Concordia UNIVERSITY

COURSE	NUMBER	SECTION
GENERAL CHEMISTRY II	CHEM 206	/4 01 & 52
EXAMINATION	**DATE**	**TIME**
Final Examination	April 20, 2006	1900-2200
INSTRUCTOR	Dr. Cerrie ROGERS	

MATERIALS ALLOWED:	[X]	NO	[ ]	YES (PLEASE SPECIFY)
CALCULATORS ALLOWED:	[ ]	NO	[X]	YES programmable calculators must be reset

Chem 206 --- GENERAL CHEMISTRY II

LAST NAME: _____ FIRST NAME: _____

STUDENT NUMBER: _____ LECTURE SECTION (circle one): 01 or 52

Instructions: PLEASE READ THIS PAGE WHILE WAITING TO START!

- ***Make sure your exam has 13 pages, including this cover page & a periodic table.***
- ***Write your student ID number on all pages.***
- ***Write all answers <u>legibly</u> in the space provided (use the backs of pages for rough work).***
- ***Non-programmable calculators are allowed; cell phones & electronic dictionaries are not.***
- ***You may detach the periodic table and "potentially useful information" pages.***
- ***Read ALL questions quickly BEFORE starting the exam; do the "easy" questions first.***
- ***Suggestion: spend <15 minutes per page to have 30 minutes left to check your work.***

<u>Mark breakdown</u>: *approx. 15 min per page ⇨ 30 minutes extra to check your work.*

Page 2.	/ 10	
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Page 7.	/ 10	
Page 8.	/ 8	
Page 9.	/ 15	
Page 10.	/ 12	
Page 11.	/ 12	**TOTAL: / 100 (MAXIMUM MARK = 105)**

 # 1. (__/ 10 marks) TRUE OR FALSE? Circle T or F to describe each of these statements.

T / F Chemical equilibrium is described as a dynamic state, because the concentrations of all species involved in the reaction change at equal rates at equilibrium.

T / F Most substances have higher solubility at higher temperatures, which suggests that dissolution is usually entropically favourable according to the system *(where system = solute + solvent)*.

T / F If two reactions occur in sequence, the equilibrium constants for the reactions must be added together.

T / F During a chemical reaction that leads to an explosion, the system *(i.e., the reactants &/or products)* performs work on the surroundings.

T / F Hess's law can be used to calculate changes in thermodynamic functions that vary depending on the mechanism or path of the process.

T / F To minimize indicator error during the titration of an acid, it is best to choose an indicator that undergoes a dramatic colour change at a pH very close to the pK_a of the acid being titrated.

T / F When an attractive interaction is broken, energy is released by the system.

T / F Brønsted and Lowry derived an equation that helps explain why not all collisions between reactant molecules lead to reaction.

T / F A 1.0 M solution of sodium chloride (NaCl) would exert a lower osmotic pressure than a 1.0 M solution of glucose ($C_6H_{12}O_6$).

T / F It is always possible to predict the relative solubilities of two ionic substances by comparing the values of their solubility product (K_{sp}) constants, without doing calculations.

 # 2. (__/ 7 marks) The freezing point of a solution prepared by dissolving 1.00 mol of hydrogen fluoride (HF) in 500 g of water is -3.8°C, but the freezing point of a solution prepared by dissolving 1.00 mol of hydrogen chloride (HCl) in 500 g of water is -7.4°C. Explain. *[Calculations are not required.]*

 # 3. (__/ 11 marks) A simple humidity sensor consists of a cardboard square that is blue in dry weather and red in humid weather. The colour change is due to the formation of a hydrated compound:

$$CoCl_2(s) + 6\ H_2O(g) \rightleftharpoons [Co(H_2O)_6]Cl_2(s)$$ *note: same as $CoCl_2 \cdot 6H_2O(s)$*

a) **(1 mark)** The water molecules become bound to the cobalt ion via coordinate covalent bonds. Which of these two species is the Lewis acid, and which species is the Lewis base?

b) **(4 marks)** Consider the reaction shown above. Briefly explain what causes this reaction to be:

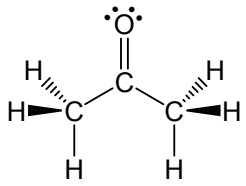
i. Exothermic ($\Delta H°_{rxn}$ = -352 kJ·mol^{-1} at 25°C)

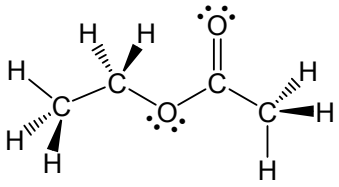
ii. Entropically unfavourable ($\Delta S°$ = -899 J·mol^{-1}·K^{-1} at 25°C)

c) **(4 marks)** Calculate the standard Gibbs free energy change for this reaction on a hot summer day when the temperature is 35°C.

d) **(2 marks)** Comment on the expected magnitude of the equilibrium constant for this reaction at this temperature.

 # 4. (__/ 12 marks) Acetone, C_3H_6O, and ethyl acetate, $C_4H_8O_2$, are volatile liquids often used as solvents.

acetone 

ethyl acetate 

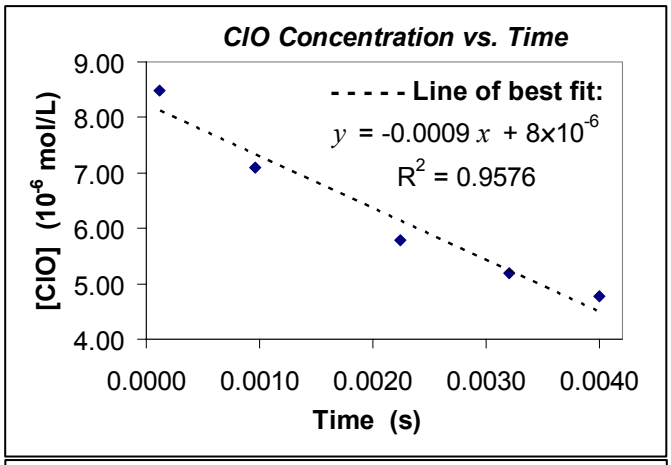
a) **(5 marks)** Name and describe two intermolecular forces that would exist between acetone and ethyl acetate molecules, and clearly indicate which parts of the molecules would be involved for each.

b) **(7 marks)** Consider a mixture of 25.0 g acetone and 25.0 g ethyl acetate, which you might use as a cleaning fluid. If this mixture behaves ideally, what would be the vapour pressure above the solution at 30°C? The pure liquids' vapour pressures at 30°C are: P^{o}_{acetone} 285 mm Hg; $P^{o}_{\text{ethyl acetate}}$ 118 mm Hg.

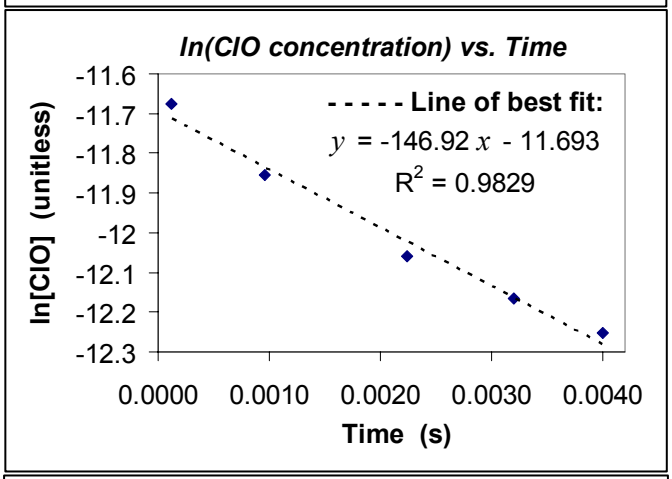
 # 5. (__/ 8 marks) Chlorine oxide (ClO), which plays an important role in the depletion of ozone, decays rapidly at room temperature:

$$2\ ClO(g) \rightarrow Cl_2(g) + O_2(g)$$

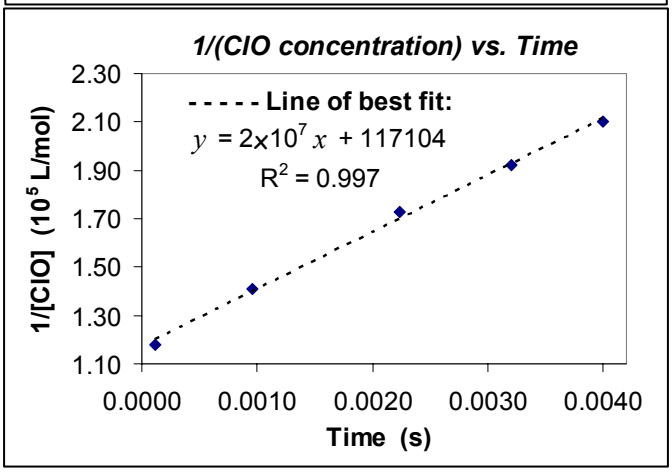
A single kinetics experiment was performed, and the data set was plotted in the three ways shown here.



a) **(2 marks)** What is the rate law for this reaction? How were you able to come to this conclusion?



b) **(1 mark)** What is the value of the rate constant?



c) **(5 marks)** How long would it take for the concentration of ClO to drop from 4.77×10^{-6} M to 1.0×10^{-8} M?

 # 6. (__/ 10 marks) Potassium metal reacts violently with water to yield aqueous potassium hydroxide plus hydrogen gas:

$$K(s) + H_2O(l) \rightarrow KOH(aq) + \tfrac{1}{2} H_2(g)$$

a) **(2 marks)** Calculate the standard enthalpy change for this reaction at 298 K.

Thermodynamic data for 298 K		
Substance	**ΔH°_f ($kJ \cdot mol^{-1}$)**	**S°_f ($J \cdot mol^{-1} \cdot K^{-1}$)**
K(s)	0	64.2
$H_2O(l)$	-285.8	69.9
KOH(aq)	-482.4	91.6
$H_2(g)$	0	130.6

b) **(8 marks)** Imagine you drop a piece of potassium metal weighing 7.55 g into 400.0 g of water at 25.0°C. What would be the final temperature of the solution if all the heat released by the reaction is used to warm up the solution? *[Assume the heat capacity of the solution is the same as water.]*

 # 7. (__/ 8 marks) The following three-step mechanism has been proposed for the reaction of chlorine and chloroform. The numerical value (*i.e.,* without units) of the rate constant for each step is provided. *[Assume that the three steps have similar pre-exponential factors (frequency factors), A.]*

STEP 1: $Cl_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Cl(g)$ $k_1 = 4.8\text{x}10^3$ and $k_{-1} = 3.6\text{x}10^3$

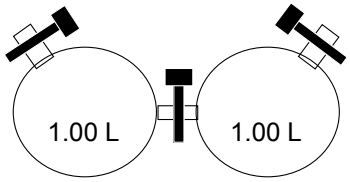
STEP 2: $Cl(g) + CHCl_3(g) \xrightarrow{k_2} HCl(g) + CCl_3(g)$ $k_2 = 1.3\text{x}10^{-2}$

STEP 3: $CCl_3(g) + Cl(g) \xrightarrow{k_3} CCl_4(g)$ $k_3 = 2.7\text{x}10^2$

Based on this mechanism, derive the predicted overall rate law for this reaction (include comments / explanation), and calculate the numerical value of the predicted overall rate constant.

 # 8. (__/ 15 marks) At 525 K, the exothermic reaction shown below has $K_p = 2.1 \times 10^2$ *(data modified for this exam)*:

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$



a) **(9 marks)** A 0.974 mol quantity of Br_2 is added to the 1.00 L flask on the left (see diagram), which already contains 1.22 mol of H_2 gas. What will be the total pressure in the flask at equilibrium at 525 K?
Assume that all three black valves remain closed, so the volume is 1.00 L.

b) **(6 marks)** Now consider disturbing this equilibrium mixture. How would the following changes affect the quantity of Br_2 present in the flask when equilibrium is re-established? Very briefly explain why.

Disturbance	***Will the quantity of Br_2 increase, decrease or stay the same? Why?***
Adding a substance that reacts with HBr	
Decreasing the temperature to 400 K	
Opening the valve that connects the two flasks	

 # 9. (__/ 12 marks) Many home swimming pools are disinfected by adding calcium hypochlorite, $Ca(OCl)_2$. Calcium hypochlorite is fully soluble in water, and the K_a of its conjugate acid HOCl is 3.5×10^{-8}.

a) **(4 marks)** Write balanced chemical equations to illustrate the two equilibria this substance participates in when $Ca(OCl)_{2(s)}$ is added to water. Include the appropriate equilibrium constant expressions.

b) **(8 marks)** Calculate the pH of a pool with 0.100 M $Ca(OCl)_2$. Is the water acidic, basic or neutral?

 # 10. (__/ 12 marks) Imagine you are preparing to perform an experiment on a pH-sensitive compound, and you need the solution to be kept at pH 8.75 throughout the experiment.

a) **(4 marks)** Evaluate <u>each</u> of the pairs below in terms of their usefulness in a buffer for your experiment.

PAIR	Acid	K_a	Base	Good choice or bad choice? WHY?
1	$HClO_4$	> 1	$NaClO_4$	
2	HCOOH	1.8×10^{-4}	NaHCOO	
3	NH_4Cl	5.6×10^{-10}	NH_3	
4	H_2O_2	1.8×10^{-12}	Na_2O_2	

b) **(3 marks)** For the best choice from part (a), what is the ratio of [acid form] to [base form] necessary to maintain a pH of 8.75?

c) **(5 marks)** If the total initial buffer concentration ($[acid]_o + [base]_o$) must be 0.75 M in your experiment, what mass of each compound should you dissolve in water in order to prepare 1.0 L of buffer?
(Note that you would be able to make <u>minor</u> adjustments to your buffer's pH <u>after</u> preparing it.)

POTENTIALLY USEFUL INFORMATION

Constants:

$R = 8.314\ J \cdot mol^{-1}K^{-1} = 0.08206\ L \cdot atm \cdot mol^{-1}K^{-1}$

1 atm = 760 mm Hg = 760 torr = 101.325 kPa

Data:

Properties of liquid water:

bp (at 1 atm) = 100.00°C

$C_{H_2O(l)} = 4.184\ J \cdot g^{-1}K^{-1}$

$d_{H_2O(l)} = 1.00\ g \cdot mL^{-1}$

$K_{f\ H_2O} = 1.86\ °C \cdot kg \cdot mol^{-1}$

$K_{b\ H_2O} = 0.52\ °C \cdot kg \cdot mol^{-1}$

$K_w = 10^{-14}$

Properties of solid water:

mp (at 1 atm) = 0.00°C

$C_{H_2O(s)} = 2.06\ J \cdot g^{-1}K^{-1}$

$d_{H_2O(s)} = 0.917\ g \cdot mL^{-1}$

Formulae:

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

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

$\Delta G^o = -RT \ln K_{eq}$

$PV = nRT$

$C = k\,P \quad (\text{or, } S = k\,P)$

$P = \chi\, P^o$

$\Delta T = K\, m$

$\pi V = nRT$

$k = A\, e^{(-Ea/RT)}$

$[A]_t = -kt + [A]_o$

$\ln[A]_t = -kt + \ln[A]_o$

$1/[A]_t = kt + 1/[A]_o$

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

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

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$