.00$ at 400 K.

$$Br_2(g) + Cl_2(g) \rightleftharpoons 2BrCl(g)$$

Calculate the equilibrium concentrations of all three species that should result when 2.50 mol of $BrCl(g)$ are introduced into an empty one-liter vessel at 400 K.

$$Br_2(g) + Cl_2(g) \rightleftharpoons 2BrCl(g)$$
$$x \qquad x \qquad 2.50 - 2x$$

$$K_c = 7.00 = \frac{[BrCl]^2}{[Br_2][Cl_2]} = \frac{(2.50-2x)^2}{x^2}$$

$$\frac{2.50-2x}{x} = 2.64_{58} \Rightarrow 2.64_{58}x = 2.50 - 2x$$

$$4.64_{58}x = 2.50 \Rightarrow x = 2.50/4.64_{58} = 0.538$$

$$[Br_2] = [Cl_2] = 0.538\,mol/L$$
$$[BrCl] = 2.50 - (2)(0.538) = 1.42\,mol/L$$

$$Q = \frac{(1.42)^2}{(0.538)^2} = 6.96_6 \approx 7.00 \Rightarrow OK$$

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6. (18 points) Formic acid, HCO_2H, has $K_a = 1.9 \times 10^{-4}$ for its hydrolysis

$$HCO_2H + H_2O \rightleftharpoons H_3O^+ + HCO_2^-$$

a. (6 points) What is the pH of 0.10 M solution of formic acid?

$$[H_3O^+] = \sqrt{(0.10)(1.9 \times 10^{-4})} = 4.3_6 \times 10^{-5}$$

$$\Rightarrow pH = 2.36$$

b. (3 points) What is the pH of a solution in which the concentration of formic acid is 0.10 M and concentration of sodium formate is 0.10 M?

Equimolar buffer; i.e., $[HCO_2H] = [HCO_2^-] \Rightarrow pH = pK_a$

$$pH = -\log(1.9 \times 10^{-4}) = 3.72$$

c. (9 points) What is the pH of a 0.10 M sodium formate solution?

$$K_b^{HCO_2^-} = \frac{K_w}{K_a^{HCO_2H}} = 5.2_6 \times 10^{-11}$$

$$HCO_2^- + H_2O \rightleftharpoons HCO_2H + OH^- \quad K_b = 5.2_6 \times 10^{-11}$$

$$[OH^-] = \sqrt{(0.10)(5.2_6 \times 10^{-11})} = 2.3 \times 10^{-6}$$

$$pOH = 5.64 \Rightarrow pH = 8.36$$

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7. (18 points) Consider the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Given the following thermodynamic data:

Substance	ΔH°_f (kJ/mol)	ΔG°_f (kJ/mol)	S° (J/K·mol)
$PCl_5(g)$	–398.9	–324.6	352.7
$PCl_3(g)$	–306.4	–286.3	311.7
$Cl_2(g)$	0	0	223.0

a. (3 points) What is the value of ΔG° for the reaction at 25 °C? Is the reaction spontaneous at this temperature?

$\Delta G^\circ = -286.3 - (-324.6) = +38.3$ kJ/mol

$\Rightarrow$ Non-spontaneous

b. (6 points) What is the value of K_p for the reaction at 25 °C?

$K_p = \exp(-\Delta G^\circ/RT) = \exp[-38.3\text{ kJ/mol}/(8.314\times10^{-3}\text{ kJ/K·mol})(298\text{ K})]$

$= \exp(-15.458_{68}) = 1.93\times10^{-7}$

c. (9 points) Assuming ΔH and ΔS are constant with changes in temperature, calculate the value of ΔG for the reaction at 300 °C. Is the reaction spontaneous at this temperature?

$\Delta G \cong \Delta H^\circ - T\Delta S^\circ$ $\quad T = 300 + 273 \rightarrow 573\text{K}$

$\Delta H^\circ = -306.4 - (-398.9) = +92.5$ kJ/mol

$\Delta S^\circ = 311.7 + 223.0 - 352.7 = +182$ J/K·mol

$\Delta G \cong 92.5\text{ kJ} - (573\text{K})(0.182\text{ kJ/K·mol})$

$= -11.7_{86}$ kJ/mol $= -11.8$ kJ/mol

$\Rightarrow$ Spontaneous