SAMPLE QUESTION PAPER

BLUE PRINT

Time Allowed : 3 hours **Maximum Marks :** 70

S. No.	Chapter	Passage based/ MCQs/A & R (1 mark)	SA-I (2 marks)	SA-II (3 marks)	LA (5 marks)	Total
1.	The Solid State	1(1)	1(2)	1(3)	–	**12(23)**
2.	Solutions	1(1)	1(2)	–	–	
3.	Electrochemistry	1(1)	–	–	1(5)	
4.	Chemical Kinetics	2(2)	1(2)	–	–	
5.	Surface Chemistry	1(1)	–	1(3)	–	
6.	The *p*-Block Elements	1(4)	1(2)	–	–	**8(19)**
7.	The *d*- and *f*-Block Elements	2(2)	–	–	1(5)	
8.	Coordination Compounds	1(1)	1(2)	1(3)	–	
9.	Haloalkanes and Haloarenes	2(2)	1(2)	–	–	**13(28)**
10.	Alcohols, Phenols and Ethers	1(1)	2(4)	–	–	
11.	Aldehydes, Ketones and Carboxylic Acids	1(1)	1(2)	1(3)	–	
12.	Amines	1(1)	–	–	1(5)	
13.	Biomolecules	1(4)	–	1(3)	–	
	Total	**16(22)**	**9(18)**	**5(15)**	**3(15)**	**33(70)**

Subject Code : 043

CHEMISTRY

Time allowed : 3 hours ***Maximum marks : 70***

General Instructions : Read the following instructions carefully.

(a) There are 33 questions in this question paper. All questions are compulsory.

(b) Section A : Q. No. 1 to 16 are objective type questions. Q. No. 1 and 2 are passage based questions carrying 4 marks each while Q. No. 3 to 16 carry 1 mark each.

(c) Section B : Q. No. 17 to 25 are short answer questions and carry 2 marks each.

(d) Section C : Q. No. 26 to 30 are short answer questions and carry 3 marks each.

(e) Section D : Q. No. 31 to 33 are long answer questions carrying 5 marks each.

(f) There is no overall choice. However, internal choices have been provided.

(g) Use of calculators and log tables is not permitted.

SECTION - A (OBJECTIVE TYPE)

1. **Read the passage given below and answer the following questions :**

A carbohydrate is a chemical compound which is made up of carbon, oxygen and hydrogen which are primarily produced by plants .These are formed in plants by a process known as photosynthesis and makeup about 70% of the solid plant material.

$$xCO_2 + yH_2O \xrightarrow[\text{Chlorophyll}]{\text{Sunlight}} \underset{\text{Carbohydrate}}{C_x(H_2O)_y} + xO_2$$

The carbohydrates are present in starch, sugars and cellulose. Carbohydrate happen to be the energy supplying nutrients. They are required in greater quantities for not only growing children but also for those who usually do hard physical labour. It is both an economical and quick source of calories. In earlier days, the carbohydrates were regarded as the hydrates of carbon with general formula $C_x(H_2O)_y$. For example, carbohydrates such as glucose ($C_6H_{12}O_6$), fructose ($C_6H_{12}O_6$) and sucrose ($C_{12}H_{22}O_{11}$).

When sucrose is boiled with dilute HCl or H_2SO_4 in alcoholic solution, glucose and fructose are obtained in equal amounts. Glucose consists of one aldehydic group, four 2° alcoholic groups and one 1° alcoholic group. Fructose consists of one ketonic group, three 2° alcoholic groups and two 1° alcoholic groups.

The following questions are multiple choice questions. Choose the most appropriate answer.

(i) Which of the following biomolecules simply refers to as "staff of life"?

(a) Lipids (b) Proteins (c) Vitamins (d) Carbohydrates

(ii) Fructose is a

(a) aldose (b) ketose (c) both (a) and (b) (d) none of these.

OR

Glucose is a

(a) aldose (b) ketose (c) both (a) and (b) (d) neigher (a) nor (b).

(iii) Which of the following groups is simplest form of a carbohydrates?

(a) carboxyl groups
(b) Aldehyde and ketone groups
(c) Alcohol and carboxyl groups
(d) Hydroxyl groups and hydrogen groups

(iv) Which of the following carbohydrates form is the majority found in human body?

(a) *D*-type
(b) *L*-type
(c) D, *L*-type
(d) None of these

2. **Read the passage given below and answer the following questions:**

Scientists had always believed that noble gases also known as inert or rare gases, were chemically unable to react. Scientific wisdom held that noble gas elements could not form compounds because their electronic structure was extremely stable. In 1933, Walther Kossel predicted that highly reactive atoms such as fluorine might form compounds with xenon, the heaviest of the noble gas elements and whose electrons, they observed, were not as tightly bound as those of the lighter gases.

In 1961 Neil Bartlett while experimenting with fluorine and platinum, had accidently produced a deep red solid whose exact chemical composition remained a mystery. After much research, he found that the known gaseous fluoride, platinum hexafluoride (PtF_6) was able to oxidize oxygen and produce the red solid which had identified as $O_2^+ PtF_6^-$.

Bartlett conducted a simple experiment to test this compound $O_2^+ PtF_6^-$. He set up a glass apparatus containing, $Pt\,F_6^-$ red gas, in one container and xenon, a colourless gas in an adjoining container separated by a seal. The reaction took place at root temperature and he prepared the orange-yellow solid, the world first noble gas compound. Today, noble gas chemistry has become a powerful tool for developing new compounds with useful properties. Bartlett estimates that more than 100 noble gas compounds are known today.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** Xenon forms fluorides.
Reason : Because 5*d*-orbitals are available for valence expansion.

(ii) **Assertion :** Compared to other noble gases, Xe is chemically reactive.
Reason : Xe has low ionisation potential value.

(iii) **Assertion :** Most of known noble gas compounds are those of xenon.
Reason : The ionization enthalpy of xenon is very close to that of oxygen.

(iv) **Assertion :** Noble gases are least reactive.
Reason : Noble gases have completely filled *s*- and *p*-orbital and attain stable electronic configuration.

OR

Assertion : All of the noble gases compounds are know except helium and neon.
Reason : Ionisation potential values of helium and neon are close to xenon.

Following questions (Q. No. 3-11) are multiple choice questions carrying 1 mark each :

3. Rate of a reaction can be expressed by following rate expression, Rate = $k[A]^2[B]$, if concentration of A is increased by 3 times and concentration of B is increased by 2 times, how many times rate of reaction increases?

(a) 9 times
(b) 27 times
(c) 18 times
(d) 8 times

4. Cerium ($Z = 58$) is an important member of the lanthanoids. Which of the following statements about cerium is incorrect?
(a) The common oxidation states of cerium are +3 and +4.
(b) Cerium (IV) acts as an oxidizing agent.
(c) The +4 oxidation state of cerium is not known in solutions.
(d) The +3 oxidation state of cerium is more stable than the +4 oxidation state.

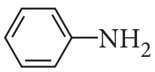
5. Ratio of the total volume of *bcc* to simple cubic structure is
(a) $3\sqrt{3}:8$ (b) $8:3\sqrt{3}$
(c) $24\sqrt{3}:1$ (d) $1:24\sqrt{3}$

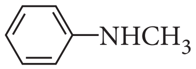
OR

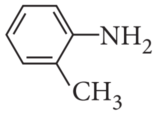
The flame colours of metal ions are due to
(a) Frenkel defect (b) Schottky defect
(c) metal deficiency defect (d) metal excess defect.

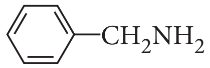
6. $(CH_3)_2CO \xrightarrow[HCl]{NaCN} A \xrightarrow{H_3O^+} B$
In the above sequence of reactions (A) and (B) are
(a) $(CH_3)_2C(OH)CN, (CH_3)_2C(OH)COOH$
(b) $(CH_3)_2C(OH)CN, (CH_3)_2C(OH)_2$
(c) $(CH_3)_2C(OH)CN, (CH_3)_2CHCOOH$
(d) $(CH_3)_2C(OH)CN, (CH_3)_2C{=}O$

7. Which of the following is the strongest base?

(a) 

(b) 

(c) 

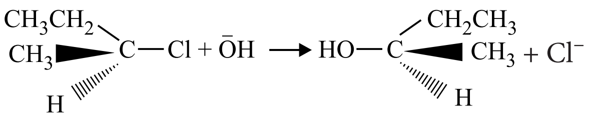
(d) 

OR

The name of the compound '*B*' in the following series of reactions, is

Acetone $\xrightarrow{H_2N{-}OH}$ 'A' $\xrightarrow{H_2/Pt}$ 'B'
(a) propan-1-amine (b) propan-2-amine
(c) butan-1-ol (d) butan-2-ol.

8. In the reaction given below :

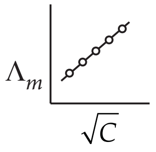


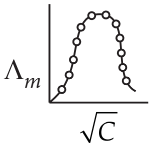
Which of the following statements is correct?
(a) The reaction proceeds *via* S_N2 mechanism hence inversion of configuration takes place.
(b) The reaction proceeds *via* S_N1 mechanism hence inversion of configuration takes place.
(c) The reaction proceeds *via* S_N2 mechanism hence their is no change in the configuration.
(d) The reaction proceeds *via* S_N1 mechanism hence there is no change in the configuration.

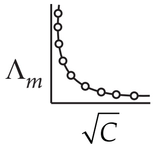
9. For a spontaneous reaction, the ΔG, equilibrium constant (K) and E°_{cell} will be respectively
(a) – ve, <1, – ve (b) – ve, >1, – ve
(c) – ve, >1, + ve (d) + ve, >1, – ve.

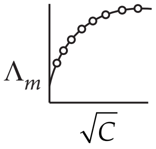
OR

The variation of Λ_m of acetic acid with concentration is correctly represented by

(a) 

(b) 

(c) 

(d) 

10. Vapour pressure of dilute aqueous solution of glucose is 750 mm of mercury at 373 K. The mole fraction of solute is
(a) 1/76 (b) 1/7.6 (c) 1/38 (d) 1/10

11. In an octahedral crystal field, the t_{2g} orbitals are
(a) raised in energy by 0.4 Δ_o
(b) lowered in energy by 0.4 Δ_o
(c) raised in energy by 0.6 Δ_o
(d) lowered in energy by 0.6 Δ_o.

OR

Primary and secondary valency of platinum in the complex $[\mathrm{Pt}(en)_2\mathrm{Cl}_2]$ are
(a) 4, 6 (b) 2, 6 (c) 4, 4 (d) 6, 4

In the following questions (Q. No. 12-16), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.
(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

12. **Assertion :** In rate law, unlike in the expression for equilibrium constants, the exponents for concentrations do not necessarily match the stoichiometric coefficients.
Reason : It is the mechanism and not the balanced chemical equation for the overall change that governs the reaction rate.

13. **Assertion :** Phenol undergoes Kolbe's reaction whereas ethanol does not.
Reason : Phenoxide ion is more basic than ethoxide ion.

OR

Assertion : Phenol forms 2, 4, 6-tribromophenol on treatment with Br_2- water at 273 K.
Reason : Phenol is *o*, *p*- directing group.

14. **Assertion :** Hydrolysis of (–)-2-bromooctane proceeds with inversion of configuration.
Reason : This reaction proceeds through the formation of a carbocation.

15. **Assertion :** Ionic radii of Ta and Nb are same.
Reason : The lanthanide contraction cancels almost exactly the normal size increase on descending a group of transition elements.

16. **Assertion :** Fe^{3+} can be used for coagulation of As_2S_3 sol.
Reason : Fe^{3+} reacts with As_2S_3 to give Fe_2S_3.

SECTION - B

The following questions Q. No. 17-25 are short answer type and carry 2 marks each.

17. (i) When propanone is subjected to Wolff-Kishner reduction, what product will be obtained? Give chemical equation.

(ii) How will you convert acetaldehyde to acetone?

18. (i) For a reaction, $A + B \rightarrow$ Product, the rate law is given by, Rate $= k[A]^1[B]^2$. What is the order of the reaction?

(ii) Write the unit of rate constant 'k' for the first order reaction.

(iii) For the reaction $A \rightarrow B$, the rate of reaction becomes twenty seven times when the concentration of A is increased three times. What is the order of reaction?

OR

Hydrogen peroxide, $H_2O_{2(aq)}$ decomposes to $H_2O_{(l)}$ and $O_{2(g)}$ in a reaction that is first order in H_2O_2 and has a rate constant $k = 1.06 \times 10^{-3}$ min^{-1}. How long will it take for 15% of a sample of H_2O_2 to decompose?

19. Why does phenol give tribromophenol on bromination with bromine water while monobromophenol in presence of CS_2 as solvent?

20. (i) Name the two factors on which the vapour pressure of the liquid depends.

(ii) What happens to vapour pressure of water, if a tablespoon of glucose is added to it?

21. (i) How will you differentiate between *hcp* and *ccp* lattice?

(ii) If the radius of anion in an ionic solids is 100 pm, what should be the radius of cation that fits in the (a) cubic hole, (b) octahedral hole, (c) tetrahedral hole?

22. (i) Why all halogens are coloured?

(ii) In interhalogen compounds of the type AB_5 and AB_7, B is invariably fluorine. Why?

OR

(a) Arrange NF_3, PF_3, AsF_3, BiF_3 in increasing ionic character. Give reason.

(b) Acidity of oxoacids of nitrogen increases with increase in oxidation state, why?

23. Draw a figure to show splitting of degenerate d-orbitals in an octahedral crystal field. How does the magnitude of Δ_o decide the actual configuration of orbitals in a complex entity?

24. Answer the following :

(i) Haloalkanes easily dissolve in organic solvents, why?

(ii) Of the two bromoderivatives, $C_6H_5CH(CH_3)Br$ and $C_6H_5CH(C_6H_5)Br$, which one is more reactive in S_N1 substitution reaction and why?

OR

An optically active compound having molecular formula $C_7H_{15}Br$ reacts with aqueous KOH to give a racemic mixture of products. Write the mechanism involved for this reaction.

25. (i) Why is it difficult to prepare ethyl methyl ether by dehydration of alcohols?

(ii) *o*-Nitrophenol is steam volatile while *p*-nitrophenol is not. Why?

SECTION - C

Q. No. 26-30 are short answer type II carrying 3 marks each.

26. How are the colloids classified on the basis of the nature of interaction between dispersed phase and dispersion medium? Describe an important characteristics of each class. Which of these sols need stabilising agents for preservation?

27. (i) How are proteins classified on the basis of molecular shape?
(ii) What is base pairing principle?

28. (a) Two moles of organic compound '*A*' on treatment with a strong base give two compounds '*B*' and '*C*'. Compound '*B*' on dehydrogenation with Cu gives '*A*' while acidification of '*C*' yields carboxylic acid '*D*' having molecular formula of CH_2O_2. Identify the compounds *A*, *B*, *C* and *D*.
(b) Explain Hell–Volhard–Zelinsky reaction.

OR

(*A*), (*B*) and (*C*) are three non-cyclic functional isomers of a carbonyl compound with molecular formula C_4H_8O. Isomers (*A*) and (*C*) give positive Tollens' test whereas isomer (*B*) does not give Tollens' test but gives positive iodoform test. Isomers (*A*) and (*B*) on reduction with Zn(Hg)/conc. HCl give the same product (*D*).
(a) Write the structures of (*A*), (*B*), (*C*) and (*D*)
(b) Out of (*A*), (*B*) and (*C*) isomers, which one is least reactive towards addition of HCN?

29 Using crystal field theory, draw energy level diagram, write electronic configuration of the central metal atom/ion and determine the magnetic moment value in the following :
(a) $[CoF_6]^{3-}$ (b) $[FeF_6]^{3-}$ (c) $[Fe(CN)_6]^{4-}$

OR

Write the IUPAC names of the following coordination compounds :
(i) $[Cr(NH_3)_3Cl_3]$
(ii) $K_3[Fe(CN)_6]$
(iii) $[CoBr_2(en)_2]^+$, (*en* = ethylenediamine)

30. (i) In a compound *AX*, the radius of A^+ ion 95 pm and that of X^- is 181 pm. Predict the crystal structure of *AX* and write the coordination number of each of the ion.
(ii) Predict the close packed structure of an ionic compound $A^+ B^-$ in which the radius of cation is 148 pm and radius of anion is 195 pm. What is the coordination number of cation?

SECTION - D

Q. No. 31 to 33 are long answer type carrying 5 marks each.

31 (i) Can lanthanum ($Z = 57$) exhibit +4 oxidation state?
(ii) Nb and Ta exhibit similar properties. Give reason.
(iii) Among the ionic species, Sc^{3+}, Ce^{4+} and Eu^{2+}, which one is a good oxidising agent.
(iv) Trivalent lanthanoid ions are coloured. Why?
(v) Explain the cause of paramagnetism in lanthanoid ions.

OR

(i) Transition metals have very high melting and boiling points. Why?
(ii) Enthalpies of atomisation of 2nd and 3rd transition series are higher than the corresponding metals of first transition series. Why?

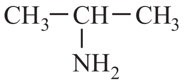
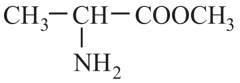
(iii) In *d*-block element, ionic radii of ions of the same charge decreases progressively with increasing atomic number in a series. Why?

(iv) How does ionisation enthalpy change along a transition series?

(v) Explain why Cu has a positive $E°$ value, if transform $Cu_{(s)}$ to $Cu^{2+}_{(aq)}$.

32. (a) An organic compound *A* having molecular formula C_2H_7N on treatment with HNO_2 gave an oily yellow substance. Identify '*A*'. Give equation.

(b) Which amine in each of the following pairs is a stronger base? Give reason.

(i) 
$CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_3$
and 
$CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOCH_3$

(ii) $CH_3CH_2CH_2NH_2$ and $CH_3NHCH_2CH_3$

(c) Account for the following :

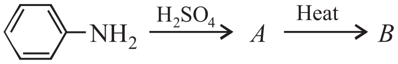
(i) Tertiary amines do not undergo acylation reaction.

(ii) Amines are more basic than comparable alcohols.

OR

(a) Suggest a convenient scheme for separating aniline, *N*-methylaniline, toluene and phenol present together in mixture. Distillation is not to be used.

(b) Identify *A* and *B*.



(c) Account for the following :

(i) Ammonolysis of alkyl halides does not give a corresponding amine in pure state.

(ii) If – NO_2 or – COOH group is attached to a carbon of benzene ring, electrophilic substitution becomes difficult.

33. (a) Calculate standard emf of the cell in which following reaction takes place at 25°C.

$Cu_{(s)} + Cl_{2(g)} \rightleftharpoons Cu^{2+} + 2Cl^-$

$E°_{Cl_2/Cl^-} = +1.36$ V, $E°_{Cu^{2+}/Cu} = +0.34$ V

Also calculate standard free energy change and equilibrium constant of the reaction.

(b) Calculate standard electrode potential for the following half cell $Fe^{3+} + 3e^- \rightleftharpoons Fe$ from the following data

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$; $E° = 0.77$ V

$Fe^{2+} + 2e^- \rightleftharpoons Fe$; $E° = -0.44$ V

OR

(a) Out of HCl and NaCl, which do you expect will have greater value for $\Lambda°_m$ and why?

(b) The equivalent conductivity of 0.05 N solution of a monobasic acid is 15.8 mho cm^2 eq^{-1}. If equivalent conductivity of the acid at infinite dilution is 350 mho cm^2 eq^{-1}, calculate the (i) degree of dissociation of acid (ii) dissociation constant of acid.

(c) The resistance of 100 cm^3 aqueous solution of 0.025 M $CuSO_4$ is 520 ohm at 298 K. Calculate the molar conductivity if the cell constant of the conductivity cell is 153.7 m^{-1}.

SOLUTIONS

1. (i) (d) : Carbohydrates belong to a group of complex biomolecules commonly regarded as the “staff of life”.

(ii) (b) OR (a)

(iii) (b)

(iv) (a)

2. (i) (a) : Due to presence of empty 5*d*-orbitals, electrons can be excited and higher valency of xenon can be produced.

(ii) (a)

(iii) (b) : Oxygen has ionisation enthalpy 1166 kJ/mol. Xenon has ionisation enthalpy 1170 kJ/mol.

(iv) (a)

OR

(d) : Ionisation potential values of helium and neon are very high as compared to xenon.

3. (c) : Given, $R_1 = k[A]^2\,[B]$

According to question, $R_2 = k[3A]^2\,[2B]$

$= k \times 9\,[A]^2 \times 2\,[B] = 18 \times k\,[A]^2\,[B] = 18\,R_1$

4. (c) : $Ce^{3+} : 4f^1 5d^0 6s^0$ and $Ce^{4+} : 4f^0 5d^0 6s^0$

+4 oxidation state of cerium is also known in solution.

5. (b) : Volume of unit cell = a^3

For *bcc*, $r = \frac{\sqrt{3}}{4}a$ or $a = \frac{4r}{\sqrt{3}}$

Thus, volume of *bcc* unit cell = $\left(\frac{4r}{\sqrt{3}}\right)^3 = \frac{64r^3}{3\sqrt{3}}$

For simple cubic, $r = \frac{a}{2}$ or $a = 2r$

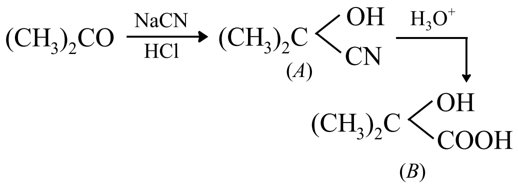
Thus, volume of simple cubic unit cell = $(2r)^3 = 8r^3$

$$\frac{\text{Volume of } bcc \text{ unit cell}}{\text{Volume of simple cubic}} = \frac{64r^3/3\sqrt{3}}{8r^3} = \frac{64}{8\times 3\sqrt{3}} = \frac{8}{3\sqrt{3}}$$

OR

(d) : The flame colours of metal ions are due to metal excess defect. These type of crystals are generally coloured. This is due to the presence of free electrons. These electrons get excited easily to higher energy levels by absorption of certain wavelengths from the visible light and therefore, the compounds appear coloured.

6. (a) :

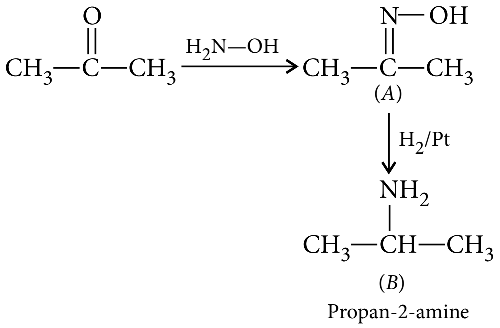


$$(CH_3)_2CO \xrightarrow[HCl]{NaCN} \underset{(A)}{(CH_3)_2C{<}^{OH}_{CN}} \xrightarrow{H_3O^+} \underset{(B)}{(CH_3)_2C{<}^{OH}_{COOH}}$$

7. (d) : In compounds given in options (*A*), (*B*) and (*C*) the lone pair of electrons on nitrogen atom is in resonance with aromatic ring and thus not available for donation.

OR

(b) :



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{H_2N-OH} \underset{(A)}{CH_3-\overset{\overset{N-OH}{\|}}{C}-CH_3} \xrightarrow{H_2/Pt} \underset{(B)}{CH_3-\overset{\overset{NH_2}{|}}{CH}-CH_3}$$

Propan-2-amine

8. (a) : Inversion of configuration takes place in S_N2 mechanism.

9. (c) : For spontaneous process:

$\Delta G < 0$, $K > 1$ and $E^\circ_{cell} > 0$

OR

(c) : For weak electrolytes (CH_3COOH), Λ_m first increases slowly and then rapidly with dilution but does not become constant.

10. (a) : $p_s = p_1^\circ(1 - x_2)$

$\Rightarrow 750 = 760(1 - x_2)$ or, $\frac{750}{760} = 1 - x_2$

or, $\frac{750}{760} - 1 = -x_2 \Rightarrow x_2 = \frac{1}{76}$

11. (b)

OR

(b) : Primary valency corresponds to oxidation number while secondary valency corresponds to coordination number.

12. (a)

13. (c) : Phenol undergoes Kolbe’s reaction (an electrophilic substitution reaction) because conjugate base (phenoxide ion) is less basic than ethoxide ($C_2H_5O^-$) ion.

OR

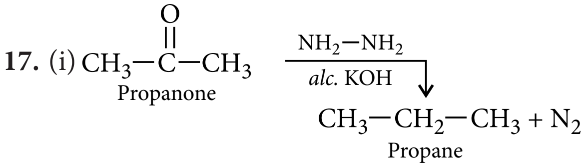
(b) : Phenol forms 2, 4, 6-tribromophenol on treatment with Br_2- water. In phenols, the polarisation of bromine takes place even in the absence of Lewis acid.

14. (c) : Reaction follows S_N2 mechanism which does not proceed through a carbocation formation.

15. (a) : The elements following the lanthanides in the periodic are influenced by the lanthanide contraction as lanthanide contraction cancels almost exactly the normal size increase on descending a group of transition elements.

16. (c) : Fe^{3+} is positively charged whereas As_2S_3 is negatively charged sol. Their charges are neutralised on mixing hence, mutual precipitation (coagulation) occurs.

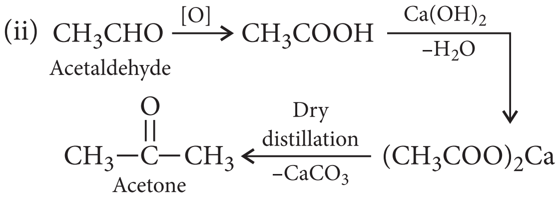
17. (i)



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[alc.\ KOH]{NH_2-NH_2} CH_3-CH_2-CH_3 + N_2$$

Propanone → Propane

(ii)



$$CH_3CHO \xrightarrow{[O]} CH_3COOH \xrightarrow[-H_2O]{Ca(OH)_2} (CH_3COO)_2Ca \xrightarrow[-CaCO_3]{\text{Dry distillation}} CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

Acetaldehyde → Acetone

18. (i) Order of reaction is sum of powers of concentration terms,

$\therefore$ Order of reaction = 1 + 2 = 3

(ii) Unit of rate constant for first order reaction is s^{-1}.

(iii) Let $r = k[A]^n$

Then, $27r = k[3A]^n$

$$\frac{27r}{r} = \frac{k[3A]^n}{k[A]^n} \text{ or } 3^3 = 3^n$$

$n = 3$

$\therefore$ Thus, order = 3

OR

$$t = \frac{2.303}{k}\log\frac{[A]_0}{[A]}$$

Given $k = 1.06 \times 10^{-3}\ \text{min}^{-1}$, $\dfrac{[A]_0}{[A]} = \dfrac{100}{85}$

$$t = \frac{2.303}{1.06\times10^{-3}\ \text{min}^{-1}}\log\frac{100}{85}$$

$$t = \frac{2303}{1.06}[2\log 10 - \log 85]\ \text{min}$$

$$t = \frac{2303}{1.06}[2\times1 - 1.9294] = \frac{2303\times0.0706}{1.06}$$

$t = 153.39\ \text{min} \simeq 153.4\ \text{min}$

19. The solvents like CS_2 and $CHCl_3$ are of low polarity which make the medium inert and only monobromophenol is formed. When it is treated with bromine water it gives tribromophenol because the high polarity of water molecule ionises phenol to phenoxide ion which increases electron density at the *o*-and *p*-position of benzene ring.

20. (i) Nature of liquid (intermolecular force) and temperature.

(ii) Water is a volatile solvent. When a non-volatile solute such as glucose is added to it, then its vapour pressure is lowered.

21. (i) In *hcp* lattice, each third layer is parallel to first layer. It is *ABAB* .... type.

In *ccp* lattice, each fourth layer is parallel to the first layer. It is *ABCABC*......... type.

(ii) (a) For cubic hole, $r = 0.732\,R = 0.732 \times 100 = 73.2$ pm

(b) For octahedral hole, $r = 0.414\,R = 0.414 \times 100 = 41.4$ pm

(c) For tetrahedral hole, $r = 0.225\,R = 0.225 \times 100 = 22.5$ pm

22. (i) Halogens absorb a part of the light in the visible region which causes excitation of outer electrons to higher energy levels. The excitation energy depends on the size of the halogen atom, the smaller the atom, the greater is the excitation energy. Thus, fluorine absorbs violet light and thus appears yellow (complementary colour). As different colours are absorbed by halogens, they display different complementary colours.

(ii) The higher interhalogen compounds like AB_5 and AB_7 are formed by large atoms (like Br and I) with small atoms (like F), it is due to more small atoms can arrange around a large atom.

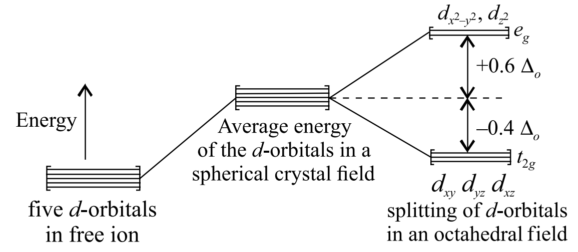
OR

(a) $NF_3 < PF_3 < AsF_3 < BiF_3$

For same anion if size of cation increases, the tendency of polarisation decreases and correspondingly ionic character also increases.

(b) Increase in oxidation state tends to withdraw the N–O electron cloud towards nitrogen as a result O– H bond becomes weak and hence more easily breaks. So, acidity increases.

23. Greater the value of Δ_o, the greater is the electron pairing.



Splitting of degenerate *d*-orbitals in an octahedral crystal field.

The actual configuration adopted is decided by the relative value of Δ_o and *P*. *P* represents energy required for electron pairing.

(i) If $\Delta_o < P$ in case of weak field ligand high spin situation, fourth electron enters one of the e_g orbital giving the configuration $t_{2g}^3e_g^1$.

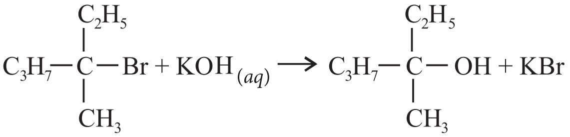
(ii) If $\Delta_o > P$, in case of strong field ligand low spin situation, pairing occurs in the t_{2g} level with the e_g level remaining unoccupied in entities up to d^6. From d^7 electron starts occupying e_g level.

24. (i) Haloalkanes tend to dissolve in organic solvent because new intermolecular attraction between haloalkanes and solvent molecules have almost same strength as the ones being broken in separating haloalkane and solvent molecules.

(ii) $C_6H_5CH(C_6H_5)Br$ is more reactive than $C_6H_5CH(CH_3)Br$ for S_N1 reaction because its carbocation is resonance stabilised by two phenyl groups.

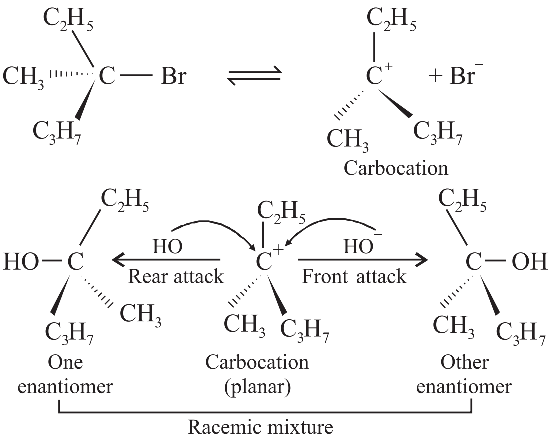
OR

Clearly $C_7H_{15}Br$ is a tertiary halide.



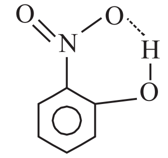
$$C_3H_7-\overset{C_2H_5}{\underset{CH_3}{C}}-Br + KOH_{(aq)} \longrightarrow C_3H_7-\overset{C_2H_5}{\underset{CH_3}{C}}-OH + KBr$$

Mechanism :

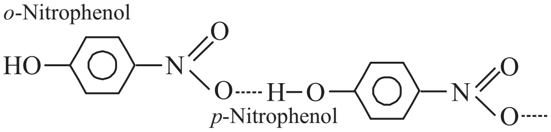


25. (i) For the preparation of ethyl methyl ether two different types of alcohols are needed. As a result a mixture of products is formed which is difficult to separate.

(ii) *o*-Nitrophenol is steam volatile due to intramolecular H–bonding. *p*-Nitrophenol is not steam volatile due to presence of intermolecular H–bonding.



o-Nitrophenol



p-Nitrophenol

26. Depending upon the nature of interaction between the dispersed phase and the dispersion medium, colloids are divided into two categories :

(i) Lyophilic sols : The colloidal in which the particles of the dispersed phase have a strong affinity for the dispersion medium are called lyophilic sols.

These colloidal sols, even if precipitated, change back to the colloid form simply by adding dispersion medium. So lyophilic sols are reversible in nature *e.g.,* glue, starch, rubber, etc.

(ii) Lyophobic sols : The colloidals in which particles of the dispersed phase have no or very little affinity for dispersion medium are called lyophobic sols. These are irreversible in nature, *i.e.,* once precipitated, they have little tendency to get back into the colloidal form on simply adding dispersion medium, *e.g.,* As_2S_3 solution.

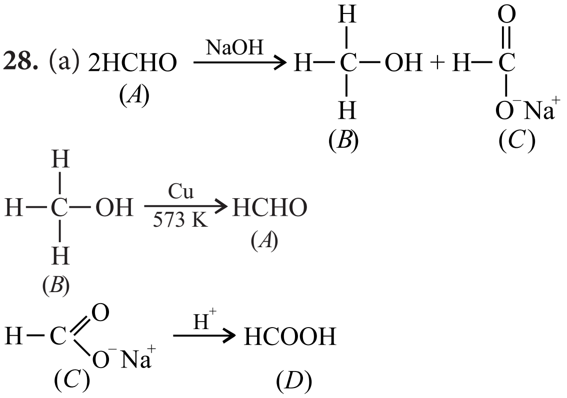
Lyophobic sols need stabilising agents for their preservation.

27. (i) (a) Fibrous protein : When polypeptide chains run parallel and are held together by hydrogen and sulphide bonds then the fibre-like structure is formed. These are insoluble in water. *e.g.,* keratin, myosin.

(b) Globular proteins : In this, chains of polypeptides coil around to give a spherical shape. These are usually soluble in water. *e.g.,* albumin, insulin.

(ii) In DNA structure hydrogen bonds are formed between specific pair of bases. Adenine forms 2 H-bonds with thymine and cytosine forms 3 H-bonds with guanine. This is called base pairing principle.

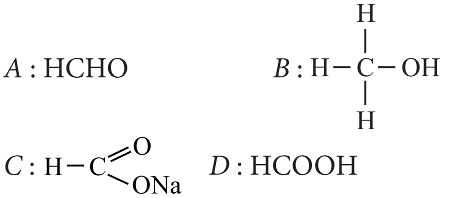
28. (a)



$$\underset{(A)}{2HCHO} \xrightarrow{NaOH} \underset{(B)}{H-\overset{H}{\underset{H}{C}}-OH} + \underset{(C)}{H-\overset{O}{\overset{\|}{C}}-O^-Na^+}$$

$$\underset{(B)}{H-\overset{H}{\underset{H}{C}}-OH} \xrightarrow[573\ K]{Cu} \underset{(A)}{HCHO}$$

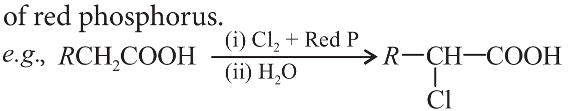
$$\underset{(C)}{HCOO^-Na^+} \xrightarrow{H^+} \underset{(D)}{HCOOH}$$



$A : HCHO$ $\quad B : H-\overset{H}{\underset{H}{C}}-OH$

$C : HCOONa$ $\quad D : HCOOH$

(b) Carboxylic acids having α-hydrogen are halogenated at the α-position on treatment with chlorine or bromine in the presence of small amount of red phosphorus.

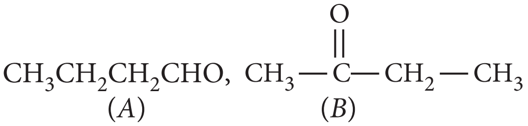


e.g., $RCH_2COOH \xrightarrow[(ii)\ H_2O]{(i)\ Cl_2\ +\ Red\ P} R-\underset{Cl}{CH}-COOH$

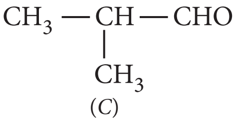
OR

(a) As (*A*) and (*C*) given positive Tollens' test thus these two should be aldehyde while (*B*) should be a ketone (does not give Tollen's test) with $-\underset{\underset{O}{\|}}{C}-CH_3$

group (as it gives positive iodoform test).
Three isomers are,

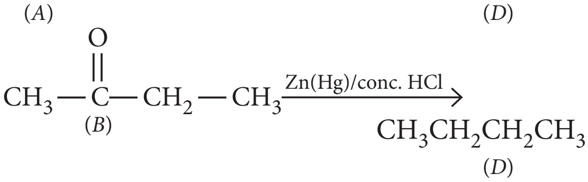


$$\underset{(A)}{CH_3CH_2CH_2CHO},\ \underset{(B)}{CH_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_2-CH_3}$$



$$\underset{(C)}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CHO}$$

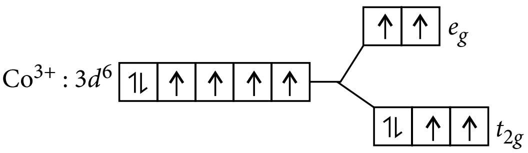
$$\underset{(A)}{CH_3CH_2CH_2CHO} \xrightarrow{Zn(Hg)/conc.\ HCl} \underset{(D)}{CH_3CH_2CH_2CH_3}$$



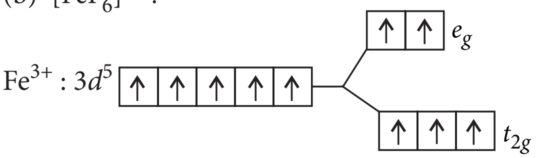
$$\underset{(B)}{CH_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_2-CH_3} \xrightarrow{Zn(Hg)/conc.\ HCl} \underset{(D)}{CH_3CH_2CH_2CH_3}$$

(b) Out of *A*, *B*, *C* isomers, *B* is least reactive towards addition of HCN.

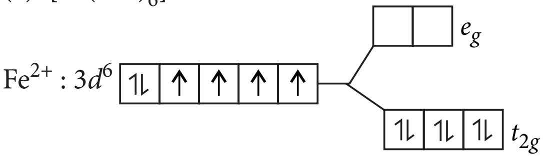
29. (a) $[CoF_6]^{3-}$:



No. of unpaired electrons = 4, $\mu = \sqrt{4(4+2)} = 4.9$ B.M.
(b) $[FeF_6]^{3-}$:



No. of unpaired electrons = 5, $\mu = \sqrt{5(5+2)} = 5.92$ B.M.
(c) $[Fe(CN)_6]^{4-}$:



No. of unpaired electrons = 0, $\mu = 0$

OR

(i) Triamminetrichloridochromium(III)
(ii) Potassium hexacyanidoferrate(III)
(iii) Dibromido*bis*(ethane-1,2-diamine)cobalt(III) ion

30. (i) Given, $r_c = 95$ pm, $r_a = 181$ pm, structure = ?
∴ C.N. = ?

$$\frac{r_c}{r_a} = \frac{95\,\text{pm}}{181\,\text{pm}} = 0.525$$

Radius ratio lies between 0.414 to 0.732 hence cations are in the octahedral voids of *ccp* of anions.
Hence, structure is *fcc*, C.N = 6.
(ii) Given, $r_c = 148$ pm, $r_a = 195$ pm, structure = ?
C.N = ?

$$\frac{r_c}{r_a} = \frac{148\,\text{pm}}{195\,\text{pm}} = 0.758$$

Radius ratio > 0.732. Hence, structure is *bcc* C. N. = 8.

31. (i) La^{3+} has a stable configuration of an inert gas $[Xe]5d^06s^0$. To obtain +4 oxidation state, the stable configuration is to be disturbed which is not possible under ordinary conditions and hence, La^{4+} does not exist.
(ii) Due to lanthanoide contraction, their sizes are same. Hence, their properties are similar.
(iii) Ce^{4+}. The stable oxidation state of lanthanoides is +3. Ce^{4+} tends to accept an electron to change to +3 state. Hence, it acts as a good oxidising agent.
(iv) Trivalent lanthanoids are coloured due to presence of *f*-electrons. The excitation of electron in *f*-level imparts colour to them. This colour is caused due to *f-f* transition. Some compounds show colour due to charge transfer also.
(v) Due to presence of unpaired electrons in *f*-orbital, lanthanoid ions are paramagnetic in nature.

OR

(i) The high melting and boiling points of transition metals are attributed to the involvement of greater number of electrons from (*n* – 1) *d*-orbital in addition to the *ns* electrons in the interatomic metallic bonding (*d-d* overlap).

(ii) This fact can be explained on the basis that heavy transition metals have much more strong metal-metal bonding.

(iii) As the atomic number increases the new electron enters the *d*-orbital and expected to increase in atomic size, but due to poor shielding effect of *d*-orbitals the electrostatic attraction between nucleus and outermost orbital increases and hence, the ionic radii decreases.

(iv) From left to right in each series of transition elements there is an increase in ionisation enthalpy due to increase in nuclear charge.

(v) $E°(M^{2+}/M)$ for any metal is related to the sum of enthalpy changes taking place in the following steps :
$M_{(s)} + \Delta_aH \rightarrow M_{(g)}$; $M_{(g)} + \Delta_iH \rightarrow M^{2+}_{(g)}$
$M^{2+}_{(g)} + aq. \rightarrow M^{2+} + \Delta_{hyd}H$
Copper has high enthalpy of atomisation (Δ_aH) and low enthalpy of hydration (*i.e.* low energy released). The high energy required to transform $Cu_{(s)}$ to $Cu^{2+}_{(aq)}$ is not balanced by its hydration enthalpy. Hence $E°(Cu^{2+}/Cu)$ is positive.

32. (a) The compound *A* gives a yellow oily substance on treatment with HNO_2. So, it must be 2°-amine. So, *A* is $(CH_3)_2NH$.

$$(CH_3)_2NH + HNO_2 \longrightarrow \underset{(A)}{(CH_3)_2N{-}N{=}O} + H_2O$$

(b) (i) $CH_3-\overset{\overset{\displaystyle NH_2}{|}}{CH}-CH_3$ is more basic than $CH_3-\underset{\underset{\displaystyle NH_2}{|}}{CH}-COOCH_3$ because $-COOCH_3$ is an electron withdrawing group which decrease the electron density on nitrogen atom.

(ii) 2° amines are more basic than 1° amines, because in 2° amine there are two electron releasing groups and in 1° amine only one electron releasing group is present, so, $CH_3NHCH_2CH_3$ is more basic than $CH_3CH_2CH_2NH_2$.

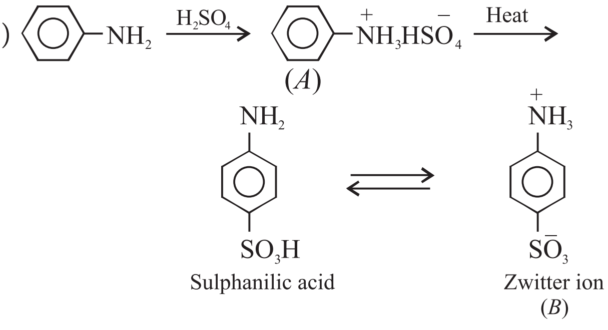
(c) (i) In tertiary amines there are no acidic hydrogen due to which they do not undergo acylation reaction.

(ii) N being less electronegative than O gives lone pair of electron more easily than O atom. Therefore, amines are more basic than alcohols.

OR

(a) First the mixture is washed with HCl when aniline and *N*-methylaniline are dissolved in it. Then the remaining part is washed with NaOH, when phenol dissolves leaving behind pure toluene. Phenol dissolved in alkali is precipitated by adding HCl. The hydrochloric acid solution of aniline and *N*-methyl aniline is treated first with benzene sulphonyl chloride and then sodium hydroxide. Benzene sulphonyl derivative of aniline dissolves in NaOH. It is filtered off, the filtrate as well as the residue are treated separately first with HCl and then with KOH to obtain pure and *N*-methylaniline separately.

(b)



(c) (i) If alkyl halide is in excess, the hydrogen atoms of ammonia are successively replaced by alkyl group to form primary, secondary and tertiary amines which further react with alkyl halide to form quaternary ammonium salt as follows :

$$NH_{3(alc.)} \xrightarrow[-HX]{+RX} \underset{1^\circ \text{ Amine}}{RNH_2} \xrightarrow[-HX]{+RX} \underset{2^\circ \text{ Amine}}{R_2NH}$$

$$\xrightarrow{+RX} \underset{3^\circ \text{ Amine}}{R_3N} \xrightarrow{+RX} \underset{\substack{\text{Tetraalkyl}\\ \text{ammonium halide}}}{R_4N^+X^-}$$

(ii) Both $-NO_2$ and $-COOH$ groups are electron withdrawing groups. They decrease the electron density at the benzene ring and hence deactivate it towards electrophilic substitution reactions.

33. (a) The given cell may be represented as

$Cu_{(s)}|Cu^{2+}|\,|Cl_2|Cl^-$

(i) $E^\circ_{cell} = E^\circ_c - E^\circ_a = (+1.36\text{ V}) - (+0.34\text{ V}) = 1.02\text{ V}$

(ii) $\Delta_r G^\circ = -nFE^\circ = -2 \times 96500\text{ C} \times 1.02\text{ V} = 196.86\text{ kJ}$

(iii) $E^\circ_{Cell} = \dfrac{0.0591}{n}\log K$

$$K = \text{antilog}\,\frac{2 \times 1.02\text{ V}}{0.0591} = \text{antilog}\,(34.51)$$

$K = 3.236 \times 10^{34}$

(b) Given :

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+};\ E^\circ_1 = +\,0.77\text{ V}$

$Fe^{2+} + 2e^- \rightleftharpoons Fe;\ E^\circ_2 = -\,0.44\text{ V}$

The desired equation is $Fe^{3+} + 3e^- \rightleftharpoons Fe;\ E^\circ_3 = ?$

The desired equation is obtained by adding above two equations. Therefore,

$$E^\circ_3 = \frac{n_1 E^\circ_1 + n_2 E^\circ_2}{n_3}$$

$$\text{or, } E^\circ_3 = \frac{1 \times 0.77\text{ V} + 2 \times (-0.44\text{ V})}{3} = \frac{-0.11}{3} = -0.04\text{ V}$$

OR

(a) HCl. Because H^+ ions are smaller than Na^+ ions and hence H^+ ions have greater ionic mobility than Na^+ ions.

(b) (i) Degree of dissociation, $\alpha = \dfrac{\Lambda_{eq}}{\Lambda^\infty_{eq}}$

$$\therefore\ \alpha = \frac{15.8}{350} = 0.04514$$

(ii) For monobasic acid, $HA \rightleftharpoons H^+ + A^-$

$$K = \frac{C\alpha^2}{(1-\alpha)} = C\alpha^2$$

As $\alpha <<< 1$ hence $(1 - \alpha) \approx 1$

$\therefore\ K = 0.05 \times (0.04514)^2,\ K = 1.019 \times 10^{-4}$

(c) Given : $V = 100\text{ cm}^3$, $M = 0.025$ M, $R = 520$ ohm

$G^\circ = 153.7\text{ m}^{-1} = 1.537\text{ cm}^{-1}$, $\Lambda_m = ?$

$$\kappa = G^\circ \times \frac{1}{R} = 1.537\text{ cm}^{-1} \times \frac{1}{520\text{ ohm}}$$

$$= 2.95 \times 10^{-3}\text{ ohm}^{-1}\text{cm}^{-1}$$

$$\text{Again, } \Lambda_m = \frac{\kappa \times 10^3}{M}$$

$$= \frac{2.95 \times 10^{-3}\text{ ohm}^{-1}\text{ cm}^{-1} \times 10^3}{0.025\text{ mol cm}^{-3}}$$

$$\Lambda_m = 118.0\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$$

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