THE COLLEGE OF THE BAHAMAS

FINAL EXAMINATION

SEMESTER 01-2013

FACULTY OF
SCHOOL OF CHEMISTRY ENVIRONMENTAL AND LIFE SCIENCES

Campus/Centre:	( ) Grosvenor Close ( ) Northern Bahamas (X) Oakes Field ( ) Abaco ( ) Eleuthera ( ) Exuma ( ) Other (Specify)

Examination Day:	Thursday	**Examination Date:**	April 25th, 2013
Examination Time:	9:00AM	**Duration:**	3 Hours

Course Abbreviation & Number:	CHEM 225
Course Title:	College Chemistry II

Name of Student: ______________________________ -------
(Please print)

Student Number: ______________________________ -------

Name of Lecturer: ______________________________ -------
(Please print)

INSTRUCTIONS TO CANDIDATES

1. Please follow instructions given in each section.

INFORMATION FOR STUDENTS

- Gas constant, $R = 8.31\ \mathrm{J\ mol^{-1}\,K^{-1}} = 0.0821\ \mathrm{dm^3\,atm\ mol^{-1}\,K^{-1}}$
- $pV = nRT$, $1\ \text{atm} = 760\ \text{mmHg} = 101\ 325\ \text{Pa}$
- $F = 96487\ \mathrm{C\,mol^{-1}}$

Kinetics

- Rate$=k[\mathrm{A}]^x[\mathrm{B}]^y[\mathrm{C}]^z \ldots$

Table 1: Characteristics of first, second and zeroth order reaction of the type $A \rightarrow$ products

First-Order	Second-Order	Zeroth-Order
$\text{Rate} = -\dfrac{\Delta[A]}{\Delta t} = k[A]$	$\text{Rate} = -\dfrac{\Delta[A]}{\Delta t} = k[A]^2$	$\text{Rate} = -\dfrac{\Delta[A]}{\Delta t} = k[A]^0 = k$
$\ln[A]_t = -kt + \ln[A]_0$	$\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$	$[A]_t = -kt + [A]_0$
Form: $y = mx + b$	Form: $y = mx + b$	Form: $y = mx + b$
$y = \ln[A]_t, m = -k, x = t, b = \ln[A]_0$	$y = \dfrac{1}{[A]_t}, m = k, x = t, b = \dfrac{1}{[A]_0}$	$y = [A]_t, m = -k, x = t, b = [A]_0$
$t_{1/2} = \dfrac{\ln 2}{k} = \dfrac{0.693}{k}$	$t_{1/2} = \dfrac{1}{k[A]_0}$	$t_{1/2} = \dfrac{[A]_0}{2k}$

- $k = Ae^{-E_a/RT}$
- $\ln\left(\frac{k_1}{k_2}\right) = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

Equilibrium

- $A = \epsilon lc$
- $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
- $\mathrm{pH} = -\log[\mathrm{H^+}]$, $\mathrm{pOH} = -\log[\mathrm{OH^-}]$
- $\mathrm{pH} + \mathrm{pOH} = 14.00$ at 25 °C.
- $\mathrm{p}K_a = -\log K_a$, $\mathrm{p}K_b = -\log K_b$
- $K_w = [\mathrm{H^+}][\mathrm{OH^-}] = K_a \times K_b = 1.01 \times 10^{-14}$ at 25 °C.
- $\mathrm{pH} = \mathrm{p}K_a + \log\left(\dfrac{C_b}{C_a}\right)$
- $K_p = K_c\left(\dfrac{c_0RT}{p_0}\right)^{\Delta n_{gas}} = K_c(0.0821\,T)^{\Delta n_{gas}}$ where $c_0 = 1\,\mathrm{M}$ and $p_0 = 1\,\mathrm{atm}$.

Electrochemistry

- $E^{\ominus}_{cell} = E^{\ominus}_{red}(\text{cathode}) + E^{\ominus}_{ox}(\text{anode})$
- $\mathrm{E} = \mathrm{E}^{\ominus} - \dfrac{RT}{nF}\ln Q$
- $\mathrm{E} = \mathrm{E}^{\ominus} - \dfrac{0.0257}{n}\ln Q$ at 25 °C
- $\ln K = \dfrac{nE^{\ominus}}{0.0257}$ at 25 °C

Section 1: Multiple Choice Questions

Five possible answers are given to each question in this section. Choose the best answer in each case. (33 marks)

1) Ammonia is oxidized according to the equation,

$$4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g)$$

If, during a certain time interval, $\Delta[H_2O]$ is $0.004\,\text{mol dm}^{-3}$, then $\Delta[NH_3]$, in mol dm^{-3}, during the same time interval, is

A $-3/2 \times 0.004$

B $3/2 \times 0.004$

C $-2/3 \times 0.004$

D $2/3 \times 0.004$

E $4 \times 6 \times 0.004$

2) *Relatively* slow rates of chemical reaction are most closely associated with

A the presence of a catalyst

B high temperatures

C high reactant concentrations

D strong bonds in reactant molecules

E low activation energies

3) If concentrations are measured in M and time in seconds, the unit for the rate constant of a zeroth order reaction is:

A s^{-1}

B $M\,s^{-1}$

C $M^{-1}\,s^{-1}$

D $M^{-2}\,s^{-1}$

E unitless

4) A chemical reaction, $A + B \longrightarrow$ products, has a rate law of the form,

$$\text{rate} = k[A][B]^2.$$

The concentration of A is tripled and that of B is doubled. If the temperature remains constant, the rate of reaction increases by a factor of:

A 2

B 5

C 6

D 12

E 18

5) Which statement about the *overall order* of a reaction is *true*?

A The overall order of a reaction can be determined from the correctly balanced net ionic equation for the reaction.

B The overall order of a reaction increases with increasing temperature.

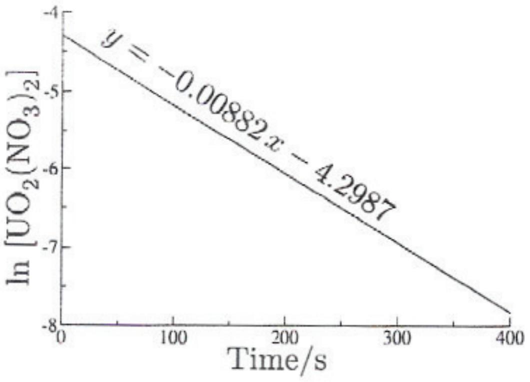
C The overall order must be a positive integer.

D The overall order of an elementary reaction is always equal to its molecularity.

E The overall order is the sum of the squares of the exponents in the observed rate law.

Questions 6 to 7 refer to the graph below showing the result of a rate study for the decomposition of uranyl nitrate.
Uranyl nitrate decomposes according to the equation,

$$UO_2(NO_3)_2(aq) \longrightarrow UO_3(s) + 2\,NO_2(g) + \tfrac{1}{2}O_2(g).$$



6) The rate law for this reaction is

A $\text{Rate}=k$

B $\text{Rate}=k[UO_2(NO_3)_2]$

C $\text{Rate}=k[UO_2(NO_3)_2]^2$

D $\text{Rate}=k[UO_2(NO_3)_2]^{-1}$

E Impossible to determine from the information given.

7) The rate constant, k for the reaction is

A -4.29

B 4.29

C 0.00882

D -0.00882

E k can not be determined from the graph

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8) For a first-order chemical reaction, an expression for the half-life of a reactant is,

$$t_{1/2} = \frac{\ln 2}{k}.$$

Which statement is *true* about the half-life of this first-order reaction?

A The $t_{1/2}$ is independent of temperature.

B The $t_{1/2}$ increases with increasing temperature.

C The $t_{1/2}$ decreases with increasing temperature.

D The $t_{1/2}$ increases with the increasing initial concentration of reactant.

E The $t_{1/2}$ decreases with the decreasing initial concentration of reactant.

9) Which statement is *true* for the reaction

$$Cr_2O_7^{2-}(aq) + 6\,I^-(aq) + 14\,H^+(aq) \longrightarrow 2\,Cr^{3+}(aq) + 3\,I_2(aq) + 7\,H_2O(l)$$

A The oxidation number of O does not change.

B The oxidation number of H changes from +1 to −1.

C The oxidation number of I changes from −6 to 0.

D The oxidation number of Cr changes from 6 to +6.

E I^- is the oxidising agent.

10) The rate of reaction between A and B follows the rate law,

$$\text{Rate} = k[\text{A}]^2[\text{B}].$$

Which change(s) will affect the value of the *rate constant* for this reaction?

I Decreasing the temperature.
II Adding a catalyst.
III Increasing the [A].

A I only.
B II only.
C III only.
D I and II only.
E II and III only.

11) When wine spoils, ethanol is oxidized to ethanoic acid by dissolved oxygen. The K_c for the equilibrium

$$C_2H_5OH(aq) + O_2(aq) \rightleftharpoons CH_3COOH(aq) + H_2O(l),$$

is 1.2×10^{82} at 25 °C. The magnitude of the equilibrium constant at this temperature indicates that

A Wine spoils through a single step process.
B Wine spoils very fast.
C Wine spoils very slowly.
D The $[C_2H_5OH(aq)] >> [CH_3COOH(aq)]$ at equilibrium.
E The $[CH_3COOH(aq)] >> [C_2H_5OH(aq)]$ at equilibrium.

12) For which reaction does K_p equal K_c?

A $2\,CO(g) + O_2(g) \rightleftharpoons 2\,CO_2(g)$
B $CH_4(g) + 2\,O_2(g) \rightleftharpoons CO_2(g) + 2\,H_2O(g)$
C $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
D $NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$
E $2\,O_3(g) \rightleftharpoons 3\,O_2(g)$

13) For the equilibrium system

$$2\,NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g) \quad \Delta H > 0$$

which change(s) will increase the amount of $CO_2(g)$?

I Adding $NaHCO_3(s)$
II Increasing the volume of the container
III Increasing the temperature

A I only
B II only
C III only
D II and III only
E I, II and III

4) Which one of the following statements regarding the ionic product of water (K_w) is *not* true?

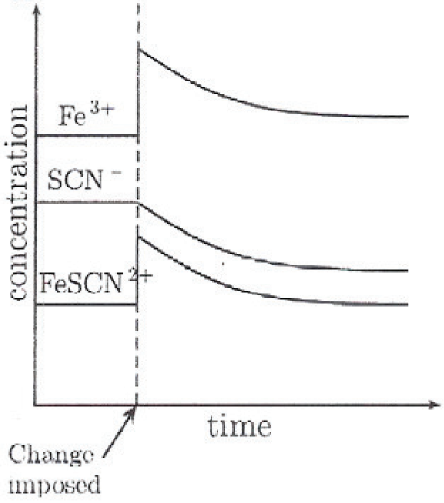
A K_w is the product of the hydrogen ion concentration and the hydroxide ion concentration in pure water.
B K_w is lower for acidic solutions than for basic solutions at the same temperature.
C K_w is altered by a change in temperature.
D K_w is 1.0×10^{-14} at 298K.
E K_w is constant for any dilute aqueous solution at 298K.

15) Consider the equilibrium system represented by the equation:

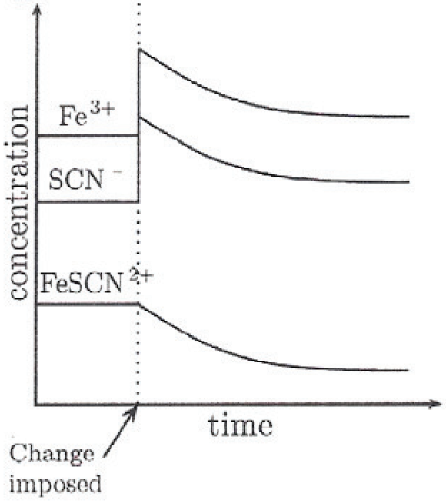
$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq).$$

If some OH^- is added (instantaneously) to this equilibrium system, keeping the volume constant, which diagram best shows the changes in $[Fe^{3+}]$, $[SCN^-]$, and $[FeSCN^{2+}]$ which occur before equilibrium is restored?

A



B



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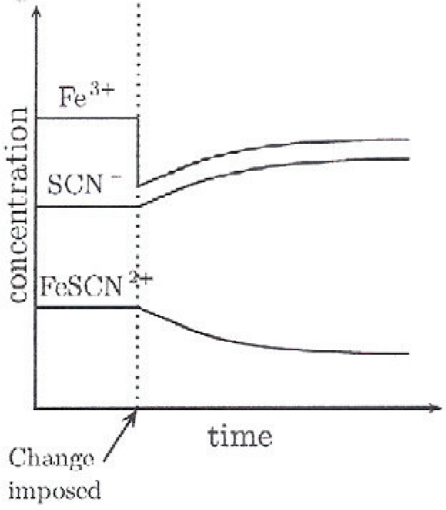

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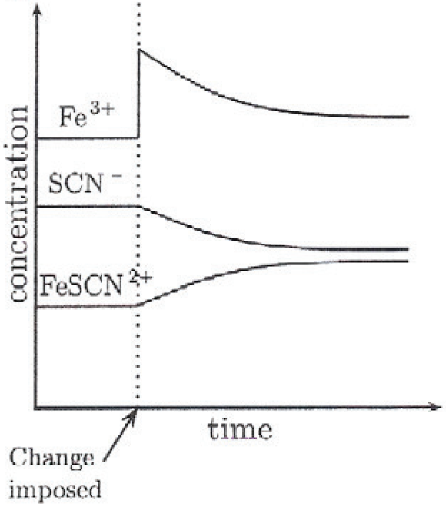
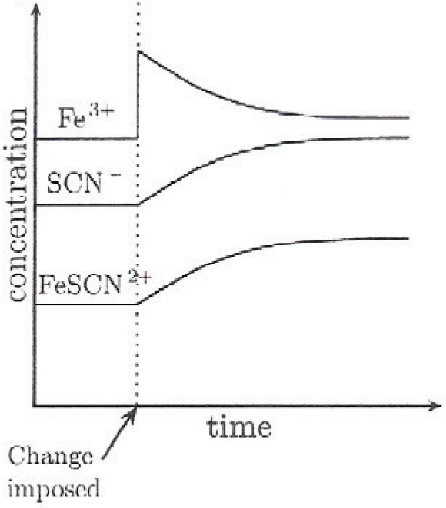


E



.6) How many electrons on the left or right will be required to balance the following half-reaction?

$$H^{+}(aq) + ClO^{-}(aq) \rightleftharpoons Cl^{-}(aq) + H_2O(l),$$

A 0

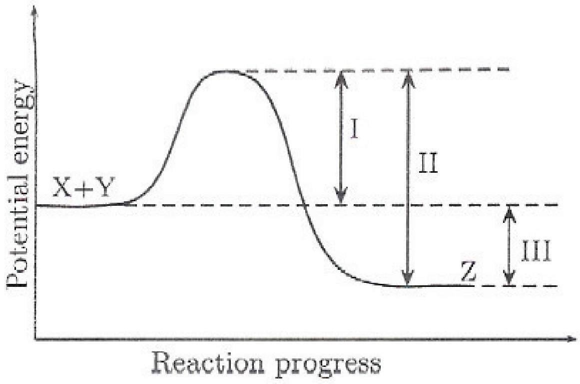
B 1

C 2

D 3

E 4

17) The energy profile diagram for the reaction X + Y $\longrightarrow$ Z is shown below.



The addition of a catalyst to this reaction would cause a change in which of the indicated energy differences?

A I only

B II only

C III only

D I and II only

E I, II and III

18) The acid dissociation constant for the weak acid HA is 3.5×10^{-6}. The pK_a of this acid is nearest to

A 1.0×10^{-14}

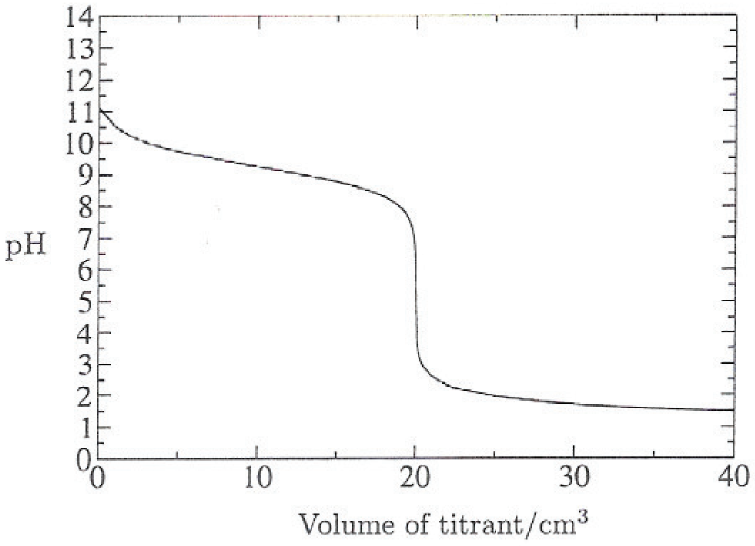
B 2.9×10^{-9}

C 5.5

D 8.5

E 14

19) Which indicator is most suitable for detecting the end-point of the titration represented by the following titration curve?



	Indicator	pH range
A	thymol blue	1.2 to 2.8
B	phenol red	6.8 to 8.4
C	methyl red	4.2 to 6.2
D	bromothymol blue	6 to 7.6
E	phenolphthalein	8.3 to 10.0

20) Which molecule or ion is the *strongest* acid?

A CH_3COO^-
B CH_3COOH
C CFH_2COOH
D CF_2HCOOH
E CF_3COOH

21) In aqueous solution, each of the following species can act as *both* a Brønsted acid and a Brønsted base, *except:*

A HCO_3^-
B $H_2PO_4^-$
C NH_4^+
D H_2O
E HS^-

22) Hydrogen sulphide, H_2S, is a diprotic acid with $K_{a1} = 9.5 \times 10^{-5}$ and $K_{a2} = 1.3 \times 10^{-13}$. In 0.05 M $H_2S(aq)$, which species is present with the *lowest* concentration?

A H_2O
B H_3O^+
C H_2S
D HS^-
E S^{2-}

23) A buffer is prepared by mixing equal volumes of 0.25 M HOAc(aq) and 0.25 M NaOAc(aq) solutions. What is the pH of the resulting solution? HOAc has $K_a = 1.74 \times 10^{-5}$, $pK_a = 4.76$.

A 1.12
B 2.68
C 4.76
D 7.00
E 9.24

24) In which species does S have the *same* oxidation number as it does in H_2SO_4?

A H_2SO_3
B $S_2O_3^{2-}$
C S^{2-}
D S_8
E SO_2Cl_2

Questions 25 to 28 refer to aqueous solutions containing equal concentrations (0.1 M) of the following substances. *Note*: $K_a(CH_3COOH)=1.8 \times 10^{-5}$, $K_b(NH_3)=1.8 \times 10^{-5}$.

A NaCl
B HCl and NaCl
C CH_3COOH and $NaCH_3COO$
D NaOH and NH_3
E NH_3 and CH_3COOH

25) The solution with the lowest pH

26) The most nearly neutral solution

27) A buffer with a pH ≈ 5

28) The solution with the highest pH.

29) Equal volumes of 0.25 M HNO_2(a weak acid) and 0.25 M HNO_3 (a strong acid) are titrated separately with 0.25 M KOH. Which would nearly be the same for both titrations?

A The K_a of the acids.
B The initial pH.
C The indicator used.
D The pH at the equivalence point.
E The pH when 5 cm^3 of excess KOH has been added.

30) The relationship between the K_{sp} of AgBr and the molar solubility, s, of AgBr in 0.10 M KBr is that K_{sp} is approximately equal to

A s^2
B $s/0.10$
C $\sqrt{s}$
D $4s^3$
E $0.10\,s$

31) Which of the following reactions reactions might consist of a single *elementary* step?

I $CH_3C{\equiv}N \longrightarrow CH_3\overset{\oplus}{N}{\equiv}\overset{\ominus}{C}$
II $H_2(g) + I_2(g) \longrightarrow 2\,HI(g)$
III $2\,Fe^{3+}(aq) + 3\,H_2S(aq) \longrightarrow 2\,FeS(s) + S(s) + 6\,H^+(aq)$

A I only.
B II only.
C I and II only.
D II and III only.
E I, II and III.

32) Based on the standard electrode potentials given which is the strongest *oxidizing agent*?

$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ $E^\circ = +0.80$
$Cu^{2+}(aq) + 2\,e^- \rightleftharpoons Cu(s)$ $E^\circ = +0.34$
$Pb^{2+}(aq) + 2\,e^- \rightleftharpoons Pb(s)$ $E^\circ = -0.13$

A Ag(s)
B Ag^+(aq)
C Cu(s)
D Pb(s)
E Pb^{2+}(aq)

33) When the contents of an electrochemical (voltaic) cell are at equilibrium, the e.m.f. of the cell, E_{cell}, is

A zero.
B negative.
C positive.
D at a maximum.
E is equal to E°_{cell}.

Section II: Structured Questions

Answer each of the following five questions in the spaces provided on the question paper. Clear and concise expression is an essential part of a good answer. (62 marks)

1) The following sequence of elementary steps is a proposed mechanism for a hypothetical reaction in the gas phase. Step II is the rate determining step.

$$\text{Step I} \qquad A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

$$\text{Step II} \qquad B \xrightarrow{k_2} C + D$$

a) Write the *net overall* equation associated with this mechanism. [1 mark]

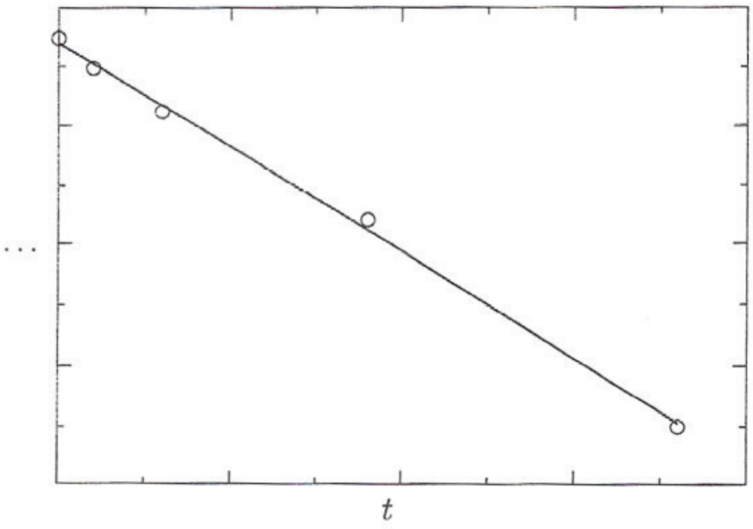
b) Is B behaving as a catalyst or intermediate? Justify your answer. [2 marks]

c) Show that the rate law consistent with this mechanism is

$$\text{Rate} = k_{obs}[A],$$

where k_{obs} is the observed experimental rate constant. [4 marks]

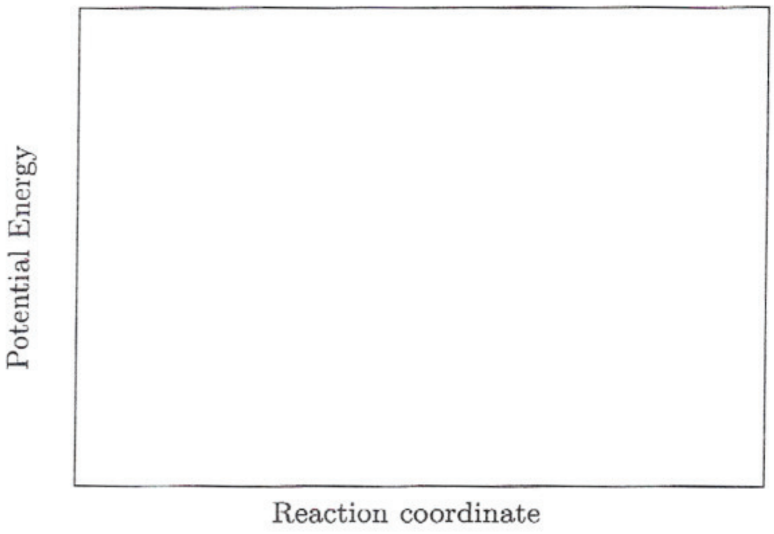
d) Experiments were performed to determine the [A] for this reaction at various times, t. Data from these experiments were used to produce the graph below.



i) Label the vertical axis. [1 mark]

ii) Explain how to determine the rate constant, k_{obs}, from this graph. [2 marks]

e) Given that the *overall* reaction is *exothermic*, sketch an energy profile diagram for this reaction on the axes provided. [4 marks]



2) At 600 K, the K_p for the decomposition reaction

$$2\,\mathrm{BrCl(g)} \rightleftharpoons \mathrm{Cl_2(g)} + \mathrm{Br_2(g)} \qquad (1)$$

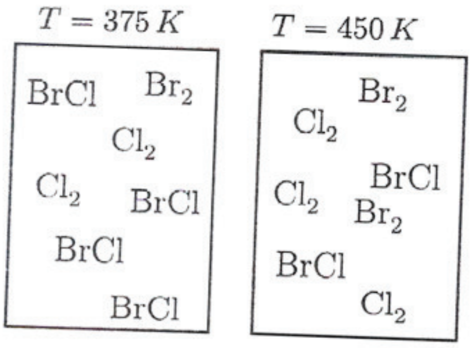
is 4.00. Some BrCl(g), Cl_2(g) and Br_2(g) are placed in a container and at the instant of mixing the *non-equilibrium* partial pressures of these gases are 1.00 atm for BrCl(g), 3.00 atm for Cl_2(g) and 3.00 atm for Br_2(g).

a) Confirm that this initial mixture of gases is a *non-equilibrium* mixture. [3 marks]

b) Complete an 'ICE' table and find the equilibrium partial pressures of each gas when the system reaches equilibrium at 600 K. [5 marks]

c) What effect, if any, will a decrease in the volume of the container have on the equilibrium position? Justify your answer. [2 marks]

d) The pictures below represent *equilibrium* mixtures at 375 K and 450 K for the reaction represented by Eq. (1). Is this reaction exothermic or endothermic. Justify your answer. [3 marks]



e) Given (same temperature throughout):

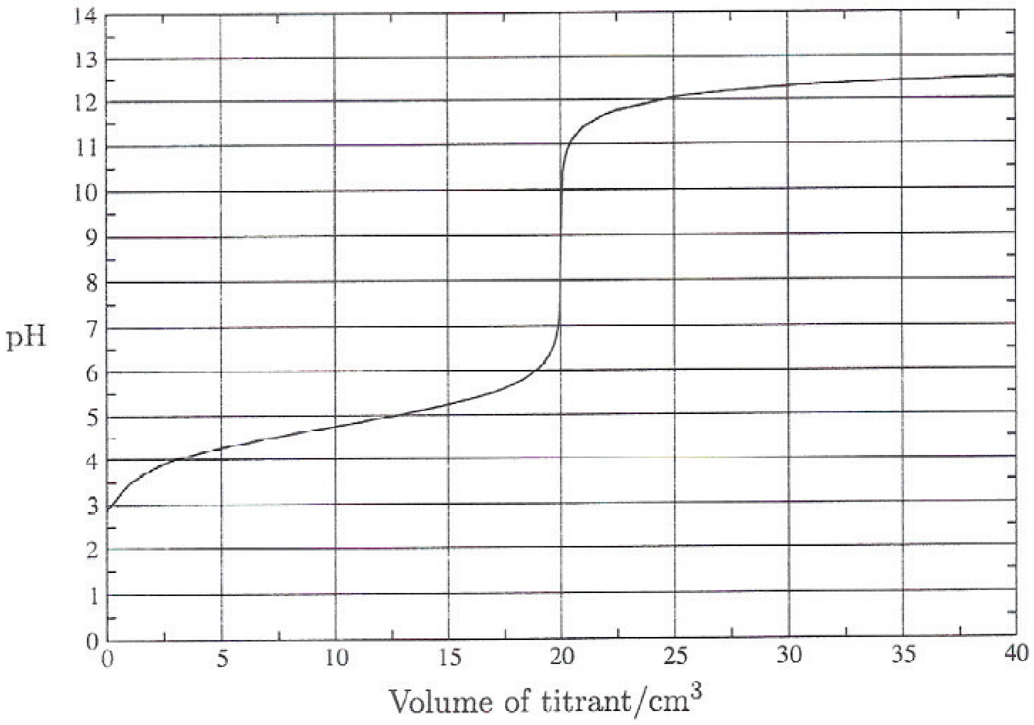
$$2\,BrCl(g) \rightleftharpoons Cl_2(g) + Br_2(g) \qquad (1) \qquad K_{p1} = 0.269$$
$$2\,IBr(g) \rightleftharpoons Br_2(g) + I_2(g) \qquad (2) \qquad K_{p2} = 0.0149$$

Determine K_{p3} for the reaction

$$BrCl(g) + \tfrac{1}{2}I_2(g) \rightleftharpoons IBr(g) + \tfrac{1}{2}Cl_2(g) \qquad (3)$$

[3 marks]

3) The graph below illustrates the result of titrating 20 cm^3 of a 0.10 M solution of the weak acid, HA(aq), with a 0.10 M solution of the strong base, NaOH(aq). The K_a of the weak acid HA is 6.3×10^{-5} at 25 °C.



a) Name the titrant. [1 mark] ....

b) Describe two features of the curve which identify HA as a weak acid. [2 marks]

c) Calculate the pH of the solution after 10 cm^3 of titrant has been added. [3 marks]

d) On the graph provided above, sketch the curve resulting from the titration of 20 cm^3 of 0.1M HCl with 0.10M NaOH. [3 marks]

4) a) The equation for the dissolution of $Mn(OH)_2(s)$ in water at 25 °C is

$$Mn(OH)_2(s) \rightleftharpoons Mn^{2+}(aq) + 2\,OH^-(aq).$$

In a saturated solution of $Mn(OH)_2(s)$ the $[OH^-] = 3.63 \times 10^{-5}$. Calculate the value of K_{sp}, for $Mn(OH)_2(s)$ at 25 °C. [4 marks]

b) $Mn(OH)_2(s)$ is oxidized to $MnO_2(s)$ by the bismuthyl(III) cation, BiO^+ in basic solution. The $BiO^+(aq)$ is simultaneously reduced to Bi(s). Write balanced half-reactions and the overall net ionic equation for this redox reaction. [5 marks]

5) Consider the following spontaneous redox reaction:

$$5\,\mathrm{Fe}^{2+}(\mathrm{aq}) + \mathrm{MnO}_4^-(\mathrm{aq}) + y\mathrm{H}^+(\mathrm{aq}) \rightleftharpoons 5\,\mathrm{Fe}^{3+}(\mathrm{aq}) + \mathrm{Mn}^{2+}(\mathrm{aq}) + \frac{y}{2}\mathrm{H}_2\mathrm{O}(\mathrm{l}). \qquad (2)$$

a) Deduce, from Eq. (2), that the value of y must be 8. Show your reasoning. [3 marks]

b) Determine how many electrons are transferrred in the reaction represented by Eq. (2)? [2 marks]

c) Identify the reducing agent in this reaction. [1 mark] ....

d) Calculate the standard e.m.f. (E°_{cell}) for this reaction, given the standard reduction potentials in the table below. [2 marks]

Reduction half-reaction	E°/volt at 25 °C
$\mathrm{Fe}^{3+}(\mathrm{aq}) + \mathrm{e}^- \rightleftharpoons \mathrm{Fe}^{2+}(\mathrm{aq})$	+0.770
$\mathrm{MnO}_4^-(\mathrm{aq}) + 8\,\mathrm{H}^+(\mathrm{aq}) + 5\,\mathrm{e}^- \rightleftharpoons \mathrm{Mn}^{2+}(\mathrm{aq}) + 4\,\mathrm{H}_2\mathrm{O}(\mathrm{l})$	+1.51

e) Write the expression for the reaction quotient, Q from Eq. (2) with $y = 8$. [1 mark]

f) If all ion concentrations are 1 M, except H^+ ions, determine the pH of the solution in the cathode half-cell compartment if the measured cell potential is +0.58 v at 25 °C. [4 marks]