Last Name _____ Student Number _____

First Name _____

Quiz 1 – 7 February 2013

Chemical Dynamics
Chem 1001M
Department of Chemistry
York University

Notes: All final answers must be in ink. All questions are to be answered.
Calculators are allowed.

Time allowed: 50 minutes; Total marks: 30

$R = 0.0821$ L atm mol^{-1} K^{-1} = 0.08315 L bar mol^{-1} K^{-1} = 8.314 J mol^{-1} K^{-1}.

$t_{1/2} = \frac{\ln 2}{k}$, $[A] = [A]_0 - akt$, $[A] = [A]_0 e^{-akt}$, $PV = nRT$, $\ln\left(\frac{P_{A,0}}{P_A}\right) = akt$

$\frac{1}{[A]_t} = akt + \frac{1}{[A]_0}$, $k = Ae^{-\frac{E_a}{RT}}$, $\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

Marks

[5] **1** **a**. If you had a third order reaction, what would the units of the rate constant be?

Answer: M^{-2} time^{-1}

b. Does the presence of a catalyst change the stoichiometry of the overall reaction?

Answer: NO

c. What is the value of E_a if increasing the reaction temperature does not change the value of the rate constant?

Answer: 0

d. For the reaction A → products, is a plot of 1/ln[A] vs. time is a straight line for a second order reaction?

Answer: NO

e. For an enzyme to be most efficient as a catalyst which structure should it bind best? (circle one)

substrate transition state product

[3] **2.** The rate constant of a first order reaction is $4.60 \times 10^{-4}\ s^{-1}$ at 350 °C. If the activation energy is 104 kJ mol^{-1}, calculate the temperature at which its rate constant is $5.28 \times 10^{-2}\ min^{-1}$.

644 K

[6] **3.** Data for the reaction $2NO\ (g) + 2H_2\ (g) \rightarrow N_2\ (g) + 2H_2O$ are given below.

Experiment	[NO] (M)	$[H_2]$ (M)	Initial rate (M/s)
1	10.0×10^{-3}	2.0×10^{-3}	5.0×10^{-5}
2	10.0×10^{-3}	4.0×10^{-3}	10.0×10^{-5}
3	14.0×10^{-3}	2.0×10^{-3}	9.8×10^{-5}

a. What is the rate of reaction?

$$\text{rate} = K[NO]^2[H_2]^1$$

b. What is the value of *k*?

$$250\ m^{-2}s^{-1}$$

c. What is the rate of the reaction when $[NO] = 13.0 \times 10^{-3}$ M and $[H_2] = 6.0 \times 10^{-3}$ M

$$2.54 \times 10^{-4}\ m/s$$

[6] **4.** For a first order reaction A → products.

a. What is the half-life if 75% of A decomposes in 60 min?

30 min

b. What is the instantaneous reaction rate at 120 seconds if [A] = 0.100 M at 120 seconds?

0.0023 m/min

c. How long will it take for the concentration of A to drop to a quarter of the initial concentration?

60 min

[4] **5.** For the reaction N_2 (g) + $3H_2$(g) → $2NH_3$ (g); if a some point during the reaction hydrogen is decomposing at a rate of 0.074 M s^{-1}:

a. What is the rate of formation of ammonia?

0.0493 m/s

Answer:_____

b. What is the rate of decomposition of nitrogen?

0.025 m/s

Answer:_____

[6] **6**. Under certain conditions the following mechanism exists:

step 1:	$Br_2 \rightleftharpoons 2Br$	(fast reversible)
step 2:	$Br + H_2 \rightarrow HBr + H$	(slow)
step 3	$H + Br \rightarrow HBr$	(fast)

a. What is the overall reaction?

$$Br_2 + H_2 \rightarrow 2HBr$$

b. What is the rate law predicted by this mechanism?

$$\text{rate} = K_2\left(\frac{K_1}{K_{-1}}\right)^{1/2}[Br_2]^{1/2}[H_2]$$

Answer:_____

Last Name _____ Student Number _____

First Name _____

Quiz 2 – 7 March 2013

Chemical Dynamics
Chem 1001M
Department of Chemistry
York University

Notes: All final answers must be in ink. All questions are to be answered.
Calculators are allowed.

Time allowed: 50 minutes; Total marks: 30

$R = 0.0821$ L atm mol^{-1} K^{-1} $= 0.08315$ L bar mol^{-1} K^{-1} $= 8.314$ J mol^{-1} K^{-1}.

$pH = pK_a + \log \frac{[A^-]}{[HA]}$, $PV = nRT$, $K_p = K_c(RT)^{\Delta n_{gas}}$, $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Marks

[4] **1.** For the following questions circle the correct answer

(a) Is the solution of the salt KCl:

acidic basic (neutral)

(b) Is the solution of the salt KF:

acidic (basic) neutral

(c) Is a solution of 0.1 M NaCl and 0.1 $NaNH_4$ a buffer?

yes (no) only during a full moon

(d) Could a solution of NaOH and H_3PO_2 be a buffer?

(yes) no

[3] **2.** The reaction below occurs with a $\Delta H^o = -20\ 5$ kJ mol^{-1}:

$$2PbS\ (s) + 3O_2\ (g) \rightleftharpoons 2PbO\ (s) + 2SO_2\ (g)$$

What effect will the following changes have on the position of the equilibrium? Circle the correct answer

(a) He (g) is added, volume stays fixed:

shift left shift right (stay the same)

(b) He (g) is added, volume increases:

(shift left) shift right stay the same

(d) the temperature is increased:

(shift left) shift right stay the same

[9] **3.** A mixture of 0.364 bar H_2, 0.242 bar I_2 and 1.31 bar HI was placed in a 10.00 L flask at 430°C. The K_p value for the reaction below is 54.3. Calculate the number of moles of H_2, I_2 and HI present at equilibrium.

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

moles H_2 = 0.0467 moles I_2 = 0.0258 moles HI= 0.255

[9] **4.** A commonly used buffer in biochemistry is phosphate buffer. How many grams of $NaHPO_4$ and Na_2PO_4 would you use to prepare prepare 0.500 L of a 0.100 M phosphate buffer at pH 7.60 mM? (molecular weights for H = 1.01; O = 16.00; P = 30.97; Na = 22.99). The pK_a of $H_2PO_4^-$ is 7.2.

$NaHPO_4$ = 1.79 g

Na_2PO_4= 5.08 g

[2] **5.** For the reaction below, K_c is 1.2 at 375 C.

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

If the initial concentration of N_2 is 0.60 M, H_2 is 0.76 M and NH_3 is 0.48 M is the system at equilibrium? If not, in which direction will it proceed?

No, moves right

[3] **6.** Determine the pH of a 0.50 M solution of HCN. The pK_a of HCN is 9.31.

4.8

Last Name _____ Student Number _____

First Name _____

Quiz 3 – 28 March 2013

Chemical Dynamics
Chem 1001M
Department of Chemistry
York University

Notes: All final answers must be in ink. All questions are to be answered.
Calculators are allowed.

Time allowed: 50 minutes; Total marks: 30

$R = 0.0821\ L\ atm\ mol^{-1}\ K^{-1} = 0.08315\ L\ bar\ mol^{-1}\ K^{-1} = 8.314\ J\ mol^{-1}\ K^{-1}$ $k=1.38\text{-}66\ JK^{-1}$ $N_a=6.022\times10^{23}$

$pH = pK_a + \log\frac{[A^-]}{[HA]}$, $\Delta G = \Delta H - T\Delta S$, $S = k\ \ln W$, $\Delta S = \frac{q_{rev}}{T}$, $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$\Delta G = \Delta G^\circ + RT\ \ln Q_{eq}$, $\ln K_{eq} = -\frac{\Delta H^\circ}{R}\frac{1}{T} + \frac{\Delta S^\circ}{R}$, $\Delta G^\circ = -RT\ \ln K_{eq}$, $pH = pK_a + \log\frac{[A^-]}{[HA]}$

Marks

[2] **1.** For the following reactions and their corresponding ΔH° and ΔS° values, circle the correct statement about the reaction.

(a) $N_2(g) + 3F_2(g) \leftrightarrows 2NF_3(g)$ $\Delta H^\circ = -264.2\ kJ\ mol^{-1}$ $\Delta S^\circ = -277.8\ J\ mol^{-1}K^{-1}$

spontaneous at all temperatures — spontaneous only at high temperatures

spontaneous only at low temperatures — never spontaneous

(b) $C(gr) + O_2(g) \leftrightarrows CO_2(g)$ $\Delta H^\circ = -393.5\ kJ\ mol^{-1}$ $\Delta S^\circ = 3.1\ J\ mol^{-1}K^{-1}$

spontaneous at all temperatures — spontaneous only at high temperatures

spontaneous only at low temperatures — never spontaneous

[2] **2.** For each reaction, indicate the whether sign of ΔS is positive, negative or not possible to determine from the information given. Briefly justify your answers (use less than 12 words).

(a) $H_2O\ (l) \rightarrow H_2O\ (s)$ negative Liquid to solid

(b) $2NO\ (g) + O_2\ (g) \rightarrow 2N_2O\ (g)$ negative Fewer moles of gas on right

[3] **3.** Will a precipitate of $BaSO_4$ form if 200 mL of 0.0040 M of $BaCl_2$ is added to a 600 mL of a solution of 0.008 M K_2SO_4? The K_{sp} of $BaS0_4$ is $1.1x10^{-10}$. Support your answer with a calculation.

$Q > K_{sp} \rightarrow$ ppt forms

[4] **4.** What is the solubility of MgF_2 ($K_{sp} = 3.70 \times 10^{-8}$) in the presence of a 1.00 mM solution of NaF?

$3.7 \times 10^{-8} = 4s^3 + 4 \times 10^{-3} s^2 + 1 \times 10^{-6} s$

[7] **5.** For a titration of 25 mL of 0.100 M NH_3 (K_b=1.8x10^{-5}) with a solution of 0.100 M HCl.

(a) What is the pH at the half equivalent point?

9.26

(b) What is the pH at the equivalent point?

5.3

[8] **6.** Use the data below to determine ΔH°, ΔS°, ΔG° and K_{eq} for the following reaction at 25 °C.

$$2MgO(s) \leftrightarrows 2Mg(s) + O_2(g)$$

	ΔH°_f (kJ mol^{-1})	S° (J mol^{-1} K^{-1})
MgO(s)	-60.18	26.78
Mg(s)	0.000	32.7
O_2(g)	0.000	205.0

ΔH°= 120.36 KJ/mol ΔS°= 216.84 J/mol k

ΔG°= 55.71 KJ/mol K_{eq}= 1.74×10^{-10}

[4] **7.** What is the standard molar entropy (ΔS°_{fus}) for the melting of hydrazine (N_2H_4) at its normal freezing point of 2.0 °C? The enthalpy of fusion (ΔH°_{fus}) for hydrazine is 12.66 kJ mol^{-1}.

ΔS°_{fus} = 46.01 J/Kmol

YORK UNIVERSITY
SC/CHEM 1001 3.0 Section N W2013

NAME (in ink):_____

STUDENT NUMBER:_____

Quiz No. 1 – February 5th

50 minutes

30 Marks

NOTE: ALL FINALS ANSWERS MUST BE WRITTEN IN NK
Calculators are permitted: sharing calculators is not permitted
All cell phones must be turned off and out of reach.
They cannot be used as clocks or calculators.

Equations and Data

$R = 8.314472\ J.K^{-1}.mol^{-1} = 0.08205\ L.atm.K^{-1}.mol^{-1}$; 1 atm = 1.013 x 105 Pa = 760 torr (mmHg)
$\ln k = \ln A - (Ea/RT)$; $[A]_t=[A]_0-akt$; $\ln[A]_t=\ln[A]_0 - akt$; $1/[A]_t = 1/[A]_0 + akt$
$Kp=Kc(RT)^{\Delta n}$; 0 °C=273 K ; $x= (-b \pm \sqrt{(b^2-4ac)})/2a$

Question. [Marks]

1. Three different sets of data of [A] versus time are given in the following table for the reaction A → products.

I		II		III	
Time (s)	Conc. [mol/L]	Time (s)	Conc. [mol/L]	Time (s)	Conc. [mol/L]
0	1.000	0	1.00	0	1.00
60	0.662	60	0.712	60	0.238
120	0.495	120	0.424	120	0.135
180	0.395	180	0.136	180	0.094

[3] a) Which of these sets of data corresponds to a zero-order, first-order, and second-order reaction?

I → 2nd order
II → Zero order
III → 2nd order

(use this space for Question 1a)

[1] b) What is the value of the rate constant k of the zero-order reaction?

4.8×10^{-3} m/s

[2] c) What is the rate of reaction at t=120s for reactions I and II?

I)

Rate = 2.08×10^{-3} M/s

II)

Rate = 4.8×10^{-3} M/s

[2] d) What is the concentration of [A] remaining after 4 min for reactions II and III?

II) [A] = 0 M

III) [A] = 7.2×10^{-2} M

2. [4] What are the units of the constant rate ***k*** for a reaction of order p? Rate = $k\,[A]^p$, (p=0,1,2,3,4...). Use **M** (mol/L) for concentration and **s** for time.

$M^{(1-p)} \cdot s^{-1}$

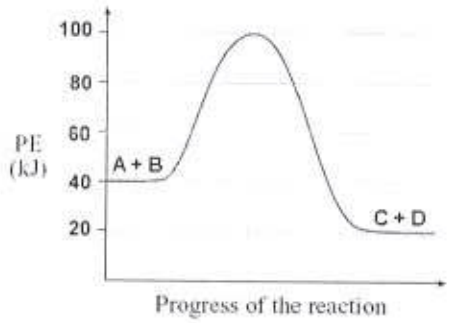
3. [6] For the reaction:

$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ at 70.5°C, Kp = 1.05.

If one starts with 1.80 atm pressure of $PCl_3(g)$, 1.72 atm pressure of $Cl_2(g)$, and no $PCl_5(g)$, what is the partial pressure of $PCl_5(g)$ at equilibrium?

0.86 atm

4. A potential energy diagram for the reaction A+B → C+D is given below:



[1] a) Does the graph represent an endothermic or exothermic reaction? Exothermic

[1] b) What is the potential energy (PE) of the reactants A+B? 40 KJ

[1] c) Determine the heat of reaction, ΔH, for this reaction. - 20 KJ

[1] d) What is the energy of the activated complex (transition state) for this reaction? 100 KJ

[1] f) Determine the activation energy (Ea) for this reaction. 60 KJ

[1] e) If a catalyst reduces the Ea to 50 kJ, what is the new PE for the products C+D? 20 KJ

5. [6] The reaction $Br_2 + 2NO \rightarrow 2NOBr$ has the rate law: Rate of reaction= $k[NO]^2[Br_2]$. Two two-step mechanisms were proposed for this reaction. Which mechanism is more likely to occur? Why?

Mechanism I

$Br_2 \rightleftharpoons 2Br$ (fast, reversible)

$2Br + 2NO \rightarrow 2NOBr$ (slow)

Mechanism II

$Br_2 + NO \rightleftharpoons NOBr_2$ (fast, reversible)

$NOBr_2 + NO \rightarrow 2NOBr$ (slow)

Both mechanisms are plausible.

(II) is more likely to occur

YORK UNIVERSITY
SC/CHEM 1001 3.0 Section N W2013

NAME (in ink):_____

STUDENT NUMBER:_____

Quiz No. 2 – March 5th

50 minutes

30 Marks

NOTE: ALL FINALS ANSWERS MUST BE WRITTEN IN INK

Calculators are permitted: sharing calculators is not permitted

All cell phones must be turned off and out of reach. They cannot be used as clocks or calculators.

Table I - Acid/Base Ionization Constants at 25°C

Acid	Formula	K_{a1}	K_{a2}
Acetic acid	CH_3CO_2H	1.8×10^{-5}	
Ascorbic acid	$H_2C_6H_6O_6$	7.9×10^{-5}	1.6×10^{-12}
Carbonic acid	H_2CO_3	4.5×10^{-7}	4.7×10^{-11}
Formic acid	HCO_2H	1.8×10^{-4}	
Hydrocyanic acid	HCN	6.2×10^{-10}	
Hydrofluoric acid	HF	7.2×10^{-4}	
Nitrous acid	HNO_2	4.5×10^{-4}	
Base	**Formula**	K_b	
Caffeine	$C_8H_{10}N_4O_2$	4.1×10^{-4}	
Codeine	$C_{18}H_{21}O_3N$	8.9×10^{-7}	
Diethylamine	$(C_2H_5)_2NH$	6.9×10^{-4}	
Hydroxylamine	NH_2OH	9.1×10^{-9}	
Pyridine	C_5H_5N	1.5×10^{-9}	

Table II – Solubility Product Constants at

Compound	Formula	K_{sp}
Nickel (II) hydroxide	$Ni(OH)_2$	2.0×10^{-15}
Calcium carbonate	$CaCO_3$	2.8×10^{-9}
Copper (II) hydroxide	$Cu(OH)_2$	1.6×10^{-19}
Iron (III) hydroxide	$Fe(OH)_3$	4.0×10^{-38}
Lead(II) iodide	PbI_2	7.1×10^{-9}
Silver bromide	AgBr	5.0×10^{-13}
Silver chloride	AgCl	1.8×10^{-10}
Tin (II) hydroxide	$Sn(OH)_2$	1.4×10^{-28}

$HA + H_2O \rightarrow H_3O^+ + A^-$ $\quad pH=pKa+\log([A^-]/[HA])$

$B + H_2O \rightarrow BH^+ + OH^-$ $\quad pOH=pKb+\log([BH^+]/[B])$

$[H_3O^+].[OH^-] = 10^{-14} = Kw$

$Ka \cdot Kb = Kw$

Table III – pH indicators

Indicator	pK	pH range for color changing	Corresponding color change
m-cresol purple	1.5	1.2 - 2.8	Red to yellow
Methyl orange	3.4	3.1 - 4.4	Red to orange
Methyl red	4.9	4.4 - 6.2	Red to yellow
Bromothymol blue	7.1	6.2 - 7.6	Yellow to blue
m-cresol purple	8.3	7.6 - 9.2	Yellow to purple
Thymolphalein	10.0	9.4 - 10.6	Colorless to blue
Alizarin yellow R	11.2	10.0 - 12.0	Yellow to violet

Question. [Marks]

1. Calculate the pH (to two decimal places) of the following aqueous solutions:

[2] a) 4.70×10^{-1} M pyridine.

9.42

[2] b) 2.4×10^{-1} M of potassium cyanide.

11.29

[2] c) 3.5×10^{-1} M of sodium chloride.

7.00

[4] d) A solution with final concentrations of 8.80×10^{-1} M of hydrocyanic acid and 5.30×10^{-1} M of sodium cyanide.

8.99

[4] **2.** A volume of 250 mL of a 2.00×10^{-1} M solution of NaI is added to 150 mL of 1.00×10^{-1} M solution of $Pb(NO_3)_2$. Will a precipitate form? Explain.

Yes. $Q_{sp} > K_{sp}$

[4] **3.** a) Explain (in a few sentences) what an indicator is and what it is used for.

Indicator is a weak acid that changes its colour depending on pH. The acid and the conjugate base have different colours. It is used to monitor the pH of aqueous solutions (eg. in titrations)

[6] b) What indicator (from Table III) should be used for the titration (determination of the end point) of 25mL of 0.25 M codeine with 0.50 M of HCl? Why?

Methyl red

[6] **4.** What are the concentrations of H_2CO_3, HCO_3^-, CO_3^{2-}, and H_3O^+ in a 5.0×10^{-2} M aqueous solution of carbonic acid?

$[H_3O^+] = [HCO_3^-] = 1.5 \times 10^{-4}\ M$

$[H_2CO_3] \simeq 5.0 \times 10^{-2}\ M$

$[CO_3^{2-}] = 4.7 \times 10^{-11}\ M$

YORK UNIVERSITY

NAME (in ink):_____

SC/CHEM 1001 3.0 Section N W2013

STUDENT NUMBER:_____

Quiz No. 3 – March 26th

50 minutes

30 Marks

NOTE: ALL FINALS ANSWERS MUST BE WRITTEN IN INK

Calculators are permitted: sharing calculators is not permitted. All cell phones must be turned off and out of reach. They cannot be used as clocks or calculators.

Equations

$$\Delta G = \Delta H - T\Delta S \qquad \Delta G = \Delta G^\circ + RT\ln Q$$

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

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \ln K_{eq} = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln Q \qquad E^\circ_{cell} = \frac{RT}{nF}\ln K_{eq}$$

Constants and Conversion Factors

0.00 °C = 273.15 K

1.000 bar = 1.000×10^5 Pa ≈ 1.0 atm

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

$N_A = 6.022\times10^{23}$ mol^{-1}

$K_W = 1.00\times10^{-14}$ at 25° C

1 V = 1 J C^{-1}

F = 96485 J V^{-1} mol^{-1} = 96485 C mol^{-1}

[6] **1.** Write **"T"** if the statement is **true** and **"F"** if the statement is **false**.

a.	A spontaneous reaction is one that must have a negative value of ΔH.	F
b.	A spontaneous process will occur only if some external action is continually applied.	F
c.	ΔG is positive for a spontaneous reaction.	F
d.	If a process is spontaneous, the reverse process is nonspontaneous.	T
e.	A zero ΔG means the system is at equilibrium.	T
f.	$E°_{cell}$ is the standard cell potential.	T
g.	When $E_{cell} < 0$, the reaction is spontaneous.	F
h.	A cathode is where reduction occurs.	T
i.	The anode is on the left in a cell diagram.	T
j.	Half cells in a cell diagram are separated by a single vertical line.	F
k.	An anode is where reduction occurs.	F
l.	A cell diagram is a symbolic way to show cell components.	T

[4] **2.** Consider the reaction for decomposition of carbon tetrachloride gas:

$$CCl_4(g) \rightarrow C\ (s,\ graphite) + 2\ Cl_2(g) \qquad \Delta H = 95.7\ kJ/mol;\ \Delta S = 142.2\ J/(mol.K)$$

Determine at what temperature the reaction becomes spontaneous assuming that both ΔH and ΔS are independent of the temperature.

673 K

[6] **3.** The overall reaction for the corrosion (rusting) of iron by oxygen is:

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s) \qquad (25C°)$$

Using the following data, calculate $\Delta G°$ and the equilibrium constant for this reaction.

Substance	$\Delta H°$ ($kJ.mol^{-1}$)	$\Delta S°$ ($J.K^{-1}.mol^{-1}$)
$Fe_2O_3(s)$	-826	90
Fe(s)	0	27
O2(g)	0	205

$\Delta G^{\circ} = -1.49 \times 10^{6}$ J/mol

$K = e^{601}$

4. Consider the reaction: 2 Cr(s) + 3 Cu^{2+}(aq) → 2 Cr^{3+}(aq) + 3 Cu(s) and the following table:

Half Reaction	$E°$ (volts)
(1) $Cr^{3+} + 3\ e^- \rightarrow Cr$	-0.74
(2) $Cr^{3+} + e^- \rightarrow Cr2+$	-0.41
(3) $Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \rightarrow 2\ Cr^{3+} + 7\ H2O$	1.33
(4) $Cu^+ + e^- \rightarrow Cu$	0.52
(5) $Cu^{2+} + 2\ e^- \rightarrow Cu$	0.34
(6) $Cu^{2+} + e^- \rightarrow Cu^+$	0.16

a. [2] Draw the cell diagram of the voltaic cell.

$Cr_{(s)} \mid Cr^{3+}_{(aq)} \parallel Cu^{2+}_{(aq)} \mid Cu_{(s)}$

b. [3] Predict the numerical value of the standard cell potential ($E°_{cell}$) of the reaction.

1.08 V

c. [3] What is the $\Delta G°$ for this reaction?

$\Delta G^\circ = -625.22$ KJ/mol

[6] 5. The decomposition of the poisonous gas phosgene is represented by the equation $COCl_2(g) \leftrightarrow CO(g) + Cl_2(g)$. Values of K_p for this reaction are $K_p = 6.7 \times 10^{-9}$ at 99.8°C and $K_p = 4.44 \times 10^{-2}$ at 395°C. At what temperature is $COCl_2$ 15% dissociated when the total gas pressure is maintained at 1.00 atm?

647 K

General Chemistry CHEM 1001

Student ID: _____ **Student Name:** _____

FIRST TEST

CHEM 1001

FEBRUARY 05, 2013

DURATION: 50 MINUTES

Aid allowed: non-programmable calculators.

Answer all questions in the space provided on the examination paper. Please read each question carefully and answer only what is asked in each question.

Neat writing is highly appreciated. Read each question carefully before answering.
All answers must be in ink.

This test has 8 pages
Total Marks are 30

Question	Question 1	Question 2	Question 3	Question 4	Total
Grade	10	10	6	4	30
Marks					

Q.1.a) Consider following reaction that occurs at 300K:

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

Following data for the initial concentrations was obtained for the reaction;

Experiment	[NO]	$[Cl_2]$	Initial Rate ($molL^{-1}s^{-1}$)
1	0.010	0.010	1.2×10^{-4}
2	0.010	0.020	2.3×10^{-4}
3	0.020	0.020	9.6×10^{-4}

i) write the rate law of this reaction? **[0.5]**

Rate $= K[NO]^2[Cl]$

ii) What is the order of reaction with respect to NO and with respect to Cl_2? **[1]**

Order for NO is 2

Order for Cl_2 is 1

iii) What is the overall order of this reaction? **[0.5]**

3

iv) What is the value of rate constant k at 300K for this reaction? **[2]**

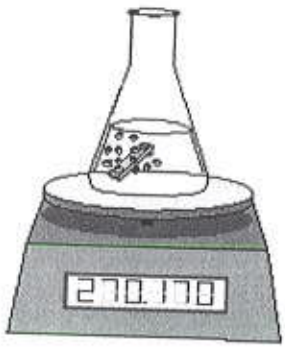
$1.2 \times 10^2 \ \frac{L^2}{mol^2 s}$

v) What will be rate of reaction when $[NO] = 0.030\ molL^{-1}$ and $[Cl_2] = 0.040\ molL^{-1}$ **[2]**

$4.3 \times 10^{-3} \ \frac{mol}{Ls}$

b) An experiment is done to determine the rate of the following reaction:

$$2Al_{(s)} + 6HCl_{(aq)} \rightarrow 3H_{2(g)} + 2AlCl_{3(aq)}$$



The following data are collected:

TIME (s)	MASS OF FLASK PLUS CONTENTS (g)
0.0	270.230
30.0	270.200
60.0	270.170

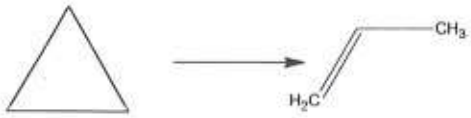
i) Calculate the rate of formation of H_2 in mol/min. **[2]**

$0.03 \frac{mol}{min}$

ii) Calculate the rate of consumption of Al in g/sec **[2]**

9.0×10^{-3} g/sec

Q.2.a) In the past cyclopropane, C_3H_6, was used in a mixture with oxygen as an anesthetic. (This practice has almost ceased today, because the compound is very flammable.) When cyclopropane is heated, it is converted to propene in a first order process:



The rate constant k is $2.41 \times 10^{-10} s^{-1}$ at 300°C. At 400°C, $k = 1.16 \times 10^{-6} s^{-1}$.

i) What is the activation energy for this reaction? **[2]**

271 KJ/mol

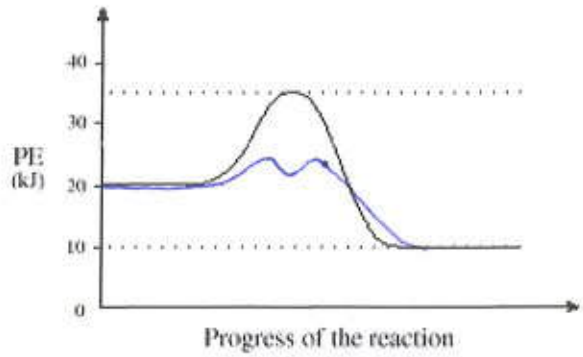
ii) What will be the rate constant at 450°C for this reaction? **[2]**

$3.34 \times 10^{-5} s^{-1}$

iii) If the initial concentration of cyclopropane is 0.050 $molL^{-1}$, how much time (in hours) must laps for its concentration to drop to 0.010 $molL^{-1}$? **[2]**

1.86×10^{6} hr

b) Consider the following potential energy diagram for a reversible reaction:



i) Calculate the activation energy for the forward reaction. **[1]**

15 kJ

ii) Calculate ΔH for the forward reaction. **[1]**

- 10 kJ

iii) Calculate the activation energy for the reverse reaction. **[1]**

25 kJ

iv) On the diagram above, sketch a curve that could result when a catalyst is added. **[1]**

Q.3.a) Radioactive radon-222 gas (^{222}Rn) from natural sources can seep into the basement of a home. The half-life of ^{222}Rn is 3.8 days. If a basement has 4×10^{13} atoms of ^{222}Rn per liter of air, and the radon gas is trapped in the basement, how many atoms of ^{222}Rn will remain after one month (30 days)? **[3]**

$1.7 \times 10^{11} \frac{\text{atom}}{L}$

b) Consider the following reaction mechanism:

Step 1	?
Step 2	$H_2 + Cl \rightarrow HCl + H$
Step 3	$H + Cl_2 \rightarrow HCl + Cl$
Step 4	$Cl + Cl \rightarrow Cl_2$
Overall	$H_2 + Cl_2 \rightarrow 2HCl$

i) Write the equation for Step 1. **[1]**

$Cl_2 \rightarrow 2Cl$

ii) Define the term "reaction intermediate" and identify the reaction intermediate(s) in the above reaction mechanism. **[2]**

Usually unstable species produced by some elementary reactions and consumed by others. They do not appear in overall reaction or overall rate law.

Cl & H are intermediates.

Q.4) Ozone (O_3) naturally decomposes to oxygen (O_2) by the following reaction:

$$2O_3(g) \longrightarrow 3O_2(g)$$

The experimentally observed rate law for this reaction is as follows:

$$\text{Rate} = k[O_3]^2[O_2]^{-1}$$

Show that the following proposed mechanism is consistent with the experimentally observed rate law. [4]

$$O_3(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2(g) + O(g) \qquad \text{Fast}$$

$$O_3(g) + O(g) \xrightarrow{k_2} 2O_2(g) \qquad \text{Slow}$$

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

$1/[A]_t = 1/[A]_o + akt$ $t_{1/2} = [A]_o/2k$

$t_{1/2} = 0.693/k$ $t_{1/2} = 1/k[A]_o$

$k = Ae^{-Ea/RT}$

$\ln k = \ln A-(Ea/RT)$ $l_n\left(\frac{k_2}{k_1}\right) = \frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$PV = nRT$, $\ln (P_{a,o}/P_a) = akt$

$R = 8.314 J.mol^{-1}K^{-1} = 0.8206 L.atm.mol^{-1}K^{-1}$
$N_A = 6.022 \times 10^{23} mol^{-1}$ $0.00\ ^\circ C = 273.15K$
$k = 1.38066 \times 10^{-23} JK^{-1}$
$1\ atm = 1.013 \times 10^5 pa = 760\ torr\ (mmHg)$

Molar mass (g/mol)
C = 12.01
N = 14.01
Al = 26.98
H = 1.008
O = 16.00
Cl = 35.45
Rn = 222.02

General Chemistry CHEM 1001

Student ID: _____ Student Name: _____

SECOND TEST

CHEM 1001

MARCH 05, 2013

DURATION: 50 MINUTES

Aid allowed: non-programmable calculators.

Answer all questions in the space provided on the examination paper. Please read each question carefully and answer only what is asked in each question.

Neat writing is highly appreciated. Read each question carefully before answering.
All answers must be in ink.

This test has 6 pages
Total Marks are 30

Question	Question 1	Question 2	Question 3	Question 4	Total
Grade	7	7	7	9	30
Marks					

Q.1.a) Phosphorus pentachloride decomposes at higher temperature.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

An equilibrium mixture at some temperature consists of 3.120 g of PCl_5, 3.845 g of PCl_3, and 1.787 g of Cl_2 in a 1.00 L flask. If you add 1.418 g of Cl_2, how will the equilibrium be affected? **What will the concentrations of PCl_5, PCl_3 and Cl_2** be when equilibrium is reestablished? [4.5]

$[PCl_5] \approx 0.0198\ M$

$[PCl_3] \approx 0.023\ M$

$[Cl_2] \approx 0.040\ M$

b) Heating a metal carbonate leads to decomposition.

$$BaCO_3(s) \rightleftharpoons BaO(s) + CO_2(g)$$

Predict the effect on equilibrium of each change listed below. [2.5]

i) add $BaCO_3$ no change

ii) add CO_2 Shift left

iii) add BaO no change

iv) raise the temperature Shift right

v) increase the volume of the flask containing the reaction. Shift right

Q.2.a) Calcium hydroxide (slaked lime) is a major component of mortar, plaster, and cement, and solutions of $Ca(OH)_2$ are used in industry as a cheap, strong base. **What is its solubility in 0.10 M $Ca(NO_3)_2$?** K_{sp} of $Ca(OH)_2$ in pure water = 6.5×10^{-6} [4]

4.0×10^{-3} M

b) Write the formula for the **conjugate base** of each of the following substances. [3]

i) HCl Cl^-

ii) H_2SO_3 HSO_3^-

iii) $HCHO_2$ CHO_2^-

iv) HF F^-

v) NH_3 NH_2^-

vi) H_3PO_4 $H_2PO_4^-$

Q.3.a) For the equilibrium :

$$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq) \qquad K_{sp} = 1.3 \times 10^{-33}$$

What is the minimum pH at which $Al(OH)_3(s)$ will precipitate from a solution that is 0.075M in Al^{3+}? [3]

3.41

b) A common laboratory method for preparing a precipitate is to mix solutions containing the component ions. **Does a precipitate form** when 0.100 L of 0.30 M $Ca(NO_3)_2$ is mixed with 0.200 L of 0.060 M NaF? K_{sp} for $CaF_2 = 3.2 \times 10^{-11}$ [4]

Yes

Q.4.a.) Sodium acetate (CH_3COONa) is used in photographic development and textile dyeing. **What is the pH** of 0.25 M CH_3COONa? K_a (CH_3COOH) = 1.8×10^{-5} [4]

9.08

b) A particular vinegar is found to contain 5.7% acetic acid, CH_3COOH, by mass. **What mass** of this vinegar should be diluted with water to produce **0.750 L of a solution with pH = 4.52?** [4]

0.063g

c) Which of the following are **Arrhenius bases**? [1]

i) H_3AsO_4 *ii*) $Ba(OH)_2$ *iii*) HClO *iv*) KOH

WebElements: the periodic table on the world-wide web

www.webelements.com

1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
hydrogen 1 **H** 1.0079																		helium 2 **He** 4.0026
lithium 3 **Li** 6.941	beryllium 4 **Be** 9.0122												boron 5 **B** 10.811	carbon 6 **C** 12.011	nitrogen 7 **N** 14.007	oxygen 8 **O** 15.999	fluorine 9 **F** 18.998	neon 10 **Ne** 20.180
sodium 11 **Na** 22.990	magnesium 12 **Mg** 24.305												aluminium 13 **Al** 26.982	silicon 14 **Si** 28.086	phosphorus 15 **P** 30.974	sulfur 16 **S** 32.065	chlorine 17 **Cl** 35.453	argon 18 **Ar** 39.948
potassium 19 **K** 39.098	calcium 20 **Ca** 40.078		scandium 21 **Sc** 44.956	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.942	chromium 24 **Cr** 51.996	manganese 25 **Mn** 54.938	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.933	nickel 28 **Ni** 58.693	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.38	gallium 31 **Ga** 69.723	germanium 32 **Ge** 72.61	arsenic 33 **As** 74.922	selenium 34 **Se** 78.96	bromine 35 **Br** 79.904	krypton 36 **Kr** 83.80
rubidium 37 **Rb** 85.468	strontium 38 **Sr** 87.62		yttrium 39 **Y** 88.906	zirconium 40 **Zr** 91.224	niobium 41 **Nb** 92.906	molybdenum 42 **Mo** 95.96	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07	rhodium 45 **Rh** 102.91	palladium 46 **Pd** 106.42	silver 47 **Ag** 107.87	cadmium 48 **Cd** 112.41	indium 49 **In** 114.82	tin 50 **Sn** 118.71	antimony 51 **Sb** 121.76	tellurium 52 **Te** 127.60	iodine 53 **I** 126.90	xenon 54 **Xe** 131.29
caesium 55 **Cs** 132.91	barium 56 **Ba** 137.33	57-70 *	lutetium 71 **Lu** 174.97	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.95	tungsten 74 **W** 183.84	rhenium 75 **Re** 186.21	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.22	platinum 78 **Pt** 195.08	gold 79 **Au** 196.97	mercury 80 **Hg** 200.59	thallium 81 **Tl** 204.38	lead 82 **Pb** 207.2	bismuth 83 **Bi** 208.98	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
francium 87 **Fr** [223]	radium 88 **Ra** [226]	89-102 **	lawrencium 103 **Lr** [262]	rutherfordium 104 **Rf** [267]	dubnium 105 **Db** [268]	seaborgium 106 **Sg** [271]	bohrium 107 **Bh** [272]	hassium 108 **Hs** [270]	meitnerium 109 **Mt** [276]	darmstadtium 110 **Ds** [281]	roentgenium 111 **Rg** [280]	ununbium 112 **Uub** [285]	ununtrium 113 **Uut** [284]	ununquadium 114 **Uuq** [289]	ununpentium 115 **Uup** [288]	ununhexium 116 **Uuh** [293]	ununseptium 117 — Uus	ununoctium 118 **Uuo** [294]

Key:

element name
atomic number
symbol
atomic weight (mean relative mass)

*lanthanoids	lanthanum 57 **La** 138.91	cerium 58 **Ce** 140.12	praseodymium 59 **Pr** 140.91	neodymium 60 **Nd** 144.24	promethium 61 **Pm** [145]	samarium 62 **Sm** 150.36	europium 63 **Eu** 151.96	gadolinium 64 **Gd** 157.25	terbium 65 **Tb** 158.93	dysprosium 66 **Dy** 162.50	holmium 67 **Ho** 164.93	erbium 68 **Er** 167.26	thulium 69 **Tm** 168.93	ytterbium 70 **Yb** 173.06
**actinoids	actinium 89 **Ac** [227]	thorium 90 **Th** 232.04	protactinium 91 **Pa** 231.04	uranium 92 **U** 238.03	neptunium 93 **Np** [237]	plutonium 94 **Pu** [244]	americium 95 **Am** [243]	curium 96 **Cm** [247]	berkelium 97 **Bk** [247]	californium 98 **Cf** [251]	einsteinium 99 **Es** [252]	fermium 100 **Fm** [257]	mendelevium 101 **Md** [258]	nobelium 102 **No** [259]

Symbols and names: the symbols and names of the elements, and their spellings are those recommended by the International Union of Pure and Applied Chemistry (IUPAC - http://www.iupac.org/). Names have yet to be proposed for the most recently discovered elements beyond 112 and so those used here are IUPAC's temporary systematic names. In the USA and some other countries, the spellings **aluminum** and **cesium** are normal while in the UK and elsewhere the common spelling is **sulphur**.
Group labels: the numeric system (1–18) used here is the current IUPAC convention.
Atomic weights (mean relative masses): Apart from the heaviest elements, these are the IUPAC 2007 values and given to 5 significant figures. Elements for which the atomic weight is given within square brackets have no stable nuclides and are represented by the element's longest lived isotope reported at the time of writing.

General Chemistry CHEM 1001

Student ID: _____ Student Name: _____

THIRD TEST

CHEM 1001

MARCH 26, 2013

DURATION: 50 MINUTES

Aid allowed: non-programmable calculators.

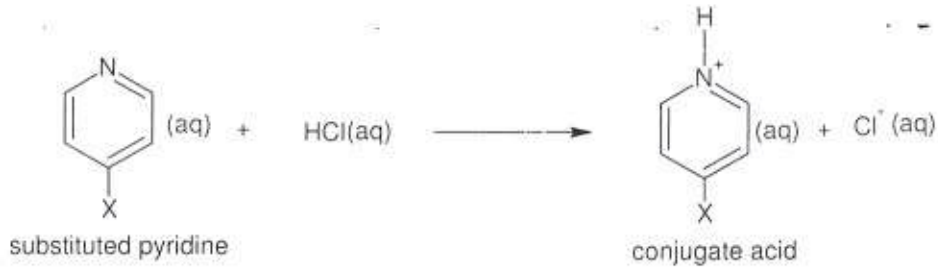
Answer all questions in the space provided on the examination paper. Please read each question carefully and answer only what is asked in each question.

Neat writing is highly appreciated. Read each question carefully before answering.
All answers must be in ink.

This test has 7 pages
Total Marks are 30

Question	Question 1	Question 2	Question 3	Question 4	Total
Grade	10	5	8	7	30
Marks					

Q.1) A hydrogen atom in the organic base pyridine, C_5H_5N, can be substituted by various atoms or groups to give XC_5H_4N, where X is an atom such as Cl or a group such as CH_3. The table give K_a values for the conjugate acids of a variety of substituted pyridines.



Atom or Group X	K_a of Conjugate Acid
NO_2	5.9×10^{-2}
Cl	1.5×10^{-4}
H	6.8×10^{-6}
CH_3	1.0×10^{-6}

a) Suppose each conjugate acid is dissolved in sufficient water to give a 0.050M solution. Which solution would have the highest pH? The lowest pH? [2]

NO_2 lowest pH

CH_3 highest pH

b) Identify Lewis acid and Lewis base from the following reactions: [2]

i) $H^+ + NH_3 \rightarrow NH_4^+$

ii) $OH^- + H^+ \rightarrow H_2O$

iii) $BF_3 + O(CH_3)_2 \rightarrow FB_3O(CH_3)_2$

iv) $B(OH)_3 + OH^- \rightarrow [B(OH)_4]^-$

Lewis Acids: H^+, H^+, BF_3, $B(OH)_3$

Lewis bases: NH_3, OH^-, $O(CH_3)_2$, OH^-

c) A chemist prepared a buffer solution by dissolving 2.00 g each of benzoic acid, C_6H_5COOH, and sodium benzoate, NaC_6H_5COO, in 750.0 mL of water.

What is the pH of this buffer? Assume that the solution volume is 750.0 mL. [3]

K_a (C_6H_5COOH) = 6.3×10^{-5}

4.13

d) Which buffer component, and how much (in grams), would the chemist need to add to the 750.0 mL of buffer solution to change its pH to 4.00? [3]

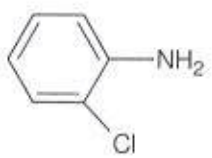
0.7 g

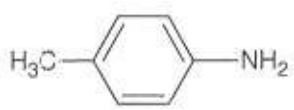
Q.2.a) You have three solutions labeled **A**, **B** and **C**. You know only that each contains a different cation Na^+, NH_4^+, or H^+. Each has an anion that does not contribute to the solution pH (e.g., Cl^-). You also have two other solutions, **Y** and **Z**, each containing a different anion, Cl^- or OH^-, with a cation that does not influence solution pH (e.g., K^+). If equal amounts of **B** and **Y** are mixed, the results is an acidic solution. Mixing **A** and **Z** gives a neutral solution, whereas **B** an **Z** give a basic solution. Identify the five unknown solutions. [3]

	Y	Z
A		neutral
B	acidic	basic
C		

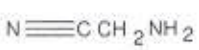
A HCl
B NH_4Cl
C NaCl
Y KCl
Z KOH

b) From the following bases, select the one with the smallest K_b and the one with the largest K_b, and give reasons of your choices. [2]

(i) 

(ii) 

(iii) $CH_3CH_2CH_2NH_2$

(iv) 

i) Smallest K_b Nitrogen lone pair spread out over ring, making less available to accept proton.

ii) largest K_b Hydrocarbon chain being lowest electronegative actually e^--donor

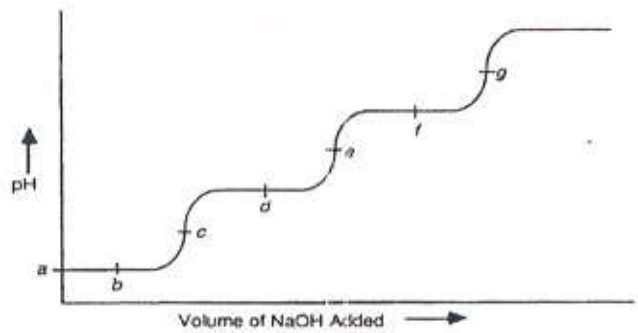
(Q.3.a) Calculate the ratio of conjugate base to conjugate acid for a hypothetical buffer that was made by dissolving a hypothetical base (pK_b 3.95) and the salt of its conjugate acid. The pH of this hypothetical buffer solution was found to be 10.05. [3]

$$\frac{A^-}{HA} = 1$$

b) Will the solution be a good buffer? Explain with reasoning. [2]

Yes $\frac{A^-}{HA}$ is between 0.1 and 10.

c) Label each component of the titration curve of a polyprotic acid with NaOH shown below: [3]



(b) 1st half neutralization (c) First equivalence point
(d) 2nd half neutralization (e) Second equivalence point
(f) 3rd half neutralization (g) Third equivalence point.

Q.4.a) Predict the sign of the entropy change for each of the following reactions: [3]

i) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ -ive

ii) $Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$ -ive

iii) $I_2(s) \rightarrow I_2(g)$ +ive

iv) $2C_6H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$ +ive

v) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ -ive

vi) $Al_2Cl_6(g) \rightarrow 2AlCl_3(g)$ +ive

b) Consider the oxidation of iron metal:

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

By determining the sign of ΔS_{total}, show whether the reaction is spontaneous at 25°C.

ΔH°_f (Fe_2O_3) = -824.2 kJ/mol [4]

ΔS_{Total} is +ive, the reaction is spontaneous.

Standard Molar Entropies for Some Common Substances at 25°C

Substance	Formula	S° [J/(K · mol)]	Substance	Formula	S° [J/(K · mol)]
Gases			**Liquids**		
Acetylene	C_2H_2	200.8	Acetic acid	CH_3CO_2H	160
Ammonia	NH_3	192.3	Ethanol	CH_3CH_2OH	161
Carbon dioxide	CO_2	213.6	Methanol	CH_3OH	127
Carbon monoxide	CO	197.6	Water	H_2O	69.9
Ethylene	C_2H_4	219.5	**Solids**		
Hydrogen	H_2	130.6	Calcium carbonate	$CaCO_3$	92.9
Methane	CH_4	186.2	Calcium oxide	CaO	39.7
Nitrogen	N_2	191.5	Diamond	C	2.4
Nitrogen dioxide	NO_2	240.0	Graphite	C	5.7
Dinitrogen tetroxide	N_2O_4	304.2	Iron	Fe	27.3
Oxygen	O_2	205.0	Iron(III) oxide	Fe_2O_3	87.4

Part of the modern PERIODIC TABLE showing atomic (proton) numbers AND the elements's relative atomic mass

																	2 He 4.003
							1 H 1.008					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 Li 6.939	4 Be 9.012											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
11 Na 22.99	12 Mg 24.31											31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.71	29 Cu 63.55	30 Zn 65.39	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
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 (99)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
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						
87 Fr (223)	88 Ra 226.0	89 Ac 227.0															

the top number is the atomic or proton number.
the bottom number is the relative atomic mass.
(which used to be called the 'atomic weight')

York University
Department of Chemistry
Final Examination
CHEM 1001 Chemical Dynamics
Winter 2013
10 April 2013, 2:00 to 4:00 pm

Last Name _____ Student Number _____

First Name _____

Instructors: D. Ifa, H. Mirza & P. Johnson

Notes: This exam consists of 11 pages, including this one. There is a data table, a periodic table and a table of useful equations and constants following the last page of this examination. You may detach them.

You have two hours to complete this exam. There are a total of 100 marks. All questions are to be answered. Answer all questions in the space provided. Additional paper for rough work is not permitted.

Calculators are allowed, but may not be shared. All other electronic devices (such as cell phones) are not permitted

page	marks
2	
3	
4	
5	
6	
7	
8	
9	
10	
11	
total	

Marks

[15] **1.** Consider the equation for the decomposition of SO_2Cl_2.

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

The concentration of SO_2Cl_2 was monitored at a fixed temperature as a function of time during the decomposition reaction and the data are tabulated on the right.

Time (s)	$[SO_2Cl_2]$ (M)
0	0.1000
100	0.0844
200	0.0712
300	0.0600
400	0.0507
500	0.0427
600	0.0361
700	0.0304
800	0.0257
900	0.0217
1000	0.0183
1100	0.0154
1200	0.0130

(a) Is this reaction a zero-order, first-order or second-order reaction?

First -order

(b) What is the value of the constant k of the reaction?

1.7×10^{-3} 1/s

(c) What is the average rate of the reaction at $t = 100$ s?

1.44×10^{-4} M/s

(d) What is the instantaneous rate of the reaction at $t = 1100$ s?

2.62×10^{-5} M/s

(e) What is the concentration of SO_2Cl_2 remaining after 25 min?

7.80×10^{-3} M

[7] **2.** From the following initial-rate data, (a) write the rate law and (b) calculate the rate constant (with units) for the reaction: $2\ H_2(g) + 2\ NO(g) \rightarrow N_2(g) + 2\ H_2O(g)$.

$[H_2]$ (M)	[NO] (M)	**Initial Rate** ($M\ s^{-1}$)
0.0010	0.0020	1.2×10^{-4}
0.0010	0.0030	1.8×10^{-4}
0.0020	0.0020	4.8×10^{-4}

$Rate = K[H_2]^2[NO]^1$

$K = 6 \times 10^4\ M^{-2} \cdot S^{-1}$

rate law: _____ rate constant: _____

[8] **3.** A mixture of SO_2, SO_3, and O_2 gases is maintained in a 10.0 L flask at a temperature that $K_c = 100$ for the reaction $2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$.

(a) If the number of moles of SO_2 and SO_3 in the flask are equal, how many moles of O_2 are present at equilibrium?

0.1 moles

(b) If the number of moles of SO_3 in the flask is twice the number of moles of SO_2, how many moles of O_2 are present at equilibrium?

0.4 moles

[4] **4 (a)** Aldrich, a leading chemical supplier in the world, sells various buffers used in the pharmaceutical and chemical industry to standardize pH meters in order to adjust the pH of mobile phases used in HPLC. A chemist decided to prepare a carbonate buffer pH 10.00. What mass of Na_2CO_3 must the chemist add to 1.5 L of 0.20 M $NaHCO_3$ to make the buffer?
$K_a (HCO_3^-) = 4.7 \times 10^{-11}$

15g

[6] **(b)** Muscles may ache after strenuous exercise because lactic acid is formed faster than it is metabolized to CO_2 and H_2O. What is the pH of the fluid in muscle when the lactic acid concentration reaches 1.0×10^{-3} mol L^{-1}. K_a (lactic acid) = 8.4×10^{-4}

3.23

5. A 40.0 mL sample of 0.100 mol L^{-1} HNO_2 ($K_a = 7.2 \times 10^{-4}$) is titrated with 0.200 mol L^{-1} KOH. Calculate:

[2] (a) the volume required to reach the equivalence point

20.0 mL

[3] (b) the pH after adding 5.00 mL of KOH

2.66

[5] (c) the pH at one-half the equivalence point.

3.14

[6] **6 (a)** Milk of magnesia, commonly used as a remedy for stomach upset due to acidity, is an aqueous suspension of magnesium hydroxide, $Mg(OH)_2$ ($K_{sp} = 1.8 \times 10^{-11}$). What is the pH of milk of magnesia?

10.53

[2] **(b)** How will addition of sodium acetate to an acetic acid solution affect the pH? Circle the correct answer.

i) It will lower the pH.
ii) The pH will not change.
iii) The solution becomes hotter.
iv) The pH cannot be measured.
v) It will raise the pH.

[2] **(c)** The Henderson-Hasselbach equation, used to calculate the pH of simple conjugate-pair buffer systems, would be expressed for an ammonia/ammonium chloride buffer, for which $K_b(NH_3)$ is 1.8×10^{-5}, as: (circle the correct answer)

i) $pH = 4.74 + \log([NH_3]/[NH_4^+])$
ii) $pH = 4.74 + \log([NH_4^+]/[NH_3])$
iii) $pH = 9.25 + \log([NH_3]/[NH_4^+])$
iv) $pH = 9.25 + \log([NH_4^+]/[NH_3])$
v) $pH = 14.00 - \log(1.8 \times 10^{-5})$

[10] **7.** Answer the following questions based on the reaction below:

$$Co\ (s) + Fe^{2+}\ (aq) \leftrightarrows Co^{2+}\ (aq) + Fe\ (s)$$

(a) Write the half-reaction that takes place at the anode:

$Co_{(s)} \rightleftharpoons Co^{2+}_{(aq)} + 2e^-$

(b) Write the half-reaction that takes place at the cathode:

$Fe^{2+}_{(aq)} + 2e^- \rightleftharpoons 2\,Fe_{(s)}$

(c) What is the value of E°_{cell}?

$-0.16\ V$

(d) If $[Fe^{2+}] = 0.68$ M and $[Co^{2+}] = 0.15$ M, would the reaction proceed spontaneously? Support your answer with a calculation.

rxn not spontaneous

[10] **8.** (a) Below is an unbalanced redox equation:

$$Fe^{3+} + NH_3OH^+ \leftrightarrows Fe^{2+} + N_2O$$

Write the balanced reaction in acid solution below:

$2NH_3OH^+ + 4Fe^{3+} \rightleftharpoons N_2O + Fe + 6H^+ + H_2O$

(b) Below is an unbalanced redox equation:

$$Fe(OH)_3 + OCl^- \leftrightarrows FeO_4^{2-} + Cl^-$$

Write the balanced reaction in basic solution below:

$2Fe(OH)_3 + 3OCl^- + 4OH^- \rightleftharpoons 3Cl^- + 2FeO_4^{2-} +$

$5H_2$

(c) Silver ions react with elemental iron at standard conditions.

$$2Ag^+ (aq) + Fe (s) \leftrightarrows Fe^{2+} (aq) + 2Ag (s)$$

(i) Circle the oxidizing agent in this reaction:

(Ag$^+$ (aq)) Fe (s) H_2O Fe^{2+} (aq) Ag (s)

(ii) Which species is at the cathode in this reaction (circle your answer):

Ag$^+$ (aq) Fe (s) H_2O Fe^{2+} (aq) (Ag (s))

(iii) Write the cell diagram (line diagram) for an electrochemical cell based on this reaction.

$Fe_{(s)} \mid Fe^{2+}_{(aq)} \parallel Ag^+_{(aq)} \mid Ag_{(s)}$

[8] **9.** (a) For the reaction below, calculate ΔG° at 25 °C and 1000 °C. Assume ΔH° and ΔS° are independent of temperature.

$$NH_3\,(g) + HCl\,(g) \leftrightharpoons NH_4Cl\,(s)$$

	ΔH°_f (kJ mol^{-1})	S° (J mol^{-1} K^{-1})
NH_3 (g)	-45.9	192.8
HCl (g)	-92.3	187.0
NH_4Cl (s)	-314.4	94.6

Answer for 25 °C. -91.2 KJ/mol Answer for 1000 °C. 186.9 KJ/mol

(b) At what temperature, if any, does ΔG° become zero?

Answer: 618° K

[12] **10**. For the reaction:

$$CO\ (g) + 3\ H_2\ (g) \leftrightarrows CH_4\ (g) + H_2O\ (g)$$

K_p is 2.15×10^{11} at 200 °C and 4.56×10^{8} at 260 °C.

(a) What is the value of $\Delta H°$ for this reaction?

-215.2 kJ/mol

(b) For a plot of $\ln K_p$ versus 1/T for this reaction, what is the value of the slope?

25.9×10^{3} K

(c) Using the data in the table below and your calculation in part (a), determine $\Delta H°_f$ for CH_4 (g).

	$\Delta H°_f$ (kJ mol^{-1})
CO (g)	-110.5
H_2O (g)	-241.8
H_2 (g)	0.0

-83.7 kJ/mol

Equations

$$k = A\, e^{-E_a/RT}$$

$$\ln\left(\frac{k_2}{k_1}\right) = \left(\frac{E_a}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$[A]_t = [A]_o - akt$

$[A]_t = [A]_o \exp(-akt)$

$[A]_t^{-1} = [A]_o^{-1} + akt$

$pH_{buffer} = pK_a + \log([A^-]/[HA])$

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

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

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

$\Delta G = -zFE_{cell}$

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^o}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln K_{eq} = \frac{-\Delta H^o}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^o}{R}$$

$$E_{cell} = E^o_{cell} - \frac{RT}{zF} \ln Q$$

$$E^o_{cell} = \frac{RT}{zF} \ln K_{eq}$$

Constants and Conversion Factors

0.00 °C = 273.15 K

1.000 bar = 1.000 X 10^5 Pa ≈ 1.0 atm

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

N_A = 6.022 X 10^{23} mol^{-1}

K_w = 1.00 X 10^{-14} at 25 °C

1 V = 1 J C^{-1}

F = 96485 J V^{-1} mol^{-1} = 96485 C mol^{-1}

The Periodic Table of the Elements

1 **H** Hydrogen 1.00794																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012182											5 **B** Boron 10.811	6 **C** Carbon 12.0107	7 **N** Nitrogen 14.00674	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.9984032	10 **Ne** Neon 20.1797
11 **Na** Sodium 22.989770	12 **Mg** Magnesium 24.3050											13 **Al** Aluminum 26.981538	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.973761	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.4527	18 **Ar** Argon 39.948
19 **K** Potassium 39.0983	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.955910	22 **Ti** Titanium 47.867	23 **V** Vanadium 50.9415	24 **Cr** Chromium 51.9961	25 **Mn** Manganese 54.938049	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933200	28 **Ni** Nickel 58.6934	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92160	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.80
37 **Rb** Rubidium 85.4678	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.90585	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.90638	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.90550	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.8682	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.710	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90447	54 **Xe** Xenon 131.29
55 **Cs** Cesium 132.90545	56 **Ba** Barium 137.327	57 **La** Lanthanum 138.9055	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.9479	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.078	79 **Au** Gold 196.96655	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98038	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (263)	107 **Bh** Bohrium (262)	108 **Hs** Hassium (265)	109 **Mt** Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114				

58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.90765	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.92534	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93032	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93421	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
90 **Th** Thorium 232.0381	91 **Pa** Protactinium 231.03588	92 **U** Uranium 238.0289	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)

Half-Reaction	$\mathcal{E}°$(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

Increasing strength as oxidizing agent ↑

Increasing strength as reducing agent ↓