BROCK UNIVERSITY

Final Examination:	**April 2003**	**Number of pages:**	**22**
Course:	**CHEM 1F92/1P81/1P90**	**Number of students:**	**240**
Date of Examination:	**Thursday 17 April 2003**	**Number of hours:**	**3**
Time of Examination:	**7:00pm -10:00pm**	**Instructors:**	**H.L. Gordon / M.F. Richardson**

TOTAL MARKS: 95

No examination aids other than those specified are permitted. Use or possession of unauthorized materials will automatically result in the award of a zero grade for this examination.

THE FOLLOWING INFORMATION IS PROVIDED:

Formula sheet.
Thermodynamic data.
List of physical constants and conversions.

CALCULATORS AND MODEL KITS ARE PERMITTED.

A minimum of 30% must be obtained on this final examination in order to achieve a passing grade in the course.

All questions are to be answered on the examination paper. If you need more space please write on blank pages at end of this paper.

Name:_______________________________________ **ID#:**____________________

Lab section: _______________________________________

Q. 1	Q. 2	Q. 3	Q. 4	Q. 5	Q. 6	Q. 7
/5	/10	/10	/10	/10	/5	/10
Q. 8	Q. 9	Q. 10	Q. 11	BONUS	TOTAL	
/10	/5	/10	/10	/5	/95	

QUESTION 1. *(5 marks)*

A 5.00 g sample of antimony, Sb (*s*), and a 2.00 g sample of sulfur, S_8 (*s*), are heated to produce Sb_2S_3.

(a) **Name** the product Sb_2S_3.

(b) **Compute** the % yield of product if 0.01752 moles of product are produced.

QUESTION 2. *(10 marks)*

(a) (5 marks) Draw acceptable Lewis structures for the following ions:

(i) ClF_4^-	(ii) XeO_3^{2-}
(iii) N_3^- (one N is the central atom, the other two are bonded to it but not to each other).	(iv) BF_3
(v) ClO_3^-	

(b) (5 marks). Refer to your Lewis structures in part (a) above and answer the following questions. There may be no correct answer to a given question. State "None" if no structure fits the question. Some structures may be used more than once, others may not be used at all.

Which ion is pyramidal? **Answer:** ______________

Which ion has an octahedral electron-pair geometry? **Answer:** ________________

Which ion has at least one bond angle of 120°? **Answer:** ______________

Which ion has a tetrahedral molecular shape? **Answer:** ________________

Which ion has a central atom with sp^3d hybridization? **Answer:** ______________

QUESTION 3. *(10 marks)*

(a) (4 marks) Give the formulas of the following compounds:

(i) Sodium nitride ________________________

(ii) Magnesium nitrite________________________

(iii) Ammonium perchlorate ________________________

(iv) Copper(II) phosphate ________________________

(b) (3 marks) Complete and balance the following equations:

(i) $CH_3NH_2 + H_2SO_4 \rightarrow$

(write the equation for complete neutralization of H_2SO_4)

(ii) $Mg + HCl\,(aq) \rightarrow$

(a gas is produced)

(iii) $NaOH\,(aq) + Fe_2(SO_4)_3\,(aq) \rightarrow$

(a precipitate is produced)

(c) (3 marks) Write the net ionic equations for each of the reactions in Part (b) above.

(i)

(ii)

(iii)

QUESTION 4. *(10 marks)*

Consider the reaction

$$P_4\ (g) \rightleftharpoons 2P_2\ (g)$$

In an experiment where originally pure P_4 (g) is placed into a container at 1325 K, once equilibrium has been attained, the mixture has a total pressure of 1.00 atm. $K_p = 0.100$ at 1325 K

(a) Let the equilibrium partial pressure of $P_2(g) = x$
Therefore, the equilibrium partial pressure of $P_4(g) = 1.00$ atm – x.

What is the **name** of the gas law that allows us to do this? _________________

(b) Write down the symbolic expression for K_p. Then calculate the equilibrium partial pressures of $P_4(g)$ and $P_2(g)$, using the suggested replacements in (a). *You will need to use the quadratic equation, given in the formula sheet, to solve for x!*

(b) Calculate the mole fraction of $P_4(g)$ that has dissociated to reach equilibrium.

QUESTION 5. *(10 marks)*

Remember to think CAREFULLY about number of particles into which solute dissociates!!!

A. Which of the following will have the **lowest** total vapour pressure at 25°C?

(a) pure water (P_{vap} = 23.8 torr at 25°C)
(b) a solution of glucose in water, with mole fraction glucose = 0.01
(c) a solution of sodium chloride in water, with mole fraction sodium chloride = 0.01
(d) a solution of magnesium chloride in water, with mole fraction magnesium chloride = 0.01

B. Which of the following will have the **highest** total vapour pressure at 25°C?

(a) pure water (P_{vap} = 23.8 torr at 25°C)
(b) a solution of glucose in water, with mole fraction glucose = 0.01
(c) a solution of sodium chloride in water, with mole fraction sodium chloride = 0.01
(d) a solution of magnesium chloride in water, with mole fraction magnesium chloride = 0.01

C. Which of the following solutions will have the same boiling point at 0.040 molal glucose ($C_6H_{12}O_6$) in water?

(a) 0.10 molal Na_3PO_4 (*aq*)
(b) 0.20 molal $CaBr_2$ (*aq*)
(c) 0.020 molal KCl (*aq*)
(d) 0.020 molal HF (*aq*), $K_a = 7.2 \text{ H } 10^{-4}$

QUESTION 5. *(continued ...)*

D. From the following solutions:

(a) 0.10 molal Na_3PO_4 (*aq*)

(b) 0.20 molal $CaBr_2$ (*aq*)

(c) 0.020 molal KCl (*aq*)

(d) 0.020 molal HF (*aq*), $K_a = 7.2 \times 10^{-4}$

The one with the **highest freezing point** is: _______________

The one with the **lowest freezing point** is: ________________

The one with the **highest boiling point** is: _________________

The one with the **lowest boiling point** is: _________________

The one with the **highest osmotic pressure** is: _______________

E. A 2.00 g sample of a large biomolecule was dissolved in 15.0 g of carbon tetrachloride. The boiling point of this solution was determined to be 77.85°C. Calculate the molar mass of the biomolecule. For carbon tetrachloride, the boiling-point constant is 5.03 °C kg/mol, and the boiling point of pure carbon tetrachloride is 76.50°C. *Assume that the biomolecule does not dissociate.*

QUESTION 6. *(5 marks)*

The bombardier beetle uses an explosive discharge as a defensive measure. The chemical reaction involved is the oxidation of hydroquinone by hydrogen peroxide to produce quinone and water:

$$C_6H_4(OH)_2\ (aq) + H_2O_2\ (aq) \rightarrow C_6H_4O_2\ (aq) + 2H_2O\ (l)$$

Calculate ΔH^o_{rxn} for the above reaction from the following data:

(a) $C_6H_4(OH)_2\ (aq) \rightarrow C_6H_4O_2\ (aq) + H_2\ (g)$ $\Delta H^o_{rxn} = +177.4$ kJ

(b) $H_2\ (g) + O_2\ (g) \rightarrow H_2O_2\ (aq)$ $\Delta H^o_{rxn} = -191.2$ kJ

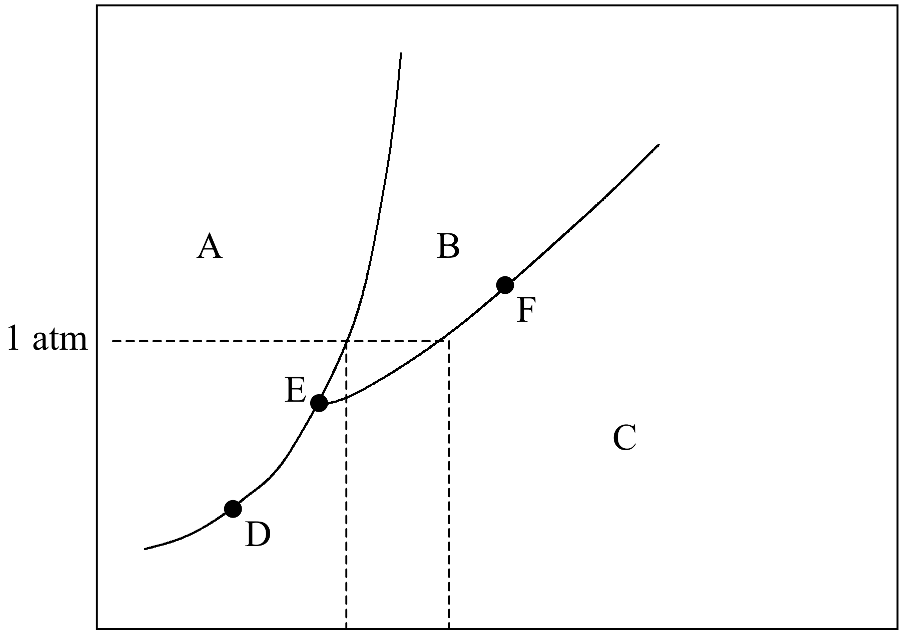
(c) $H_2\ (g) + \frac{1}{2}\ O_2\ (g) \rightarrow H_2O\ (g)$ $\Delta H^o_{rxn} = -241.8$ kJ

(d) $H_2O\ (g) \rightarrow H_2O\ (l)$ $\Delta H^o_{rxn} = -43.8$ kJ

QUESTION 7. *(10 marks)*

Consider the phase diagram given below for an unknown substance X.

(a) **Label** the axes of the graph.



(b) Identify **ALL** phases present at the following labelled points:

A: ____________________________ **D:** ______________________________

B: ____________________________ **E:** ______________________________

C: ____________________________ **F:** ______________________________

(c) On the above phase diagram, use the following symbols to **clearly label**:

J: normal boiling point **K:** normal freezing point

(d) **Draw** an arrow on the above phase diagram representing the following overall process:

X (*g*) at 1.5 atm → X(*s*) at 1.5 atm

QUESTION 7. *(continued ...)*

(e) Is the overall process

$$X\ (g) \text{ at } 1.5 \text{ atm} \rightarrow X(s) \text{ at } 1.5 \text{ atm}$$

endothermic or exothermic? ______________________________

represent an increase, decrease or no change in entropy? __________________________

(f) If you were to compute the total heat **q** associated with the overall process

$$X\ (g) \text{ at } 1.5 \text{ atm} \rightarrow X(s) \text{ at } 1.5 \text{ atm}$$

as you have illustrated on the graph, the total number of different contributions to **q** you would have to compute would be: *(Circle the correct answer)*:

(i): 1 (ii): 2 (iii): 3 (iv): 4 (v): 5 (vi): > 5

(Your answer MUST be both correct and consistent with the arrow you drew on the phase diagram in part (d). If incorrect, part marks may be awarded if you show your reasoning below. NO CALCULATIONS REQUIRED

QUESTION 8. *(10 marks)*

Hydrogen for use in ammonia production is produced by the reaction:

$$CH_4(g) + H_2O(g) \overset{\textit{Ni catalyst}}{\mathbf{O}} CO(g) + 3H_2(g) \qquad \Delta H^o_{rxn} = 206 \text{ kJ}, \ \Delta S^o_{rxn} = 216 \text{ J K}^{-1}$$

(a) **Check** the appropriate boxes in the following table, using LeChatelier's principle to predict what will happen to the reaction above if:

		Thermodynamic Equilibrium Shifts:		
		Towards reactants	**No change**	**Towards products**
(i)	$H_2O(g)$ is removed:			
(ii)	The temperature is increased:			
(iii)	The volume of the container is tripled:			
(iv)	$CO(g)$ is removed:			
(v)	Pressure is increased:			
(vi)	Ni catalyst is removed:			

(b) **Compute** ΔG^o_{rxn} and K_p at 25ºC for this reaction.

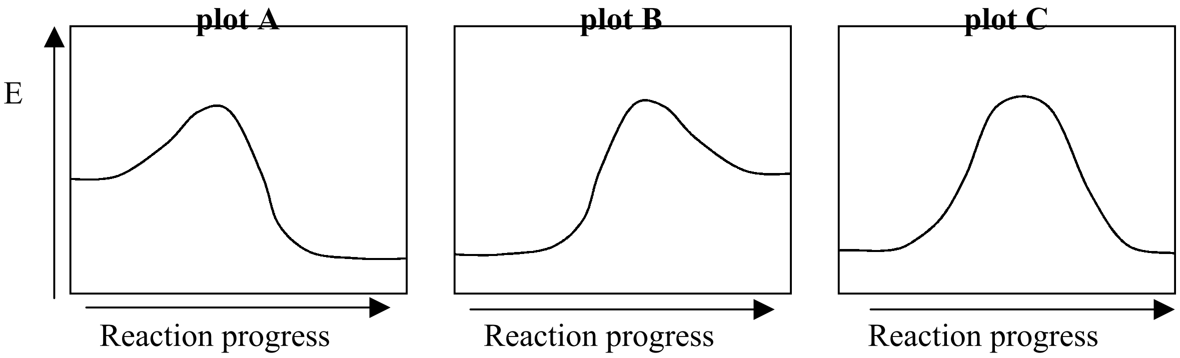
(c) Is this reaction spontaneous or not spontaneous at 25ºC? ___________________________

(d) **Compute** the temperature range over which this reaction is spontaneous:

QUESTION 8. *(continued ...)*

(e) $CH_4(g) + H_2O(g) \xrightarrow{Ni\ catalyst} CO(g) + 3H_2(g)$ $\Delta H^o_{rxn} = 206$ kJ, $\Delta S^o_{rxn} = 216$ J K^{-1}

Which of the following plots is correct for the reaction progress of the above reaction:
(i): plot A
(ii): plot B
(iii): plot C



(f) **Sketch and label** on the plot you selected, ΔH^o_{rxn} and the energy of activation, E_a, for the catalysed reaction.

(g) **Sketch** on the plot you selected, what happens when the Ni catalyst is NOT used.

(h) How does ΔH^o_{rxn} change for the reaction if the Ni catalyst is NOT used?
(i): ΔH^o_{rxn} increases
(ii): ΔH^o_{rxn} does not change
(iii): ΔH^o_{rxn} decreases

(i) How does E_a change for the reaction if the Ni catalyst is NOT used?
(i): E_a increases
(ii): E_a does not change
(iii): E_a decreases

QUESTION 9. *(5 marks)*

The following rate data were obtained for the reaction

$$2\ ClO_2\ (aq) + 2\ OH^-\ (aq) \rightarrow ClO_3^-(aq) + ClO_2^-\ (aq) + H_2O\ (l)$$

Initial $[ClO_2]$ (M)	Initial $[OH^-]$ (M)	Initial Reaction rate (M/s)
0.0500	0.100	5.75×10^{-2}
0.100	0.100	2.30×10^{-1}
0.100	0.0500	1.15×10^{-1}

(a) Determine the rate law for the reaction.

(b) What is the **overall order** of the reaction? ____________________

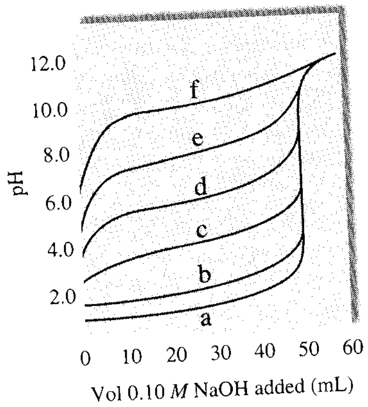
What is the order of the reaction with respect to $[ClO_2]$? ______________

What is the order of the reaction with respect to $[OH^-]$? ________________

(c) Determine the value of the rate constant. Include units!

QUESTION 10. *(10 marks)*
No calculations are required for these questions. Think CAREFULLY.

The following plot shows the pH curves for several acid-base titrations. In each case, 50.00 mL acid is titrated with 0.10 M NaOH.



(a) Which curve corresponds to the weakest acid? _____________

(b) Which curve corresponds to the strongest acid? _____________

(c) Which curve corresponds to the acid with Ka = $1H10^{-6}$? _____________

(d) Which of the following acid-base colour indicators would be most appropriate to use for titration curve **e**? _________________

Indicator:	Thymol blue	Thymolphthalein	Phenolphthalein	Methyl Red
pH range:	1.2-2.8	9.5-10.5	8.3-10.0	4.2-6.3

(e) What volume of 0.10 M NaOH should be added to acid **c** to make a buffer?__________

(f) Over what pH range could a buffer made from acid **c** be used? _______________

(g) Which of the curves represents the titration of a diprotic acid? ________________

(h) What is the pH at the equivalence point of titration curve **d**? _________________

(i) All of the acids depicted above are at the **same** initial concentration. What is the initial acid concentration? _______________

(j) How many times would you have to fill a standard buret in order to complete one of the above titrations? _______________

QUESTION 11. *(10 marks)*

Tris(hydroxymethyl)aminomethane $(HOCH_2)_3CNH_2$ is often used as a buffer in biochemistry. The chemical equilibrium is:

$$(HOCH_2)_3CNH_2\,(aq) + H_2O\,(l) \rightleftharpoons (HOCH_2)_3CNH_3^+(aq) + OH^-(aq)$$

K_b for the above equilibrium is 1.19×10^{-6}.

A buffer is prepared by diluting 50.0 g $(HOCH_2)_3CNH_2$ (MW 121.14) and 65.0 g $(HOCH_2)_3CNH_3Cl$ (MW 157.60) to a total volume of exactly 2.000 L.

(a) What is the pH of this buffer?

(b) What is the pH after 0.50 mL of 12 M HCl is added to 200.0 mL of the above buffer?

BONUS *(5 marks)*

A student intends to titrate a solution of a weak monoprotic acid with 0.1000 M NaOH solution, but reverses the two solutions and instead pipettes 50.00 mL NaOH solution into the Erlenmeyer flask, and puts the weak acid solution into the buret. After 23.75 mL of weak acid solution has been added to the 50.00 mL NaOH, the pH of the resulting solution is 10.50.

Calculate the original concentration of the solution of weak acid.

EXTRA PAGE FOR CALCULATIONS .....

EXTRA PAGE FOR CALCULATIONS .....

PHYSICAL CONSTANTS and CONVERSION FACTORS:

Avogadro's Number		**6.022×10^{23} mol^{-1}**	
Planck's Constant	**h**	**6.6256×10^{-34} J s**	
Speed of light	**c**	**2.998×10^{8} m s^{-1}**	
Rydberg constant	**R_H**	**2.18×10^{-18} J**	
Ideal Gas Constant	**R**	**0.08205 L atm / K mol** **8.314 J / K mol**	
Pressure		**1 atm = 760 mmHg** **1 mm Hg = 1 torr**	
Energy		**1 L atm = 101.3 J**	
Molar heat capacity $H_2O(l)$		**75.4 J K^{-1} mol^{-1}**	**between 0°C and 100°C**
Specific heat capacity $H_2O(l)$		**4.183 J K^{-1} g^{-1}**	**between 0°C and 100°C**
Molar heat capacity $H_2O(g)$		**33.76 J K^{-1} mol^{-1}**	**at constant pressure**
Specific heat capacity $H_2O(g)$		**1.874 J K^{-1} g^{-1}**	**at constant pressure**
Molar heat capacity $H_2O(s)$		**38.07 J K^{-1} mol^{-1}**	**at constant pressure**
Specific heat capacity $H_2O(s)$		**2.113 J K^{-1} g^{-1}**	**at constant pressure**
Heat of vaporization $H_2O(l)$		**2257 J g^{-1}** **40.79 kJ mol^{-1}**	**at 100°C** **at 100°C**
Heat of condensation $H_2O(g)$		**= - Heat of vaporization $H_2O(l)$**	
Heat of fusion $H_2O(l)$		**-333.4 J g^{-1}**	**at 0°C**
For H_2O (l)		**K_f = -1.86 ºC kg/mol** **K_b = 0.52 ºC kg/mol**	

Relationship between energy and wavelength or frequency of light: $E = h\nu$ or $E = {hc}/{\lambda}$	Energy of an electron in the nth shell of Bohr model of hydrogen-like atom: $E_n = -R_H\left({1}/{n^2}\right)$
Charles' Law: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$	Heat change due to change of phase: $q = \Delta H_{vap} m$ $q = \Delta H_{fus} m$
Boyle's Law: $P_1V_1 = P_2V_2$	Heat change due to change of temperature at constant P: $q = C_P(T_2 - T_1)$ or $q = m\overline{C_P}(T_2 - T_1)$
Ideal Gas Law: $PV = nRT$	Standard enthalpy change for a reaction: $\Delta H^o_{rxn} = \sum n\Delta H^o_f(products) - \sum m\Delta H^o_f(reac\tan ts)$
Dalton's Law of Partial Pressures: $P_{total} = P_A + P_B + P_C + \ldots$	Standard entropy change for a reaction: $\Delta S^o_{rxn} = \sum nS^o_f(products) - \sum mS^o_f(reac\tan ts)$
Relationship of partial pressure to mole fraction: $P_A = X_A \cdot P_{total}$	Standard free energy change for a reaction: $\Delta G^o_{rxn} = \sum n\Delta G^o_f(products) - \sum m\Delta G^o_f(reac\tan ts)$
Relationship between equilibrium constant and ΔG: $\Delta G^o = -RT\ln K_P$ or $\Delta G^o = -RT\ln K_C$	Gibbs free energy: $\Delta G = \Delta H - T\Delta S$
van der Waal's equation: $\left[P + \frac{an^2}{V^2}\right][V - nb] = nRT$	Internal energy: $\Delta E = q + w$
Pressure-volume work: $w = -P_{ext}(V_2 - V_1)$	Enthalpy change for constant pressure process: $\Delta H = \Delta E + P(V_2 - V_1)$
Average kinetic energy of gas molecules: $\overline{KE} = \frac{1}{2}m\overline{u^2}$	Henry's Law: $c = k\,P$
	Vapour pressure lowering: $P_{solution} = X_{solvent}P^o_{solvent}$

Root-mean-square speed of gas molecules: $u_{rms} = \sqrt{\frac{3RT}{M}}$	
Simple cubic cell: 1 atom/cell; cell length = 2r	Freezing point lowering: $T^o_{fp} - T_{fp} = K_f im$
Body-centred cubic cell: 2 atoms/cell; cell length = $\frac{4}{\sqrt{3}}r$	Boiling point elevation: $T_{bp} - T^o_{bp} = K_b im$
Face-centred cubic cell: 4 atoms/cell; cell length = $\sqrt{8}r$	Osmotic pressure: $\pi = iMRT$ and $\pi = (mass)RT/FW$
Clausius-Clapeyron equation: $\ell n\left\{\frac{P_1}{P_2}\right\} = \frac{\Delta H_{vap}}{R}\left\{\frac{T_1 - T_2}{T_1 T_2}\right\}$	$k = Ae^{-Ea/RT}$ Arrhenius equation: or $\ln k = \ln A - \frac{E_a}{RT}$
$\ln[A] - \ln[A]_o = -kt$ First order rate equation: $\ln\left\{\frac{[A]}{[A]_o}\right\} = -kt$	Second order rate equation: $\frac{1}{[A]} - \frac{1}{[A]_o} = kt$
Half-life for first order reaction: $t_{1/2} = \frac{\ln(2)}{k} = \frac{0.623}{k}$	Half-life for second order reaction: $t_{1/2} = \frac{1}{k[A]_o}$
pH = - log [H$^+$]; pOH = - log [OH$^-$]; $K_w = K_a K_b = 10^{-14}$	Solution to quadratic equation: $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
Standard emf of electrochemical cell: $E^o_{cell} = E^o_{cathode} - E^o_{anode}$ Relationship between ΔG^o and standard emf: $\Delta G^o = -nFE^o_{cell}$	Relationship between standard emf of cell and K: $E^o_{cell} = \frac{RT}{nF}\ln K$ Nernst equation: $E = E^o_{cell} - \frac{RT}{nF}\ln Q$