00791

THE OPEN UNIVERSITY OF SRI LANKA

B.Sc Degree / Continuing Education Programme- Level 3

Final Examination -2016/2017

CMU1220 / CME 3220 - Basic Principles of Chemistry

(3 hours)

08.01. 2018 **9.30 a.m. - 12.30 p.m.**

- This question paper consists of two sections:
  Section I- 30 Multiple Choice Questions (Recommended time for this part is 1 hour).
  Section II – six (6) Essay type Questions (Recommended time for this part is 2 hours).
- Answer **All** questions.
- Submit the answer scripts for each section separately.
- The use of a **non-programmable** electronic calculator is permitted.
- You are **NOT allowed** to keep Mobile phones with you during the examination. **Switch off** and leave them in a safe place.

Gas constant(R)	$= 8.314\ J\ K^{-1}mol^{-1}$	Avogadro constant	$= 6.023 \times 10^{23}\ mol^{-1}$
Faraday constant (F)	$= 96{,}500\ C\ mol^{-1}$	Planck's constant (h)	$= 6.63 \times 10^{-34}\ J\ s$
Velocity of light (c)	$= 3.0 \times 10^{8}\ m\ s^{-1}$	Mass of an electron	$= 9.1 \times 10^{-31} kg$
Rydberg constant, R	$= 1.097 \times 10^{7}\ m^{-1}$	Standard Atmospheric pressure	$= 10^{5}\ Pa\ (N\ m^{-2})$

Section I- Multiple Choice Questions

- Choose the most correct answer to each of the questions and mark this answer with an "X" on the answer sheet.
- Use a **PEN (not a pencil)** to mark your answers.
- Any question with more than one answer marked will not be counted for grading.

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1. What is the oxidation number of Re in $Mg(ReO_4)_2$?

(1) +4 (2) +5 (3) +6 (4) +7 (5) +3

2. Which of the following statements regarding a carbon atom in the ground-state is **incorrect**?

(1) The carbon atom has 6 electrons; 2 are core electrons and 4 are valence electrons.
(2) The valence electrons in the carbon atom are all located in 2p orbitals.
(3) The core electrons in the carbon atom are all located in the 1s orbital.
(4) There are two unpaired electrons in the carbon atom.
(5) The carbon atom is paramagnetic.

3. Consider the following statements regarding the Bohr model.

(a) Since energy of the electron is given by $E = -k\left(\frac{1}{n^2}\right)$, a possible value for a stationary state is $-\frac{k}{2}$.
(b) Balmer series arise from transition of electron to the n = 2 level from levels above.
(c) When E = 0 the electron will be free and not attached to the nucleus any more.
(d) Only the first two energy levels in the hydrogen atom are quantized.

The **correct** statement/s from the above is/are

(1) (a) and (b) only (2) (a) and (c) only (3) (b) and (c) only
(4) (c) and (d) only (5) (a), (b) and (c) only

4. Which of the following statement is **incorrect?**

(1) Ionization energy increases across a period because with the increase of no. of protons, electrons are being pulled closer to the nucleus.

(2) The higher the shielding effect the lower is the ionization energy.

(3) Ionization energy decreases down a group because electrons are further away and require less energy to remove.

(4) The difference between the first ionization energy and the second ionization energy in sodium is negligible.

(5) The ionization energy of nitrogen is more than that of oxygen because nitrogen has half filled p orbitals.

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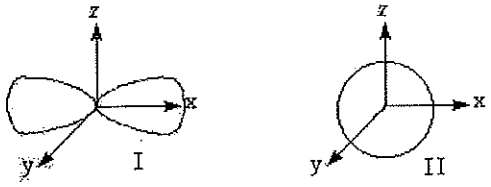
5. Shown below are the shapes of two atomic orbitals for hydrogen. Select the correct sets of quantum numbers associated with the indicated orbitals.



(1) shape I: $n = 2, l = 3$; shape II: $n = 1, l = 0$

(2) shape I: $n = 1, l = 1$; shape II: $n = 0, l = 0$

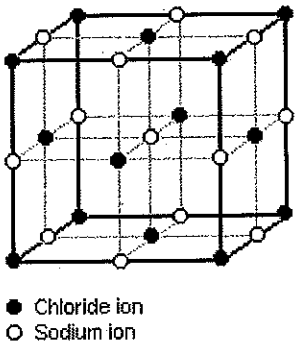
(3) shape I: $n = 1, l = 2$; shape II: $n = 1, l = 1$

(4) shape I: $n = 2, l = 1$; shape II: $n = 0, l = 0$

(5) shape I: $n = 2, l = 1$; shape II: $n = 1, l = 0$

6. In the unit cell of NaCl (rock salt) given below, the coordination numbers of Na^+ and Cl^- respectively are

(1) 4, 4 (2) 4, 6 (3) 6, 4 (4) 6, 6 (5) 6, 8



7. Which of the following statement/s is/are true about $BeCl_2$ molecule?

(a) It obeys the octet rule
(b) Its central atom is *sp* hybridized
(c) It has linear geometry
(d) Cl-Be-Cl bond angle is 120°

The answer is

(1) (a) and (b) only
(2) (b) and (c) only
(3) (c) and (d) only
(4) (a) and (d) only
(5) (a), (b) and (c) only

8. Of the following compounds, the one with the lowest boiling point is

(1) NH_3 (2) AsH_3 (3) PH_3 (4) SbH_3 (5) BiH_3

9. Select the correct statement(s) about O_2.

(a) Its bond order is 2
(b) It is paramagnetic with two unpaired electrons
(c) Its molecular orbital electron configuration is,
$\sigma_{1s}^2\ \sigma_{1s}^{*2}\ \sigma_{2s}^2\ \sigma_{2s}^{*2}\ \sigma_{2pz}^2\ \pi_{2px}^2 = \pi_{2py}^2\ \pi_{2px}^{*1} = \pi_{2py}^{*1}$
(d) O-O bond in O_2 is stronger than that in O_2^+

The answer is

(1) (a) and (b) only (2) (b) and (c) only (3) (c) and (d) only
(4) (a) and (d) only (5) (a), (b) and (c) only

10. Which one of the following molecules does not possess a dipole moment?

(a) CO_2 (b) BF_3 (c) NH_3 (d) $CHCl_3$

The answer is
(1) (a) and (b) only (2) (b) and (c) only (3) (c) and (d) only
(4) (a) and (d) only (5) (a), (b) and (c) only

11. Consider the following statements regarding reactive intermediates.
(a) Carbenes are electron rich divalent carbon intermediates.
(b) Carbanions are sp^3 hybridized pyramidal carbon intermediates.
(c) Carbocations are sp^2 hybridized planner carbon intermediates.

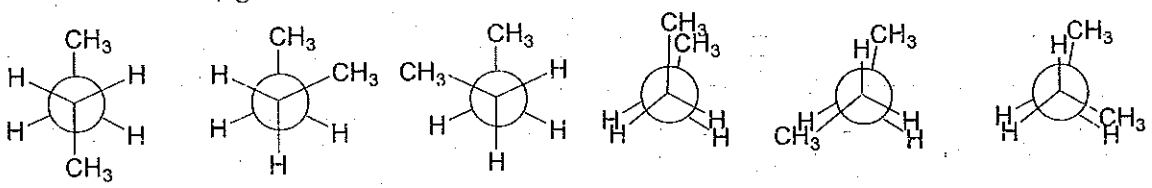
Correct statement/s is/are?

(1) (a) only (2) (a) and (b) (3) (b) and (c) (4) (a) and (c) (5) All (a),(b)and (c)

12. The **most unlikely** step during the chlorination of methane in the presence of UV radiation is:

(1) $CH_4 + Cl^{\bullet} \longrightarrow {}^{\bullet}CH_3 + HCl$
(2) ${}^{\bullet}CH_3 + HCl \longrightarrow CH_3Cl + H^{\bullet}$
(3) $CH_3Cl + Cl^{\bullet} \longrightarrow {}^{\bullet}CH_2Cl + HCl$
(4) ${}^{\bullet}CH_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + Cl^{\bullet}$
(5) ${}^{\bullet}CH_3 + Cl^{\bullet} \longrightarrow CH_3Cl$

13. Consider the following conformations of butane.

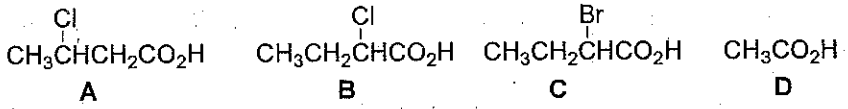


A B C D E F

Which statement is **incorrect**?

(1) Conformation A is the most stable conformation.
(2) Conformation C is more stable than conformation F.
(3) Conformations B and C show same stability
(4) Conformations D and E show same stability.
(5) Conformation D is less stable than conformation F.

14. Consider the acidities of following compounds.



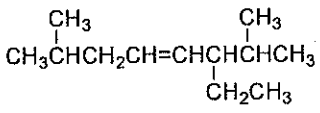
A B C D

The order of increasing acidities is:

(1) D < A < B < C (2) C < A < B < D (3) C < A < D < B

(4) C < D < A < B (5) D < A < C < B

15. IUPAC name of the following compound is:



(1) 3-ethyl-2,7-dimethyl-4-octene
(2) 2,7-dimethyl-6-ethyl-4-octene
(3) 6-ethyl-2,7-dimenthyl-4- octane
(4) 2,7-dimethyl-3-ethyl-4-octene
(5) 3-(1-methylethyl)-7-methyl-4-octene

16. Which of the following assumption is **not true** related with an ideal gas?

(1) Forces between molecules are insignificant.
(2) No energy is lost when molecules collide
(3) Molecules occupy a negligible volume
(4) Gas volume is insensitive to changes in pressure
(5) None of the above is true

17. Which of the following mathematical expression is **true** for a reversible isothermal process of an ideal gas?

(1) $q = nRTln\frac{V_2}{V_1}$ (2) $TV^{\gamma-1} = \text{constant}$ (3) $\ln P + \gamma \ln V = \text{Constant}$
(4) $PV^{\gamma} = \text{constant}$ (5) None of the above is true

18. Which of the following statement is **not true**?

(1) State functions are exact differentials.
(2) All natural processes are irreversible.
(3) Work done in a free expansion process of a gas is always zero.
(4) A system possesses only heat it does not possess any energy.
(5) Work is an expression of Energy

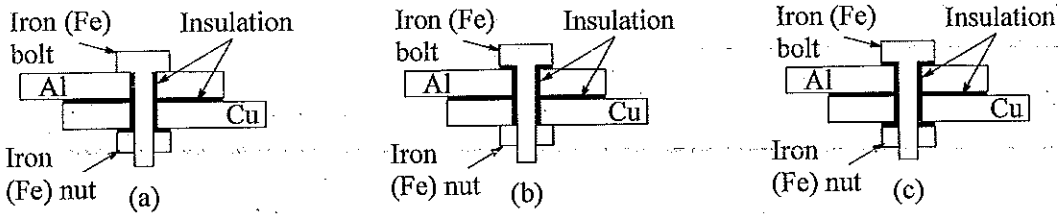
19. Which of the following is an extensive property?

(1) Dipole moment (2) Kinetic Energy (3) Vapour pressure of pure liquid
(4) The percentage of sugar in coke (5) Universal gas constant (R)

20. Which of the following is **not** a state function?

(1) Density (2) Internal energy (3) specific volume
(4) chemical composition (5) Heat

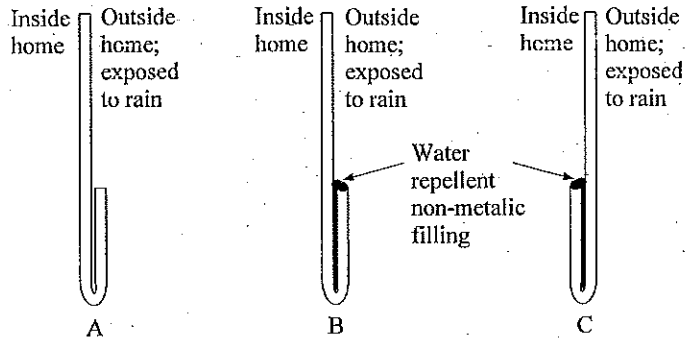
21. Cross sections of three possible ways of attaching an aluminium bar to a copper bar using an iron bolt is shown below. (An electrical insulation material is shown in black.)



Which attachment/s will **not** lead to dissimilar metal corrosion?

(1) (a) only. (2) (b) only. (3) (c) only.
(4) (a) and (b) only. (5) (b) and (c) only.

22. Consider the following statements made on three possible configurations of a tight folding of a domestic iron sheet, shown in figures A, B and C.



(a) Configurations B and C are equally good in providing long term corrosion protection at the folding.
(b) Differential aeration corrosion may take place at the folding in configuration A.
(c) No differential aeration corrosion occurs at the folding as far as the water repellent filling is in good condition in B and C.

The correct statements, out of (a), (b) and (c) above, are
(1) (a) and (b) only. (2) (a) and (c) only. (3) (b) and (c) only.
(4) All (a), (b) and (c). (5) None of the answers (1), (2), (3) or (4), is correct.

23. Under a certain set of conditions, it was found that the emf assigned to the cell diagram $P(s)\,|\,P^{3+}(aq)\,\|\,Q^{2+}(aq)\,|\,Q(s)$, where P and Q are metals, is $+1.9\ V$.

Consider the following statements.
We can say, **under the above mentioned conditions,**

(a) $P(s)\,|\,P^{3+}(aq)$ is the spontaneous anode.

(b) the reaction $3Q(s)+2P^{3+}(aq)\rightarrow 3Q^{2+}(aq)+2P(s)$ is spontaneous.

(c) the emf assigned to the cell diagram $Q(s)\,|\,Q^{2+}(aq)\,\|\,P^{3+}(aq)\,|\,P(s)$ is $-1.9\ V$.

The correct statements, out of (a), (b) and (c) above, are
(1) (a) and (b) only. (2) (a) and (c) only. (3) (b) and (c) only.
(4) All (a), (b) and (c). (5) None of the answers (1), (2), (3) or (4), is correct.

24. Consider the following statements.

The half cell having the half cell reaction $Hg_2SO_4(s) + 2e^- \rightarrow 2Hg(l) + SO_4^{2-}(aq)$

(a) may be represented by $Pt(s)\,|\,Hg(l)\,|\,Hg_2SO_4(s)\,|\,SO_4^{2-}(aq)$.

(b) may have a paste of $Hg_2SO_4(s)$ and mercury.

(c) has an interfacial potential difference which depends on the sulphate ion concentration.

The correct statements, out of (a), (b) and (c) above, are

(1) (a) and (b) only. (2) (a) and (c) only. (3) (b) and (c) only.
(4) All (a), (b) and (c). (5) None of the answers (1), (2), (3) or (4), is correct.

25. A battery is constructed by connecting two identical cells in series. The cell reaction is $Zn(s) + Cl_2(g) \rightarrow ZnCl_2(aq)$. For this reaction $\Delta G^0_{298} = -409.1\ kJ\,mol^{-1}$. The battery contains 2 kg of zinc and 2 kg of chlorine gas. The other parts, including the water, has a mass of 3.0 kg. If operated under standard conditions at 298 K, the energy density of the battery, in units of $kWh\ kg^{-1}$, is [Relative atomic masses: Zn = 65.39, Cl = 35.45]

(1) 0.65 (2) 0.46 (3) 0.32
(4) 0.23 (5) 0.58.

26. The rate of a zero order chemical reaction,(r) A →B can be expressed as

(1) $r = k \ln[A]$ (2) $r = k[A]^2$ (3) $r = k[A]$ (4) $r = k$ (5) $r = k[A]^{½}$

27. Which one of the following factors **does not affect** the rate of a chemical reaction?

(1) humidity (2) temperature (3) concentration
(4) nature of the reactants (5) light intensity

28. Consider the following statements

(a) Crushing a solid into a powder will increase reaction rate because the particles will collide with increased frequency.
(b) It is generally believed that catalysts increase reaction rates by removing the activation energy barrier.
(c) Enzymes act as catalysts in the body.

The correct statement/s is/are

(4) (a) only (2) (b) only (3) (c) only (4) (a) and (b) only (5) (a) and (c) only

29. The rate of formation of oxygen in the reaction, $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ is 2.28 $mol.L^{-1}s^{-1}$. What is the rate of formation of NO_2 in units $mol\ L^{-1}\ s^{-1}$?

(1) 0.57 (2) 9.12 (3) 2.28 4) 1.14 (5) 4.56

30. In the hydrolysis of an Alkyl chloride in the presence of a large excess of water,
$RCl + H_2O \rightarrow ROH + HCl$

(1) Molecularity is 1 but order of reaction is 2
(2) Molecularity is 2 but order of reaction is 1
(3) Molecularity and order of reaction both are 2
(4) Molecularity is 1 and order of reaction is also 1
(5) Prediction of neither molecularity nor order can be said through the given data

Section II

Answer all six questions (Recommended time 2 hours)

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1. (a) Beryllium is a lighter element compared to gold. What differences in experimental observations would you expect if beryllium foil were used instead of gold foil in the Rutherford's alpha particle scattering experiment?

(15 marks)

(b) Objects that have sizes less than the minimum wavelength of visible light do not produce clear images when observed through an optical microscope.

(i) What is the smallest size of an object that could be seen clearly through an optical microscope that uses blue light of frequency 7.06×10^{14} Hz?

(ii) An electron microscope uses fast moving electrons instead of light to probe matter. If the speed of the electrons used is 1.45×10^{7} m/s, what wavelength do the electrons have?

(iii) How many times smaller objects can the electron microscope see compared to optical microscope using blue light?

(35 marks)

(c) Expression for the energy of the electron in a helium atom is given by $E = -\frac{kz^2}{n^2}$ where $k = 2.18 \times 10^{-18}$ J.

(i) Identify all other terms in the equation.

(ii) Calculate the energy required to ionize one atom of helium.

(30 marks)

(d)(i) The following electron configuration represents an atom in an excited state. Identify the element and write its ground state electron configuration.

Electron configuration of excited state	Element	Electron configuration of ground state
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4\ 4s^1$		

(ii) Write your observation when the above element in its gaseous form if bubbled through a damp red dye stain.Explain. Translate your observation to a chemical equation.

(20 marks)

2. (a)(i) Define the term, 'lattice energy'.
(ii) Draw a fully labelled Born- Haber cycle for the formation of $Mg_3N_2(s)$. Write the expression for the lattice energy of Mg_3N_2 using the energy terms in the cycle.

(35 marks)

(b)(i) Using the concept of hybridization, predict the geometry of PCl_3 and PCl_5.
(ii) Draw the resonance structures for PO_4^{3-}

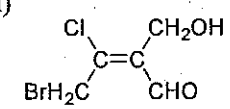
(30 marks)

(c)(i) Draw the molecular orbital energy diagram of O_2.
(ii) Draw and label the molecular orbitals formed by the overlap of two p_z orbitals and two p_y orbitals (z- axis is the inter- nuclear axis). (35 marks)

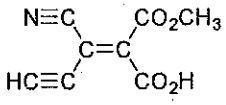
3. Answer all parts (a) – (c)
(a) Indicating the priority of groups attached to the double bond (*using numbers*) according to Cahn-Ingold-Prelog rules determine the configuration of the double bond in each of the following alkenes as *E* or *Z*.

Note: ***No marks are awarded if priority of groups is not indicated.***

(i)

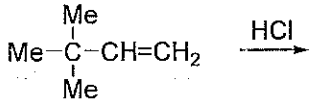


(ii)



(20 marks)

(b) Two products are formed in the following reaction.

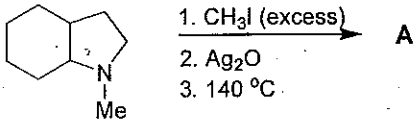


(i) Giving the mechanism postulate the structures of those two products.
(ii) Giving reasons state which one is the major product.

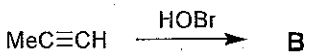
(30 marks)

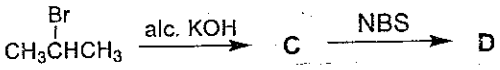
(c) Give the structures of the compounds **A** – **J** of the following reactions.

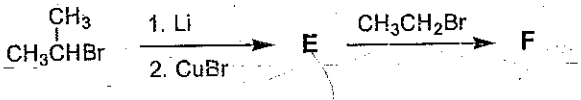
(i)

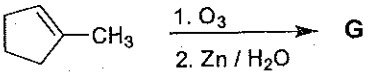


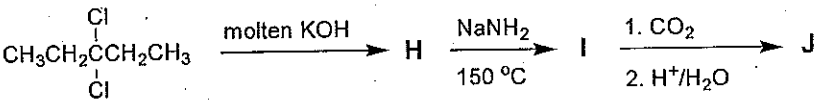
(ii)



(iii) 

(iv) 

(v) 

(vi) 

(50 marks)

4) Answer **all** parts (a), (b) and (c)

Use the following information to answer this question.

$dU = nC_v dT$ $\quad \Delta H = nC_p dT$ $\quad Cv \int_{T1}^{T2} \frac{1}{T} \cdot dT = -R \int_{V1}^{V2} \frac{1}{V} \cdot dV$

$PV^{\gamma} = \text{constant}$ $\quad \Delta S = \frac{\Delta H}{T}$ $\quad \Delta S = \int \frac{dq}{T}$

(a) Write down the mathematical expression for the 1st law of thermodynamics and 2nd law of thermodynamics? Define all the terms involved.

(10 marks)

(b) Define the following terms

(i) Closed system (ii) Isobaric process (iii) Extensive properties

(iv) State function (v) Reversible process

(30 marks)

(c) A sample of 1.0 mole of gas initially at 5.0 atm and 300 K undergoes reversible and adiabatic expansion until its pressure reaches 2.5 atm. Given that it's molar constant pressure heat capacity is 20.5 J $mol^{-1}K^{-1}$. Calculate q, w, ΔU, ΔH and the final temperature and final volume.

(60 marks)

$$\Delta G = -nFE \qquad I = 0.5 \times \sum_j c_j Z_j^2 \qquad \log(\gamma_\pm) = -\frac{A|Z_+ Z_-|\sqrt{I}}{1 + aB\sqrt{I}} \qquad E = E^0 - \frac{RT}{nF}\ln(Q)$$

$$\left[\text{Data: } F = 96500\ \text{C mol}^{-1},\ R = 8.314\ \text{J K}^{-1}\text{mol}^{-1},\ A = 0.509\ \text{dm}^{3/2}\ \text{mol}^{-1/2}\right.$$
$$\left.aB = 1.25\ \text{dm}^{3/2}\ \text{mol}^{-1/2}\right]$$

5. Answer any **TWO (02)** parts out of (a), (b) and (c).

(a) (i) Explain the importance of the Debye-Huckel laws for activity coefficient in studying Galvanic cells.

(ii) Consider an aqueous solution of $CaCl_2$ at 298 K with $[CaCl_2] = 0.1\ \text{mol dm}^{-3}$.

(α) Calculate the ionic strength of this solution.

(β) Calculate the mean activity coefficient of $CaCl_2$ in this solution using the Debye-Huckel limiting law.

(50 marks)

(b) (i) Define the electrode potential of an electrode.

(ii) Using the definition of electrode potential show that the electrode potential of the standard hydrogen electrode is zero.

(iii) Consider a metal-metal ion electrode whose half reaction is $P^{3+}(aq) + 3e^- \rightarrow P(s)$ at 298 K when $a_{P^{3+}} = x$. Explain why the electric potential of this electrode can be different from its electrode potential.

(50 marks)

(c) At 298 K, a student conducted a potentiometric titration using an aqueous solution of $X^{n+}(aq)$ as titrant and an aqueous solution of $Y^{m+}(aq)$ as titrand. He measured the electrode potential of a platinum rod immersed in the titration vessel (titrand) during the titration. The titration reaction was $X^{n+}(aq) + Y^{m+}(aq) \rightarrow X^{(n-1)+}(aq) + Y^{(m+1)+}(aq)$.

From a book of constants he found the following information.

$X^{n+}(aq) + e^- \rightarrow X^{(n-1)+}(aq)$ $\qquad E^0_{298} = 1.1\ \text{V}$

$Y^{(m+1)+}(aq) + e^- \rightarrow Y^{m+}(aq)$ $\qquad E^0_{298} = -0.8\ \text{V}$

(i) Sketch the variation of the electrode potential of the platinum rod as a function of the volume of titrant during the titration. Denote the volume of titrant at end point by V_{end}. Indicate the following on your sketch.

(α) The end point of the titration.

(β) The values of the electrode potential of the redox electrode formed at the platinum electrode when the volume of titrant added is $\frac{1}{2}V_{end}$ and $2V_{end}$.

(ii) Denoting the activity of an ionic species α by a_α, write down the thermodynamic equilibrium constant of the titration reaction in terms of the activities of the ionic species.

(iii) Calculate the thermodynamic equilibrium constant of the titration reaction at 298 K.

(50 marks)

6. (a) Draw the potential energy diagram for an endothermic reaction.
Indicate on the diagram
(i) activation energy for the forward reaction
(ii) activation energy for the reverse reaction
(iii) enthalpy of reaction.

(25 marks)

(b)(i) Given that the rate law for a first order reaction is of the form, $\frac{d[A]}{dt} = k[A]$, derive a mathematical expression for its half life.

(ii) The half-life for the acid-catalyzed hydrolysis of sucrose to form glucose and fructose, which is first order overall, is 3.20 h at 25°C.

(α) Calculate the rate constant for the reaction at this temperature.

(β) If the concentration of the reactant was doubled what would happen to the rate? Give reasons.

(35 marks)

(c) Consider the results of the following set of Experiments studying the rate of the chemical reaction, $2A + B \rightarrow 3C + D$.

Experiment no	Initial [A]/mol dm $^{-3}$	Initial [B]/mol dm $^{-3}$	Rate/ mol dm $^{-3}$hr $^{-1}$
1	0.240	0.120	2.00
2	0.120	0.120	0.500
3	0.240	0.060	0.100

(i) Use the above data to determine the rate law expression.

(ii) Calculate the rate constant k, with units.

(iii) What is the rate of the reaction when [A] is 0.140 mol dm^{-3} and [B] is 1.35 mol dm^{-3}.

(40 marks)