

7. **AX** and **BX₂** are two sparingly soluble salts in water. At room temperature, their solubility products are K_{sp_1} and K_{sp_2} respectively. Solubility of **AX** is p while that of **BX₂** is q . When each salt is in equilibrium with its saturated solution, if $\frac{K_{sp_1}}{[A^{+}_{(aq)}]} = \frac{K_{sp_2}}{[B^{2+}_{(aq)}]}$, which of the following is correct?

(1) $p = q^2$ (2) $p^2 = q$ (3) $4p = q^2$ (4) $p = 4q^2$ (5) $p = 2q^2$

8. Which of the following statements is **false** with regard to alkali and alkaline earth metals?

(1) All alkaline earth metals react with N₂ gas at high temperature.
 (2) The melting points of alkaline earth metals are higher than the melting points of alkali metals in the same period.
 (3) Second ionization energies of alkali metals are much higher than those of alkaline earth metals in the same period.
 (4) All hydroxides formed by alkaline earth metals are strong bases.
 (5) The solubility of alkali metal hydroxides increases down the group.

9. The effective nuclear charge felt by the valence electron in lithium (Li) is, (Li, Z = 3 and relative atomic mass = 7)

(1) equal to +3 (2) less than +3 (3) greater than +3
 (4) equal to +7 (5) less than +7

10. The following equilibrium exists in a closed-rigid container at a given temperature.

$$2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$$

An extra amount of O₂(g) is added into the container at the same temperature. After the equilibrium is re-established, which of the following has a lower value compared to its value at the initial equilibrium?

(1) Equilibrium constant of the reaction. (2) The total pressure of the system.
 (3) The amount of SO₂(g) in the system. (4) The amount of SO₃(g) in the system.
 (5) The amount of O₂(g) in the system.

11. Which of the following is **true** regarding the O—N—O angle of the nitrogen species?

(1) NO₂⁺ > NO₂⁻ > NO₂ > NO₄³⁻ (2) NO₄³⁻ > NO₂⁺ > NO₂ > NO₂⁻
 (3) NO₂⁺ > NO₂ > NO₂⁻ > NO₄³⁻ (4) NO₄³⁻ > NO₂ > NO₂⁻ > NO₂⁺
 (5) NO₂⁺ > NO₂⁻ > NO₄³⁻ > NO₂

12. A lamp produces 6.0J of energy per second in the blue region (470 nm) of the visible light. For how long should the lamp be lit to generate 1.0×10^{20} photons?

(1) 2.4 s (2) 7.1 s (3) 8.5 s (4) 9.2 s (5) 10.5 s

13. A reaction is spontaneous at 298 K and 100 kPa pressure, while it is non-spontaneous at high temperature and the same pressure. Which of the following is **true** for this reaction at 298 K and 100 kPa pressure?

	ΔG	ΔH	ΔS
(1)	positive	positive	positive
(2)	negative	negative	negative
(3)	negative	negative	positive
(4)	negative	positive	negative
(5)	positive	positive	negative

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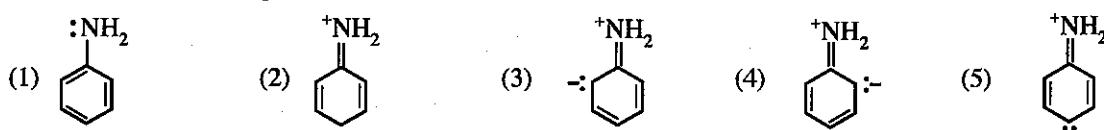
14. The following procedure was used to determine the molar mass of an unknown gas X. First, the mass of a rigid container of volume V containing dry air was measured as m_1 . Then the dry air was removed and the container was filled with an unknown gas X and the mass was measured as m_2 . Both the dry air and unknown gas, were at the same temperature (T) and pressure (P). Density of dry air is d . Which of the following expressions gives the molar mass of the unknown gas?

(1) $\frac{dRT}{P}$ (2) $\frac{[m_2 - (m_1 - dV)]RT}{PV}$ (3) $\frac{(m_1 - m_2)RT}{PV}$
 (4) $\frac{(m_2 - m_1)RT}{PV}$ (5) $\frac{[m_1 - (m_2 - dV)]RT}{PV}$

15. A buffer solution is prepared by mixing a volume V_1 of a monobasic weak acid with a volume V_2 of a monoacidic strong base. The initial concentrations of the weak acid and the strong base are C_1 and C_2 , respectively. The acid dissociation constant of the weak acid is K_a . If the pH of the buffer solution is to be maintained between $pK_a - 1$ and $pK_a + 1$, which of the following expressions gives the correct relationship for C_1 , C_2 , V_1 and V_2 ?

(1) $\frac{1}{10} < \frac{C_2 V_2}{C_1 V_1 - C_2 V_2} < 10$ (2) $\frac{1}{10} < \frac{C_1 V_1}{C_1 V_1 - C_2 V_2} < 10$ (3) $\frac{1}{10} < \frac{C_2 V_2}{C_1 V_1} < 10$
 (4) $\frac{1}{10} < \frac{C_1 V_1 - C_2 V_2}{C_2 V_2} < 10$ (5) $1 < \frac{C_1 V_1}{C_2 V_2} < 10$

16. Which of the following is **not** a resonance structure of aniline?



17. The initial rate of a zero-order reaction is R_0 and its rate constant is k . The rate of the reaction when the initial concentration is reduced by 50% is,

(1) k (2) $\frac{1}{k}$ (3) $\frac{k}{2}$ (4) $\frac{R_0}{2}$ (5) $\frac{R_0}{4}$

18. An electrochemical cell was constructed by connecting half-cells of $\text{Ni}^{2+}(\text{aq}, 1.0 \text{ M})/\text{Ni}(\text{s})$ and $\text{Cu}^{2+}(\text{aq}, 1.0 \text{ M})/\text{Cu}(\text{s})$ with a voltmeter and a salt bridge. The overall cell reaction and the initial reading of the voltmeter when the half-cells are connected are,

$$\left(E_{\text{Ni}^{2+}/\text{Ni}}^{\circ} = -0.24 \text{ V} \text{ and } E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = +0.34 \text{ V} \right)$$

(1) $\text{Ni}^{2+}(\text{aq}) + \text{Cu}(\text{s}) \longrightarrow \text{Ni}(\text{s}) + \text{Cu}^{2+}(\text{aq})$; 0.00 V
 (2) $\text{Cu}^{2+}(\text{aq}) + \text{Ni}(\text{s}) \longrightarrow \text{Cu}(\text{s}) + \text{Ni}^{2+}(\text{aq})$; +0.58 V
 (3) $\text{Cu}^{2+}(\text{aq}) + \text{Ni}(\text{s}) \longrightarrow \text{Cu}(\text{s}) + \text{Ni}^{2+}(\text{aq})$; -0.58 V
 (4) $\text{Cu}^{2+}(\text{aq}) + \text{Ni}(\text{s}) \longrightarrow \text{Cu}(\text{s}) + \text{Ni}^{2+}(\text{aq})$; 0.00 V
 (5) $\text{Cu}(\text{s}) + \text{Ni}(\text{s}) \longrightarrow \text{Cu}^{2+}(\text{aq}) + \text{Ni}^{2+}(\text{aq}) + 4\text{e}^-$; +0.58 V

19. Solid diiodine pentoxide (I_2O_5) reacts with carbon monoxide at room temperature to give carbon dioxide and iodine. This can be used to measure the amount of carbon monoxide in a sample of air. An air sample of 5.0 dm^3 was passed through a tube containing I_2O_5 and the liberated iodine was collected in an aqueous KI solution (KI in excess). The resulting solution was titrated with $0.005 \text{ mol dm}^{-3}$ $\text{Na}_2\text{S}_2\text{O}_3$ solution using starch as the indicator. The volume of $\text{Na}_2\text{S}_2\text{O}_3$ required was 10.00 cm^3 . The concentration (in ppm) of carbon monoxide in the air sample is, ($\text{C} = 12$, $\text{O} = 16$, density of the air sample = $1.40 \times 10^{-3} \text{ g cm}^{-3}$)

(1) 100 (2) 250 (3) 500 (4) 700 (5) 1000

20. Which of the following statements is **false** with regard to sulfur and its compounds?

(1) S is a non metal with oxidation states in the range -2 to +6.
 (2) S reacts with conc. H_2SO_4 giving SO_3 as one of the products.
 (3) SO_2 can act both as an oxidizing agent and as a reducing agent.
 (4) Burning large quantities of S contributes to acid rain.
 (5) Concentrated H_2SO_4 can act as a strong acid, an oxidizing agent and a dehydrating agent.

21. At 298 K, for the reaction $\text{N}_2(\text{g}) + 3\text{F}_2(\text{g}) \longrightarrow 2\text{NF}_3(\text{g})$, $\Delta H^\circ = -263 \text{ kJ mol}^{-1}$. Bond dissociation enthalpies of $\text{N}\equiv\text{N}$ and $\text{N}-\text{F}$ are 946 kJ mol^{-1} and 272 kJ mol^{-1} , respectively. The value (in kJ mol^{-1}) of the bond dissociation enthalpy of the F-F bond is,

(1) -423 (2) -393 (3) -141 (4) 141 (5) 423

22. Which of the following statements is **false** with regard to 3d-block elements?

(1) Sc, Ti and Zn do not exhibit variable valency.
 (2) 3d-block elements are good industrial catalysts.
 (3) Mn forms acidic, amphoteric and basic oxides.
 (4) Zn has the lowest melting point among all 3d-block elements.
 (5) Positive oxidation states of V range from +2 to +5.

23. The following thermochemical data are given for the reaction.

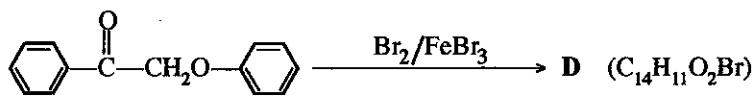


$$\Delta H_{f\text{NO}_2\text{(g)}}^{\circ} = 35 \text{ kJ mol}^{-1}, \quad \Delta H_{f\text{N}_2\text{O(g)}}^{\circ} = 80 \text{ kJ mol}^{-1}, \quad \Delta H_{f\text{NO(g)}}^{\circ} = 90 \text{ kJ mol}^{-1}$$

Which of the following statements is true for the reaction above?

- (1) $\Delta H^{\circ} = -155 \text{ kJ mol}^{-1}$ while the value of the equilibrium constant of the reaction decreases with increasing temperature.
- (2) $\Delta H^{\circ} = 155 \text{ kJ mol}^{-1}$ while the value of the equilibrium constant of the reaction decreases with increasing temperature.
- (3) $\Delta H^{\circ} = -25 \text{ kJ mol}^{-1}$ while the value of the equilibrium constant of the reaction decreases with increasing temperature.
- (4) $\Delta H^{\circ} = 25 \text{ kJ mol}^{-1}$ while the value of the equilibrium constant of the reaction decreases with increasing temperature.
- (5) $\Delta H^{\circ} = -155 \text{ kJ mol}^{-1}$ while the value of the equilibrium constant of the reaction increases with increasing temperature.

24. Consider the following reaction.



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The most likely structure of **D** is,

- (1)
- (2)
- (3)
- (4)
- (5)

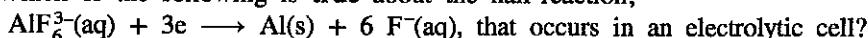
25. Compound **A** reacts with LiAlH_4 to give **B**. **B** is more basic than **A**. **B** liberates N_2 when treated with NaNO_2/HCl at $0-5^{\circ}\text{C}$. Both **A** and **B** react with ammoniacal AgNO_3 to give precipitates. The structure of **A** could be,

- (1)
- (2)
- (3)
- (4)
- (5)

26. Which of the following statements is true with regard to ozone layer depletion?

- (1) Chlorofluorocarbons (CFCs) react directly with ozone and deplete the ozone layer.
- (2) Falling of IR radiation on the earth surface is encouraged by the depletion of the ozone layer.
- (3) Hydrofluorocarbons (HFCs) contribute to ozone layer depletion.
- (4) Ozone in the ozone layer undergoes natural decomposition in the presence of ultraviolet radiation.
- (5) Ozone layer depletion takes place only by ClO^- free radicals.

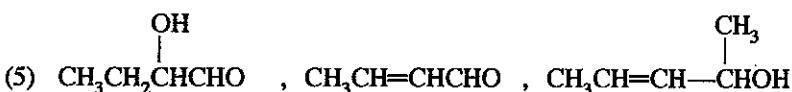
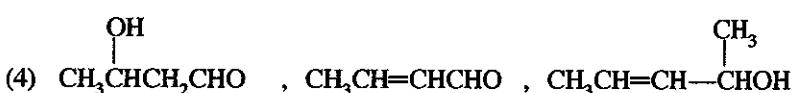
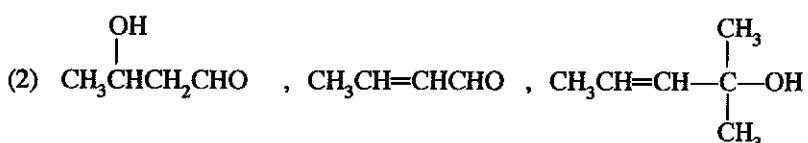
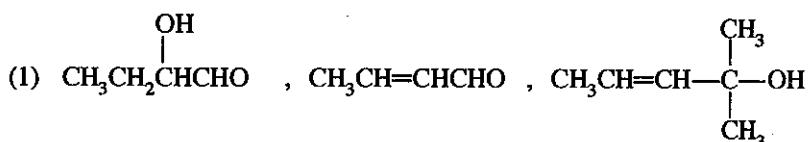
27. Which of the following is **true** about the half-reaction,



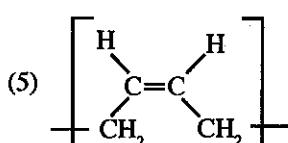
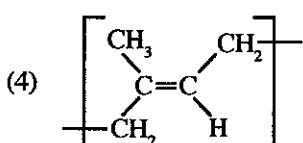
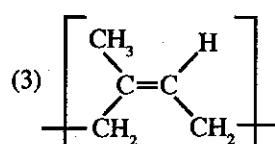
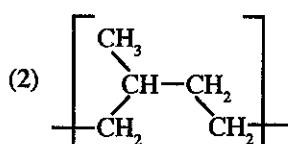
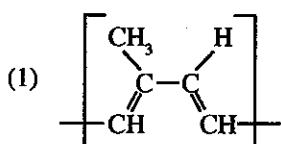
- Al is oxidized.
- AlF_6^{3-} is reduced.
- Oxidation state of Al is changed from -3 to 0.
- F^- acts as a reducing agent.
- F^- is reduced.



In the reaction scheme given above, the structures of **P**, **Q** and **R** respectively are,

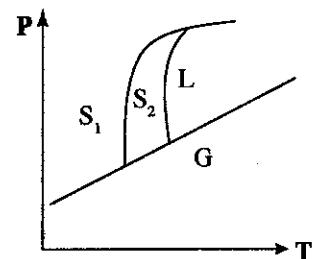


29. The repeating unit of natural rubber is,



30. The phase diagram of an element is shown in the figure. Which of the following statements is **false** with regard to the phase diagram of this element?

- There is one **T**, **P** condition at which the phases S_1 , S_2 and **G** are in equilibrium.
- There is one **T**, **P** condition at which the phases S_1 , S_2 and **L** are in equilibrium.
- There is one **T**, **P** condition at which the phases S_2 , **L** and **G** are in equilibrium.
- There is one **T**, **P** condition at which the phases S_1 , **L** and **G** are in equilibrium.
- Three **T**, **P** conditions at which more than two phases are in equilibrium are shown in the phase diagram.



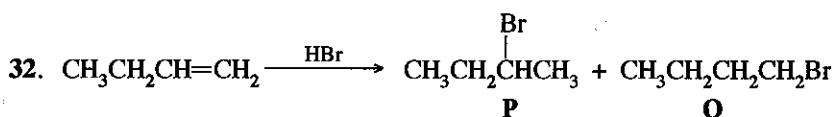
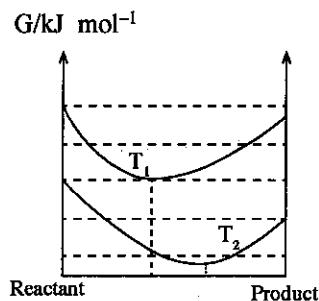
- For each of the questions **31 to 40**, one or more responses out of the four responses *(a)*, *(b)*, *(c)* and *(d)* given is/are correct. Select the correct response/responses. In accordance with the instructions given on your answer sheet, mark
 - if only *(a)* and *(b)* are correct.
 - if only *(b)* and *(c)* are correct.
 - if only *(c)* and *(d)* are correct.
 - if only *(d)* and *(a)* are correct.
 - if **any other** number or combination of responses is correct.

Summary of above Instructions

(1)	(2)	(3)	(4)	(5)
Only (a) and (b) are correct	Only (b) and (c) are correct	Only (c) and (d) are correct	Only (d) and (a) are correct	Any other number or combination of responses is correct

31. The variation of standard Gibbs energy of $A(g) \rightleftharpoons B(g)$ with the extent of reaction at two temperatures T_1 , T_2 ($T_2 > T_1$) and constant pressure is shown in the figure. Which of the following statements is/are correct for this reaction?

- Equilibrium constant at T_2 is greater than that at T_1 .
- The reaction is endothermic.
- The reaction has a positive ΔS° value.
- The reaction is exothermic.



Which of the following statements is/are **correct** regarding the above reaction?

- This reaction is a nucleophilic addition reaction.
- P** is the major product.
- A carbocation is formed in the first step of the reaction.
- Q** is the major product.

33. The following statements refer to certain industrial processes. Which of the following statements is/are **correct**?

- Baby soap is manufactured using KOH.
- Reaction of SO_2 with O_2 to give SO_3 in the contact process is favoured under low pressures.
- K_2CO_3 can be synthesised using the Solvay process.
- Cathode and anode compartments are separated by a diaphragm to prevent the reaction between Na and chlorine gas in the manufacture of Na using the Down's cell.

34. Which of the following is/are always **correct** for the slowest step of a multi-step reaction?

- Its molecularity is an integer.
- Its molecularity is higher than the overall order of the reaction.
- Overall rate of the reaction depends on its rate.
- Its molecularity is equal to the number of steps in the reaction.

35. Which of the following reaction steps is/are most **unlikely** to take place, when Cl_2 reacts with CH_4 in the presence of light?

- $\text{CH}_3 + \text{Cl}_2 \longrightarrow \text{CH}_3\text{Cl} + \text{Cl}$
- $\text{CH}_3 + \text{Cl}^\cdot \longrightarrow \text{CH}_3\text{Cl}$
- $\text{CH}_4 + \text{Cl}^\cdot \longrightarrow \text{CH}_3\text{Cl} + \text{H}^\cdot$
- $\text{Cl}^\cdot + \text{H}^\cdot \longrightarrow \text{HCl}$

36. Which of the following statements is/are **correct** with regard to NH_3 and NF_3 ?

- Bonded pair repulsions are weaker in NF_3 than in NH_3 .
- NF_3 has a higher dipole moment than NH_3 .
- NF_3 is a stronger Lewis base than NH_3 .
- The electronegativity difference between N and H in NH_3 and that between N and F in NF_3 are nearly equal.

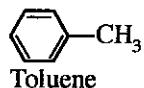
37. The equilibrium constant for the reaction $2\text{NO(g)} + \text{Br}_2\text{(g)} \rightleftharpoons 2\text{NOBr(g)}$ at 1000 K is $1.25 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3$. At this temperature, which of the following statements is/are correct?

- Equilibrium mixture consists mainly of NO(g) and $\text{Br}_2\text{(g)}$ and the equilibrium constant for the reverse reaction is 80 mol dm^{-3} .
- Equilibrium mixture consists mainly of NOBr(g) and the equilibrium constant for the reverse reaction is 80 mol dm^{-3} .
- Equilibrium mixture consists mainly of NO(g) and $\text{Br}_2\text{(g)}$ and the equilibrium constant for the reverse reaction is $1.25 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3$.
- Equilibrium mixture consists mainly of NOBr(g) and the equilibrium constant for the reverse reaction is $1.25 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3$.

38. Which of the following statements is/are correct regarding an elementary bimolecular reaction in the gas phase?

- The experimentally determined order of the reaction is two only when the concentrations of reactants are equal.
- The experimentally determined order of the reaction becomes three when the concentrations of reactants are in the 1:3 ratio.
- When the concentration of one of the reactants is in large excess compared to the other, the rate of the reaction becomes independent of the concentration of that reactant.
- When the volume of the container containing reactants is reduced at a constant temperature, the rate of collision between reactant molecules increases.

39. Which of the following statements regarding methyl benzene (toluene) is/are correct?



- All carbon atoms lie in the same plane.
- Lengths of all carbon carbon bonds are equal to each other.
- Lengths of all carbon hydrogen bonds are equal to each other.
- Any C—C—C bond angle is 120° .

40. Which of the following statements is/are correct regarding air pollution?

- Sulphates in water bodies is a source of atmospheric H_2S .
- Conversion of $\text{SO}_2\text{(g)}$ to $\text{SO}_3\text{(g)}$ is accelerated by NO(g) .
- NO(g) emitted during fossil fuel combustion is not considered as an air pollutant.
- $\text{SO}_2\text{(g)}$ in the atmosphere is removed by lightning.

● In question Nos. 41 to 50, two statements are given in respect of each question. From the Table given below, select the response out of the responses (1), (2), (3), (4) and (5) that best fits the two statements and mark appropriately on your answer sheet.

Response	First Statement	Second Statement
(1)	True	True, and correctly explains the first statement
(2)	True	True, but does not explain the first statement correctly
(3)	True	False
(4)	False	True
(5)	False	False

	First Statement	Second statement
41.	C—O bonds in the bicarbonate ion are identical.	Bicarbonate ion is a resonance hybrid of three stable resonance structures.
42.	It is not possible to prepare a Grignard reagent by reacting $\text{HOCH}_2\text{CH}_2\text{Br}$ with Mg in dry ether.	Grignard reagent does not react with compounds having a hydroxyl group.
43.	Increasing the pressure of the equilibrium mixture $2\text{H}_2\text{(g)} + \text{CO(g)} \rightleftharpoons \text{CH}_3\text{OH(g)}$ at constant temperature shifts the position of equilibrium to the right.	When the pressure of a gas mixture at chemical equilibrium is increased at constant temperature, the reaction occurs in such a way as to decrease the number of moles.

First Statement		Second statement
44. Solubility of group II sulphates and carbonates decreases down the group whereas the opposite is observed for hydroxides.		Solubility of an ionic compound depends only on its hydration energy.
45. The reactivity of alkanes with electrophiles is less than that of alkenes.		The C—H bonds in hydrocarbons have a low polarity due to the small difference in electronegativity between carbon and hydrogen atoms.
46. The entropy of the surroundings increases when water vapour in a closed container undergoes condensation.		Heat absorbed by a closed system increases the thermal motion of surroundings.
47. The cathode compartment and anode compartment of the membrane cell used in the manufacture of NaOH are separated by an ion selective membrane.		The ion selective membrane used in the membrane cell does not allow the transfer of cations.
48. 2-butene shows diastereoisomerism.		There are two possible structures for 2-butene, which are not mirror images of each other.
49. Solubility of MnS(s) in water at room temperature does not depend on pH.		S ^{2-(aq)} is the conjugate base of a weak acid.
50. The melting points of <i>d</i> -block elements are higher than the melting points of <i>s</i> -block elements.		<i>d</i> and <i>s</i> electrons are available to take part in delocalization in forming metallic bonds in <i>d</i> -block elements.

* * *

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The Periodic Table

1	1 H	2	2 He
2	3 4 Li Be		
3	11 12 Na Mg		
4	19 20 21 22 23 24 25 26 27 28 29 30 K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn	31 32 33 34 35 36 Ga Ge As Se Br Kr	
5	37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe		
6	55 56 La- Cs Ba Lu	72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn	
7	87 88 Ac- Fr Ra Lr	104 105 106 107 108 109 110 111 112 113 Rf Db Sg Bh Hs Mt Uun Uuu Uub Ut	...

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

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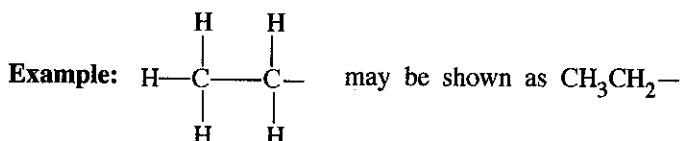
ரසாயன வீட்டுவில்
இரசாயனவியல்
Chemistry

02 E II

రైయ రూహాజి
ముంఱు మణిత్తథియాలమ్
Three hours

Index No.:

- * A Periodic Table is provided on page 15.
- * Use of calculators is not allowed.
- * Universal gas constant, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
- * Avogadro constant, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
- * In answering this paper, you may represent alkyl groups in a condensed manner.



PART A – Structured Essay (pages 2 - 8)

- * *Answer all the questions on the question paper itself.*
- * *Write your answer in the space provided for each question. Please note that the space provided is sufficient for the answer and that extensive answers are not expected.*

PART B and PART C – Essay (pages 9 - 14)

- * Answer four questions selecting two questions from each part. Use the papers supplied for this purpose.
- * At the end of the time allotted for this paper, tie the answers to the three Parts A, B and C together so that Part A is on top and hand them over to the Supervisor.
- * You are permitted to remove only Parts B and C of the question paper from the Examination Hall.

For Examiner's Use Only

Part	Question No.	Marks
A	1	
	2	
	3	
	4	
B	5	
	6	
	7	
C	8	
	9	
	10	
Total		
Percentage		

Final Mark

In Numbers	
In Letters	

Code Numbers

Marking Examiner 1	
Marking Examiner 2	
Checked by :	
Supervised by :	

PART A — STRUCTURED ESSAY

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

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1. (a) (i) I. Complete the expression given below to determine the charge (Q) of an atom in a Lewis structure by inserting the terms N_A , N_{LP} and N_{BP} in the appropriate boxes, where,

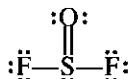
N_A = number of valence electrons in the atom

N_{LP} = number of electrons in lone pairs

N_{BP} = number of electrons in bonding pairs around the atom

$$Q = \boxed{} - \boxed{} - \frac{1}{2} \boxed{}$$

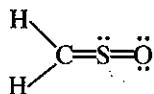
II. Fill in the values for N_A , N_{LP} and N_{BP} in the appropriate boxes and calculate the charge on S, Q(sulfur), in the structure SO_2 , given below.



$$Q(\text{sulfur}) = \boxed{} - \boxed{} - \frac{1}{2} \boxed{} = \dots$$

(ii) Draw the **most** acceptable Lewis structure for the ion, ClO_2F^+ .

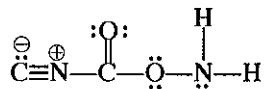
(iii) The most stable Lewis structure for the molecule CH_2SO (sulfine) is shown below. Draw another two Lewis structures (resonance structures) for this molecule.



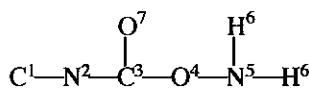
(iv) Based on the hypothetical Lewis structure given below, state the following regarding the C, N and O atoms given in the table below.

- I. VSEPR pairs around the atom
- III. shape around the atom

- II. electron pair geometry around the atom
- IV. hybridization of the atom



The atoms are numbered as follows:



	N^2	C^3	O^4	N^5
I. VSEPR pairs				
II. electron pair geometry				
III. shape				
IV. hybridization				

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(v) Identify the atomic/hybrid orbitals involved in the formation of the following σ bonds in the Lewis structure given in part (iv) above. (Numbering of atoms is as in part (iv).)

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

II. O^4-N^5 O^4, N^5

III. N^5-H^6 N^5, H^6

IV. C^3-O^7 C^3, O^7

(5.5 marks)

(b) (i) Identify the sub-shells (atomic orbitals) along with their azimuthal quantum number (l), and magnetic quantum number/s (m_l) for the energy level with principal quantum number $n=3$ in an atom. What is the maximum number of electrons present in each sub-shell?

Write your answers in the table given below.

Sub-shell	Azimuthal quantum number (l)	Magnetic quantum number/s (m_l)	Maximum number of electrons in each sub-shell
.....
.....
.....

(ii) Identify the type/s of intermolecular forces present in I, II and III given below.

I. Ar gas

.....

II. NO gas

.....

III. water sample containing a small amount of dissolved KCl

.....

(iii) "The boiling point of *n*-butane (C_4H_{10}) is higher than the boiling point of propane (C_3H_8)."
Giving reasons, state whether this statement is true or false.

.....
.....
.....

(iv) Arrange the following in the decreasing order of the property indicated in parentheses. (Reasons are not required.)

I. Li_2CO_3 , Na_2CO_3 , K_2CO_3 (solubility in water)

..... > >

II. NF_3 , NH_3 , NOCl , NO_2^+ (bond angle)

..... > > >

III. COCl_2 , CO_2 , HCN , CH_3Cl (electronegativity of carbon)

..... > > >

(4.5 marks)

100

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2. (a) **X**, **Y** and **Z** are elements that belong to the same group in the Periodic Table. They are in three successive periods respectively on descending the group. **Y** exists as a non-metallic coloured liquid at room temperature.

(i) Identify **X**, **Y** and **Z**. (Give atomic symbols.)

X = **Y** = **Z** =

(ii) Indicate the relative magnitudes of the following with regard to **X**, **Y** and **Z**.

I. Atomic size

> >

II. Electron affinity

> >

III. First ionization energy

> >

(iii) You are provided with aqueous solutions of the anions of **X**, **Y** and **Z**, each in a separate test-tube. Suggest a **single** reagent that could be used to identify these anions.

[Note: You are required to state the observation for each anion.]

Reagent:

Observation: (for the anions) **X**:

Y:

Z:

(iv) Give balanced chemical equations for the reactions of $\mathbf{X}_2(\mathbf{g})$ with the following.

I. $\mathbf{NH}_3(\mathbf{g})$

II. dil. \mathbf{NaOH}

(v) Draw the structures of **two** oxoacids of **X**.

(vi) Name **one** natural source of **X**.

(vii) I. A monomer that contains **X** forms an addition polymer that is widely used in the manufacture of water pipes. Draw the structure of the monomer.

II. Write the **full name** of the polymer.

(5.0 marks)

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(b) An aqueous solution **Q** contains **three** anions. The following tests were carried out to identify these anions. (Fresh portions of solution **Q** were used for each test ① to ⑤).

Test		Observation
①	I	Dilute HCl was added. A colourless gas was evolved. A clear solution was obtained.
	II	The gas evolved was tested with filter paper moistened with lead acetate. No colour change
②	I	A BaCl ₂ solution was added. A white precipitate was obtained.
	II	The white precipitate was separated by filtration, and dil. HCl was added to it. The white precipitate dissolved with the evolution of a gas.
	III	The gas evolved was tested with a filter paper moistened with acidified potassium dichromate. The colour changed from orange to green.
③	Conc. HNO ₃ and an excess of ammonium molybdate solution were added and the mixture was warmed.	
④	Devarda's alloy and NaOH solution were added and the mixture was heated. A gas that turned Nessler's reagent brown was evolved.	
⑤	A FeCl ₃ solution was added. A blood red coloured solution was obtained.	

(i) Identify the **three** anions in solution **Q**.

....., and

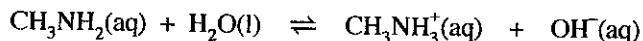
(ii) Write the balanced chemical equation for the reaction taking place in test number ② III.

.....

(5.0 marks)

100

3. (a) Methylamine, CH₃NH₂ is a weak base. The following equilibrium exists in an aqueous solution of methylamine.



(i) Write the expression for K_b of methylamine.

.....
.....

(ii) At 25 °C, the pH value of a 0.20 mol dm⁻³ aqueous solution of methylamine is 11.00. Calculate K_b .

.....
.....
.....
.....
.....
.....

(iii) A volume of 25.00 cm^3 of the solution in (ii) above was titrated with 0.20 mol dm^{-3} HCl at 25°C . Calculate the pH value of the solution at the equivalence point. ($K_w = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at 25°C .)

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(5.0 marks)

(b) In an experiment, a limited volume of 1.00 mol dm^{-3} HNO_3 was added to a precipitate MX(s) and the system was allowed to reach equilibrium at 25°C . This resulted in partial dissolution of the precipitate giving rise to a clear solution. The HX(aq) formed behaves as a weak acid.

(i) Write chemical reactions for the equilibria existing in the above solution.

.....
.....
.....

(ii) Calculate $[X^-(aq)]$ in the solution assuming that the dissociation of $HX(aq)$ is negligible. (Solubility product of MX at $25^\circ C$, $K_{sp(MX)} = 3.6 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$.)

(iii) Giving reasons explain whether $[X^-(aq)]$ in a saturated aqueous solution of MX at 25 °C is equal to, smaller than or greater than the value obtained in (b)(ii) above.

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(5.0 marks)

4. (a) The alcohols **A**, **B**, **C** and **D** are structural isomers of each other having the molecular formula $C_5H_{12}O$. **A**, **B** and **C** show optical isomerism.

(i) Draw possible structures for A, B and C.

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When **B**, **C** and **D** are reacted with acidic $\text{K}_2\text{Cr}_2\text{O}_7$, **X**, **Y** and **Z** are formed respectively. The products **X**, **Y** and **Z** can be converted back to **B**, **C** and **D** respectively by reacting with NaBH_4 .

(ii) What is the structure of A?

1100

A

On heating with conc. H_2SO_4 **A** and **B** gave **E** and **F**, respectively, while **C** and **D** gave the same product **G**. **G** shows diastereoisomerism. All three compounds **E**, **F** and **G** have the molecular formula C_5H_{10} . When **E** and **F** are reacted with HBr the same product **H** was formed.

(iii) Draw the structures of **B**, **C**, **D**, **E**, **F** and **H**.

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B

6

D

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E

F

H

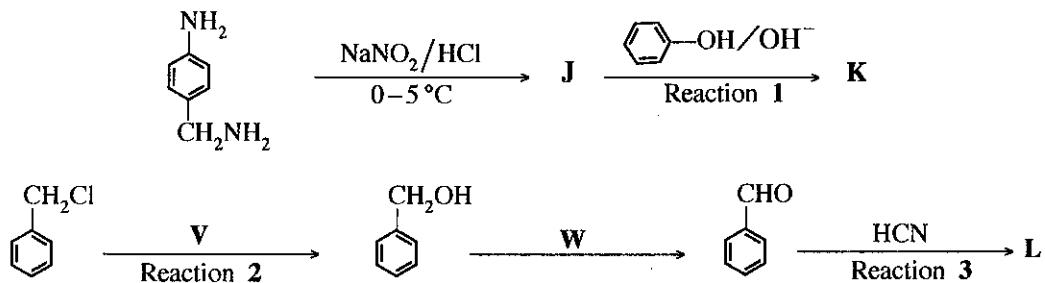
(iv) Draw the structures of the diastereoisomers of G.

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(4.8 marks)

(b) Consider the two reaction schemes given below.



(i) Draw the structures of J, K and L in the boxes given below.

J	K	L
---	---	---

(ii) Write the reagents V and W in the boxes given below.

V = **W** =

(iii) Writing A_E , A_N , S_E , S_N or E in the appropriate box, classify each of the reactions 1, 2 and 3 as electrophilic addition (A_E), nucleophilic addition (A_N), electrophilic substitution (S_E), nucleophilic substitution (S_N) or elimination (E) reaction.

Reaction 1 <input type="text"/>	Reaction 2 <input type="text"/>	Reaction 3 <input type="text"/>
---------------------------------	---------------------------------	---------------------------------

(4.0 marks)

(c) (i) What is the structure of the major product of the reaction between $\text{CH}_3\text{CH}=\text{CH}_2$ and HBr ?

(ii) Write the mechanism of the above reaction.

100

(1.2 marks)

உலகக் கலை கல்விக் கழ (உயிர் கலை) விழுது, 2017 கல்விக் கல்விப் பொதுக் காலதூப் பத்திரி (உயிர் கழ)ப் பிரிவை, 2017 கல்விக் General Certificate of Education (Adv. Level) Examination, August 2017

ரසாயன விடையில்
இரசாயனவியல்
Chemistry

02 E II

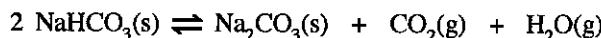
* Universal gas constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

* 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) The following reaction occurs when $\text{NaHCO}_3(s)$ is heated to a temperature above 100°C .



A sample of $\text{NaHCO}_3(s)$ was placed in an evacuated closed rigid container of 5.00 dm^3 volume and heated to $328 \text{ }^\circ\text{C}$. After the equilibrium was reached, a small amount of $\text{NaHCO}_3(s)$ still remained in the container. The pressure of the container was found to be $1.0 \times 10^6 \text{ Pa}$. Assume that the volume of the solids remaining in the container is negligible. $RT = 5000 \text{ J mol}^{-1}$ at $328 \text{ }^\circ\text{C}$.

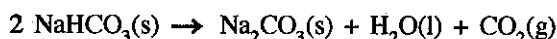
(i) Calculate the number of moles of $\text{H}_2\text{O(g)}$ in the container when the equilibrium is reached at 328 °C.

(ii) Calculate K_p for the above equilibrium at 328 °C, and hence calculate K_c .

(iii) An extra amount of $\text{CO}_2(\text{g})$ was added into the container described above at 328 °C. When the equilibrium is re-established, the partial pressure of $\text{CO}_2(\text{g})$ was four (4) times the partial pressure of $\text{H}_2\text{O(g)}$. Calculate the partial pressures of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O(g)}$ under this condition.

(7.5 marks)

(b) In order to determine the standard enthalpy change (ΔH°) of the reaction,



the following experiment consisting of two steps (I and II) was carried out at room temperature.

Step I: 0.08 mol of $\text{NaHCO}_3(s)$ was added to 100.00 cm^3 of 1.0 mol dm^{-3} HCl acid solution in a beaker. The maximum temperature fall was found to be 5.0 $^{\circ}\text{C}$.

[The reaction taking place: $\text{NaHCO}_3(\text{s}) + \text{HCl}(\text{aq}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$]

Step II: 0.04 mol of $\text{Na}_2\text{CO}_3(s)$ was added to 100.00 cm^3 of 1.0 mol dm^{-3} HCl acid solution in a beaker. The maximum temperature rise was found to be 3.5 $^{\circ}\text{C}$.

[The reaction taking place: $\text{Na}_2\text{CO}_3(\text{s}) + 2 \text{HCl}(\text{aq}) \rightarrow 2 \text{Na}^+(\text{aq}) + 2 \text{Cl}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$]

Specific heat capacity at constant pressure and density of HCl acid solution are $4.0 \text{ J g}^{-1} \text{ K}^{-1}$ and 1.0 g cm^{-3} respectively. Assume that the changes in volume and density of the solutions after the addition of solids in the above two steps are negligible.

(i) Calculate the enthalpy changes (in kJ mol^{-1}) of the reactions given in steps I and II above.

(ii) Using the values obtained in (i) above and a **thermochemical cycle**, calculate ΔH° of the reaction,

$$2 \text{NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g}).$$

(iii) State the condition under which a heat change of a reaction is equal to its enthalpy change.

(iv) Identify **two** sources of error in the above experimental procedure.

(7.5 marks)

[see page ten]

6. (a) (i) Explain why the rate of a reaction increases when the concentrations of the reactants are increased.
(ii) Give two reasons to explain why in general, the rate of a reaction increases with increasing temperature.
(iii) What is the relationship between order and molecularity of an elementary reaction?
(iv) Sketch the structure of the activated complex of the elementary reaction, $\text{NO} + \text{O}_2 \rightarrow \text{NO}_2 + \text{O}$.
Label the bonds that are being formed as 'forming' and the bonds that are being broken as 'breaking'.
(v) Write the rate expression for the elementary reaction, $x\text{A} + y\text{B} \rightarrow z\text{C}$, where the rate constant is k , and stoichiometric coefficients are x, y, z .

(5.0 marks)

(b) The reaction $x\text{A} + y\text{B} \rightarrow z\text{C}$ was studied in a two phase system consisting of an organic solvent and water. The compound **A** is soluble in both phases while compounds **B** and **C** are soluble only in the aqueous phase. The partition coefficient for the distribution of **A** between phases, $K_D = \frac{[\text{A}_{(\text{org})}]}{[\text{A}_{(\text{aq})}]}$ = 4.0.

The compound **A** was added to the two phase system and allowed to reach equilibrium. The reaction was started by injecting the compound **B** to the aqueous phase. Temperature of the system was maintained at a constant value. The results of the experiments carried out are given below.

Experiment No.	Volume of the organic phase (cm ³)	Volume of the aqueous phase (cm ³)	Amount of A added to the system (mol)	Amount of B injected (mol)	Initial rate, $\left(\frac{-\Delta C_A}{\Delta t} \right)$ (mol dm ⁻³ s ⁻¹)
I	—	100.00	1.00×10^{-2}	1.00×10^{-2}	1.20×10^{-5}
II	100.00	100.00	1.25×10^{-1}	1.00×10^{-2}	7.50×10^{-5}
III	50.00	50.00	6.25×10^{-2}	1.00×10^{-2}	1.50×10^{-3}

Note: Experiment I was carried out without the organic phase.

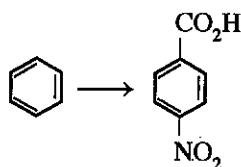
(i) Calculate the initial concentration of **A** in the aqueous phase in experiments I, II and III above.
(ii) Find the order of the reaction with respect to **A**.
(iii) Find the order of the reaction with respect to **B**.
(iv) Calculate the rate constant of the reaction.
(v) In the experiment III above, after adding **A** and allowing the system to reach equilibrium, if a volume of 10.00 cm³ was removed from the organic phase, what can be stated about the initial rate of the reaction? Give reason/reasons for your answer.

(5.0 marks)

(c) A mixture of liquids **X** and **Y** behaves ideally. At a constant temperature, when the liquid phase in equilibrium with the vapour phase in a closed rigid vessel contains 1.2 moles of **X** and 2.8 moles of **Y**, the total vapour pressure is 3.4×10^4 Pa. At the same temperature, when the composition of the liquid phase in equilibrium with the vapour phase is 1.2 moles of **X** and 4.8 moles of **Y**, the total vapour pressure is 3.6×10^4 Pa. Calculate the saturated vapour pressures of **X** and **Y** at this temperature.

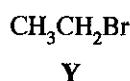
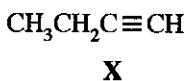
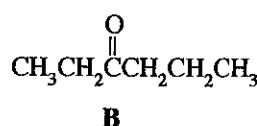
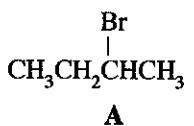
(5.0 marks)

7. (a) Show how you would carry out the following conversion in **not more than five (5) steps**.



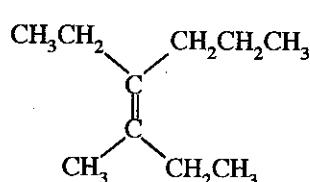
(3.0 marks)

(b) Two compounds **A** and **B** are required to be prepared in the laboratory.



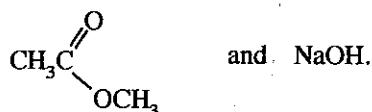
(i) Show how you would prepare **A** and **B** in **not more than five (5) steps** in each case, using **X** and **Y** as required.

(ii) Show how you would prepare the compound **C** using **A** and **B** given above, in **not more than five (5) steps**.

**C**

(9.0 marks)

(c) Using your knowledge of the mechanism of the reaction between acetyl chloride and NaOH, propose a mechanism for the reaction between



(3.0 marks)

PART C — ESSAY

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

8. (a) Solution **Y** contains three cations.

(A) The following tests were carried out to identify these cations.

	Test	Observation
①	Dilute HCl was added to a small portion of Y .	A white precipitate (P ₁)
②	P ₁ was separated by filtration and H ₂ S was bubbled through the solution.	A black precipitate (P ₂)
③	P ₂ was separated by filtration. The filtrate was boiled to remove the H ₂ S, cooled, and NH ₄ OH/NH ₄ Cl was added.	No precipitate
④	H ₂ S was bubbled through the solution.	A black precipitate (P ₃)

(B) The following tests were carried out for precipitates P_1 , P_2 and P_3 .

Precipitate	Test	Observation
P_1	I. Water was added to P_1 and the mixture was boiled. II. The mixture from I above was filtered while warm and the following tests were carried out on the filtrate (F_1) and residue (R_1). Filtrate (F_1) <ul style="list-style-type: none"> Dilute H_2SO_4 was added to warm F_1. Residue (R_1) <ul style="list-style-type: none"> R_1 was washed thoroughly with warm water and dilute NH_4OH was added. Thereafter, a KI solution was added. 	Part of P_1 dissolved. A white precipitate R_1 dissolved. A dark yellow precipitate
P_2	P_2 was dissolved in warm dil. HNO_3 and a potassium chromate solution was added.	A yellow precipitate
P_3	I. P_3 was dissolved in warm conc. HNO_3 . II. The following were added to solution 1 above. <ul style="list-style-type: none"> conc. HCl dil. NH_4OH 	A pink coloured solution (solution 1) A blue coloured solution (solution 2) A yellow-brown coloured solution (solution 3)

(i) Identify the **three** cations. (Reasons are **not** required.)

(ii) Identify,

I. precipitates P_1 , P_2 and P_3

II. species responsible for the colours of **solutions, 1, 2 and 3**.

(Note: Write chemical formulae **only**.)

(iii) Explain **briefly** why the cation/s that precipitate/s in (A) ④ above does not/do not precipitate in acidic medium. **(7.5 marks)**

(b) A solid sample was found to contain $(NH_4)_2SO_4$, NH_4NO_3 and non-reactive substances. The following procedures were used to determine the amount of ammonium salts present in this sample.

A 1.00 g portion of the solid sample was dissolved in water and diluted to 250.00 cm³ in a volumetric flask (hereafter referred to as **solution S**).

Procedure 1

A 50.00 cm³ portion of **solution S** was treated with an excess amount of a strong alkali (NaOH) and the gas liberated was passed into 30.00 cm³ of 0.10 mol dm⁻³ HCl. The volume of 0.10 mol dm⁻³ NaOH required to neutralize the remaining HCl (using phenolphthalein as the indicator) was 10.20 cm³.

Procedure 2

To a 25.00 cm³ portion of **solution S**, Al powder was added followed by an excess of strong alkali, and the mixture was heated. The gas liberated was passed into 30.00 cm³ of 0.10 mol dm⁻³ HCl. The volume of 0.10 mol dm⁻³ NaOH required to neutralize the remaining HCl (using phenolphthalein as the indicator) was 15.00 cm³.

(Note: Completion of gas evolution in procedures 1 and 2 was checked using litmus paper.)

(i) Identify the **gas** liberated in procedure 1.

(ii) Identify the **gas** liberated in procedure 2.

(iii) Write balanced chemical equations for the reactions taking place in procedures 1 and 2.

(iv) Calculate the mass percentage of each of the compounds $(NH_4)_2SO_4$ and NH_4NO_3 in the solid sample. (H = 1, N = 14, O = 16, S = 32) **(7.5 marks)**

9. (a) Consider the following industrial processes.

- I. Manufacture of bleaching powder
- II. Manufacture of calcium carbide
- III. Manufacture of urea
- IV. Manufacture of sulphuric acid (contact process)

- (i) State the starting materials used in each process.
- (ii) Write balanced chemical equations for the reactions taking place in each process, along with proper conditions wherever necessary.
- (iii) State **two** uses for each of the following:
bleaching powder, calcium carbide, urea and sulphuric acid

(7.5 marks)

(b) The major environmental problems we are facing at present are ozone layer depletion (OLD), global warming (GW) and acid rain (AR). The questions given below are related to the environment and the problems mentioned above.

- (i) The carbon and nitrogen cycles are two important chemical cycles that operate in the environment.
 - I. With regard to the carbon cycle, state **one** main form of carbon that is present in each of the following:
atmosphere, plants, water, Earth's crust
 - II. State briefly how N_2 gas in the atmosphere is removed and replenished in the nitrogen cycle.
 - III. State **two** ways by which microorganisms participate in the carbon cycle.
- (ii) Identify the **two** main nitrogen containing compounds present in the atmosphere that contribute to acid rain. With the aid of balanced chemical equations show how these compounds make rain water acidic.
- (iii) Identify **two** contributing industrial processes **per** environmental problem stated above (OLD, GW, AR). Identify **one** chemical compound that is liberated to the atmosphere by **each** of these industrial processes.
- (iv) Identify the main industrial process that contributes significantly to the addition of nitrogen compounds to water and soil. Comment on the pathways by which these compounds are added to water and soil.
- (v) Inappropriate disposal of solid municipal waste as in the Meethotamulla event contributes significantly to one of the three environmental issues stated above. Identify this environmental issue and state briefly how the disposal of solid municipal waste contributes to it.

(7.5 marks)

10. (a) (i) $TiCl_3$ is a violet coloured solid. In water, two hydrated species of $TiCl_3$, **A** and **B** are formed. **A** and **B** are coordination compounds of titanium with an octahedral geometry, containing H_2O and Cl^- as ligands.

A and **B** were separated and their atomic compositions were determined. The compounds were further analysed using the procedures given below.

Analysis of **A**

When excess $AgNO_3$ (aq) was added to 50.00 cm^3 of a 0.20 mol dm^{-3} solution of **A**, a white precipitate that was soluble in dilute ammonia was obtained. The mass of the precipitate after washing and oven drying (to a constant mass) was 4.305 g .

Analysis of **B**

When excess $AgNO_3$ (aq) was added to 50.00 cm^3 of a 0.30 mol dm^{-3} solution of **B**, the same white precipitate was obtained as in analysis, **A**. The mass of the precipitate after washing and oven drying (to a constant mass) was also 4.305 g .

($H = 1$, $O = 16$, $Cl = 35.5$, $Ti = 48$, $Ag = 108$)

- I. Write the electronic configuration of titanium in **A** and **B**.
- II. Deduce the structures of **A** and **B**.
- III. Give the IUPAC names of **A** and **B**.

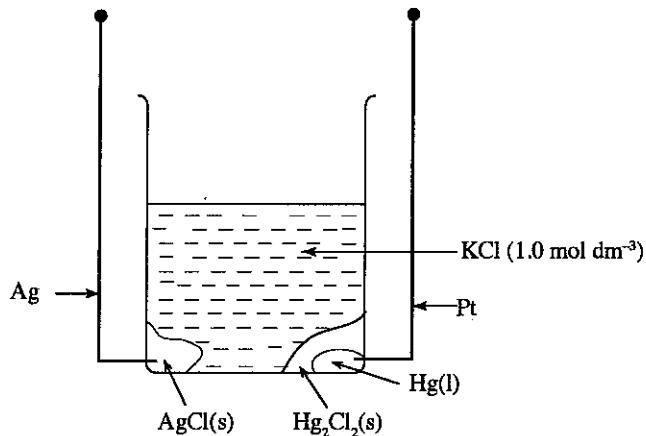
(ii) **X, Y and Z** are coordination compounds of the metal ion **M(II)**. They have a square planar geometry. **X** is a neutral compound. On addition of $\text{BaCl}_2(\text{aq})$ to an aqueous solution of **Y**, a white precipitate that is insoluble in dilute acids is obtained. **Z** gives three ions in aqueous solution.

Write the structural formulae of **X, Y** and **Z** selecting the appropriate species from the list given below.



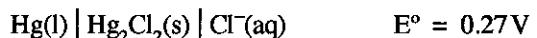
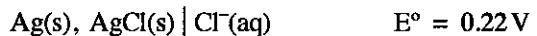
(7.5 marks)

(b)



An electrochemical cell is made as shown in the diagram above.

The following data are provided.



- Write the reduction half reaction of the above cell.
- Write the oxidation half reaction of the above cell.
- Construct the cell reaction.
- Using the E° values given, calculate the electromotive force of the cell.
- Give the standard cell notation of the above electrochemical cell.
- Does the electromotive force of the above electrochemical cell depend on the chloride ion concentration? Give reason/s for your answer.
- Calculate the change in the mass of $\text{Ag}(\text{s}) + \text{AgCl}(\text{s})$, when a current of 0.10 A was drawn for a period of 60 minutes from the cell.
- What would be the chloride ion concentration in the solution after drawing the current in (vii) above?

(Faraday constant, $F = 96,500 \text{ C mol}^{-1}$, $\text{Cl} = 35.5$, $\text{Ag} = 108$)

(7.5 marks)

The Periodic Table

1	1 H													2 He				
2	3 Li	4 Be																
3	11 Na	12 Mg																
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	La- Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	Ac- Lr	104 Rf	105 Db	106 Sg	Bh Bh	Hs Hs	Mt Mt	109 Uun	111 Uuu	112 Uub	113 Uut	...				

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr