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| GENERAL CHEMISTRY II | CHEM206 | /4 01 |
| Final Examination | April 28, 2005 | 0900-1200 |
| Dr. Cerrie ROGERS | | |

x periodic table and formula sheet provided

x non-programmable calculators allowed

# Chem 206 --- GENERAL CHEMISTRY II

LAST NAME: _____ FIRST NAME: _____

STUDENT NUMBER: _____ SIGNATURE: _____

***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.***
- ***SUGGESTION: Read ALL questions quickly BEFORE starting the exam.***

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

| | | |
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| Page 11. | / 8 | **TOTAL: / 100 (MAXIMUM MARK = 101)** |

**# 1. (__/ 13 marks)** Circle the word(s) that correctly completes each of the following statements.

a) An object with a small heat capacity will feel warm to the touch after it absorbs a ( LARGE / SMALL ) amount of heat.

b) A solution containing 0.500 M NaCl will freeze at a ( HIGHER / LOWER ) temperature than a solution containing 0.500 M $CaCl_2$.

c) When a system is at equilibrium, the free energy of the system is at a ( MAXIMUM / MINIMUM ).

d) When an ionic compound is observed to have a van't Hoff factor ($i$) less than we expect, we conclude that some ions remain ( PAIRED / UNPAIRED ) when the substance dissolves.

e) If the equations for two reactions are added together, the equilibrium constants for the reactions must be ( ADDED TO EACH OTHER / MULTIPLIED BY EACH OTHER ).

f) Based on the relative sizes of nitrogen and phosphorus atoms, we would predict ammonia, $NH_3$, to be a ( STRONGER / WEAKER ) base than phosphine, $PH_3$.

g) A solution of pH 12.0 would more likely contain ( 0.01 M NaOH / 0.01 M $NH_3$ ).

h) A reaction that is thermodynamically favourable in the forward direction will always have a larger rate constant in the ( FORWARD / REVERSE ) direction.

i) To minimize indicator error during a titration, it is best to choose an indicator that changes colour at a pH very close to the ( EQUILIBRIUM / EQUIVALENCE ) point of the titration.

j) When a chemical bond forms, energy is ( RELEASED / REQUIRED ).

k) All Brønsted bases are also ( LEWIS ACIDS / LEWIS BASES ).

l) A hydrogen bond can exist between a hydrogen atom bonded to nitrogen, oxygen or fluorine and any atom with a ( LONE PAIR / OPEN VALENCE ).

m) Parts per million is a concentration unit based on the ( MASS / MOLES ) of solute per million equivalent units of solvent.

**# 2. (__/ 5 marks)** A scientist from the 19th century, Marcellin Berthoulet, stated that "all exothermic reactions are spontaneous". Is his statement correct? Explain. *[Evaluate the science, not the historical reference….]*

**# 3. (__/ 15 marks)** Sodium bicarbonate can decompose via the following reaction:

$$2\ NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

| SUBSTANCE (at 298K) | $\Delta H^o_f$ (kJ/mol) | $S^o_f$ (J/mol·K) |
|---|---|---|
| $NaHCO_3(s)$ | -948 | 102 |
| $Na_2CO_3(s)$ | -1131 | 136 |
| $CO_2(g)$ | -394 | 214 |
| $H_2O(g)$ | -242 | 189 |

a) **(3 marks)** Calculate $\Delta H^o_{rxn}$ and $\Delta S^o_{rxn}$ for this reaction.

b) **(3 marks)** Calculate $\Delta G^o_{rxn}$ for this reaction at 125°C (398K). *[Assume $\Delta H^o_{rxn}$ and $\Delta S^o_{rxn}$ do not change.]*

## # 3. CONTINUED FROM PREVIOUS PAGE…

c) **(2 marks)** Calculate the value of the thermodynamic equilibrium constant $K_p$ for this reaction at 125°C. *[Note: if you cannot do part (c), use a $K_p$ value of 15.0 (which is not correct) to answer parts (d) and (e).]*

d) **(1 mark)** Is the reaction product-favoured or reactant-favoured at 125°C? How can you tell?

e) **(6 marks)** If solid $NaHCO_3$ and solid $Na_2CO_3$ are placed into a sealed container that initially contains 0.500 atm of $CO_2(g)$ and 0.100 atm of $H_2O(g)$, what will be the total pressure in the container when the system reaches equilibrium at 125°C?

**# 4. (__/ 13 marks)** Dichloromethane ($CH_2Cl_2$) and chloroform ($CHCl_3$) are industrially important solvents. They are prepared by the reaction of methane with chlorine, followed by distillation of the product mixture.

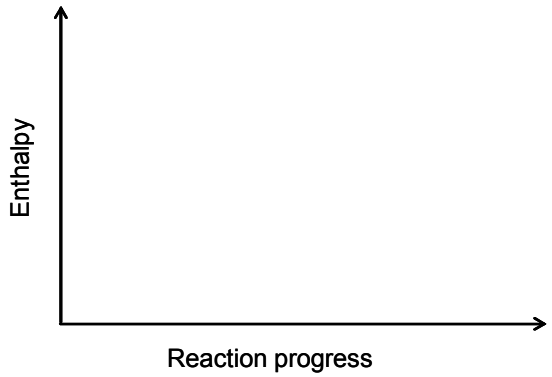
a) **(2 marks)** Which <u>two</u> intermolecular forces exist between $CHCl_3$ and $CH_2Cl_2$ molecules? Which is the stronger of these two forces?

b) **(6 marks)** At 25°C, the vapour pressure of pure $CHCl_3$ is 205 mm Hg, and the vapour pressure of pure $CH_2Cl_2$ is 415 mm Hg. What is the predicted vapour pressure (in mm Hg) at 25°C above a mixture of 15.0 g of $CHCl_3$ and 27.5 g of $CH_2Cl_2$? *[ Assume the mixture behaves as an ideal solution.]*

c) **(5 marks)** Using kinetics arguments (*i.e.,* discussion of rates…), explain how a volatile liquid comes to equilibrium with its vapour when it is placed into an evacuated, sealed container.

**# 5. (__/ 8 marks)** A certain chemical reaction A → 2 B follows a one-step mechanism and has an activation energy of 32 kJ/mol. The enthalpy change for the reaction is -15 kJ per mole of A reacted.

a) **(2 marks)** Draw an energy *vs.* reaction progress diagram that describes this reaction. Clearly label your diagram with any of the following labels that apply to this reaction:
reactants, products, transition state, intermediate, rate-limiting step, activation energy, $\Delta H_{rxn}$




b) **(6 marks)** If you wanted to slow down this reaction by a factor of 1000 compared to its rate at room temperature (25°C), to what temperature should you cool the reaction mixture? [*Assume the initial concentrations of reactants are the same at both temperatures and that the mechanism does not change.]*

**# 6. (__/ 8 marks)** Initial rates data were collected for the reaction of nitric oxide and hydrogen at 1100 K:

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

| | Reactant Concentration (M) | | Reaction rate (M/s) |
|---|---|---|---|
| Run | $[NO]_o$ | $[H_2]_o$ | $RATE_o$ |
| 1 | $5.00\times10^{-3}$ | $2.50\times10^{-3}$ | $3.0\times10^{-3}$ |
| 2 | $15.0\times10^{-3}$ | $2.50\times10^{-3}$ | $9.0\times10^{-3}$ |
| 3 | $15.0\times10^{-3}$ | $10.0\times10^{-3}$ | $3.6\times10^{-2}$ |

a) **(2 marks)** Use the initial rates data in the table to determine the observed rate law for this reaction.

b) **(2 marks)** Based on this experimentally observed rate law, does the balanced chemical equation for the reaction accurately summarize the mechanism of the reaction? Explain.

c) **(2 marks)** Calculate the average rate constant for this reaction at 1100 K.

d) **(2 marks)** Calculate the initial rate of this reaction at 1100 K if $[NO]_o = [H_2]_o = 8.0\text{x}10^{-3}$ mol/L.

**# 7. (__/ 11 marks)** Imagine you are preparing a solution of ammonium fluoride, $NH_4F$, in water. The following data may be helpful: $K_b$ of $NH_3 = 1.8\times10^{-5}$ $K_a$ of $HF = 7.2\times10^{-4}$ $K_w = 1\times10^{-14}$

a) **(3 marks)** Write balanced equations to illustrate <u>all</u> chemical processes that occur when $NH_4F_{(s)}$ dissolves in water.

b) **(4 marks)** Will a solution of $NH_4F$ be acidic, basic or neutral? EXPLAIN your conclusion (include any calculations that support your claims).

c) **(4 marks)** Imagine you are preparing a saturated solution of $NH_4F$ using water that already contains some calcium fluoride, $CaF_2$. Will the solubility of $NH_4F$ be higher or lower than it is in pure water? Provide a written explanation of this phenomenon (note: naming the phenomenon is not enough). Include all relevant chemical equations, but do not perform calculations.

**# 8. (__/ 10 marks)** Imagine you have isolated an interesting new compound from a marine organism. You have determined that its formula is $C_{17}H_{21}NO_4$. You are now investigating its acid-base properties.

a) **(1 mark)** You notice that an aqueous solution of this compound turns litmus paper blue, and is therefore weakly basic. Write the chemical equation that illustrates this compound acting as a weak base in aqueous solution.

b) **(3 marks)** A certain aqueous solution of this compound was found to have an osmotic pressure of 52.7 torr at 15°C. What was the total concentration of dissolved particles in this solution?

c) **(6 marks)** The solution analyzed in (b) was found to have a pH of 8.53. What is the compound's $K_b$?
*[If you did not answer part (b), just explain what you would do].*

**# 9. (__/ 10 marks)** This question involves demonstrating and then explaining the nature of buffers.

a) **(2 marks)** Calculate the change in pH that occurs when 10.0 mL of 0.10 M NaOH is added to 90.0 mL of pure water. [$K_w = 1.0 \times 10^{-14}$].

b) **(6 marks)** What is the change in pH that occurs if 10.0 mL of 0.10 M NaOH is added to 90.0 mL of a solution containing 1.0 M $CH_3COOH$ and 1.0 M $CH_3COONa$? [The $K_a$ of $CH_3COOH$ is $1.8 \times 10^{-5}$].

c) **(2 marks)** Briefly explain why the solution in part (b) was able to resist the change in pH whereas water could not.

**# 10. (__/ 8 marks)** People develop kidney stones when insoluble compounds like calcium phosphate, $Ca_3(PO_4)_2$, precipitate out of their urine. [The $K_{sp}$ of calcium phosphate is $1\times10^{-25}$].

a) **(1 mark)** Write a balanced chemical equation for the equilibrium that occurs in a saturated solution of calcium phosphate.

b) **(1 mark)** Write an expression for the $K_{sp}$ of $Ca_3(PO_4)_2$.

c) **(6 marks)** Urine normally contains about 5.33 g/L of $Ca^{2+}$ ions. What concentration of phosphate ions (in molarity) would cause calcium phosphate to begin precipitating from urine? Show calculations AND very briefly explain your answer.

## POTENTIALLY USEFUL INFORMATION

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

1 atm = 760 mm Hg = 760 torr

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

$K_w = 10^{-14}$

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

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

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

$PV = nRT$

$C = k P$

$P = \chi P^o$

$\pi V = nRT$

$\Delta T = K\ m$

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

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

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

$(1/[A]) = kt + (1/[A]_o)$

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

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

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