KWANTLEN UNIVERSITY COLLEGE
DEPARTMENT OF CHEMISTRY

NAME: _____

CHEM. 1210 FINAL EXAMINATION
December 13, 2001
Time: 3 hours

INSTRUCTIONS:

1. Read all questions thoroughly and answer each question completely. EXCEPT FOR MULTIPLE CHOICE QUESTIONS **ALL WORK** MUST BE SHOWN IN ORDER TO RECEIVE ANY CREDIT.

2. You will only be allowed to use the provided sheet of thermodynamic equations and periodic table.

3. Ensure that this exam paper has **35 questions** and **12 pages (including this cover sheet).** Formula sheet and periodic table are also included with this exam.

4. Answers to mutiple choice questions should be indicated on the question sheet. Work for all other questions should be done in the exam booklet. If you dissagree with all choices in a multiple choice question, enter your own.

5. Both the exam booklet and question sheet must be handed in by the end of the examination period.

6. Good Luck!

ADDITIONAL INFORMATION:

Clausis-Clapeyron equation: $\ln(P_2/P_1) = \frac{\Delta H_{vap}}{R}(1/T_1 - 1/T_2)$

Trouton's Rule (for non-polar liquids): $\Delta S_{vap} = \frac{\Delta H_{vap}}{T_{nbp}} \cong 88\ J\ mol^{-1}\ K^{-1}$

Total Marks = 124½

1. (6 MARKS) For the following oxidation-reduction reaction which takes place in **<u>basic</u>** solution.

$$CrO_4^{2-}(aq) + HSnO_2^-(aq) \text{ ---> } HSnO_3^-(aq) + CrO_2^-(aq)$$

a) Balance the above chemical equation. **(4)**

b) Which species is the reducing agent? **(1)**

c) What is the equivalent weight of K_2CrO_4 (molar mass = 194.20) used in the above reaction for CrO_4^{2-} ? **(1)**

2. (14 MARKS) A hydrogen-oxygen fuel cell, which is used in the space program, is made up from half cells which utilize the following half reactions:

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $\quad \mathscr{E}^o = -0.828$ V

$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ $\quad \mathscr{E}^o = +0.401$ V

a) Write the conventional cell notation for this fuel cell in which the net cell reaction is

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

Note: the fuel cell utilizes graphite electrodes. **(3)**

b) Calculate $\mathscr{E}_{298}^o$ and ΔG^o_{298} for this cell. **(3)**

c) Calculate ΔG for this cell when $P(H_2) = 2.00 \times 10^{-3}$ atm and $P(O_2) = 1.00 \times 10^{-5}$ atm. Is the reaction spontaneous under these conditions? **Explain**. **(3)**

d) Using the provided standard Gibbs free energies of formation, calculate ΔG_{298} and $\mathscr{E}_{298}^o$ for a fuel cell in which hydrogen gas has been replaced by methane gas. **(3)**

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$\Delta G_f^o(CH_4(g)) = -50.72$ kJ/mol $\qquad \Delta G_f^o(CO_2(g)) = -394.36$ kJ/mol

$\Delta G_f^o(H_2O(l)) = -237.13$ kJ/mol

e) Determine the maximum useful work (ΔG) that could be obtained from each of the two cells (per gram of H_2 and CH_4 reacted). **(2)**

3. (5 MARKS) It took 6.30 minutes using a current of 2.00 amperes to plate out all of the gold from 250.0 mL of a solution containing $Au_2(SO_4)_3$.

a) What was the original concentration of Au^{3+} in the solution? **(3)**

b) On which electrode was the gold plated out? Write the balanced half reaction occuring at this electrode. **(2)**

4. (5 MARKS) The K_{sp} for silver chromate, Ag_2CrO_4, is 1.2×10^{-12}.

a) Calculate the molar solubility of Ag_2CrO_4 in pure water. **(2)**

b) If 25.0 mL of 1.00×10^{-5} *M* Ag_2SO_4 solution were mixed with 25.0 mL of 0.020 *M* Na_2CrO_4, would a precipitate of silver chromate form? **(SHOW YOUR CALCULATIONS!) (3)**

5. (10 MARKS) One possible reaction which may occur in air polluted with nitrogen oxide is

$$2NO(g) + O_2(g) \text{ ---> } 2NO_2(g)$$

The following data were obtained in a series of kinetic studies, in terms of the **rate of appearance** of $NO_2(g)$:

Run #	**[NO]**	**[O_2]**	**Rate of Appearance (M/s)**
1	0.00300	0.00300	1.89×10^{-4}
2	0.00300	0.00600	3.78×10^{-4}
3	0.00450	0.00450	6.38×10^{-4}

a) What is the order of the reaction with respect to each reactant? **(3)**

b) Write the rate law for the reaction and calculate the rate constant, k.
INCLUDE THE UNITS OF k. **(2)**

c) Calculate the rate of disappearance of O_2, when $[NO] = [O_2] = 0.0100M$. **(2)**

d) The following mechanism has been proposed for the above reaction:

$$2NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} N_2O_2(g) \qquad \text{(Both fast with equal rates)}$$

$$N_2O_2(g) + O_2(g) \xrightarrow{k_2} 2NO_2(g) \qquad \text{(Slow)}$$

Does this mechanism agree with the rate law determined in part **b)** above?
SHOW YOUR WORK (3)

6. (14 MARKS) A 25.0 mL solution of a 0.20 *M* weak base, B , is titrated with 0.1000 *M* HCl.

$$B(aq) + H_2O(l) \rightleftarrows BH^+(aq) + OH^-(aq) \quad K_b = 1.0 \times 10^{-4}$$

a) Determine the initial pH before any HCl was added. **(2)**

b) Calculate the pH when 40.00 mL of HCl has been added. **(3)**

c) Calculate the pH at the equivalence point. **(3)**

d) Calculate the pH when 60.00 mL of HCl has been added **(2)**

e) The pK_a for the indicator methyl orange is 3.8. If this indicator is used in the titration, the color change will occur when what volume of HCl has been added? State any assumptions you are making. **(3)**

f) Would this be a good indicator to use? **Explain! (1)**

7. (11 MARKS) The normal boiling point of benzene, C_6H_6, is 80.1 ^oC. Its triple point is 5.0 ^oC and 0.028 atm, and its critical point is 289 ^oC and 48 atm. The density of liquid benzene is 0.894 g/cm^3, and the density of solid benzene is 1.005 g/cm^3.

a) Sketch the phase diagram of benzene (**not necessarily to scale**). Label all axes, lines, areas. Indicate: the approximate normal melting point, normal boiling point, critical point, and triple point on your diagram. **(4)**

b) What happens to benzene if the pressure is held constant at 0.010 atm and the temperature is gradually increased from 0 ^oC to 100 ^oC? **(1)**

c) Calculate the boiling point of benzene at 3.00 atm if ΔH_{vap} = 30.8 kJ/mol. **(3)**

d) Estimate the entropy of vaporization of benzene at its normal boiling point, using ΔH_{vap} given in part **c)** above. What does the sign and magnitude of ΔS_{vap} indicate about the phase transition:

$C_6H_6(l)$ ---> $C_6H_6(g)$? **(2)**

e) Would you expect benzene to be polar or non-polar based on your calculations in part **d)** above? **(1)**

8. (4 MARKS) For the reaction:

$H^+(aq) + OH^-(aq) \rightleftarrows H_2O(l)$ $\quad \Delta H^o = -55.8$ kJ; $K_w = 1.0 \times 10^{-14}$ (at 25.0 °C)

Calculate the pOH of a 0.0100 *M* HCl solution at 50.0 °C.

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MULTIPLE CHOICE SECTION: Circle only one answer for each of the following questions. Indicate answers on THIS question sheet.

9. Electrolysis of water produces at the anode:

(2) a) H^+ **b)** H_2O **c)** O_2 **d)** H_2 **e)** H_2O_2

10. Given the following standard reduction potentials in acid solution:

		$\mathscr{E}^o$ (V)
(2)	$Al^{3+} + 3\ e^- \rightleftarrows Al(s)$	-1.66
	$AgBr(s) + e^- \rightleftarrows Ag(s) + Br^-$	+0.07
	$Sn^{4+} + 2\ e^- \rightleftarrows Sn^{2+}$	+0.14
	$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$	+0.77

The strongest oxidizing agent of those shown above is:

a) Fe^{3+} **b)** Fe^{2+} **c)** Br^- **d)** Al^{3+} **e)** Al(s)

11. The reaction rates of many spontaneous reactions are actually very slow. Which of the following is the best explanation of this observation?

a) K_p for the reaction is less than one.

b) The activation energy of the reaction is large.

(1) **c)** ΔG^o for the reaction is positive.

d) These reactions are endothermic.

e) The entropy change is negative.

12. The reaction, $2\ NO_2(g)$ ---> $2NO(g) + O_2(g)$, is suspected to be second order in NO_2. Which of the following kinetic plots would be used to confirm that the reaction is second order?

a) a plot of $[NO_2]^{-1}$ vs t **b)** a plot of $\log[NO_2]$ vs t

(3) **c)** a plot of $[NO_2]$ vs t **d)** a plot of $\log[NO_2]^{-1}$ vs t

e) a plot of $[NO_2]^2$ vs t

13. A catalyst:

a) increases the activation energy.

b) alters the reaction mechanism.

(2) **c)** increases the average kinetic energy of the reactants.

d) increases the concentration of reactants.

e) increases the collision frequency of the reacting molecules.

14. The isomerization of cyclopropane to form propene:

C_3H_6(cyclopropane) ---> C_3H_6(propene)

is a first order reaction. At 700 K the rate constant is $6.2 \times 10^{-4}\ min^{-1}$. How many minutes are required for 20% of a sample of cyclopropane to isomerize to propene?

(3) **a)** 1120 min. **b)** 360 min. **c)** 3710 min. **d)** 1.4×10^{-4} min. **e)** 2.80 min.

15. An increase in the temperature of the reactants causes an increase in the rate of reaction. The best explaination is: As the temperature increases;

a) the concentration of reactants increases.

b) the activation energy increases.

(1) **c)** the activation energy decreases.

d) the number of energetic molecules increases.

e) ΔG will increase.

16. If the energy of activation, E_a, for a certain biological reaction is 50 kJ/mol, by what factor (how many times) will the rate of this reaction increase when body temperature increases from 37 ^oC (normal) to 40 ^oC (fever)?

(3) **a)** 1.15 times **b)** 1.20 times

c) 2.0×10^5 times **d)** 1.0002 times

e) 2 times

17. For the following endothermic process:

$$HCN(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + CN^-(aq)$$

What will happen to the % ionization of HCN if:

a) the temperature is increased INCREASE DECREASE NO CHANGE

b) the temperature is decreased INCREASE DECREASE NO CHANGE

(2½) **c)** sodium cyanide, NaCN, is added INCREASE DECREASE NO CHANGE

d) the solution is diluted INCREASE DECREASE NO CHANGE

e) HCl(g) is bubbled into the solution (assume no volume change) INCREASE DECREASE NO CHANGE

18. Phosgene, $COCl_2$, a poisonous gas decomposes according to the equation:

$$COCl_2(g) \rightleftarrows CO(g) + Cl_2(g)$$

If $K_c = 0.083$ at 900 °C, what is the value of K_p ?

(2) **a)** 0.125 **b)** 8.0 **c)** 6.1 **d)** 0.16 **e)** 0.083

19. For the reaction:

$$SO_2(g) + NO_2(g) \rightleftarrows SO_3(g) + NO(g) \qquad K_c = 18.0 \text{ at } 1200\ ^oC$$

If 1.0 mole of SO_2 and 2.0 mole of NO_2 are placed in a 20. L container, what concentration of SO_3 will be present at equilibrium?

(3) **a)** 0.048 *M* **b)** 0.11 *M* **c)** 0.095 *M* **d)** 0.22 *M* **e)** 1.39 *M*

20. In which one of the following solutions will acetic acid have the greatest percent ionization?

a) 0.1 *M* CH_3COOH

b) 0.2 *M* CH_3COOH

(3) **c)** 0.1 *M* CH_3COOH dissolved in 1.0 *M* HCl

d) 0.1 *M* CH_3COOH plus 0.1 *M* CH_3COONa

e) 0.1 *M* CH_3COOH plus 0.2 *M* CH_3COONa

21. Which is a true statement with regard to a 0.10 *M* H_2SO_4 solution?

a) $[HSO_4^-] > [H^+]$

b) $[SO_4^{2-}] > [H^+]$

(1) **c)** $[H^+] > [HSO_4^-]$

d) $[H_2SO_4] > [H^+]$

e) $[SO_4^{2-}] > [HSO_4^-]$

22. The pH at the equivalence point of a titration may differ from 7.0 because of:

a) the initial concentration of the standard solution.

b) the indicator used.

(1) **c)** the self ionization of H_2O

d) the initial pH of the unknown.

e) hydrolysis of the salt formed.

23. Hydrosulfuric acid is a diprotic acid. Its two stages of ionization are:

$$H_2S(aq) \rightleftarrows H^+(aq) + HS^-(aq) \quad K_{a1} = 5.7 \times 10^{-8}$$

$$HS^-(aq) \rightleftarrows H^+(aq) + S^{2-}(aq) \quad K_{a2} = 1 \times 10^{-19}$$

Determine the concentration of S^{2-} ions in a 0.10 M H_2S solution.

(2) **a)** 0.10 *M* **b)** 7.5×10^{-5} *M* **c)** 5.7×10^{-9} *M* **d)** 1×10^{-19} *M*

e) 1×10^{-20} *M*

24. Calculate the pH of a solution made by mixing 78.0 mL of 3.67×10^{-2} M NH_3 with 50.0 mL of 0.2 M HCl. $K_b = 1.79 \times 10^{-5}$ for ammonia.

(3) **a)** 11.25 **b)** 13.25 **c)** 4.75 **d)** 1.25 **e)** 0.15

25. Which of the following reactions or processes would you predict to have large negative values for **both** ΔH and ΔS:

a) $O_2(g) \rightarrow 2O(g)$

b) $CH_3OH(l) \rightarrow CH_3OH(g)$

(2) **c)** $H_2O(g) \rightarrow H_2O(l)$

d) $CO_2(s) \rightarrow CO_2(g)$

e) $Hg(s) \rightarrow Hg(l)$

26. Arrange the following compounds in order of increasing standard molar entropy at 25° C: $C_6H_{14}(l)$, $C_2H_4(g)$, ZnS(s), and $H_2O(l)$

a) $ZnS(s) < H_2O(l) < C_6H_{14}(l) < C_2H_4(g)$

b) $C_2H_4(g) < H_2O(l) < C_6H_{14}(l) < ZnS(s)$

(2) **c)** $ZnS(s) < C_6H_{14}(l) < C_2H_4(g) < H_2O(l)$

d) $C_6H_{14}(l) < C_2H_4(g) < H_2O(l) < ZnS(s)$

e) $ZnS(s) < H_2O(l) < C_2H_4(g) < C_6H_{14}(l)$

27. When 0.7521 g of benzoic was burned in a calorimeter containing 1000 g of water, a temperature rise of 3.60 °C was observed. What is the heat capacity of the bomb calorimeter, excluding water? The specific heat of water is 4.184 J/g-°C and the heat of combustion of benzoic acid is 26.42 kJ/g.

(3) **a)** 15.87 kJ/°C **b)** 4.18 kJ/°C **c)** 5.52 kJ/°C **d)** 1.34 kJ/°C

e) 752.1 kJ/°C

28. For the reaction $2\ P(s) + 3\ H_2(g) \rightarrow 2\ PH_3(g)$

ΔH^o = 18.5 kJ/mol and ΔS^o = +420.0 J/mol.K. Which of the following statements is **true**?

a) The reaction is only spontaneous at low temperatures.

b) The reaction is spontaneous at all temperatures.

(1) **c)** ΔG^o becomes less favorable as T is increased.

d) The reaction is spontaneous only at high temperatures.

e) The reaction is at equilibrium at 25° C under standard conditions.

29. For the reaction $I_2(g) \rightarrow 2\ I(g)$, we would expect at all temperatures:

(1) **a)** $\Delta H > 0$ and $\Delta S > 0$ **b)** $\Delta H < 0$ and $\Delta S < 0$ **c)** $\Delta H < 0$ and $\Delta S > 0$

d) $\Delta H > 0$ and $\Delta S < 0$

30. Given that the normal freezing point of ammonia is -78° C. Predict the sign of ΔH, ΔS, and ΔG for ammonia when it freezes at -80° C and 1 atm pressure.

		ΔH	ΔS	ΔG
	a)	-	-	0
	b)	-	+	-
(2)	**c)**	+	-	+
	d)	+	+	0
	e)	-	-	-

31. For the following process:

$CHCl_3(s)$ ---> $CHCl_3(l)$, ΔH° = 9.2 kJ/mol and ΔS° = 43.8 J/mol·K

What is the melting point of chloroform?

(2) **a)** -63 °C **b)** 210 °C **c)** 5 °C **d)** 63 °C **e)** -5.0 °C

32. The element oxygen was prepared by Joseph Priestley in 1774 by heating mercury (II) oxide:

$HgO(s)$ ---> $Hg(l) + \frac{1}{2} O_2(g)$ ΔH° = 90.84 kJ

Make use of the following data to estimate the temperature at which this reaction will be spontaneous under standard conditions.

S° (HgO(s)) = 70.29 J/mol·K S° (Hg(l)) = 76.02 J/mol·K

S° (O_2(g)) = 205.0 J/mol·K

(3) **a)** 108 K **b)** 430 K **c)** 620 K **d)** 775 K **e)** 840 K

33. Nitrosyl Chloride (NOCl) decomposes at elevated temperatures according to the equation:

$$2\ NOCl \rightleftarrows 2\ NO(g) + Cl_2(g)$$

Use the following information to calculate the value of *K*p for this reaction at 227 °C.

$\Delta H^o = +81.2$ kJ; $\Delta S^o = +128$ J/K

(3) **a)** 1.60×10^{-2} **b)** 2.1×10^{-7} **c)** 62.8 **d)** 4.9×10^{6} **e)** 3.20×10^{9}

34. A certain solution (prepared by mixing 35 mL of $CHCl_3$ and 25 mL of C_2H_5OH) shows <u>negative deviation</u> from Raoult's Law (i.e. the solution has a higher boiling point than either of the two pure liquids). For this solution:

a) The volume is 60 mL and ΔH for the mixing process is zero.

b) The volume is > 60 mL and ΔH for the mixing process is positive.

(2) **c)** The volume is > 60 mL and ΔH for the mixing process is negative.

d) The volume is < 60 mL and ΔH for the mixing process is positive.

e) The volume is < 60 mL and ΔH for the mixing process is negative.

35. What is the molar mass of an unknown (non-electrolyte) solute if 0.85 g of the unknown depresses the freezing point of 100 g of benzene by 0.47 °C? $K_f = 5.12$ °C/m.

(2) **a)** 92.6 g/mol **b)** 78.0 g/mol **c)** 106.7 g/mol **d)** 81.8 g/mol

e) 927 g/mol
