

2019

CHEMISTRY

PAPER-I

Time Allowed — 3 Hours

Full Marks — 200

If the questions attempted are in excess of the prescribed number, only the questions attempted first up to the prescribed number shall be valued and the remaining ones ignored.

The figures in the margin indicate full marks for each question.

SECTION – I

[This section comprises 15 questions in three groups.]

Answer any **ten** questions taking at least **three** questions from each group.]

Group – A

4×5=20

1. PF_5 exists, but PH_5 does not exist. — Explain.
2. Predict the shapes of
 - (a) TeF_5^-
 - (b) SF_4 molecules.
3. Determine the lowest possible energy for the electron in the He^+ ion. HeH exists. — Explain.
4. Cuprous ion is not stable in solution. — Explain.
5. Zinc(II) salts are colourless, while nickel(II) salts are coloured. — Explain.

Group – B

4×5=20

6. Calculate the reversible PV work when an ideal gas undergoes a polytropic expansion ($PV^k = \text{Const}$) and show that as $k \rightarrow 1$, the work takes on the form of an isothermal reversible expansion.
7. The Maxwell's speed distribution function dependent on the molar mass of the gas and the temperature. Show that, in terms of the reduced speed, defined as $C_r = \frac{C}{C_{mp}}$, the distribution function is independent of M and T .
8. Calculate the viscosity coefficient of O_2 at 0°C and 1 atm from the kinetic theory expression. Given $\sigma = 2.5 \text{ \AA}$.
9. Find the ratio of wall collision frequency Z_{wall} and binary collision frequency Z_A . What will be the value for O_2 molecules at 1 atm and 27°C ?
10. What is the expression for the Joule co-efficient μ_J ? Obtain μ_J for n moles of a Van der waals gas.

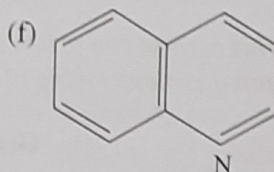
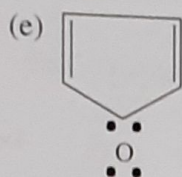
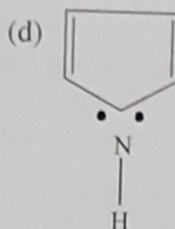
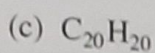
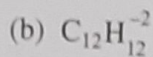
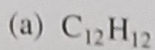
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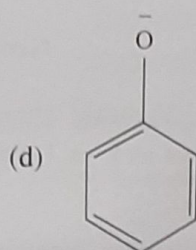
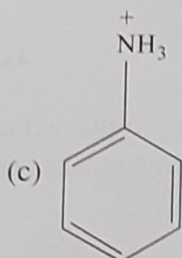
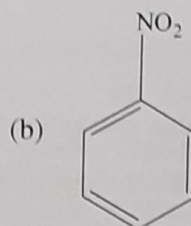
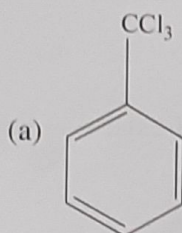
Group - C

4x5=20

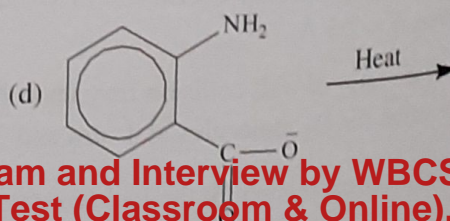
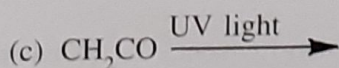
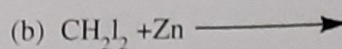
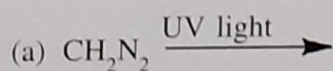
11. Select ring compounds of the following which obeys the Huckel's rule.



12. In which cases of the following, electrophile NO_2^+ ion preferentially attacks metaposition? Cite reasons.

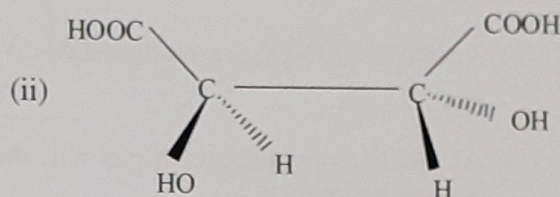
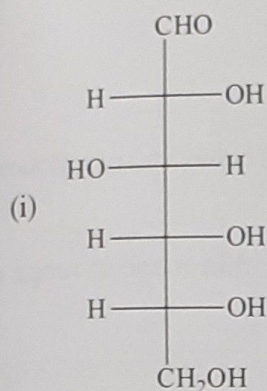


13. Identify the reactions of the following which proceeds via generation of Carbene:



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14. Designate R, S configuration of the following structure:



15. Predict the products giving mechanism when azulene reacts with acetyl chloride in the presence of anhydrous AlCl_3 .

SECTION – II

[This section comprises 6 questions in three groups.]

Answer any four questions taking at least one question from each group.]

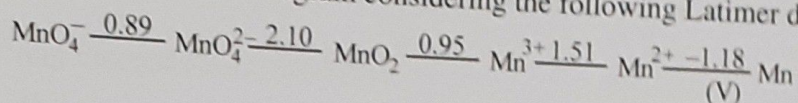
Group – A

16. (a) Define 'inert pair effect' with examples. 6
- (b) Compare the O–O bond length of H_2O_2 with O_2F_2 and explain. 8
- (c) Analyze the dimeric structures of $\text{Al}(\text{CH}_3)_3$ and BH_3 . 6
- (d) Calculate the spin states and bond orders of C_2 , C_2^- and C_2^{2-} . 9
- (e) Establish the expression of lattice energy defining all the terms involved in it. 7
- (f) Explain the nature of conducting electricity in water and gaseous state of PCl_5 . 4
17. (a) Illustrate the MO diagram of NO and predict the spin states of NO, NO^+ and NO^- . 6
- (b) Illustrate the structures of N_2O_5 . 4
- (c) For the following cell,
- $$\text{Zn}(s) \mid \text{ZnSO}_4(aq) \parallel \text{CuSO}_4(aq) \mid \text{Cu}(s)$$
- when the concentration of Zn^{2+} ion is 10 times the concentration of Cu^{2+} ion, find the expression for ΔG (in J mol^{-1}). 6
- (d) Compare the hydrolysis reactions of NF_3 and NCl_3 . 4
- (e) Compare the reactivities of borazine with benzene. 6
- (f) Find the expression of pH of the aqueous solution of sodium acetate. 6

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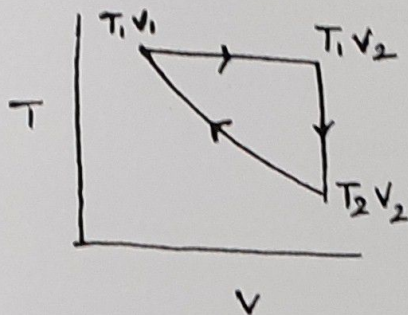
(g) Construct the Frost diagram considering the following Latimer diagram:



Group - B

18. (a) Justify 'At 60 K, $C_{v,m}$ measurements revealed that H_2 resembles the behaviour of a monoatomic gas'. 5
- (b) At what temperature of a gas will the number of molecules within a speed range dc , be the greatest?
Start from a 3-dimensional speed distribution. 6
- (c) One mole of water at 20°C is converted into steam at 250°C at 1 atm pressure. Given:
 $C_{p,m(l)} = 75.6 \text{ JK}^{-1} \text{ mol}^{-1}$, $\frac{C_{p,m}(\text{vap})}{R} = a + bT$ with $a = 3.634$ and $b = 1.195 \times 10^{-3} \text{ K}^{-1}$
and $\Delta H_{\text{vap}} = 40.68 \text{ kJ mol}^{-1}$ at 373 K. Calculate ΔS_{sys} , ΔS_{sum} , ΔS_{univ} . 10
- (d) Show that for a van der Waals gas, $C_p - C_v = R \left\{ 1 + \frac{2aP}{R^2 T^2} \right\}$
Starting from the general relation of $C_p - C_v$. 8
- (e) Calculate the dissociation pressure of CaCO_3 at 25°C . Given:
 $\mu_{\text{CaCO}_3}^0 = -1128.8 \text{ kJ mol}^{-1}$, $\mu_{\text{CO}_2}^0 = -394.36 \text{ kJ mol}^{-1}$ and $\mu_{\text{CaO}}^0 = -604.03 \text{ kJ mol}^{-1}$. 6
- (f) Chromium crystallises as a body-centered cubic structure with a density of 7.20 g cm^{-3} at 20°C . Calculate the length of a unit cell and the distance between successive 110 and 111 planes. 5
19. (a) Show that, $\frac{d \ln K_c}{dT} = \frac{\Delta u^0}{RT^2}$. 4
- (b) Obtain an expression for excess pressure across a curved surface. Consider a soap bubble where there are two interfaces. 6
- (c) Calculate the entropy change of the source, sink, engine and of the universe for
(i) a reversible Carnot cycle.
(ii) an irreversible Carnot cycle. 4+4=8
- (d) A 3-step reversible ideal gas cycle consists of
(i) an isothermal expansion at T_1 ,
(ii) constant volume cooling to T_2 and
(iii) an adiabatic compression to the initial state. Show that the efficiency is

$$\eta = 1 - \frac{(T_1 - T_2)}{T_1 \ln \frac{T_1}{T_2}}$$

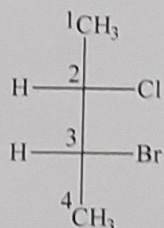


- (e) Consider the dissociation of $PCl_5 \rightleftharpoons PCl_3 + PCl_3$. Obtain an expression for ξ , the extent of the reaction given $K_p = 0.46$ at 300°C , show that the percent dissociation of PCl_5 decreases from 56 to 21 on increasing the pressure from 1 to 10 atm at 300°C . $4+4=8$
- (f) Consider an orthorhombic unit cell with dimensions $a = 487$ pm, $b = 646$ pm, $c = 415$ pm. Calculate the perpendicular distance between
- the 110 planes; and
 - the 222 planes of this crystal.

6

Group - C

20. (a) Write Sawhorse projection and Newman projection of the following compound having Fischer projection.



4

- (b) Arrange the following Carbocations in the increasing order of stability. — Justify.

- $\text{C}_6\text{H}_5\text{CH}_2^+$
- $\text{C}_6\text{H}_5\text{CH}^+\text{CH}_3$
- $(\text{C}_6\text{H}_5)_2\text{CH}^+$
- $(\text{C}_6\text{H}_5)_3\text{C}^+$

6

- (c) 'Haloalkanes undergo nucleophilic substitution reactions whereas halo arenes undergo electrophilic substitution reactions'. Illustrate with suitable examples.

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(6)

- (d) Describe the following reactions giving mechanisms of each conversion of your choice. 4×5=20
- (i) Claisen condensation
 - (ii) Reimer-Tiemann reaction
 - (iii) Diels-Alder reaction
 - (iv) Beckmann rearrangement
 - (v) Hofmann rearrangement
21. (a) Explain why S_N^1 leads to racemic mixture whereas S_N^2 gives rise to inverted product. 8
- (b) Describe the conformational isomers of *n*-butane. Draw the potential energy diagrams of various conformations of *n*-butane and comment on the relative stabilities of the conformers. 8+8=16
- (c) How quinoline can be synthesised from aniline by SKraup method stating the functions of each reagent? 4
- (d) (i) Furan undergoes Gatterman reaction followed by hydration. 4×2=8
 (ii) Anthracene is subjected to photochemical reaction in presence of oxygen and Na_2SO_3 .
- (e) Mention the products obtained by room temperature photolysis of acetone via Norrish type 1 cleavage. 4

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