DAWSON COLLEGE

DEPARTMENT OF CHEMISTRY & CHEMICAL TECHNOLOGY

FINAL EXAMINATION CHEMISTRY 202-NYB-05
May 18, 2012
14:00 – 17:00

Print your Name: _____

Student Number: _____

INSTRUCTORS: ***Please circle the name of your instructor:***

J. Ali	D. Baril	Y. Brouillette
I. Dionne	M. Di Stefano	M. Haniff
	S. Mutic	G. Rahil

INSTRUCTIONS:

This exam set consists of **16** questions. Please ensure that your copy of this examination is complete.

Answer all questions in the space provided.

1. Calculators may not be shared. Programmable calculators are not permitted.
2. No books or extra paper are permitted.
3. In order to obtain full credit, you must show the method used to solve all problems involving calculations and express your answers to the correct number of significant figures.
4. Your attention is drawn to the College policy on cheating.
5. A Periodic Table with constants is provided.
6. If a mathematical equation is used to solve a problem, the equation should be clearly written.

USEFUL DATA:

Avogadro's Number $N_A = 6.022 \times 10^{23}\ mol^{-1}$

Gas Constant $R = 0.08206\ L{\cdot}atm{\cdot}K^{-1}{\cdot}mol^{-1}$

$= 8.314\ L{\cdot}kPa{\cdot}K^{-1}{\cdot}mol^{-1}$

$= 8.314\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

1 atm = 101.3 kPa = 760 mmHg = 760 torr

$1\ J = 1\ kg{\cdot}m^2{\cdot}s^{-2} = 1\ kPa{\cdot}L$

$101.3\ J = 1\ L{\cdot}atm$

MARK DISTRIBUTION

1.	/	8
2.	/	5
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4.	/	5
5.	/	9
6.	/	6
7.	/	8
8.	/	3
9.	/	6
10.	/	6
11.	/	6
12.	/	9
13.	/	6
14.	/	7
15.	/	5
16.	/	4
Sig. fig.	/	1
Total:	**/**	**100**

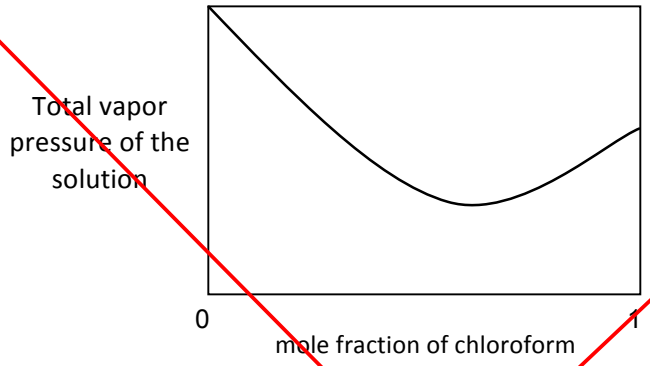
Question 1

a. A 1.00 L concentrated KOH solution contains 655 g KOH. The solution density is 1.456 g/mL. Calculate the molality (*m*) of this solution. *(4 marks)*

b. You are asked to prepare an aqueous solution of ethylene glycol ($HOCH_2CH_2OH$) with a mole fraction of 0.095. If you use 545 g of water, what mass of ethylene glycol should you use? *(4 marks)*

Question 2

a. The following plot shows the vapor pressure of various solutions of chloroform and acetone at some temperature.



Indicate whether the following statements are true or false: *(2.5 marks)*

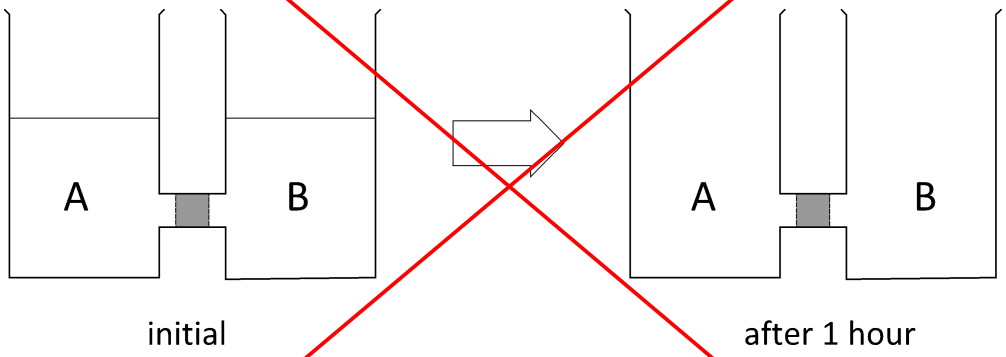
		True	False
i.	The solution exhibits negative deviation from Raoult's law.	☐	☐
ii.	ΔH for mixing this solution is endothermic.	☐	☐
iii.	The intermolecular forces between chloroform and acetone are weaker in solution than in either pure chloroform or pure acetone.	☐	☐
iv.	Pure chloroform has a higher vapor pressure than pure acetone.	☐	☐
v.	The solution with a mole fraction of chloroform of 0.6 will have a lower boiling point than either pure chloroform or pure acetone.	☐	☐

b. The vapor pressure of a solution containing 53.6 g glycerin ($C_3H_8O_3$, 92.10 g/mol nonvolatile, covalent compound) in 133.7 g ethanol (C_2H_5OH, 46.07 g/mol) is 113 torr at 40°C. Calculate the vapor pressure of pure ethanol at 40°C. Assume ideal behavior. *(2.5 marks)*

answer:_____

Question 3

a. A solution called A is prepared by dissolving 56.75 g glucose, $C_6H_{12}O_6$, (180.15 g/mol, a soluble non ionic solid) in enough distilled water to make 1.00 L solution at room temperature (25°C). This solution is isotonic with human blood (same osmotic pressure) and placed in part A of the container. A sodium chloride aqueous solution, called B, with an osmotic pressure of 6.0 atm is added to part B. Both parts are separated by a semi permeable membrane (only water molecule can pass). Draw on the container "after 1 hour" the level of the two liquids in both sides when the equilibrium will be reached. Assume NaCl is 100% dissociated. *(3 marks)*



b. A red blood cell is actually a small "container" made up of a semipermeable membrane. What would happen to the volume of the red blood cell if it is submerged in: *(1 mark)*

	bigger	no change	smaller
i. solution A at 10°C (assume red blood cell to be at 25°C)	☐	☐	☐
ii. solution B at 25°C	☐	☐	☐

c. Consider the following aqueous solutions of salts completely ionized:
   i. 4 *m* potassium Iodite, KI
   ii. 3 *m* sodium sulfate, Na_2SO_4
   iii. 3.5 *m* ammonium phosphate $(NH_4)_3PO_4$

List the given solutions in increasing order of freezing point: *(2 marks)*

_____ < _____ < _____

lowest freezing point *highest freezing point*

Question 4

a. For the following reaction, *(1 marks)*

$$2HgC\ell_2(aq) + C_2O_4^{2-}(aq) \longrightarrow 2C\ell^-(aq) + 2CO_2(g) + Hg_2C\ell_2(s)$$

if the rate of disappearance (or consumption) of $C_2O_4^{2-}$ is $5.6x10^{-5}$ M/min what is the rate of formation of $C\ell^-$?

answer :_____

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b. The initial rate for the reaction, *(4 marks)*

$$2A + 2B \longrightarrow C + D$$

was measured using initial concentrations of A and B. The results are summarized in the table:

Experiment	[A], M	[B], M	Initial rate, $M \cdot s^{-1}$
1	0.185	0.133	$3.35x10^{-4}$
2	0.185	0.266	$1.35x10^{-3}$
3	0.370	0.133	$6.75x10^{-4}$

i. Write the rate law.

answer :_____

ii. What is the overall reaction order? answer :_____

iii. What is the value of the rate constant, with units, for experiment 3?

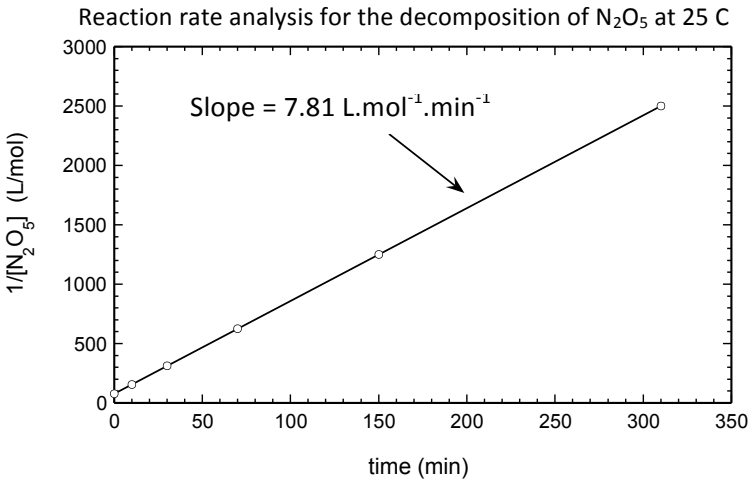
answer :_____

Question 5

a. For the reaction: *(5 marks)*

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

the following graph was made:



i. What order is the rate law for this reaction? answer :_____

ii. What is the half-life of this reaction if the initial concentration is 1.28×10^{-2} M?

answer :_____

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b. For the same reaction: $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$, a catalyst was introduced. Measurements showed the rate of reaction was directly proportional to the concentration of N_2O_5 with a rate constant of 0.055 min^{-1} at 25°C. *(4 marks)*

i. What order is the rate law for this catalyzed reaction? answer :_____

ii. Calculate the time that it will take for the $[N_2O_5]$ to fall from 1.28×10^{-2} M to 0.32×10^{-2} M with the catalyst at 25°C.

answer i. order:_____ answer ii. time with catalyst:_____

Question 6

a. Consider this two-step mechanism for a reaction *(3 marks)*

$NO_2(g) + C\ell_2(g) \longrightarrow C\ell NO_2(g) + C\ell(g)$ (slow)

$NO_2(g) + C\ell(g) \longrightarrow C\ell NO_2(g)$ (fast)

i. What is the overall reaction?

ii. Identify the intermediates in the mechanism (if any)

iii. What is the predicted rate law?

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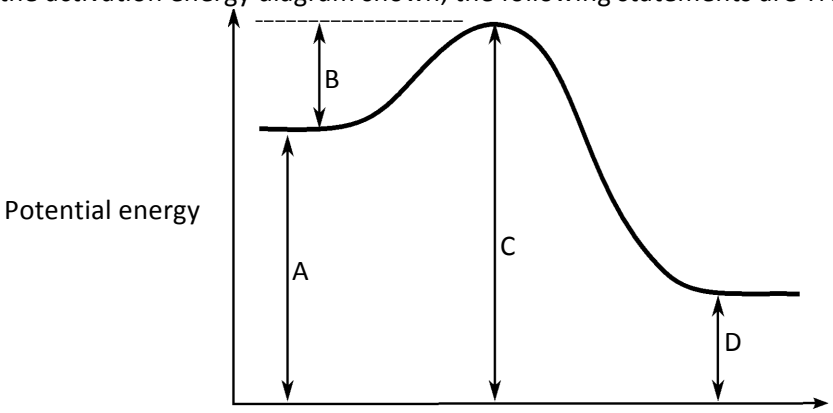
b. For the activation energy diagram shown, the following statements are True or False? *(3 marks)*



		True	False
i.	ΔE reaction = A – D	☐	☐
ii.	The reaction is exothermic	☐	☐
iii.	D represents the energy of the products	☐	☐
iv	E_a (forward) = C – A	☐	☐
v.	E_a (forward) > E_a (reverse)	☐	☐
vi.	B represents the energy of the transition state.	☐	☐

Question 7

a. Dinitrogen trioxide decomposes to nitrogen monoxide and oxygen gas in a rigid container at 300°C by the reaction written below. At equilibrium, the concentrations are $[N_2O_3] = 4.36$ M, $[NO] = 7.27$ M and $[O_2] = 1.82$ M. *(5 marks)*

$$2N_2O_3(g) \rightleftharpoons 4NO(g) + O_2(g)$$

i. For this reaction, calculate K_c

answer K_c :_____

ii. Calculate K_p

answer K_p:_____

iii. If only $N_2O_3(g)$ was initially present, what was its starting concentration?
[Hint: the equilibrium concentrations are given in part a.]

answer $[N_2O_3(g)]_o$:_____

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b. Given the equilibrium constants for the following reactions: *(3 marks)*

$$N_2(g) + \tfrac{1}{2} O_2(g) \rightleftharpoons N_2O(g) \qquad K_1 = 2.7\times10^{-18}$$

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \qquad K_2 = 4.6\times10^{-3}$$

$$\tfrac{1}{2} N_2(g) + O_2(g) \rightleftharpoons NO_2(g) \qquad K_3 = 4.1\times10^{-9}$$

Calculate the value of K for the following reaction.

$$2N_2O(g) + 3O_2(g) \rightleftharpoons 2N_2O_4(g)$$

answer :_____

Question 8

Consider the following exothermic reaction at equilibrium:

$$2C_4H_{10}(g) + 13O_2(g) \rightleftharpoons 8CO_2(g) + 10H_2O(g)$$

Predict the effect of each of the following on the equilibrium position of this system: *(3 marks)*

		shift of the equilibrium		
		to the left	no change	to the right
a.	The mixture is cooled and water vapour condenses	☐	☐	☐
b.	More $C_4H_{10}(g)$ is added	☐	☐	☐
c.	The volume of the container is increased	☐	☐	☐
d.	He gas is added to increase the total pressure	☐	☐	☐
e.	The temperature is increased	☐	☐	☐
f.	A catalyst is added	☐	☐	☐

Question 9

a. A solution is made by diluting 25.0 mL of concentrated HCℓ (stock solution) to exactly 500. mL. If this diluted solution has a pH of 0.222, calculate the molarity of HCℓ in the stock solution. *(3 marks)*

answer :_____

b. If a 0.0100 M solution of caproic acid, a monoprotic acid thought to be at least partially responsible for the unique (and generally considered foul) smell of goats, has a pH of 3.43, calculate K_a and pK_a for caproic acid. *(3 marks)*

answers : K_a _____ pK_a _____

Question 10

a. Are the aqueous solutions of the following salts acidic, basic or neutral? *(3 marks)*

		basic	neutral	acid
i.	$NaNO_2$	☐	☐	☐
ii.	$CsCl$	☐	☐	☐
iii.	$NaClO_3$	☐	☐	☐
iv.	NH_4I	☐	☐	☐
v.	KF	☐	☐	☐
vi.	Li_2SO_4	☐	☐	☐

b. At 25°C, a 250.0 mL solution has 0.814 g KCN. Calculate the pH of this solution. *(3 marks)*

answer :_____

Question 11

a. Which of the following combinations can be used to prepare a buffer? *(2.5 marks)*

		buffer	not buffer
i.	HF/KF	☐	☐
ii.	HBr/LiBr	☐	☐
iii.	HCN/NaCN	☐	☐
iv.	$Ca(OH)_2/CaBr_2$	☐	☐
v.	H_2O/oil	☐	☐

b. Calculate the pH of a solution that is 0.50 M HF and 1.00 M NaF. *(2 marks)*

answer :_____

c. Calculate the ratio $[NH_3]/[NH_4^+]$ in ammonia/ammonium chloride buffered solution with a pH of 9.50. *(1.5 marks)*

answer :_____

Question 12

A 50.0 mL aliquot of 0.300 M nitrous acid (HNO_2) is titrated with 0.500 M $Ba(OH)_2$

a. Calculate the pH of the solution after the addition of 5.00 mL of $Ba(OH)_2$ *(4 marks)*

answer :_____

b. Calculate the volume of $Ba(OH)_2$ needed to reach the equivalence point *(2 marks)*

answer :_____

c. What is the pH of the solution at equivalence point? *(3 marks)*

answer :_____

Question 13

a. A 10.00 mL aliquot of a saturated solution of barium hydroxide, $Ba(OH)_2$, requires 25.9 mL of 0.0833 M HCℓ to titrate it to the equivalence point. Calculate K_{sp} for $Ba(OH)_2$. *(3 marks)*

answer :_____

b. Calculate the solubility of $Ca(OH)_2$ in a 0.200 M NaOH solution. K_{sp} $Ca(OH)_2$: 5.0×10^{-6}. *(3 marks)*

answer :_____

Question 14

a. For a particular reaction, $\Delta H = -32$ kJ and $\Delta S = -98$ J/K. Assume that ΔH and ΔS do not vary with temperature. *(3 marks)*

i. At what temperature will the reaction occur spontaneously?

answer :_____

ii. If the temperature is increased from that in part (i), will the reaction be spontaneous or nonspontaneous?

answer :_____

c. Using the data in the table below determine whether iron(III) oxide can be reduced by carbon at 25°C. *(4 marks)*

$$Fe_2O_3(s) + 3C(s, \text{graphite}) \longrightarrow 2Fe(s) + 3CO(g)$$

Compounds	ΔH_f^o (kJ·mol^{-1})	S^o(J·mol^{-1}·K^{-1})
$Fe_2O_3(s)$	-824	87.4
C(s, graphite)	0	5.8
Fe(s)	0	27.3
CO(g)	-110.5	198

answer :_____

Question 15

The standard molar free energies of formation of $NO_2(g)$ and $N_2O_4(g)$ at 25°C are 51.840 kJ/mol and 98.085 kJ/mol, respectively.

a. What is the value of the standard molar free energy of formation (ΔG°) in Joules for the reaction written as follows at 25°C? *(2 marks)*

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

answer :_____

b. What is the value of K_p (in atm) for the same reaction at 25°C? *(3 marks)*

answer :_____

Question 16

Laboratory: Colligative properties *(4 marks)*

Objective: to find the molar mass of phenanthrene.

In this experiment, the freezing point of two substances will be measured:
Part 1. Pure cyclohexane, C_6H_{12} (solvent) K_f = 20.2 kg.°C.mol^{-1}.
Part 2. A solution of phenanthrene, a non volatile covalent compound, dissolved in cyclohexane.

The molar mass of phenanthrene will be obtained from the freezing point depression

Data sheet.

PART 1

a. Mass of the empty test tube with stopper: 131.7552 g
b. Mass of the test tube with stopper and 25.0 mL cyclohexane: 150.6133 g
c. Freezing point of pure cyclohexane: 6.348°C

PART 2

The same solution from part 1 is used for part 2

d. Mass of the test tube with stopper, cyclohexane and phenanthrene: 151.3124 g
e. Freezing point of the cyclohexane + phenanthrene solution: 2.141°C

Calculations:

Molar mass of phenanthrene: _____

Periodic Table of the Elements

	1A												3A	4A	5A	6A	7A	8A
1	1 **H** 1.008	2A																2 **He** 4.003
2	3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
3	11 **Na** 22.99	12 **Mg** 24.31	3B	4B	5B	6B	7B	8B	9B	10B	1B	2B	13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
4	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
5	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** 98.00	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
6	55 **Cs** 132.9	56 **Ba** 137.3	57 **La*** 138.9	72 **Hf** 178.5	73 **Ta** 181.0	74 **W** 183.8	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** 209.0	85 **At** 210.0	86 **Rn** 222.0
7	87 **Fr** 223.0	88 **Ra** 226.0	89 **Ac**[a] 227.0	104 **Rf** 261.0	105 **Db** 262.0	106 **Sg** 263.0	107 **Bh** 262.0	108 **Hs** 265.0	109 **Mt** 266.0	110 **Uun** 269.0	111 **Uuu** 272.0	112 **Uub** 277.0						

6 **C** 12.01 — atomic number, symbol, atomic mass

= metalloid

*Lanthanides	58 **Ce** 140	59 **Pr** 141	60 **Nd** 144	61 **Pm** 145	62 **Sm** 150	63 **Eu** 152	64 **Gd** 157	65 **Tb** 159	66 **Dy** 163	67 **Ho** 165	68 **Er** 167	69 **Tm** 169	70 **Yb** 173	71 **Lu** 175
[a]Actinides	90 **Th** 232	91 **Pa** 231	92 **U** 238	93 **Np** 237.1	94 **Pu** 244	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

Dissociation constants (all values are at 25°C)

compound	formula	K_a
hydrogen sulfate ion	HSO_4^-	1.2×10^{-2} (K_{a2})
hydrofluoric acid	HF	7.2×10^{-4}
nitrous acid	HNO_2	4.0×10^{-4}
formic acid	HCOOH	1.8×10^{-4}
benzoic acid	C_6H_5COOH	6.5×10^{-5}
acetic acid	CH_3COOH	1.8×10^{-5}
propanonic acid	C_2H_5COOH	1.3×10^{-5}
hypochlorous acid	HClO	2.9×10^{-8}
hydrocyanic acid	HCN	4.9×10^{-10}
phenol	HOC_6H_5	1.6×10^{-10}

compound	formula	K_b
ethylamine	$C_2H_5NH_2$	5.6×10^{-4}
methylamine	CH_3NH_2	4.4×10^{-4}
trimethylamine	$(CH_3)_3N$	6.4×10^{-5}
ammonia	NH_3	1.77×10^{-5}
pyridine	C_5H_5N	1.7×10^{-9}
aniline	$C_6H_5NH_2$	3.8×10^{-10}

compound	formula	K_w
water	H_2O	1.0×10^{-14}

Conversions: $R = 8.314\ L.kPa.K^{-1}.mol^{-1} = 8.314\ J.K^{-1}.mol^{-1} = 0.08206\ L.atm.K^{-1}.mol^{-1}$

1 atm = 101.3 kPa = 760.0 mmHg or torr.

K = 273.15 + °C