

COURSE	GENERAL CHEMISTRY II	NUMBER	CHEM 206	SECTION	/2 51
EXAMINATION	Final Examination	DATE	December 18, 2007	TIME	1900-2200
INSTRUCTOR	Dr. Carrie ROGERS				

MATERIALS ALLOWED: NO YES (PLEASE SPECIFY)

CALCULATORS ALLOWED: NO YES programmable calculators must be reset

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 11 pages, including this cover page & a periodic table.**
- **Write your student ID number on all pages.**
- **Write all answers legibly 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 1.5 minutes per mark to have 30 minutes left to check your work.**

Mark breakdown: PLEASE DO NOT WRITE IN THIS SPACE

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Page 3. / 12
Page 4. / 12
Page 5. / 12
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Page 7. / 12
Page 8. / 12
Page 9. / 13

TOTAL: / 100 (MAXIMUM MARK = 103)

1. (18 marks) TRUE OR FALSE? Circle T or F to describe each of these statements.

- T / F** If a gas-forming reaction takes place in an open container, it will eventually reach equilibrium (provided both forward and reverse reactions are thermally accessible).
- T / F** When a reaction with $\Delta n_{\text{gases}} < 0$ takes place at constant pressure, the surroundings perform work on the system.
- T / F** Combustion reactions involve, over all, making products with stronger bonds than those broken in the reactants (based on individual bond strengths and their numbers).
- T / F** Any pair of acids and bases will work as a buffer, as long as they are present in close to a 1:1 ratio in a relatively concentrated solution.
- T / F** The first law of thermodynamics states that the energy of the universe is constant, which means that a system's internal energy change during any process must be zero.
- T / F** When H_2S dissolves in water, hydrogen bonding occurs between the solute molecules and solvent molecules.
- 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 $\text{p}K_{\text{a}}$ of the acid being titrated.
- T / F** A Brønsted base is a type of Lewis base.

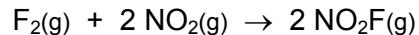
If radioactive waste must be stored until $> 97\%$ of the radioactive species has decayed, then:

- T / F** the storage time must be at least 5x the half-life of the radioactive species at that temperature.

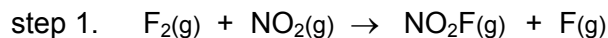
2. (12 marks) For each group of substances, circle the substance with the desired property.

<i>Desired property</i>	<i>Substances to choose from (PURE unless otherwise indicated)</i>	<i>How you decided (briefly!)</i>
Lowest melting point	Cl ₂ Br ₂ I ₂	
Highest heat of vaporization	NH ₃ H ₂ O H ₂ S	
Lowest vapour pressure at 25°C	CH ₄ CH ₃ CH ₃ CH ₃ CH ₂ CH ₃	
Highest osmotic pressure	1M HCl 1M C ₆ H ₁₂ O ₆ 1M NH ₃	
Highest temperature after absorbing 100 kJ of heat	<div style="display: flex; justify-content: space-around;"> <div style="text-align: center;">Ti(s) C_s = 0.52</div> <div style="text-align: center;">Al(s) 0.90</div> <div style="text-align: center;">SiO₂(s) 0.74 J/(g·°C)</div> </div>	
Strongest acid when dissolved in water	<div style="display: flex; justify-content: space-around;"> <div style="text-align: center;">NH₄Cl K_a = 5.6×10⁻¹⁰</div> <div style="text-align: center;">HOCl 3.0×10⁻⁸</div> <div style="text-align: center;">HNO₂ 7.1×10⁻⁴</div> </div>	

3. (8 marks) The rate law for the reaction below has been found by experiment to be $\text{rate} = k [\text{NO}_2] [\text{F}_2]$:



The mechanism of the reaction is believed to consist of the following elementary steps:



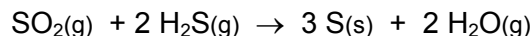
a) **(1 mark)** Write the rate law that would be expected if step 1 is the rate-limiting step.

b) **(5 marks)** Derive the rate law that would be expected if step 2 is the rate-limiting step.

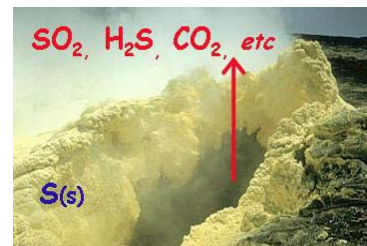
c) **(2 marks)** According to experiment, which step is rate-limiting? How can you tell?

4. (4 marks) Imagine you are a chemist working on developing a catalyst for an industrially important reaction. Will a good catalyst improve the yield of the reaction? Explain.

5. (12 marks) As discussed in class, the following reaction is involved in the formation of elemental sulfur in the vents of active volcanoes:



- a) **(2 marks)** Using logic only, explain whether this reaction is entropically favourable or entropically unfavourable.



- b) **(3 marks)** Confirm your prediction in part (a) with an appropriate calculation (using data in table).

<i>Thermodynamic data for 298 K</i>		
Species	ΔH_f° (kJ·mol ⁻¹)	S_f° (J·mol ⁻¹ ·K ⁻¹)
SO ₂ (g)	-296.8	248.2
H ₂ S(g)	-20.17	205.6
S(s)	0	32.1
H ₂ O(g)	-241.8	188.7

- c) **(5 marks)** Is this reaction spontaneous at 750°C (approximate temperature of the volcanic gases while inside the volcano)? Show calculations to support your answer.

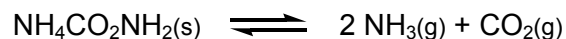
- d) **(2 marks)** Given your answer to part (c), can you explain the deposits of elemental sulfur at the mouth of volcanic vents, where it is much colder?

6. (12 marks) Ice cream is made by freezing a liquid mixture that (as a first approximation) can be considered a solution of sucrose ($C_{12}H_{22}O_{11}$) in water.

- a) **(9 marks)** Estimate the temperature at which the first ice crystals begin to appear in a mix that consists of 34% (by mass) sucrose in water.

- b) **(3 marks)** As ice crystallizes out from this freezing "ice cream", the remaining solution becomes more concentrated. Why does this happen? What happens to the solution's freezing point? Explain briefly.

7. (12 marks) Solid ammonium carbamate, $\text{NH}_4\text{CO}_2\text{NH}_2$, decomposes to ammonia and carbon dioxide when it sublimates:



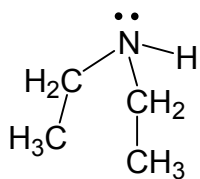
Imagine a sample of ammonium carbamate is allowed to decompose in an evacuated sealed container at 25°C . The decomposition is endothermic, and the K_p at 25°C is 2.3×10^{-4} .

a) **(7 marks)** What is the total pressure in the container at equilibrium?

b) **(5 marks)** Complete the following table about this sample of decomposing ammonium carbamate.

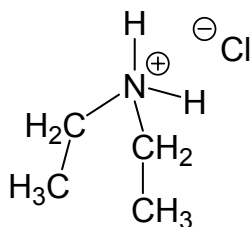
<i>Change imposed on system</i>	<i>Effect on rxn quotient, Q (larger, smaller, no change)</i>	<i>Direction of net reaction needed to reestablish eqm (right, left, or no net change)</i>	<i>Effect on equilibrium constant, K (larger, smaller, no change)</i>
<i>Add some CO_2</i>			
<i>Remove some NH_3</i>			
<i>Raise temperature</i>			
<i>Add some argon</i>			
<i>Increase flask volume</i>			

- # 8. (12 marks)** Diethylamine (shown) is a substance used in insecticides and fungicides. It is 3.9% ionized in a 0.200 M solution of diethylamine at 25°C.



- a) **(7 marks)** Calculate the pK_b of diethylamine.

- b) **(5 marks)** Would a solution of diethylammonium chloride (shown) be acidic, neutral or basic? Explain briefly, and include relevant chemical equations.



- # 9. (13 marks)** Calcium hydrogen phosphate is a component of plant fertilizers (a source of phosphate). It is a relatively insoluble hydrated ionic compound, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, with a K_{sp} of 2.7×10^{-7} at 25°C .
- a) **(2 marks)** Write a balanced equation describing a saturated solution of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, and write the K_{sp} expression.
- b) **(7 marks)** “Hard” water contains relatively high concentrations of dissolved calcium ions. Calculate the solubility (in molarity) of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ at 25°C in hard water that initially contains 95 mg/L of Ca^{2+} .
- c) **(4 marks)** Imagine you will add this fertilizer solution to soil (earth) that is acidic, because there are pine trees growing in the area. How will the low pH affect the solubility equilibrium of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$? Name the “effect” involved, explain briefly, and include relevant chemical equations.

POTENTIALLY USEFUL INFORMATION**Constants:**

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

$$1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr} = 101.325 \text{ kPa}$$

Data:***Properties of liquid water:***

$$bp \text{ (at 1 atm)} = 100.00^\circ\text{C}$$

$$C_{\text{H}_2\text{O}(l)} = 4.184 \text{ J}\cdot\text{g}^{-1}\text{K}^{-1}$$

$$d_{\text{H}_2\text{O}(l)} = 1.00 \text{ g}\cdot\text{mL}^{-1}$$

$$K_f \text{ H}_2\text{O} = 1.86 \text{ }^\circ\text{C}\cdot\text{kg}\cdot\text{mol}^{-1}$$

$$K_b \text{ H}_2\text{O} = 0.52 \text{ }^\circ\text{C}\cdot\text{kg}\cdot\text{mol}^{-1}$$

$$K_w = 10^{-14}$$

Properties of solid water:

$$mp \text{ (at 1 atm)} = 0.00^\circ\text{C}$$

$$C_{\text{H}_2\text{O}(s)} = 2.06 \text{ J}\cdot\text{g}^{-1}\text{K}^{-1}$$

$$d_{\text{H}_2\text{O}(s)} = 0.917 \text{ g}\cdot\text{mL}^{-1}$$

Formulae:

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

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

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

$$PV = nRT$$

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

$$P = \chi P^\circ$$

$$\Delta T = K m$$

$$\pi V = nRT$$

$$k_t = A e^{(-E_a/RT)}$$

$$[A]_t = -k_t t + [A]_o$$

$$\ln[A]_t = -k_t t + \ln[A]_o$$

$$1/[A]_t = k_t t + 1/[A]_o$$

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

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Periodic Table of the Elements

1 H 1.008																	2 He 4.00
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (97.91)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	La-Lu	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po 208.98	85 At 209.99	86 Rn 222.02
87 Fr 223	88 Ra 226.03	Ac-Lr	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)									

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.35	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
89 Ac 227.03	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (245)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Electronegativity Values of the Elements

H 2.1																	He
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
Cs 0.7	Ba 0.9	La-Lu	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2	Rn