DAWSON COLLEGE

DEPARTMENT OF CHEMISTRY & CHEMICAL TECHNOLOGY

FINAL EXAMINATION CHEMISTRY 202-NYB-05
May 20, 2011
9:30 – 12:30

Print your Name: _____

Student Number: _____

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

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INSTRUCTIONS:

This exam set consists of **17** 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 is provided.
6. If a mathematical equation is used to solve a problem, the equation should be clearly written.
7. Write your answer in the appropriate box when required

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

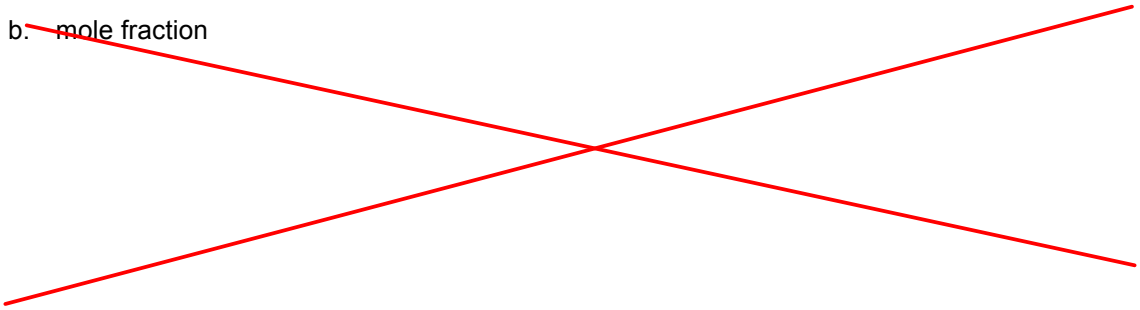
1.	/ 8
2.	/ 6
3.	/ 6
4.	/ 4
5.	/ 5
6.	/ 4
7.	/ 4
8.	/ 7
9.	/ 5
10.	/ 6
11.	/ 6
12.	/ 6
13.	/ 7
14.	/ 7
15.	/ 6
16.	/ 6
17.	/ 6
Significant Figures	/ 1
TOTAL	**/100**

Question 1 (8 marks)

To make an antifreeze solution, 40.0 mL of ethylene glycol ($C_2H_6O_2$, density: 1.08 $g \cdot mL^{-1}$) is added to 60.0 mL water (density: 1.00 $g \cdot mL^{-1}$). Assume ideal behavior for this solution (volumes are addititive). Calculate:

a. the mass percent of ethylene glycol

b. mole fraction



c. molality

d. molarity

ans. a:	*ans. b:*	*ans. c:*	*ans. d:*

Question 2

At 25°C Henry's Law constant for oxygen in water is 1.3×10^{-3} mol·L^{-1}·atm^{-1}.

a. If the partial pressure of oxygen in the atmosphere at sea level is 159 mmHg calculate the molar solubility (concentration) of oxygen in water at 25°C. (2 marks)

Ans. a:

b. When water is cooled the solubility of oxygen in water increases. Is the enthalpy of hydration of oxygen positive or negative? Explain your answer. (1 mark)

c. The vapor pressure of pure liquid benzene (C_6H_6, 78.11 g/mol) at 75°C is 640.0 torr. A solution made of 20.21 g anthracene in 117.2 g benzene has a vapor pressure of 595.0 torr at 75°C. (anthracene is a non ionic and non volatile solid). Calculate the molar mass of anthracene (3 marks)

Ans. c:

Question 3

a. What mass of ethylene glycol (non electrolyte) must be added to 1525 g of water at 1.000 atm to raise the boiling point to 103.9°C? The molal boiling point elevation constant of water is 0.52°C/*m* and the molar mass of ethylene glycol ($C_2H_6O_2$) is 62.07 g/mol. (2 marks)

Ans. a:

b. Arrange the following aqueous solutions in order of increasing boiling point: (2 marks)

i. 0.10 *m* Na_3PO_4
ii. 0.20 *m* $MgCl_2$
iii. 0.15 *m* $C_6H_{12}O_6$ (sugar)
iv. 0.15 *m* HNO_2 (weak acid)

lowest boiling point			*highest boiling point*

c. How will the following compounds change the percent dissociation of nitrous acid (HNO_2) when added to an aqueous solution of HNO_2 at equilibrium? (2 marks)

		decrease in % dissociation	no change	increase in % dissociation
i.	$Ca(NO_2)_2$	☐	☐	☐
ii.	HNO_3	☐	☐	☐
iii.	$NaNO_3$	☐	☐	☐
iv.	H_2O	☐	☐	☐

Question 4

3.70 g of calcium bromide ($CaBr_2$ mol. mass: 199.9 $g \cdot mol^{-1}$) is added to water to make a total of 100.0 mL $CaBr_2$ aqueous solution. The osmotic pressure of this solution is determined to be 10.3 atm at 25.0°C.

a. Calculate the actual van't Hoff factor *i* for this aqueous calcium bromide solution. (3 marks)

Ans. a:

b. What is the theoretical value of *i* for calcium bromide? (1 mark)

Ans. b:

Question 5

a. The balanced equation for the reaction of bromate ion with bromide ion in acidic solution is given by:

$$BrO_3^- + 5\ Br^- + 6\ H^+ \longrightarrow 3\ Br_2 + 3\ H_2O$$

At a particular instant in time, the value of $-\frac{\Delta[Br^-]}{\Delta t}$ is 2.9×10^{-3} mol·L^{-1}·s^{-1}

What is the value of $\frac{\Delta[Br_2]}{\Delta t}$ in the same units? : (1 mark)

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b. The reaction between nitric oxide (NO) and hydrogen (H_2) was studied at a constant temperature,

$$2\ NO(g) + H_2(g) \longrightarrow N_2O(g) + H_2O(g)$$

and the following results were obtained:

experiment	Initial [NO], *M*	Initial [H_2], *M*	Initial rate of NO consumption mol·L^{-1}·s^{-1}
1	6.4×10^{-3}	2.2×10^{-3}	3.0×10^{-5}
2	12.8×10^{-3}	2.2×10^{-3}	1.2×10^{-4}
3	6.4×10^{-3}	4.5×10^{-3}	6.1×10^{-5}
4	12.8×10^{-3}	4.5×10^{-3}	?

What is the rate law for this reaction? (2 marks)

c. Calculate the rate constant for this reaction, with the appropriate units. (1 mark)

d. What will the initial rate (in mol·L^{-1}·s^{-1}) be in experiment 4? (1 mark)

ans. b:	*ans. c:*	*ans. d:*

Question 6

The decomposition of hydrogen iodide follows the equation,

$$2\ HI(g) \longrightarrow H_2(g) + I_2(g)$$

The reaction is second order and has a rate constant equal to $1.60 \times 10^{-3}\ L \cdot mol^{-1} \cdot s^{-1}$ at 700°C.

a. If the initial concentration of HI in a container is 3.40×10^{-2} *M*, how many minutes will it take for the concentration to be reduced to 75.0 % of its initial value at 700°C? (2 marks)

b. What is the half–life, in minutes, for the reaction at 700°C? (2 marks)

ans. a:	*ans. b:*

Question 7 (4 marks)

A two step mechanism has been suggested for the reaction of nitric oxide with bromine:

(1) $NO(g) + Br_2(g) \longrightarrow NOBr_2(g)$

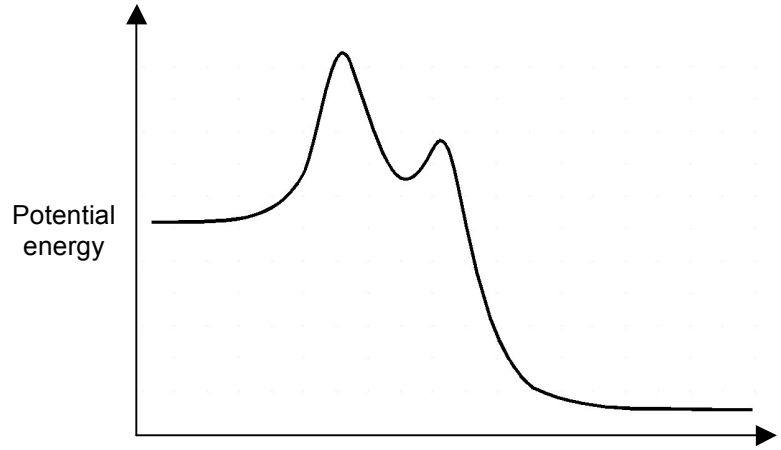
(2) $NOBr_2(g) + NO(g) \longrightarrow 2\ NOBr(g)$

a. Write the overall reaction

b. What is the role of $NOBr_2$ in this reaction?

c. Based on the proposed mechanism and the energy profile of the reaction shown below, write the rate law for this reaction?

Energy profile of the reaction



d. Write on the energy profile of the reaction the position of the chemicals: Br_2, $NOBr_2$, NOBr.

Question 8

2.0 mol of C(s) and 3.0 mol of $CO_2(g)$ were initially placed in a 6.0 L container and heated to 100°C and allowed to reach equilibrium according to the following equation.

$$C(s) + CO_2(g) \rightleftharpoons 2\,CO(g)$$

Analysis of the contents of the container at 100°C determined that 0.50 mol of C(s) remained.

a. Calculate the value of the equilibrium constant K (or K_c) for this reaction at 100°C. (2 marks)

ans. a:

b. If the initial amount of $CO_2(g)$ added to the equilibrium above was doubled to 6.0 mol instead of 3.0 mol, how would the value of K change at 100°C? (circle one answer) (1 mark)

i. Increase ii. Decrease iii. Stay the same iv. Not enough information to say

Question 8, continue on the next page…

Question 8 (Cont.)

$$C(s) + CO_2(g) \rightleftharpoons 2\,CO(g)$$

c. If the value of K for the reaction is 0.050 at 25°C, what is the value of the equilibrium constant in terms of partial pressures, K_p, at 25°C ? (2 marks)

ans. c:

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d. Find the value for the pressure equilibrium constant, K_p, at 25°C for the equilibrium (2 marks)

$$2\,H_2O(g) + O_2(g) \rightleftharpoons 2\,H_2O_2(g)$$

from the following information.

i. $H_2(g) + O_2(g) \rightleftharpoons H_2O_2(g)$ $\quad K_{p,1} = 1.0 \times 10^{6}$ at 25°C

ii. $H_2(g) + \frac{1}{2}\,O_2(g) \rightleftharpoons H_2O(g)$ $\quad K_{p,2} = 1.8 \times 10^{37}$ at 25°C

ans. d:

Question 9

Select from the equilibria (i to v) at 25°C below the one that best fits the statements in a. to d. (2 marks)

i. $H_2(g) + O_2(g) \rightleftharpoons H_2O_2(g)$ $K_{p,1} = 1.0 \times 10^{6}$

ii. $H_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons H_2O(g)$ $K_{p,2} = 1.8 \times 10^{37}$

iii. $Cl_2(g) + H_2(g) \rightleftharpoons 2\ HCl(g)$ $K_{p,3} = 3.4 \times 10^{2}$

iv. $2\ NOCl_2(g) \rightleftharpoons 2\ NO(g) + Cl_2(g)$ $K_{p,4} = 4.0 \times 10^{-1}$

v. $C(s) + CO_2(g) \rightleftharpoons 2\ CO(g)$ $K_{p,5} = 9.9 \times 10^{-10}$

a. The equilibrium that would be considered "going to completion". Answer:_____

b. The equilibrium that lies furtherest "to the left". Answer:_____

c. The equilibrium whose K_c equals its K_p. Answer:_____

d. The heterogeneous equilibrium. Answer:_____

Consider the following chemical equation:

$$CO(g) + Fe_3O_4(s) \rightleftharpoons CO_2(g) + 3\ FeO(s) \quad \Delta H° = +18\ kJ$$

How does the equilibrium position shift as a result of each of the following disturbance? (3 marks)

	shift of the equilibrium		
	to the left	no change	to the right
e. $CO(g)$ is added.	☐	☐	☐
f. $CO_2(g)$ is removed by adding solid NaOH	☐	☐	☐
g. Additional $Fe_3O_4(s)$ is added to the system	☐	☐	☐
h. Increasing the volume of the container	☐	☐	☐
i. Add a catalyst	☐	☐	☐
j. Increase temperature (while keeping pressure constant)	☐	☐	☐

Question 10 (6 marks)

What is the pH of the following aqueous solutions at 25°C (Show calculation and circle your choice)?

a. 0.012 *M* HBr
   i. 0.012
   ii. 1.92
   iii. 7.00
   iv. 12.08
   v. None of the above

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b. 0.030 *M* HOBr. K_a for HOBr is 2.0×10^{-9}
   i. 1.52
   ii. 4.35
   iii. 9.22
   iv. 9.39
   v. None of the above

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c. 0.021 *M* NaOBr K_a for HOBr is 2.0×10^{-9}
   i. 3.49
   ii. 5.19
   iii. 7.00
   iv. 8.81
   v. 10.51

Question 11

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

		basic	neutral	acid
i.	$CsNO_2$	☐	☐	☐
ii.	NaF	☐	☐	☐
iii.	KOI	☐	☐	☐
iv.	NH_4Br	☐	☐	☐
v.	CsCl	☐	☐	☐
vi.	Li_2SO_4	☐	☐	☐

b. At 25°C, a 250.0 mL KCN solution has a pH of 11.00. Calculate the initial molarity of KCN in this solution. (K_a HCN = 4.9×10^{-10} at 25°C, mol. mass KCN = 65.12 $g.mol^{-1}$) (3 marks)

Ans. b:

Question 12

a. Which of the following combinations can be used to prepare a buffer? (2 marks)

		buffer	not buffer
i.	HCl / Cl^-	☐	☐
ii.	NH_4^+ / H^+	☐	☐
iii.	HNO_2 / NO_2^-	☐	☐
iv.	HNO_3 / NO_3^-	☐	☐

b. Consider 1.0 L of a solution that is 0.85 *M* formic acid (HCOOH, $K_a = 1.7 \times 10^{-4}$) and 1.4 *M* sodium formate (HCOONa). What is the pH of this solution? (2 marks)

c. Calculate the pH of the solution in 12b above after the addition of 0.15 mol HCl. Assume the addition causes no volume change. (2 marks)

ans. b:	*ans. c:*

Question 13

A 30.0 mL sample of 0.150 mol/L HOCl solution was titrated with 0.300 mol/L KOH solution at 25°C. (K_a for HOCl is 3.5×10^{-8}).

a. What volume of KOH is needed to reach the equivalence point? (1 mark)

b. Calculate the pH of the solution in the flask at the equivalence point. (3 marks)

c. Calculate the pH in the flask upon the addition of 45.0 ml of KOH solution. (3 marks)

ans. a:	*ans. b:*	*ans. c:*

Question 14

Sodium chloride is added slowly to a solution that is 0.010 *M* in Cu^{+}, Ag^{+}, and Au^{+}. (1 mark)

a. Which compound will precipitate first? (circle one answer)
K_{sp} CuCl: 1.9×10^{-7}, AgCl: 1.6×10^{-10}, AuCl: 2.0×10^{-13}

i. CuCl
ii. AgCl
iii. AuCl
iv. All will precipitate at the same time.
v. Cannot be determined.

A solution is prepared by mixing 100.0 mL of 0.0400 *M* $ZnCl_2$ and 300.0 mL of 0.020 *M* NaOH.

b. Does precipitation occur? Show your calculations. (K_{sp} of $Zn(OH)_2 = 4.5 \times 10^{-17}$). (2 marks)

c. Calculate the concentration of Zn^{2+} at equilibrium with solid $Zn(OH)_2$. (3 marks)

ans. c:

d. How does the concentration of Zn^{2+} vary if the pH is increased (more basic conditions)? (1 mark)

☐ increases ☐ decreases ☐ does not change ☐ can not tell

Question 15

A balloon is filled with 8.00 g helium early in the morning at 15.0°C and 1.00 atm. It is then transported down south where the temperature increased to 30.0°C at 1.00 atm.

a. Assuming He behaves like an ideal gas, calculate the initial and final volumes. (2 marks)

initial V:	*final V:*

b. Calculate the work (*w*) done by the ballon (in J). (1 mark)

c. Calculate the heat (*q*) transferred (in J) assuming a specific heat capacity of 5.33 $J \cdot K^{-1} \cdot g^{-1}$ for He at P = 1.00 atm. (2 marks)

d. Calculate the change in internal energy, ΔE (in J). (1 mark)

w =	*q* =	*ΔE* =

Question 16

The fermentation of glucose ($C_6H_{12}O_6$) from corn yields ethanol (C_2H_5OH) which can then be used in automobile fuel.

$$C_6H_{12}O_6(s) \longrightarrow 2\ C_2H_5OH(\ell) + 2\ CO_2(g)$$

a. Calculate $\Delta H°$, $\Delta S°$, and $\Delta G°$ for the reaction at 25°C using the data in the table below. (3 marks)

Substance	ΔH_f° (kJ mol^{-1})	$S°$ (J K^{-1} mol^{-1})
$C_6H_{12}O_6(s)$	– 1275	212
$C_2H_5OH(\ell)$	– 278	161
$CO_2(g)$	– 393.5	214

$\Delta H° =$	$\Delta S° =$	$\Delta G° =$

b. Is the spontaneity of the reaction dependent on temperature? Explain. (1 mark)

c. Consider the Haber-Bosch process for synthesizing ammonia: (2 marks)

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$$

Knowing that ΔG_f° of $NH_3(g)$ is –16.5 kJ·mol^{-1}, calculate its equilibrium constant at 25°C

$K =$

Question 17 (6 marks)

Having studied a similar reaction during the semester you are asked to determine the nature of the rate law for the main reaction below.

$$H_2O_2(aq) + 2\,I^-(aq) + 2\,H^+(aq) \longrightarrow I_2(aq) + 2\,H_2O(\ell)$$

To monitor the main reaction, very small quantities of thiosulphate ($S_2O_3^{2-}$) and starch were also included in the reaction flask. *Thiosulphate and starch react at a much faster rate than the main reaction according to the following equations*:

$$2\,S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

$$\text{Starch} + I_2(aq) \longrightarrow \text{Starch–}I_2\text{(a blue product)}$$

a. Complete the equations below to show how the rates of each reaction compare to each other during the reaction.

$$\text{Rate} = -\frac{\Delta[H_2O_2]}{\Delta t} = \underset{\textit{answer}}{\ldots\ldots}\,\frac{\Delta[I^-]}{\Delta t} = \underset{\textit{answer}}{\ldots\ldots}\,\frac{\Delta[S_2O_3^{2-}]}{\Delta t}$$

The following solutions were used to prepare 2 flasks.

Flask 1
20 mL of 0.10 *M* KI
and
10 mL of 0.00050 *M* $Na_2S_2O_3$

Flask 2
20 mL of 0.10 *M* H_2O_2
and
10 mL of 0.30 *M* H_2SO_4
and
3 drops of Starch Solution

When Flask 1 and Flask 2 were combined it was found that it took 21 s for the solution to turn a dark blue colour.

b. Calculate the rate of the reaction $-\frac{\Delta[H_2O_2]}{\Delta t}$ for the example shown.

Hint: thiosulphate is used to monitor the main reaction rate

Question 17, continue on the next page…

Question 17 (Cont.)

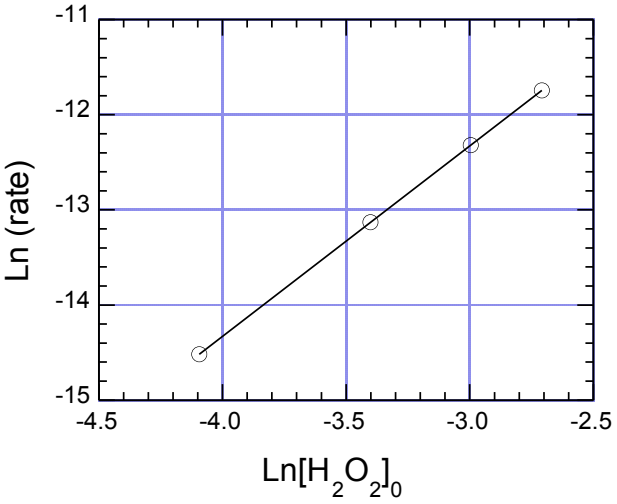
The results of a series of reactions are shown below. For each graph the reactant in the title had its initial concentration changed and the others kept constant.

c. Write the differential rate law (or rate law) for the reaction.

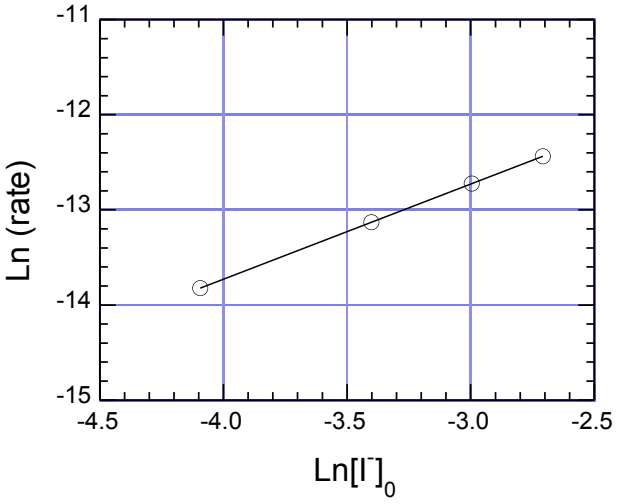
$$\text{Rate} = -\frac{\Delta[H_2O_2]}{\Delta t} = k \text{ .....}$$

answer

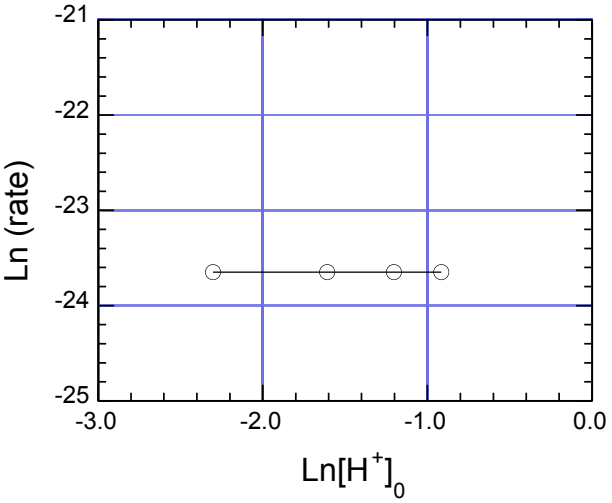
Dependence of the reaction rate on $[H_2O_2]_o$ concentration



Dependence of the reaction rate on $[I^-]_o$ concentration



Dependence of the reaction rate on $[H^+]_o$ concentration



d. Determine the value of the rate constant.

k =