CHEMVIDYA

100 Most-Expected CSIR-NET Chemistry Questions

Organic, inorganic and physical — every one with the working shown, not just an answer key.

100	36	100
QUESTIONS	CHAPTERS	WORKED SOLUTIONS

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How to use this

These hundred questions are drawn from the ChemVidya bank of 6,400+, chosen to spread across thirty-six chapters rather than cluster on a few topics. Every one has been through verification, and every one comes with a worked explanation rather than a bare answer letter.

> **Sit them first, then mark them.** The questions are in the front, the solutions in the back, deliberately. A question you answer correctly by luck and a question you know cold look identical in an answer key — and only one of them will still be right in the exam hall.

Give yourself about two minutes per question. Mark anything you guessed, even where the guess was right; those are the ones worth returning to.

When you check your work, read the explanation for the questions you got *right* as well. Roughly a third of the time the reasoning is not the one people assume, and that gap is what the paper is built to find.

Please share this file with anyone preparing for CSIR-NET, GATE or IIT-JAM chemistry. That is what it is for.

Organic Chemistry

1 AMINO ACIDS, PEPTIDES & PROTEINS

The peptide bond linking amino acids is a(n):

A ester bond
B amide bond between a carboxyl and an amino group
C ether bond
D disulphide bond

2 AROMATIC & HETEROCYCLIC

The nitro group (–NO_2) on a benzene ring is:

A Ortho/para-directing and activating
B Meta-directing and deactivating
C Ortho/para-directing and deactivating
D Meta-directing and activating

3 ASYMMETRIC SYNTHESIS & RETROSYNTHESIS

In retrosynthetic analysis, a bond “disconnection” leads to:

A synthons and their reagent (synthetic) equivalents
B the fully assembled target molecule
C a racemic mixture
D a protecting group

4 CARBOHYDRATES

Glucose and fructose are best described as:

A enantiomers
B functional isomers (aldose vs ketose)
C identical compounds
D anomers

5 GENERAL ORGANIC CHEMISTRY

Which carbocation is the most stable?

A CH_3+ (methyl)
B CH_3CH_2+ (primary ethyl)
C $(CH_3)_2CH$+ (secondary isopropyl)
D $(CH_3)_3C$+ (tertiary tert-butyl)

6 NAMED REACTIONS

Sodium borohydride ($NaBH_4$) is a mild reducing agent that readily reduces:

A Carboxylic acids to alcohols
B Aldehydes and ketones to alcohols
C Alkenes to alkanes
D Nitriles to amines

7 NATURAL PRODUCTS

Alkaloids are a class of natural products characterized by containing:

A A carboxylic acid group
B A basic nitrogen atom
C A phosphate group
D Only carbon and hydrogen

8 PERICYCLIC & PHOTOCHEMISTRY

The Diels–Alder reaction is best classified as a:

A [2+2] cycloaddition
B [4+2] cycloaddition
C Sigmatropic rearrangement
D Electrocyclic ring opening

9 PHYSICAL ORGANIC CHEMISTRY

A positive Hammett reaction constant (rho > 0) indicates a reaction favoured by:

A electron-donating substituents
B electron-withdrawing substituents
C steric bulk
D high temperature only

10 POLYMERS

Step-growth (condensation) polymerisation differs from chain-growth in that:

A it requires a radical initiator

B monomers react in steps and high molar mass is reached only at high conversion

C it uses only alkenes

D no small molecule is ever lost

11 REACTION MECHANISMS

An S_N2 reaction proceeds with:

A Retention of configuration

B Inversion of configuration (Walden inversion)

C Racemization

D No defined stereochemistry

12 SPECTROSCOPY (ORGANIC)

A strong IR absorption near 1715 cm^{-1} most likely indicates which group?

A O–H stretch

B C=O (carbonyl) stretch

C C≡N stretch

D C–H stretch

13 STEREOCHEMISTRY

A compound has two stereocentres and an internal mirror plane in one diastereomer. That achiral diastereomer is called a:

A Racemic mixture

B Meso compound

C Pair of enantiomers

D Conformational isomer

14 AMINO ACIDS, PEPTIDES & PROTEINS

Proteins are denatured by:

A mild cooling

B heat, extremes of pH, or urea

C dilution with water

D phosphorylation

15 AROMATIC & HETEROCYCLIC

Which substituent is activating and ortho/para-directing in electrophilic aromatic substitution?

A $–NO_2$

B $–OCH_3$ (methoxy)

C –COOH

D –CN

16 ASYMMETRIC SYNTHESIS & RETROSYNTHESIS

An acyl anion equivalent (a d^1 synthon, $R–C^-=O$) is most commonly provided by:

A an enolate

B a Grignard reagent

C a 1,3-dithiane (umpolung)

D an alkyl halide

17 CARBOHYDRATES

Which of the following is a non-reducing sugar?

A glucose

B fructose

C sucrose

D maltose

18 GENERAL ORGANIC CHEMISTRY

Which of the following is the most acidic C–H?

A Ethane (CH_3CH_3)

B Ethene ($CH_2=CH_2$)

C Ethyne (HC≡CH)

D Methane (CH_4)

19 NAMED REACTIONS

Hydroboration–oxidation of a terminal alkene gives predominantly:

A A Markovnikov alcohol

B An anti-Markovnikov alcohol

C A ketone

D An alkyl halide

20 NATURAL PRODUCTS

Steroids are based on which fused-ring framework?

A A single aromatic ring

B Three six-membered and one five-membered fused rings

C Two fused five-membered rings

D A macrocyclic porphyrin ring

21 PERICYCLIC & PHOTOCHEMISTRY

A thermal electrocyclic reaction of a 4n π-electron system proceeds:

A Conrotatory

B Disrotatory

C Antarafacial only

D It is thermally forbidden

22 REACTION MECHANISMS

Which conditions most favour an S_N1 reaction?

A Primary substrate, polar aprotic solvent

B Tertiary substrate, polar protic solvent

C Methyl substrate, strong nucleophile

D Primary substrate, strong base

23 SPECTROSCOPY (ORGANIC)

In mass spectrometry, an odd molecular-ion (M^+) m/z value usually indicates the molecule contains:

A An odd number of nitrogen atoms

B Only carbon and hydrogen

C An even number of oxygen atoms

D A halogen

24 STEREOCHEMISTRY

Using CIP rules, which substituent has the HIGHEST priority?

A $–CH_3$

B $–NH_2$

C –OH

D –H

25 AROMATIC & HETEROCYCLIC

Halogen substituents (–Cl, –Br) on a benzene ring are:

A Activating and ortho/para-directing

B Deactivating but ortho/para-directing

C Deactivating and meta-directing

D Activating and meta-directing

26 ASYMMETRIC SYNTHESIS & RETROSYNTHESIS

A chiral auxiliary is best described as:

A a catalyst used in substoichiometric amount

B an achiral base

C a group that remains permanently in the product

D a covalently attached chiral group that directs stereochemistry and is later removed

27 CARBOHYDRATES

Mutarotation of glucose refers to:

A its oxidation to gluconic acid

B the change in optical rotation as the alpha and beta anomers interconvert

C its hydrolysis

D racemisation of all its stereocentres

28 GENERAL ORGANIC CHEMISTRY

The most stable free radical among the following is:

A Methyl (•CH_3)
B Primary (•CH_2CH_3)
C Secondary ($(CH_3)_2$•CH)
D Tertiary ($(CH_3)_3$•C)

29 NAMED REACTIONS

The Suzuki-Miyaura coupling forms a carbon-carbon bond between an organohalide and:

A An organoboron compound
B A Grignard reagent
C An organozinc reagent
D An organotin compound

30 NATURAL PRODUCTS

The bond that links amino acid residues together in a protein is the:

A Glycosidic bond
B Peptide (amide) bond
C Phosphodiester bond
D Ester bond

31 PERICYCLIC & PHOTOCHEMISTRY

A thermal [1,5]-hydrogen sigmatropic shift is:

A Suprafacial and symmetry-allowed
B Antarafacial and symmetry-allowed
C Symmetry-forbidden thermally
D Only possible photochemically

32 REACTION MECHANISMS

A bulky base such as potassium tert-butoxide in an E_2 elimination favours the:

A Zaitsev (more substituted) alkene
B Hofmann (less substituted) alkene
C Substitution product
D Rearranged product

33 SPECTROSCOPY (ORGANIC)

An ^1H NMR signal near δ 9.7 ppm most likely corresponds to:

A An aliphatic CH_3 proton
B An aldehyde (CHO) proton
C An alkene proton
D A hydroxyl proton of an alcohol

34 STEREOCHEMISTRY

A molecule with two non-equivalent stereocentres has at most how many stereoisomers?

A 2
B 3
C 4
D 8

Inorganic Chemistry

35 BIOINORGANIC

The metal ion at the centre of the heme group in haemoglobin is:

A Mg_2+
B Fe_2+
C Cu_2+
D Zn_2+

36 CAGES & CLUSTERS

Boranes are classic examples of:

A electron-precise compounds
B electron-deficient compounds
C ionic compounds
D metallic conductors

37 CHEMICAL BONDING

Which of the following molecules is non-polar?

A H_2O **B** NH_3

C SO_2 **D** CO_2

38 COORDINATION CHEMISTRY

Using the 18-electron rule, the total valence electron count of $Ni(CO)_4$ is:

A 16 **B** 17

C 18 **D** 20

39 INORGANIC SPECTROSCOPY & CHARACTERISATION

In NMR spectroscopy, the number of signals corresponds to the number of:

A total protons **B** chemically inequivalent nuclei

C bonds in the molecule **D** electrons

40 LANTHANIDES & ACTINIDES

The 4f orbitals of the lanthanides are:

A strongly involved in covalent bonding **B** well shielded and largely non-bonding

C empty in all lanthanides **D** the orbitals used for sigma bonds

41 MAIN GROUP

Which pair of elements shows a 'diagonal relationship'?

A Li and Mg **B** Na and K

C B and Al **D** C and Si

42 METALLURGY

Concentration of a sulphide ore using oil and water with air agitation is called:

A levigation **B** froth flotation

C magnetic separation **D** leaching

43 ORGANOMETALLICS

Carbon monoxide bonds to a transition metal as a:

A σ-donor only **B** π-donor only

C σ-donor and π-acceptor **D** Purely ionic ligand

44 PERIODIC PROPERTIES

Which of the following has the largest first ionization energy?

A Na **B** Mg

C Al **D** Si

45 SOLID STATE & NUCLEAR

A Schottky defect in an ionic crystal involves:

A An ion occupying an interstitial site **B** Equal numbers of cation and anion vacancies

C Extra electrons in the lattice **D** Substitution by a foreign ion

46 TRANSITION & INNER-TRANSITION

The steady decrease in ionic radius across the lanthanide series is called:

A Lanthanide contraction
B Inert pair effect
C Diagonal relationship
D Jahn–Teller distortion

47 BIOINORGANIC

The metal ion at the centre of the chlorophyll molecule is:

A Fe^{2+}
B Mg^{2+}
C Co^{3+}
D Zn^{2+}

48 CHEMICAL BONDING

Lattice energy is greatest for an ionic compound made of:

A Large ions with low charges
B Small ions with high charges
C Large ions with high charges
D Neutral atoms

49 COORDINATION CHEMISTRY

Which ligand is the strongest-field (most likely to give a low-spin complex)?

A I^-
B Cl^-
C H_2O
D CN^-

50 INORGANIC SPECTROSCOPY & CHARACTERISATION

EPR (ESR) spectroscopy detects species containing:

A only paired electrons
B unpaired electrons (paramagnetic species)
C no electrons
D only nuclei

51 MAIN GROUP

The 'inert pair effect' is illustrated by the greater stability of:

A Pb^{4+} over Pb^{2+}
B Pb^{2+} over Pb^{4+}
C Al^{3+} over Al^{+}
D B^{3+} over B^{+}

52 METALLURGY

Refining titanium or zirconium via formation of the volatile iodide and its decomposition on a hot filament is the:

A Mond process
B van Arkel process
C zone refining
D cupellation

53 ORGANOMETALLICS

Wilkinson's catalyst, $RhCl(PPh_3)_3$, is widely used for:

A Homogeneous hydrogenation of alkenes
B Polymerization of ethene only
C Oxidation of alcohols
D Nitrogen fixation

54 PERIODIC PROPERTIES

Which element has the highest electronegativity?

A Oxygen
B Fluorine
C Chlorine
D Nitrogen

55 SOLID STATE & NUCLEAR

Doping silicon with a small amount of phosphorus produces a:

A p-type semiconductor
B n-type semiconductor
C Superconductor
D Pure insulator

56 TRANSITION & INNER-TRANSITION

Why are most Zn^{2+} (d^{10}) complexes colourless?

A Zinc is not a metal
B There are no possible d–d transitions in a filled d-shell
C Zn^{2+} is too small
D They absorb only ultraviolet light by d–d transitions

57 BIOINORGANIC

The metal ion present at the active site of carbonic anhydrase is:

A Fe^{2+}
B Cu^{2+}
C Zn^{2+}
D Mg^{2+}

58 CHEMICAL BONDING

According to VSEPR, the molecular geometry of the I_3^- (triiodide) ion is:

A Bent
B Trigonal planar
C Linear
D T-shaped

59 COORDINATION CHEMISTRY

In an octahedral crystal field, the five d-orbitals split into:

A A lower eg set and higher t2g set
B A lower t2g (3 orbitals) and higher eg (2 orbitals) set
C Two equal sets
D Five non-degenerate levels

60 INORGANIC SPECTROSCOPY & CHARACTERISATION

In ^1H NMR, the number of signals equals the number of:

A chemically inequivalent proton environments
B total protons in the molecule
C carbon atoms
D degrees of unsaturation

61 MAIN GROUP

Diborane (B_2H_6) is notable for containing:

A Normal 2-centre-2-electron bonds only
B Three-centre two-electron (banana) bonds
C A boron–boron triple bond
D Ionic B^+ and H^-

62 METALLURGY

Zone refining for ultra-pure metals (e.g. Si, Ge) is based on the principle that:

A impurities are more soluble in the molten zone than in the solid
B the metal is volatile
C the metal forms a volatile carbonyl
D of electrolytic deposition

63 ORGANOMETALLICS

Ziegler–Natta catalysts are used mainly to:

A Hydrogenate aromatic rings
B Polymerize alkenes (e.g. to polyethylene/polypropylene)
C Oxidize alcohols
D Reduce nitro groups

64 PERIODIC PROPERTIES

Across a period (left to right), atomic radius generally:

A Increases
B Decreases
C Stays constant
D Increases then decreases

65 SOLID STATE & NUCLEAR

A Frenkel defect in an ionic crystal occurs when:

A Equal cation and anion vacancies form
B An ion (usually a cation) moves to an interstitial site
C A foreign ion substitutes a host ion
D Extra electrons occupy anion vacancies

66 TRANSITION & INNER-TRANSITION

The colour of many transition-metal complexes arises mainly from:

A Nuclear transitions
B d–d electronic transitions
C Vibrational transitions
D Rotational transitions

67 BIOINORGANIC

Vitamin B_{12} (cobalamin) contains which central metal ion?

A Iron
B Cobalt
C Zinc
D Magnesium

Physical Chemistry

68 CHEMICAL EQUILIBRIUM

For a reaction at equilibrium at constant T and P, the Gibbs energy change Delta G is:

A negative
B positive
C zero
D equal to Delta G standard

69 CHEMICAL KINETICS

For a first-order reaction, the half-life t(1/2) is:

A Directly proportional to the initial concentration
B Inversely proportional to the initial concentration
C Independent of the initial concentration
D Proportional to the square of the initial concentration

70 ELECTROCHEMISTRY

By convention, the standard electrode potential of the standard hydrogen electrode (SHE) is:

A +1.23 V
B 0 V
C −0.76 V
D +0.34 V

71 GASES

By Graham's law, the rate of effusion of a gas is inversely proportional to:

A its molar mass
B the square root of its molar mass
C its molar mass squared
D its temperature

72 GROUP THEORY

How many symmetry operations are in the C2v point group?

A 2
B 3
C 4
D 6

73 QUANTUM CHEMISTRY

The maximum number of electrons that can occupy a subshell with azimuthal quantum number l = 2 (a d subshell) is:

A 2
B 6
C 10
D 14

74 SOLID STATE (PHYSICAL)

In an intrinsic semiconductor, electrical conductivity:

A decreases as temperature rises
B increases as temperature rises
C is independent of temperature
D depends only on pressure

75 SPECTROSCOPY (PHYSICAL)

A molecule shows a pure rotational (microwave) spectrum only if it has:

A A permanent dipole moment
B A centre of symmetry
C An even number of electrons
D A high molar mass

76 STATISTICAL THERMODYNAMICS

The molecular partition function q is best described as a measure of:

A The total energy of the system
B The number of thermally accessible states
C The entropy of mixing
D The activation energy

77 SURFACE & CATALYSIS

Compared with physisorption, chemisorption is characterized by:

A Weak van der Waals forces only
B Formation of chemical bonds and higher enthalpy of adsorption
C Always multilayer coverage
D No activation energy ever

78 THERMODYNAMICS

At constant temperature and pressure, a process is spontaneous when:

A $\Delta G > 0$
B $\Delta G = 0$
C $\Delta G < 0$
D $\Delta H < 0$ always

79 CHEMICAL EQUILIBRIUM

For an exothermic reaction at equilibrium, increasing the temperature will:

A shift the equilibrium toward products
B shift the equilibrium toward reactants
C have no effect on the position
D increase K

80 CHEMICAL KINETICS

The units of the rate constant for a first-order reaction are:

A $\text{mol L}^{-1}\,\text{s}^{-1}$
B $\text{L mol}^{-1}\,\text{s}^{-1}$
C s^{-1}
D $\text{L}^{2}\,\text{mol}^{-2}\,\text{s}^{-1}$

81 ELECTROCHEMISTRY

The Nernst equation describes how the cell potential depends on:

A Only temperature
B Reaction quotient (concentrations) and temperature
C Only the number of electrons
D Only the standard potential

82 GASES

The Boyle temperature of a real gas is the temperature at which:

A the gas liquefies

B the gas behaves nearly ideally over a range of low pressures (Z approx 1)

C the gas has zero volume

D the gas dissociates

83 GROUP THEORY

Which point group contains a centre of inversion (i)?

A C3v

B C2v

C D2h

D Td

84 QUANTUM CHEMISTRY

The energy of the levels of a hydrogen atom is proportional to:

A n

B n^2

C $-1/n^2$

D $-1/n$

85 SOLID STATE (PHYSICAL)

F-centres responsible for colour in some ionic crystals are:

A cation vacancies

B anion vacancies occupied by trapped electrons

C interstitial cations

D edge dislocations

86 SPECTROSCOPY (PHYSICAL)

The Beer–Lambert law states that absorbance is proportional to:

A Temperature and pressure

B Concentration and path length ($A = \varepsilon c l$)

C Wavelength only

D The square of concentration

87 STATISTICAL THERMODYNAMICS

The ratio of populations of two energy states at temperature T is governed by:

A The Boltzmann factor $\exp(-\Delta E/kT)$

B Hund's rule

C The Pauli principle

D Raoult's law

88 SURFACE & CATALYSIS

The BET isotherm extends the Langmuir model to describe:

A Monolayer adsorption only

B Multilayer adsorption

C Adsorption on liquids only

D Chemisorption only

89 THERMODYNAMICS

The first law of thermodynamics is expressed as:

A $\Delta U = q + w$

B $\Delta G = \Delta H - T\Delta S$

C $\Delta S_{universe} > 0$

D $PV = nRT$

90 CHEMICAL EQUILIBRIUM

A catalyst added to a reaction at equilibrium:

A shifts the equilibrium forward

B shifts the equilibrium backward

C does not shift the equilibrium; it only speeds attainment

D increases the value of K

91 CHEMICAL KINETICS

For a zero-order reaction, the reaction rate is:

A Proportional to [A]
B Proportional to $[A]^2$
C Independent of [A]
D Proportional to 1/[A]

92 ELECTROCHEMISTRY

One faraday (the charge of one mole of electrons) is approximately:

A 96,500 C
B 6,500 C
C 1,600 C
D 9,650,000 C

93 GROUP THEORY

The improper rotation operation S_n is equivalent to:

A A rotation followed by reflection in a plane perpendicular to the axis
B A pure rotation only
C An inversion only
D Two successive reflections in the same plane

94 QUANTUM CHEMISTRY

According to Hund's rule, electrons fill a set of degenerate orbitals by:

A Pairing up in one orbital first
B Singly occupying each orbital first, with parallel spins
C Filling them in random order
D Avoiding the orbitals entirely

95 SPECTROSCOPY (PHYSICAL)

A molecular vibration is infrared (IR) active only if, during the vibration, there is a change in the molecule's:

A Polarizability
B Dipole moment
C Bond length only
D Mass

96 STATISTICAL THERMODYNAMICS

By the equipartition theorem, each translational degree of freedom contributes how much to the average energy per molecule?

A kT
B ½kT
C 2kT
D 3kT

97 SURFACE & CATALYSIS

Enzymes are biological catalysts composed mainly of:

A Lipids
B Proteins
C Carbohydrates
D Nucleic acids only

98 THERMODYNAMICS

For any spontaneous process, the total entropy of the universe (system + surroundings):

A Decreases
B Stays constant
C Increases
D Becomes zero

99 CHEMICAL KINETICS

A catalyst increases the rate of a reaction by:

A Increasing the activation energy
B Lowering the activation energy (providing an alternative path)
C Shifting the equilibrium toward products
D Increasing ΔH of the reaction

100

ELECTROCHEMISTRY

In any electrochemical cell (galvanic or electrolytic), oxidation always occurs at the:

A Cathode

B Anode

C Salt bridge

D Reference electrode

Organic Chemistry — worked solutions

1 **B — amide bond between a carboxyl and an amino group**

A peptide bond is an amide formed between the carboxyl of one amino acid and the amino group of the next, with loss of water.

2 **B — Meta-directing and deactivating**

$–NO_2$ strongly withdraws electron density (by resonance and induction), deactivating the ring toward electrophilic substitution and directing incoming electrophiles to the meta position.

3 **A — synthons and their reagent (synthetic) equivalents**

A disconnection is the reverse of a bond-forming step; it generates idealised fragments (synthons), for which real reagents (synthetic equivalents) are then identified.

4 **B — functional isomers (aldose vs ketose)**

Glucose is an aldohexose and fructose a ketohexose; they share the formula $C_6H_{12}O_6$ but differ in functional group, so they are functional isomers.

5 **D — $(CH_3)_3C^+$ (tertiary tert-butyl)**

Carbocation stability increases with the number of alkyl groups on the positive carbon, because alkyl groups donate electron density through hyperconjugation and the inductive effect. Order: tertiary > secondary > primary > methyl. The tert-butyl cation is therefore the most stable.

6 **B — Aldehydes and ketones to alcohols**

$NaBH_4$ is a mild hydride source that reduces aldehydes and ketones to alcohols but is generally too mild to reduce carboxylic acids or esters (which need the stronger $LiAlH_4$).

7 **B — A basic nitrogen atom**

Alkaloids are naturally occurring, mostly basic organic compounds containing nitrogen (often in a heterocyclic ring) — e.g. morphine, quinine, caffeine, nicotine.

8 **B — [4+2] cycloaddition**

The Diels–Alder reaction is a [4+2] cycloaddition between a conjugated diene (4 π electrons) and a dienophile (2 π electrons), thermally allowed (suprafacial–suprafacial) by the Woodward–Hoffmann rules for 6 π electrons.

9 **B — electron-withdrawing substituents**

A positive rho means the reaction is accelerated by electron-withdrawing groups (negative charge builds up in the transition state).

10 **B — monomers react in steps and high molar mass is reached only at high conversion**

In step-growth polymerisation any two monomers/oligomers can react; high molar mass appears only near complete conversion.

11 **B — Inversion of configuration (Walden inversion)**

S_N2 is a concerted, single-step backside attack of the nucleophile opposite the leaving group, inverting the stereocentre (Walden inversion). It is second order: rate = k[substrate][nucleophile].

12 **B — C=O (carbonyl) stretch**

The carbonyl (C=O) stretch is a strong band typically around 1700–1750 cm^{-1} (ketones ~1715 cm^{-1}). O–H appears ~3200–3550 cm^{-1} (broad), nitriles ~2250 cm^{-1}, and C–H ~2850–3100 cm^{-1}.

13 **B — Meso compound**

A meso compound contains stereocentres but is superimposable on its mirror image due to an internal plane (or point) of symmetry, so it is optically inactive (achiral) despite having stereocentres. A classic example is meso-tartaric acid.

14 **B — heat, extremes of pH, or urea**

Heat, pH extremes and chaotropes such as urea disrupt the non-covalent interactions that maintain protein structure, causing denaturation.

15 **B — $–OCH_3$ (methoxy)**

The methoxy group donates electron density into the ring by resonance (lone pair on oxygen), activating the ring and directing electrophiles to the ortho and para positions. The others are deactivating, meta-directing groups.

16 **C — a 1,3-dithiane (umpolung)**

Deprotonated 1,3-dithianes are nucleophilic at the (formerly electrophilic) carbonyl carbon — classic umpolung. After alkylation the dithiane is hydrolysed to reveal the carbonyl.

17 **C — sucrose**

In sucrose both anomeric carbons are involved in the glycosidic bond, so it has no free reducing (hemiacetal) group and does not reduce Tollens or Fehling reagent.

18 **C — Ethyne (HC≡CH)**

Acidity of a terminal C–H increases with the s-character of the carbon hybrid orbital, because greater s-character holds the lone pair closer to the nucleus and stabilizes the conjugate base. sp (ethyne, ~50% s, pKa ≈ 25) > sp^2 (ethene, pKa ≈ 44) > sp^3 (ethane, pKa ≈ 50).

19 **B — An anti-Markovnikov alcohol**

Hydroboration–oxidation adds water with anti-Markovnikov regiochemistry (OH to the less substituted carbon) and syn stereochemistry, because boron adds to the less hindered carbon.

20 **B — Three six-membered and one five-membered fused rings**

Steroids share the cyclopentanoperhydrophenanthrene skeleton: three fused six-membered rings plus one fused five-membered ring (e.g. cholesterol, testosterone, cortisol).

21 **A — Conrotatory**

By the Woodward–Hoffmann rules, thermal electrocyclic reactions of 4n π-electron systems are conrotatory, while 4n+2 systems are disrotatory (the selectivities reverse photochemically).

22 **B — Tertiary substrate, polar protic solvent**

S_N1 goes through a carbocation, so it is favoured by substrates that give stable carbocations (tertiary) and by polar protic solvents that stabilize the ionic intermediate. Rate = k[substrate] (first order, independent of nucleophile).

23 **A — An odd number of nitrogen atoms**

By the nitrogen rule, a molecule with an odd nominal molecular mass contains an odd number of nitrogen atoms (a consequence of nitrogen's even mass but odd valence).

24 **C — –OH**

Cahn–Ingold–Prelog priority is assigned by atomic number of the first atom: O (8) > N (7) > C (6) > H (1). Therefore –OH outranks $–NH_2$, $–CH_3$ and –H.

25 **B — Deactivating but ortho/para-directing**

Halogens are an exception: they deactivate the ring overall (inductive electron withdrawal) yet direct ortho/para through their lone-pair resonance donation.

26 **D — a covalently attached chiral group that directs stereochemistry and is later removed**

A chiral auxiliary is bonded to the substrate to bias the facial selectivity of a reaction, then cleaved off and (ideally) recovered — e.g. Evans oxazolidinones.

27 **B — the change in optical rotation as the alpha and beta anomers interconvert**

In solution the alpha and beta anomers interconvert through the open-chain form until equilibrium, changing the observed optical rotation (mutarotation).

28 **D — Tertiary ($(CH_3)_3•C$)**

Like carbocations, carbon radicals are stabilized by hyperconjugation and the inductive donation of alkyl groups. Stability order: tertiary > secondary > primary > methyl.

29 **A — An organoboron compound**

The palladium-catalysed Suzuki-Miyaura coupling joins an aryl/vinyl halide with an organoboron species (boronic acid or ester) in the presence of base. (Coupling with organotin is Stille, with organozinc is Negishi.)

30 **B — Peptide (amide) bond**

Amino acids are joined by peptide bonds — amide linkages formed between the carboxyl group of one amino acid and the amino group of the next, with loss of water.

31 **A — Suprafacial and symmetry-allowed**

A [1,5]-H shift involves 6 electrons in the cyclic transition state; by the Woodward–Hoffmann rules it is thermally allowed in a suprafacial manner (whereas a [1,3]-H shift would have to be antarafacial and is geometrically difficult).

32 **B — Hofmann (less substituted) alkene**

Bulky bases are sterically hindered and abstract the more accessible, less hindered proton, giving the less substituted (Hofmann) alkene as the major product, rather than the usual Zaitsev product.

33 **B — An aldehyde (CHO) proton**

Aldehyde protons (R–CHO) are strongly deshielded and appear far downfield, around δ 9–10 ppm. Aliphatic CH_3 are near δ 0.9–1.5, vinylic protons δ 4.5–6.5.

34 **C — 4**

The maximum number of stereoisomers is 2^n where n is the number of stereocentres. For two non-equivalent stereocentres, 2^2 = 4. (Fewer than 4 occur only when symmetry produces a meso form.)

Inorganic Chemistry — worked solutions

35 **B — Fe_2+**

Haemoglobin carries oxygen via an iron(II) centre held in a porphyrin (heme) ring. The Fe(II) reversibly binds O_2; oxidation to Fe(III) (methaemoglobin) abolishes oxygen transport. (Mg_2+ is central in chlorophyll, not heme.)

36 **B — electron-deficient compounds**

Boranes have too few valence electrons for normal 2-centre-2-electron bonds, so they are electron-deficient and use multicentre bonding.

37 **D — CO_2**

CO_2 is linear and symmetric, so its two C=O bond dipoles cancel, giving zero net dipole moment (non-polar). H_2O and NH_3 are bent/pyramidal and SO_2 is bent — all polar.

38 **C — 18**

Ni(0) contributes 10 d-electrons and each CO is a 2-electron donor (neutral/covalent counting). 10 + 4 x 2 = 18 electrons, satisfying the 18-electron rule, which is why $Ni(CO)_4$ is a stable tetrahedral complex.

39 **B — chemically inequivalent nuclei**

Each set of chemically equivalent nuclei gives one signal, so the number of signals equals the number of inequivalent environments.

40 **B — well shielded and largely non-bonding**

The 4f orbitals are buried (well shielded), so they take little part in bonding, giving similar chemistry across the series.

41 **A — Li and Mg**

Diagonal relationships link an element to the one diagonally down-right (Li–Mg, Be–Al, B–Si) due to similar charge/size ratios and electronegativities. Lithium resembles magnesium more than its own group-1 congeners in several properties.

42 **B — froth flotation**

Froth flotation exploits the preferential wetting of sulphide ore particles by oil; they rise with the froth while gangue settles.

43 **C — σ-donor and π-acceptor**

CO donates its carbon lone pair (σ-donation) to the metal and accepts electron density from filled metal d-orbitals into its empty π* orbitals (π-back-donation). This synergic bonding stabilizes low oxidation states.

44 **D — Si**

First ionization energy generally increases across a period. Although there are dips at Al (due to removal of a 3p electron vs filled 3s) and at S, among Na, Mg, Al, Si the value rises overall left to right, so Si has the highest first ionization energy of this set.

45 **B — Equal numbers of cation and anion vacancies**

A Schottky defect is a stoichiometric vacancy defect: equal numbers of cations and anions are missing from their lattice sites, lowering the crystal's density. (A Frenkel defect instead moves an ion to an interstitial site.)

46 **A — Lanthanide contraction**

Poor shielding by the diffuse 4f electrons lets effective nuclear charge rise across the series, steadily contracting the ions (the lanthanide contraction). It makes 4d and 5d congeners (e.g. Zr/Hf) very similar in size.

47 **B — Mg^{2+}**

Chlorophyll contains a magnesium (Mg^{2+}) ion coordinated in a porphyrin-like (chlorin) ring. (For comparison: haemoglobin has Fe, vitamin B_{12} has Co, carbonic anhydrase has Zn.)

48 **B — Small ions with high charges**

By the Born–Landé/Coulomb relationship, lattice energy increases with higher ionic charges and smaller interionic distance. Thus small, highly charged ions (e.g. MgO: Mg^{2+}, O^{2-}) give very large lattice energies.

49 **D — CN^-**

In the spectrochemical series, field strength increases $I^- < Br^- < Cl^- < F^- < H_2O < NH_3 <$ en $< NO_2^- < CN^- <$ CO. CN^- is a strong-field ligand causing a large Δ and favouring low-spin configurations.

50 **B — unpaired electrons (paramagnetic species)**

EPR is sensitive to unpaired electrons, so it studies paramagnetic species such as radicals and many transition-metal ions.

51 **B — Pb^{2+} over Pb^{4+}**

Down groups 13–15, the ns^2 electrons become reluctant to ionize (inert pair effect), so heavier elements favour an oxidation state two below the group maximum. Thus Pb^{2+} is more stable than Pb^{4+} (and Tl^+ over Tl^{3+}).

52 **B — van Arkel process**

The van Arkel-de Boer method forms a volatile metal iodide that decomposes on a hot tungsten filament to deposit the pure metal.

53 **A — Homogeneous hydrogenation of alkenes**

Wilkinson's catalyst is a classic homogeneous catalyst for the hydrogenation of alkenes (and alkynes) under mild conditions, operating via oxidative addition of H_2, alkene coordination, insertion, and reductive elimination.

54 **B — Fluorine**

Fluorine is the most electronegative element (Pauling ≈ 3.98). Electronegativity increases across a period and decreases down a group, peaking at F in the top-right of the periodic table (excluding noble gases).

55 **B — n-type semiconductor**

Phosphorus (group 15) has one more valence electron than silicon (group 14). The extra, loosely bound electrons become charge carriers, giving an n-type (negative-carrier) semiconductor. Doping with group-13 elements (e.g. boron) gives p-type.

56 **B — There are no possible d–d transitions in a filled d-shell**

Colour in transition-metal complexes usually comes from d–d electronic transitions. With a completely filled d^{10} configuration, Zn^{2+} has no vacant d-orbital for such transitions, so its complexes are typically colourless.

57 **C — Zn^{2+}**

Carbonic anhydrase contains a catalytic Zn^{2+} ion that activates a water molecule for the rapid interconversion of CO_2 and bicarbonate. (Haemoglobin uses Fe; chlorophyll uses Mg.)

58 **C — Linear**

The central iodine in I_3- has 2 bonding pairs and 3 lone pairs (sp3d). The three lone pairs occupy the equatorial sites of a trigonal bipyramid, leaving the two terminal iodines axial, giving a linear ion.

59 **B — A lower t2g (3 orbitals) and higher eg (2 orbitals) set**

In an octahedral field the t2g orbitals (dxy, dxz, dyz) are stabilized (lower) and the eg orbitals (dz^2, dx^2-y^2) are raised (higher), separated by the splitting energy Δo. (The order inverts in a tetrahedral field.)

60 **A — chemically inequivalent proton environments**

Each set of chemically (and magnetically) equivalent protons gives one signal, so the signal count reports the number of distinct proton environments.

61 **B — Three-centre two-electron (banana) bonds**

Diborane is electron-deficient: two bridging hydrogens each participate in a three-centre two-electron (B–H–B 'banana') bond, in addition to four terminal 2c-2e B–H bonds.

62 **A — impurities are more soluble in the molten zone than in the solid**

Impurities concentrate in the molten zone and are swept to one end as the molten band is moved along the rod, leaving pure metal.

63 **B — Polymerize alkenes (e.g. to polyethylene/polypropylene)**

Ziegler–Natta catalysts (e.g. $TiCl_4$ with an aluminium alkyl) polymerize alkenes such as ethene and propene to high-density, stereoregular polymers — a foundation of the modern plastics industry.

64 **B — Decreases**

Across a period the nuclear charge increases while electrons enter the same shell, so the effective nuclear charge rises and pulls electrons closer — atomic radius decreases. Down a group radius increases as new shells are added.

65 **B — An ion (usually a cation) moves to an interstitial site**

In a Frenkel defect a smaller ion (typically the cation) leaves its lattice site and occupies an interstitial position, creating a vacancy–interstitial pair. The overall density is unchanged (unlike a Schottky defect, which lowers density).

66 **B — d–d electronic transitions**

When d-orbitals are split by ligands (crystal field), electrons absorb visible light to move between the split d-levels (d–d transitions); the transmitted/complementary colour is what we see.

67 **B — Cobalt**

Vitamin B_{12} contains a cobalt ion held in a corrin ring. It is the classic example of a naturally occurring organometallic compound (with a Co–C bond in some forms).

Physical Chemistry — worked solutions

68 **C — zero**

At equilibrium the system's Gibbs energy is at a minimum, so Delta G = 0 (note: Delta G standard is generally non-zero).

69 **C — Independent of the initial concentration**

For a first-order reaction t(1/2) = ln 2 / k, which contains no concentration term, so the half-life is independent of the initial concentration. (For a second-order reaction the half-life is inversely proportional to initial concentration.)

70 **B — 0 V**

The SHE is the reference electrode and is assigned a standard potential of exactly 0 V at all temperatures; all other standard electrode potentials are measured relative to it.

71 **B — the square root of its molar mass**

Graham's law: rate of effusion is inversely proportional to the square root of molar mass (lighter gases effuse faster).

72 **C — 4**

C2v contains four operations: E (identity), C_2 (two-fold rotation), and two vertical mirror planes σv and σv'. (Order of the group = 4.)

73 **C — 10**

A subshell with quantum number l has (2l+1) orbitals, each holding 2 electrons → 2(2l+1). For l = 2 (d): 2(5) = 10 electrons.

74 **B — increases as temperature rises**

Raising the temperature promotes more electrons across the band gap, so conductivity of an intrinsic semiconductor increases.

75 **A — A permanent dipole moment**

The gross selection rule for pure rotational (microwave) spectroscopy is that the molecule must have a permanent dipole moment. Thus polar molecules like HCl are microwave-active, while homonuclear diatomics like N_2 and O_2 are not.

76 **B — The number of thermally accessible states**

The partition function $q = \Sigma \exp(-\varepsilon_i/kT)$ effectively counts the number of states thermally accessible to a molecule at temperature T; it is the bridge between molecular energy levels and bulk thermodynamic properties.

77 **B — Formation of chemical bonds and higher enthalpy of adsorption**

Chemisorption involves actual chemical bond formation between adsorbate and surface, with a high enthalpy of adsorption (typically > ~40 kJ/mol), is usually monolayer, and is specific. Physisorption is weak (van der Waals), low-enthalpy, and can be multilayer.

78 **C — $\Delta G < 0$**

The Gibbs free energy criterion: at constant T and P a process is spontaneous when $\Delta G < 0$, at equilibrium when $\Delta G = 0$, and non-spontaneous when $\Delta G > 0$. (ΔH alone does not determine spontaneity.)

79 **B — shift the equilibrium toward reactants**

By Le Chatelier's principle, added heat favours the endothermic (reverse) direction, shifting an exothermic equilibrium toward reactants and lowering K.

80 **C — s^{-1}**

For first order, rate = k[A], so k = rate/[A] = (mol L^{-1} s^{-1})/(mol L^{-1}) = s^{-1} ($time^{-1}$), independent of concentration units.

81 **B — Reaction quotient (concentrations) and temperature**

The Nernst equation, $E = E° - (RT/nF) \ln Q$, relates the actual cell potential to the standard potential, temperature, number of electrons n, and the reaction quotient Q (i.e. the concentrations/activities). At 298 K the factor RT/F gives the familiar 0.059/n.

82 **B — the gas behaves nearly ideally over a range of low pressures (Z approx 1)**

At the Boyle temperature the effects of attractive and repulsive terms cancel so the gas obeys ideal behaviour over a range of low pressures.

83 **C — D2h**

D2h contains the inversion centre i (along with E, C_2 axes, mirror planes and $S_2 = i$). C2v, C3v and Td have no centre of inversion.

84 **C — $-1/n^2$**

For the hydrogen atom $E_n = -13.6\ \text{eV} / n^2$, i.e. proportional to $-1/n^2$. Levels are negative (bound) and converge toward zero as $n \to \infty$ (ionization limit).

85 **B — anion vacancies occupied by trapped electrons**

An F-centre is an anion vacancy that has trapped an electron; the trapped electron absorbs visible light, imparting colour.

86 **B — Concentration and path length ($A = \varepsilon c l$)**

Beer–Lambert: $A = \varepsilon c l$, where ε is the molar absorptivity, c the concentration, and l the path length. Absorbance is directly proportional to both concentration and path length (within the law's validity range).

87 **A — The Boltzmann factor $\exp(-\Delta E/kT)$**

The Boltzmann distribution gives $n2/n1 = (g2/g1)\exp(-\Delta E/kT)$: higher-energy states are less populated, and the gap matters relative to thermal energy kT.

88 **B — Multilayer adsorption**

The Brunauer–Emmett–Teller (BET) isotherm generalizes Langmuir's monolayer treatment to multilayer physical adsorption, and is the standard method for measuring surface areas of porous solids.

89 **A — $\Delta U = q + w$**

The first law (conservation of energy) states the change in internal energy equals heat added to the system plus work done on it: $\Delta U = q + w$ (with the IUPAC sign convention).

90 **C — does not shift the equilibrium; it only speeds attainment**

A catalyst lowers the activation energy of forward and reverse steps equally, so it speeds attainment of equilibrium without changing its position or K.

91 **C — Independent of [A]**

A zero-order reaction has rate = k, independent of reactant concentration (common when a surface or catalyst is saturated). Concentration falls linearly with time: $[A] = [A]_0 - kt$.

92 **A — 96,500 C**

The Faraday constant $F = N_A \times e \approx 96{,}485$ C/mol (often rounded to 96,500 C). It converts moles of electrons to charge in electrolysis (Faraday's laws) and appears in the Nernst equation.

93 **A — A rotation followed by reflection in a plane perpendicular to the axis**

An improper rotation S_n is a rotation by 360/n degrees about an axis followed by reflection through a plane perpendicular to that axis. Special cases: S_1 = sigma (mirror) and S_2 = i (inversion centre).

94 **B — Singly occupying each orbital first, with parallel spins**

Hund's rule of maximum multiplicity: electrons occupy degenerate orbitals singly with parallel spins before pairing, minimizing electron–electron repulsion and giving the lowest-energy (most stable) arrangement.

95 **B — Dipole moment**

The gross selection rule for IR absorption is that the vibration must change the molecule's dipole moment. (A change in polarizability is the requirement for Raman activity — the two are complementary.)

96 **B — ½kT**

The equipartition theorem assigns ½kT of average energy to each quadratic degree of freedom. A molecule has three translational degrees of freedom, contributing $3 \times \tfrac{1}{2}kT = (3/2)kT$ in total.

97

B — Proteins

Most enzymes are proteins that dramatically accelerate biochemical reactions by lowering activation energy with high specificity. (A few catalytic RNAs, ribozymes, also exist.)

98

C — Increases

The second law of thermodynamics states that the entropy of the universe increases for any spontaneous (irreversible) process, and is unchanged only for a reversible one.

99

B — Lowering the activation energy (providing an alternative path)

A catalyst provides an alternative mechanism with a lower activation energy, speeding both forward and reverse rates equally. It does not change ΔG, ΔH, or the position of equilibrium — only how fast equilibrium is reached.

100

B — Anode

By definition, oxidation (loss of electrons) occurs at the anode and reduction at the cathode, in both galvanic and electrolytic cells. (The sign of each electrode differs between the two cell types, but this definition does not.)

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