PART A — STRUCTURED ESSAY

Answer all four questions on this paper itself. (Each question carries 10 marks.)

1\. (a) Arrange the following in the decreasing order of the property indicated in parenthesis.

(i) Li, Na, Mg, Al, Si (first ionization energy)

………… > ………… > ………… > ………… > …………

(ii) C, O, F, Cl (first electron affinity)

………… > ………… > ………… > …………

(iii) $BeCl_2$, $CaCl_2$, $BaCl_2$ (melting point)

………… > ………… > …………

(iv) NCl_3, $SiCl_4$, ICl_4^- (bond angle)

………… > ………… > …………

(v) H_2O, H_3O^+, OH^- (electronegativity of oxygen atom)

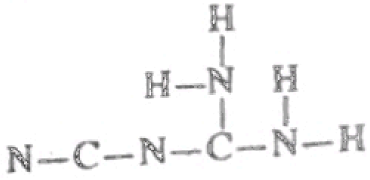
………… > ………… > …………

(vi) NO^+, FNO_2, ClNO, NH_2OH (N—O bond length)

………… > ………… > ………… > …………

(3.0 marks)

(b) 2-Cyanoguanidine ($C_2H_4N_4$) is a widely used chemical in agriculture. The following questions (i) to (v) are based on 2-Cyanoguanidine. Its skeleton is given below.



$$\mathrm{N{-}C{-}N{-}\overset{\overset{\overset{H}{|}}{H{-}N}}{\overset{|}{C}}{-}\overset{\overset{H}{|}}{N}{-}H}$$

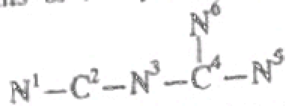
(i) Draw the most acceptable Lewis structure for this molecule.

(ii) Draw four resonance structures (excluding the structure drawn in (i) above) for this molecule.

(iii) State the following regarding the C and N atoms given in the table below:

I. electron pair geometry (arrangement of electron pairs) around the atom
II. shape around the atom
III. hybridization of the atom

The carbon and nitrogen atoms of 2–Cyanoguanidine are labelled as follows:



$$N^1-C^2-N^3-\overset{\overset{\large N^6}{|}}{C^4}-N^5$$

		C^2	N^3	C^4	N^5 or N^6
I.	electron pair geometry				
II.	shape				
III.	hybridization				

(iv) Sketch the shape of the Lewis structure drawn in part (i) above indicating approximate values of the bond angles (show all bond angles other than those involving N—H bonds).

(v) Identify the atomic/hybrid orbitals involved in the formation of the following σ–bonds in the Lewis structure drawn in part (i) above (numbering of atoms as in part (iii)).

I. N^1-C^2 N^1................................., C^2...

II. C^2-N^3 C^2................................., N^3...

III. N^3-C^4 N^3................................., C^4...

(5.0 marks)

(c) Consider the two chemical substances CH_3Cl (boiling point 249 K) and CH_3I (boiling point 316 K).

(i) Which substance has the larger dipole moment?

....

(ii) Which substance has the stronger London dispersion forces?

....

(iii) Which substance has the stronger total intermolecular attractive forces?

....

(iv) Which type of intermolecular force is dominant in comparing these two substances?

....

(electronegativity : H = 2.1, C = 2.5, I = 2.5, Cl = 3.0)

(2.0 marks)

1. (a) X is an element in the third period of the Periodic Table. Its first five successive ionization energies, in kJ mol^{-1}, are respectively, 577, 1816, 2744, 11577 and 14842. X reacts with both dilute HCl and dilute NaOH separately, liberating the same colourless and odourless diatomic gas.

(i) Identify element X. ....

(ii) Write the ground state electronic configuration of X. ....

(iii) Give the most stable positive oxidation state of X. ....

(iv) Give balanced chemical equations for the reaction of element X with

I. dilute HCl ....

II. dilute NaOH ....

(v) X burns readily in air or O_2 to form an oxide. Write the formula of the oxide.

....

(vi) Write the balanced chemical equation for the reaction of X when heated with $NaNO_3$ and dilute NaOH.

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(vii) Write the formula of the chemical species that the ion of X having the most stable oxidation state forms in an **aqueous** medium. Predict what you would expect to observe when a small amount of solid Na_2CO_3 is added to an aqueous solution of this ion.

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(viii) Give **one** use of element X.

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(5.0 marks)

(b) Test tubes labelled A to E contain solutions of $Mg(NO_3)_2$, Na_2CO_3, KCl, $ZnSO_4$ and $Pb(NO_3)_2$ (not in order). $BaCl_2$ and dilute NH_4OH solutions are added separately to portions of each solution. The observations are given in the table below.

Solution	$BaCl_2$ solution	dilute NH_4OH solution
A	a white precipitate soluble in hot water	a white precipitate
B	a white precipitate insoluble in dil. HCl	a white precipitate soluble in excess NH_4OH
C	a white precipitate soluble in dil. HCl	a clear solution
D	a clear solution	a clear solution
E	a clear solution	a gelatinous white precipitate

(i) Identify solutions A to E.

A = ...

B = ...

C = ...

D = ...

E = ...

(ii) Write balanced chemical equations for the following reactions.

I. All the reactions forming precipitates (indicate the precipitates with an arrow (↓) in the equations).

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II. All the reactions involving dissolution of precipitates.

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(5.0 marks)

3. Y is a 1.00 M solution of a weak acid HA with a pH = 3.0 at 25 °C. A 100.0 cm^3 sample of this solution was placed in a shaking bottle and 100.0 cm^3 of an organic solvent was added. After shaking the bottle it was placed in a water bath at 25 °C for 30 minutes. Thereafter, the two layers were separated and the aqueous layer was labelled as solution Z. A 25.00 cm^3 sample of solution Z was titrated with 0.50 M NaOH using phenolphthalein as the indicator. The volume of NaOH required was 40.00 cm^3.

(i) Calculate the degree of dissociation, α, of the weak acid in solution Y at 25 °C.

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(ii) Calculate the dissociation constant (K_a) of the acid HA at 25 °C.

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(iii) Calculate the degree of dissociation, α', of the acid HA in solution Z at 25 °C.

(iv) Using the values of α and α' calculated above, comment on the relationship between the degree of dissociation and concentration of the acid HA at 25 °C.

(v) Calculate the partition coefficient at 25 °C of the acid HA between water and the organic solvent. (The weak acid HA, does not associate or dissociate in an organic solvent. Disregard the dissociation of HA in aqueous medium.)

(vi) Calculate the pH of a mixture containing 25.00 cm^3 of solution Y and 25.00 cm^3 of 0.50 M NaOH solution.

(10.0 marks)

4. (*a*) A and B are structural isomers of methylpentene with the molecular formula C_6H_{12}. A exhibits geometric isomerism while B exhibits optical isomerism. On hydrogenation, A and B yield the same compound C with the molecular formula C_6H_{14}. C does not exhibit optical isomerism. Draw the structures of A, B and C in the boxes given below (It is **not necessary** to draw the stereoisomeric forms).

A B C

(1.5 marks)

(*b*) (i) Consider the following two reaction sequences (I and II) and draw the structures of the products D, E, F, G, H and I in the boxes given below.

I. $A \xrightarrow[H_2O_2]{HBr} D \xrightarrow{aq.\,KOH} E \xrightarrow{PCC} F$

II. $B \xrightarrow[H_2O_2]{HBr} G \xrightarrow{aq.\,KOH} H \xrightarrow{PCC} I$

D E F

G H I

(ii) Give a chemical test with the relevant observations to distinguish between F and I.

....

....

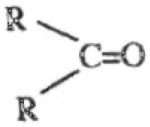
....

(iii) Compound E is a structural isomer of H. Name the type of structural isomerism that is found between these two compounds.

....

(4.0 marks)

(c) Draw the structures of the major products of the reactions given in the table below. Classify each of the reactions as nucleophilic addition (A_N), electrophilic addition (A_E), nucleophilic substitution (S_N), electrophilic substitution (S_E) or elimination (E), by writing A_N, A_E, S_N, S_E, E in the appropriate cages.

Reaction number	Reactant	Reagent	Major product	Reaction type
1	$C_2H_5CH{=}CHC_2H_5$	Br_2/CCl_4		
2		CH_3COCl/ anhydrous $AlCl_3$		
3	ROH	PCl_3		
4	RCH_2CH_2OH	anhydrous Al_2O_3/Δ		
5		RMgBr		

(2.5 marks)

(d) Write the mechanism for Reaction No. 2. Explain why the intermediate formed from benzaldehyde is stable in this reaction.

(2.0 marks)

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கல்விப் பொதுத் தராதரப் பத்திர (உயர் தர)ப் பரீட்சை, 2014 ஓகஸ்ட்
General Certificate of Education (Adv. Level) Examination, August 2014

රසායන විද්‍යාව II
இரசாயனவியல் II
Chemistry II

02 E II

✲ Universal gas constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
✲ Avogadro constant $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

PART B — ESSAY

Answer two questions only. (Each question carries 15 marks.)

5. (*a*) (i) State Raoult's law.

(ii) A and B form an ideal solution. This solution is in equilibrium with its vapour phase in a rigid container. The amounts of A and B in moles in the liquid phase are n_A and n_B respectively. The saturated vapour pressures of A and B at the temperature T are P_A^0 and P_B^0 respectively.

I. Calculate the partial pressure of A given that $n_A = 0.10$ mol, $n_B = 0.20$ mol, $P_A^0 = 1.00 \times 10^4$ Pa and $P_B^0 = 3.50 \times 10^4$ Pa.

II. Calculate the total pressure of the system.

(5.0 marks)

(*b*) The gas C dissociates into gases D and E according to the reaction given below.

$$C(g) \rightleftharpoons 2D(g) + E(g)$$

1.00 mol of C was introduced into a rigid container and allowed to reach equilibrium at temperature T_1. It was observed that 0.20 mol of C has dissociated at equilibrium and the pressure in the container was 1.00×10^5 Pa.

(i) Calculate the equilibrium constant in terms of partial pressures, K_p, for the above equilibrium writing the relevant expressions.

(ii) Calculate the equilibrium constant in terms of concentrations, K_c, if $T_1 = 500$ K.

(iii) When the temperature of the system was lowered to T_2 ($T_2 = 300$ K), it was observed that D is partially liquefied and is in equilibrium with its vapour. C and E remain as gases and are insoluble in the liquid phase of D. The saturated vapour pressure of D at 300 K is 5.00×10^2 Pa. The amount of C dissociated at T_2 is 0.10 mol. Calculate K_p.

(10.0 marks)

6. (*a*) Gas A decomposes according to the elementary reaction given below.

$$A(g) \longrightarrow B(g) + C(g)$$

(i) Write the rate law for the reaction.

(ii) The above reaction was started by introducing 1.0 mol of A into a rigid container at 300 K. The initial pressure of 30 kPa increased to 32 kPa in 10 s. When the experiment was repeated at 400 K, using the same amount of A, the initial pressure of 40 kPa increased to 45 kPa in 10 s. Rate constants of the reaction at 300 K and 400 K are k_1 and k_2 respectively.

I. Calculate the amount of A decomposed in 10 s at 300 K.

II. Calculate the amount of A decomposed in 10 s at 400 K.

III. Giving reasons show that $k_2 > k_1$

(5.0 marks)

alpy and entropy data for the dissociation of the weak acid HA are given below.

	Enthalpy change kJ mol^{-1}	Entropy change J K^{-1} mol^{-1}
$HA(aq) \rightarrow A^-(aq) + H^+(aq)$	$\Delta H_1 = 1.0$	$\Delta S_1 = 95.0$
$A^-(g) \rightarrow A^-(aq)$	$\Delta H_2 = -200.0$	$\Delta S_2 = -2000.0$
$H^+(g) \rightarrow H^+(aq)$	$\Delta H_3 = -1100.0$	$\Delta S_3 = -1200.0$
$HA(g) \rightarrow HA(aq)$	$\Delta H_4 = -150.0$	$\Delta S_4 = -100.0$

(i) Write the balanced chemical equation for the dissociation of HA in gas phase.

(ii) Calculate the following for the dissociation of HA in gas phase.

I. Enthalpy change

II. Entropy change

III. Gibbs energy change at 300 K.

(iii) Comment on the spontaneity of the dissociation of HA in the gas phase at 300 K.

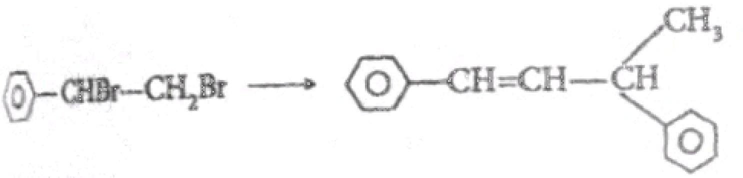
(iv) Calculate the Gibbs energy change for the dissociation of HA in the aqueous phase at 300 K.

(v) At what temperature does the Gibbs energy change of dissociation of HA in gas phase become equal to its Gibbs energy change of dissociation in the aqueous phase?

Note : Assume that ΔH and ΔS are independent of temperature.

(10.0 marks)

2. (a) Using only the chemicals given in the list, show how you would carry out the following conversion.



List of chemicals

H_2, Pd / $BaSO_4$ / Quinoline, $NaBH_4$,
Na, alcoholic KOH, $HgSO_4$,
dil. H_2SO_4, PBr_3

(5.0 marks)

(b) Show how you would synthesize compound B using compound A as the only organic starting material.

CH_3CH_2OH
A

$CH_3CHBrCHBrCH_3$
B

(7.0 marks)

(c) Draw the structures of the compounds C and D in the reaction sequence given below.

$$CH_3CH{=}CH_2 \xrightarrow{\text{conc. } H_2SO_4} C \xrightarrow[\Delta]{H_2O} D$$

It is observed that the same product D can be obtained directly by the reaction of $CH_3CH{=}CH_2$ with dilute H_2SO_4. Explain this observation by taking into account the fact that H_2O can act as a nucleophile.

(3.0 marks)

PART C — ESSAY

Answer two questions only. (Each question carries 15 marks.)

8. (*a*) The following question is based on the *s* and *p* block elements in the Periodic Table. Identify the chemical species P, Q, R, S, T, U, V, W, X and Y in the reaction scheme given below.

P (white solid) $\xrightarrow{\Delta}$ Q (white solid) + R (colourless gas)

Q $\xrightarrow{\text{dil. HCl}}$ S (reddish brown gas) + other products

$\mathrm{Q} + \mathrm{NH_4Cl(s)}$ $\xrightarrow{\Delta}$ T (white residue that gives a bright yellow colour in the flame test) + U (colourless gas) + water vapour

$\mathrm{R} + \mathrm{V}$ (colourless gas) $\xrightarrow[\text{temperature}]{\text{high}}$ U + water vapour

$\mathrm{Ca(s)} + \mathrm{U}$ $\xrightarrow{\Delta}$ W (white solid)

$\mathrm{W} + \mathrm{H_2O(l)}$ $\longrightarrow$ V + another product

$\mathrm{Mg(s)} + \mathrm{R}$ $\xrightarrow{\Delta}$ X (white solid)

$\mathrm{X} + \mathrm{H_2O(l)}$ $\longrightarrow$ Y (turns phenolphthalein pink)

(5.0 marks)

(*b*) Tests (1), (2) and (3) were carried out with an aqueous solution containing an inorganic covalent compound Z. The tests and observations are given below.

Test	Observation
(1) Added an acidified suspension of $\mathrm{MnO_2}$ to the aqueous solution.	a pale pink solution with evolution of $\mathrm{O_2}$ gas
(2) Passed $\mathrm{H_2S}$ gas through the aqueous solution.	a pale yellow (sometimes white) turbidity
(3) Passed $\mathrm{SO_2}$ gas through the aqueous solution. Removed excess $\mathrm{SO_2}$ and added a solution of $\mathrm{BaCl_2}$.	a white precipitate insoluble in dilute HCl

(i) Identify Z.

(ii) Give balanced chemical equations for the reactions that occur in tests (1), (2) and (3).

(iii) Give two uses of Z.

(iv) What is the most important intermolecular force that is present in Z?

(5.0 marks)

(c) The following procedure was used to determine the thickness of a layer of chromium coated on one surface of a rectangular sheet of an inert material.

Procedure:

A dilute acid was used to dissolve the chromium in a 8.0 cm × 5.0 cm rectangular sample of the given sheet. The resulting $\mathrm{Cr^{3+}}$, was oxidized with $\mathrm{S_2O_8^{2-}}$ (peroxydisulfate ion) in neutral medium as given below.

$$\mathrm{S_2O_8^{2-}(aq) + Cr^{3+}(aq) + H_2O(l) \longrightarrow Cr_2O_7^{2-}(aq) + H^+(aq) + SO_4^{2-}(aq)}$$

After removal of excess $\mathrm{S_2O_8^{2-}}$, the solution was acidified and an excess of ferrous ammonium sulfate, $\mathrm{(Fe(NH_4)_2(SO_4)_2.6H_2O)}$ 3.10 g was added. The unreacted $\mathrm{Fe^{2+}}$ was then titrated with 0.05 M $\mathrm{K_2Cr_2O_7}$ solution. The volume required was 8.50 cm^3.

(i) Give balanced chemical equations for the reactions of

I. $\mathrm{Cr^{3+}(aq)}$ with $\mathrm{S_2O_8^{2-}(aq)}$

II. $\mathrm{Fe^{2+}(aq)}$ with $\mathrm{Cr_2O_7^{2-}(aq)}$.

(ii) Calculate the thickness of the chromium layer on the sample.

(Density: Cr = 7.2 g cm^{-3}; Relative atomic mass: Fe = 56, Cr = 52, S = 32, O = 16, N = 14, H = 1)

(5.0 marks)

The following questions are based on the extraction of iron using the Blast Furnace.

(i) Give the common names along with their chemical formulae of the iron ore and other raw materials used in the extraction of iron.

(ii) Discuss briefly the function of each of the raw materials, except the iron ore. Use balanced chemical equations where applicable.

(iii) Write balanced chemical equations to show the stepwise conversion of iron ore to iron in the Blast Furnace.

(iv) Write the name given to the molten iron formed at the bottom of the Blast Furnace and give its approximate composition.

(v) Indicate the changes in composition required to convert the iron obtained from the Blast Furnace to stainless steel. State briefly how this is done.

(vi) Calculate the mass of the gas, (identified in part (iii)) in kg used in the stepwise conversion of iron ore to produce 2000 kg of iron.

(vii) The waste gas mixture that travels up and comes out of the Blast Furnace is known as blast furnace gas or flue gas. State the principal gases present in the mixture and identify the predominant gas.

(Relative atomic mass: Fe = 56, O = 16, C = 12)

(7.5 marks)

(i) State two major carbon species found in each of the following.

I. atmosphere

II. lithosphere (earth's crust)

III. hydrosphere

(ii) State five natural processes that provide and remove carbon species to and from the atmosphere.

(iii) Explain how human activities increase the carbon content in the atmosphere.

(iv) State two global environmental issues that are caused by the elevation of carbon content in the atmosphere.

(v) Name the chemical species/class of chemical species that are responsible for the environmental issues you mentioned in part (iv).

(vi) Write two detrimental effects caused by each of the environmental issues stated in part (iv), on global climate/human health.

(7.5 marks)

10. (*a*) (i) A domestic bleaching agent (hereafter referred to as bleaching solution) contains equal mole amounts of sodium hypochlorite (NaOCl) and Cl^-. The amount of Cl_2 gas liberated by the action of excess dilute acids on a sample of bleaching solution is called the 'available chlorine' of that sample. This is shown by the reaction below.

$$ClO^-(aq) + 2H^+(aq) + Cl^-(aq) \longrightarrow Cl_2(g) + H_2O(l)$$

Generally, the 'available chlorine' of a bleaching solution is expressed as the amount of Cl_2 gas liberated from 100 g of the bleaching solution. The following procedure was used to determine the 'available chlorine' in a bleaching solution.

Procedure:

A 25.0 cm^3 sample of the bleaching solution was diluted to 250.0 cm^3 in a volumetric flask with distilled water. To a 25.0 cm^3 sample of the diluted solution, acetic acid and excess KI were added. The I_2 liberated was then titrated with 0.30 M $Na_2S_2O_3$ solution using starch as the indicator. The volume required was 19.0 cm^3.

I. Write balanced chemical equations for the reaction of $ClO^-(aq)$ with $I^-(aq)$ and the reaction of I_2 with $Na_2S_2O_3$.

II. Calculate the percentage of 'available chlorine' by mass in the bleaching solution. (Density of the bleaching solution = 1.2 g cm^{-3}, Relative atomic mass: Cl = 35.5)

(ii) The following questions are based on the transition metal Fe and its compounds.

I. Write the ground state electronic configuration of Fe.

II. State the **two** most common positive oxidation states of Fe.

III. Aqueous $FeSO_4$ reacts with excess KCN to give a yellow octahedral ionic complex, **G**. **G** does not contain the elements H, O and S. Write the structural formula of **G**.

IV. Give the IUPAC name of **G**.

V. **G** reacts with 30% aqueous HNO_3 to give a red-brown octahedral ionic complex, **L**. The oxidation state of Fe remains unchanged during this reaction. The molecular formula of **L** is $FeK_2C_5N_6O$. Write the structural formula of **L**.

VI. The reaction taking place in part (V) above can be described as a ligand substitution reaction in an octahedral complex. From the list given below, identify the entering group and the leaving group, with their correct charges, in this substitution reaction.

$$N_2,\ NO,\ NO^+,\ NO_2^-,\ NO_3^-,\ CN^-,\ CO$$

(7.5 *marks*)

(*b*) Waste water generated in an industrial process (pH = 7.0) contains a coloured compound **D**. A treatment plant is designed to remove the colour by electrochemically oxidizing this compound. Electrochemical oxidation of compound **D** in the aqueous medium takes place as follows.

$$D(aq) \longrightarrow A^{2+}(aq) + B(aq) + 2e$$

$$2H_2O(l) + 2e \longrightarrow H_2(g) + 2OH^-(aq)$$

The concentration of compound **D** in the waste water was found to be 0.001 mol dm^{-3}.

(i) Calculate the time required for complete electrochemical oxidation of compound **D** in a 1.0 dm^3 sample of the waste water by an electrolytic cell consisting of two Pt electrodes, using a constant current of 100 mA.

(charge of 1.0 mol of electrons = 96500 C)

(ii) If $A(OH)_2$ is completely ionized in the aqueous medium, calculate the pH of the waste water sample after the electrochemical oxidation.

(iii) If the above industry releases waste water containing compound **D** at a rate of 10 dm^3 s^{-1}, calculate the minimum current that must be supplied to the electrolytic cell in order to completely oxidizie compound **D**.