

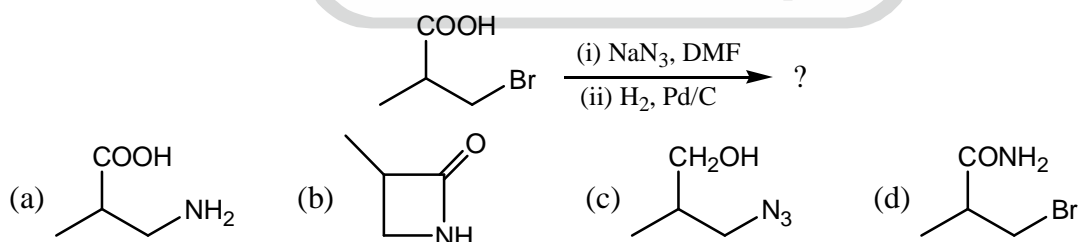
PAPER : IIT-JAM 2015
CHEMISTRY-CY

- Section-A contains 30 Multiple Choice Questions (MCQ). Each question has 4 choices (a), (b), (c) and (d), for its answer, out of which ONLY ONE is correct. From Q.1 to Q.10 carries 1 Marks and Q.11 to Q.30 carries 2 Marks each.
- Section-B contains 10 Multiple Select Questions (MSQ). Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONE or MORE than ONE is/are correct. For each correct answer you will be awarded 2 marks.
- Section-C contains 20 Numerical Answer Type (NAT) questions. From Q.41 to Q.50 carries 1 Mark each and Q.51 to Q.60 carries 2 Marks each. For each NAT type question, the value of answer is between 0 to 9.
- In all sections, questions not attempted will result in zero mark. In Section-A (MCQ), wrong answer will result in negative marks. For all 1 mark questions, 1/3 marks will be deducted for each wrong answer. For all 2 marks questions, 2/3 marks will be deducted for each wrong answer. In Section-B (MSQ), there is no negative and no partial marking provisions. There is no negative marking in Section -C (NAT) as well.

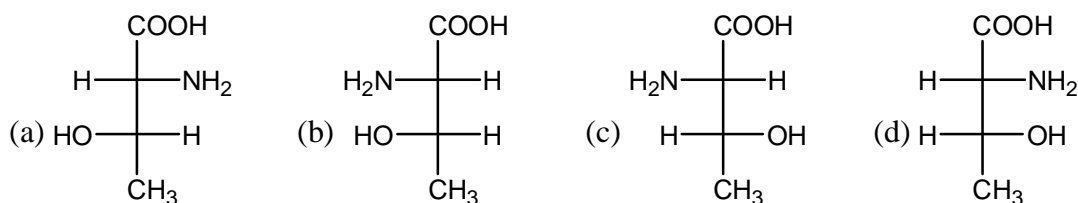
SECTION-A : MCQ (Multiple Choice Questions)

Q. 1 - Q. 10 carry one mark each.

- The first row transition metal complexes having tetrahedral geometry are high-spin due to
(a) $\Delta_t > P$ (b) $\Delta_t < P$ (c) $\Delta_t = P$ (d) $\Delta_t > \Delta_0$
- The major product formed in the following reaction is



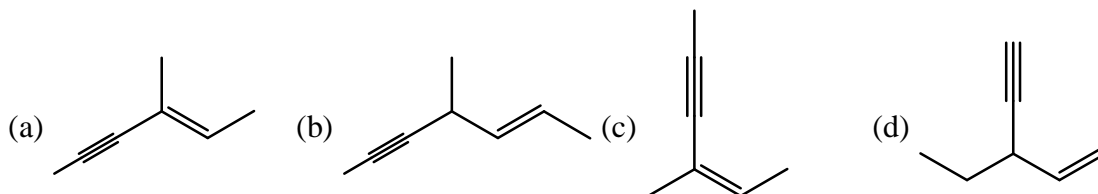
- Which one of the following is an identity matrix?
(a) $\begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$ (b) $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ (c) $\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ (d) $\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$
- The structure of (2S, 3R)-2-amino-3-hydroxy butanoic acid is



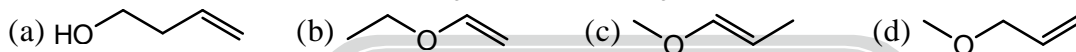
5. The intermolecular van der waals potential is inversely proportional to r^6 . The corresponding force is proportional to

- (a) $\frac{1}{r^5}$ (b) $\frac{1}{r^6}$ (c) $\frac{1}{r^7}$ (d) $\frac{1}{r^{12}}$

6. The ene-yne that produces a chiral compound upon treatment with Lindlar's catalyst is



7. An organic compound $P(C_4H_8O)$ is positive to Bayer's test, but inert to sodium metal. On treatment with conc. HCl, P gives CH_3CH_2Cl and CH_3CHO . The structure of P is



8. Low-spin iron (III) centre is present in

- (a) deoxy form of hemoglobin (b) oxy form of hemoglobin
(c) hemocyanin (d) carbonic anhydrase

9. A filter paper moistened with cadmium acetate solution turns yellow upon exposure to H_2S . The transition responsible for the yellow colour is

- (a) d-d (b) metal-to-ligand charge transfer
(c) ligand-to-metal charge transfer (d) $\sigma - \sigma^*$

10. The species responsible for the superacidity of SbF_5-HSO_3F system is

- (a) HSO_3F (b) SbF_5 (c) HF (d) $H_2SO_3F^+$

Q. 11 - Q. 30 carry two marks each.

11. The correct order of the pK_a values for the conjugate acids of heterocyclic compounds given below is



- (a) $II > III > I > IV$ (b) $IV > II > III > I$ (c) $III > II > IV > I$ (d) $III > IV > II > I$

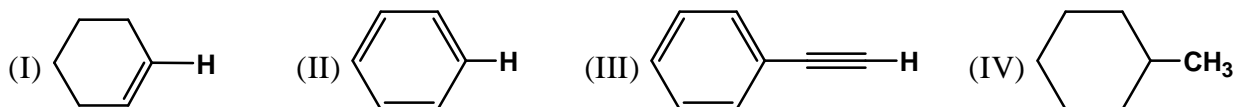
12. The species having trigonal pyramidal shape is

- (a) NO_3^- (b) CO_3^{2-} (c) BrF_3 (d) SO_3^{2-}

13. The Volhard method is used for the estimation of

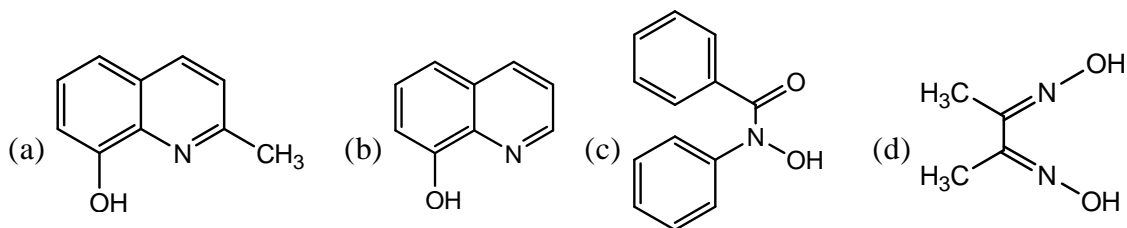
- (a) cyanide ion by titration with silver nitrate (b) silver ion directly
(c) oxygen in water (d) glucose in blood

14. The correct order of the 1H NMR chemical shift values (δ) for the indicated hydrogens (in bold) in the following compounds is

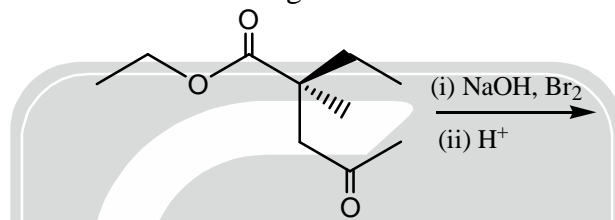


- (a) $I > II > III > IV$ (b) $II > I > III > IV$ (c) $III > II > I > IV$ (d) $II > III > IV > I$

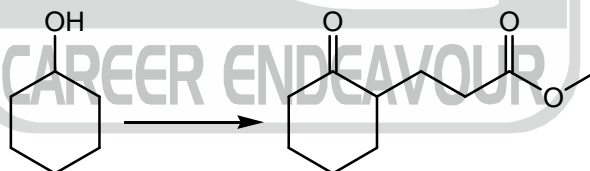
15. The reagent 'oxine' commonly used in analytical chemistry is



16. The correct statement about ionization potential (IP) is
 (a) non-metallic character of an element decreases as the IP increases
 (b) IP decreases down the group in the periodic table
 (c) second IP of Ca is larger than second IP of K
 (d) IP decreases on going from left to right in the periodic table.
17. The set of products formed in the following reaction is



- (a) CHBr_3 and a racemic acid
 (b) CHBr_3 and a chiral acid
 (c) CHBr_3 and a racemic ester
 (d) CH_2Br_2 and a chiral ester
18. The normal spinel among the following mixed metal-oxides is
 (a) CoFe_2O_4 (b) NiFe_2O_4 (c) CuFe_2O_4 (d) ZnFe_2O_4
19. The ground state term for a free ion with $3d^7$ configuration is
 (a) ${}^4F_{3/2}$ (b) ${}^4F_{9/2}$ (c) ${}^4F_{1/2}$ (d) ${}^4F_{5/2}$
20. The correct set of reagents required for the following transformation is

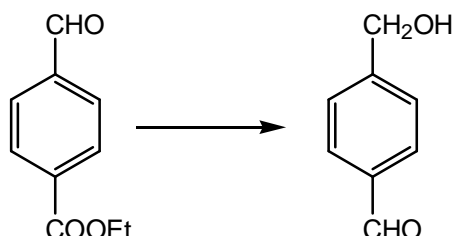


- (a) (i) CrO_3 ; (ii) acrylonitrile; (iii) H_3O^+
 (b) (i) O_2 ; (ii) methyl acrylate
 (c) (i) CrO_3 ; (ii) NaOMe/MeOH , methyl acrylate; (iii) H_3O^+
 (d) (i) H_2O ; (ii) methyl acrylate.
21. The concentration of K^+ ion inside a biological cell is 20 times higher than outside. The magnitude of potential difference between the two sides is [Given : $2.303 \text{ RT/F} = 59 \text{ mV}$]
 (a) 0 mV (b) 26 mV (c) 77 mV (d) 177 mV
22. At 25°C , the solubility product (K_{sp}) of CaF_2 in water is 3.2×10^{-11} . The solubility (in mole per kg of water) of the salt at the same temperature (ignore ion pairing) is
 (a) 4.0×10^{-6} (b) 3.2×10^{-4} (c) 2.5×10^{-4} (d) 2.0×10^{-4}
23. The complex that is expected to show orbital contribution to the overall magnetic moment is
 (a) $[\text{Cr}(\text{CN})_6]^{3-}$ (b) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ (c) $[\text{Ni}(\text{en})_3]^{2+}$ (d) $[\text{Cu}(\text{NH}_3)_6]^{2+}$

24. The correct order of the fundamental vibrational frequencies of the following diatomic molecules is

- (a) ${}^1\text{H}^{35}\text{Cl} > {}^1\text{H}^{37}\text{Cl} > {}^2\text{D}^{35}\text{Cl}$ (b) ${}^2\text{D}^{35}\text{Cl} > {}^1\text{H}^{37}\text{Cl} > {}^1\text{H}^{35}\text{Cl}$
 (c) ${}^1\text{H}^{37}\text{Cl} > {}^1\text{H}^{35}\text{Cl} > {}^2\text{D}^{35}\text{Cl}$ (d) ${}^1\text{H}^{37}\text{Cl} > {}^2\text{D}^{35}\text{Cl} > {}^1\text{H}^{35}\text{Cl}$

25. Identify the correct reagents required for the following transformation



- (a) (i) NaBH_4 ; (ii) H_3O^+
 (b) (i) LiAlH_4 ; (ii) H_3O^+
 (c) (i) $\text{HOCH}_2\text{CH}_2\text{OH}$, H^+ ; (ii) LiAlH_4 ; (iii) H_3O^+
 (d) (i) $\text{HSCH}_2\text{CH}_2\text{SH}$, H^+ ; (ii) LiAlH_4 ; (iii) H_3O^+
26. For an isothermal free expansion of an ideal gas into vacuum, which one of the following set of values is correct?

- (a) $\Delta U = 0$, $q > 0$, $w < 0$ (b) $\Delta U > 0$, $q > 0$, $w = 0$
 (c) $\Delta U = 0$, $q = 0$, $w = 0$ (d) $\Delta U < 0$, $q = 0$, $w < 0$

27. The kinetics of the reaction $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ in liquid bromine medium was measured independently for three different initial concentrations of N_2O_5 : 0.11, 0.07 and 0.05 mol L^{-1} . The half-life of the reaction was found to be 4.5 hours for all these concentrations. The order of the reaction is

- (a) 0 (b) 1 (c) 2 (d) 0.5

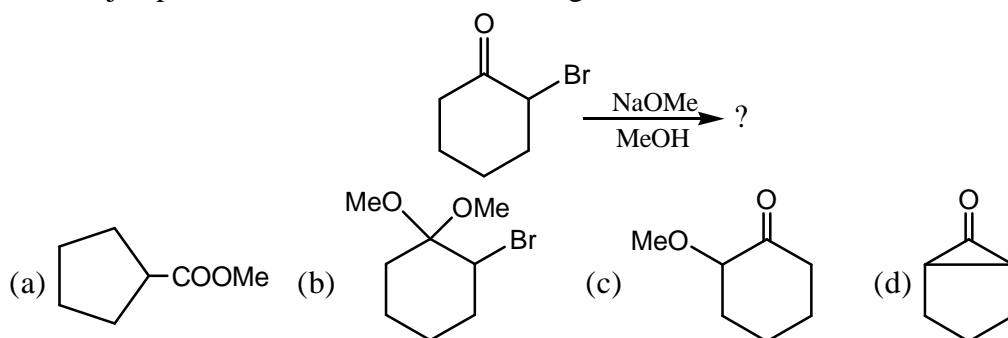
28. Which of the following statements are correct for $\text{S}_{\text{N}}\text{Ar}$ reaction?

- (i) Follows second order kinetics
 (ii) $K_{\text{H}}/K_{\text{D}} > 1$
 (iii) Involves carbanion-type intermediate
 (iv) Involves two transition states
 (a) (i) and (ii) only (b) (ii) and (iii) only (c) (i), (iii) and (iv) only (d) (i) and (iii) only

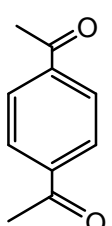
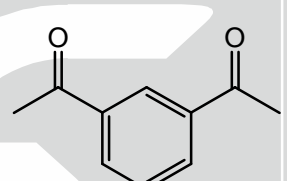
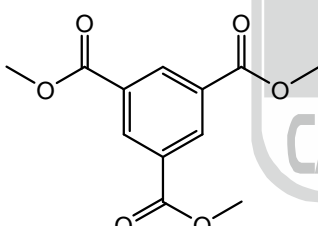
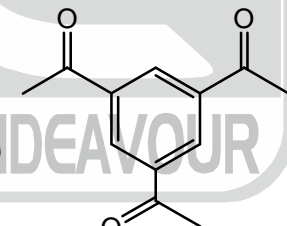
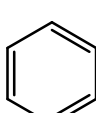
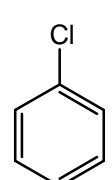
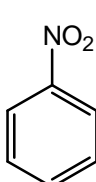
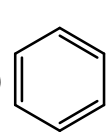
29. According to the equipartition principle, the predicted high temperature limiting value of the molar heat capacity at constant volume for C_2H_2 is

- (a) 5.5 R (b) 6.0 R (c) 9.0 R (d) 9.5 R

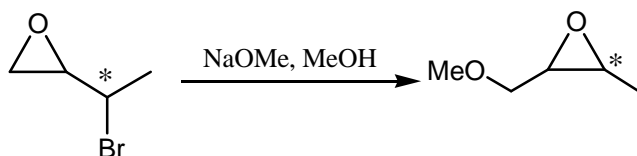
30. The major product formed in the following reaction is



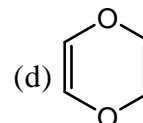
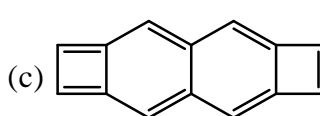
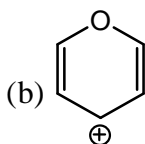
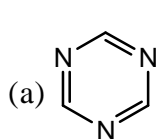
SECTION-B : MSQ (Multiple Select Questions)
Q. 1 - Q. 10 carry two marks each.

1. If $\hat{x} = x \times$ and $\hat{p}_x = \frac{h}{2\pi i} \frac{d}{dx}$, then the value(s) of $\hat{p}_x \hat{x} - \hat{x} \hat{p}_x$ is/are
- (a) $\frac{\hbar}{i}$ (b) $-i\hbar$ (c) 0 (d) $\frac{i}{\hbar}$
2. The common feature(s) of Rb^+ , Kr and Br^- is/are that they
- (a) have same number of valence electrons
 (b) have same magnitude of effective nuclear charge
 (c) have same magnitude of first ionization potential
 (d) are isoelectronic species
3. The characteristics of the blue solution of sodium in liquid ammonia is/are
- (a) diamagnetic (b) paramagnetic
 (c) reducing in nature (d) conducts electricity
4. Which of the following compound(s) show(s) only two signals in ^1H NMR and a strong IR band at $\sim 1690 \text{ cm}^{-1}$.
- (a)  (b) 
- (c)  (d) 
5. The reaction(s) which give(s) phenol is/are
- (a)  $\xrightarrow[\text{(iii) H}^+]{\text{(i) conc. H}_2\text{SO}_4, \Delta, \text{(ii) KOH}}$
- (b)  $\xrightarrow{\text{KOH, 300}^\circ\text{C}}$
- (c)  $\xrightarrow[\text{(iii) NaOH}]{\text{(i) H}_2, \text{Pd/C}, \text{(ii) NaNO}_2, \text{HCl, 0-5}^\circ\text{C}}$
- (d)  $\xrightarrow[\text{(iii) H}^+]{\text{(i) CH}_3\text{CH=CH}_2, \text{H}^+, \text{(ii) O}_2, \text{KOH}}$
6. At what angle(s) of incidence, X-rays of wavelength 5.0 \AA will produce diffracted beam from the (110) planes in a simple cubic lattice with $a = 10 \text{ \AA}$?
- (a) 6.8° (b) 10.2° (c) 20.7° (d) 45.0°

7. Which of the following statement(s) is/are true about the reaction given below?



- (a) it involves a carbocation intermediate
 (b) rearrangement is due to S_N1 reaction mechanism.
 (c) it proceeds via a concerted S_N2 pathway
 (d) it involves neighbouring group participation.
8. Which of the following species is/are aromatic in nature?



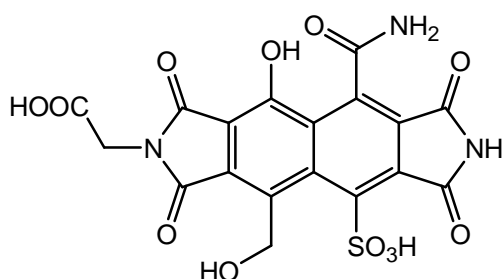
9. Which of the following statement(s) is/are true about the transition metal-alkene complexes?
- (a) Back-bonding weakens the double bond of the alkene
 (b) σ -bonding and back-bonding synergistically strengthen metal-alkene interaction
 (c) Electron-withdrawing substituents on alkene reduce back-bonding
 (d) π -acidic co-ligands on metal strengthen back-bonding
10. Which of the following thermodynamic relation(s) is/are correct?

(a) $\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V$ (b) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$ (c) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ (d) $\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$

SECTION-C : NAT (Numerical Answer Type)

Q. 1 - Q. 10 carry one mark each.

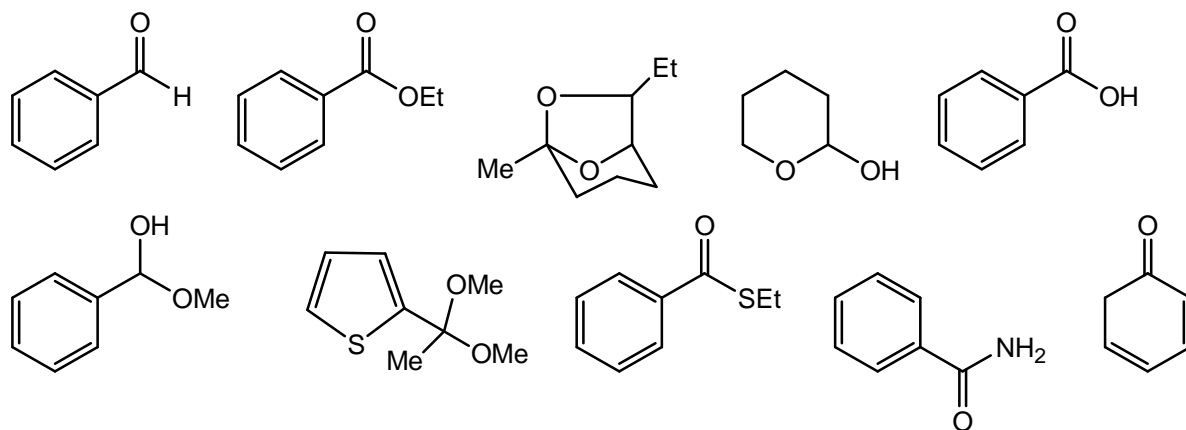
- In the gas phase, the ratio of excluded volume to molecular volume for a spherical molecule is _____
- The pK_a values of lysine are 2.18, 8.95 and 10.79. The isoelectric point of lysine is _____
- The amount (in grams) of potassium dichromate (MW = 294) present in 75 mL of 0.16 M aqueous solution is _____
- Given that the expected spin-only magnetic moment for $(Et_4N)_2[NiCl_4]$ is $2.83 \mu_B$, the total number of unpaired electrons in this complex is _____
- Given that the crystal field stabilization energy for $[Co(H_2O)_6]^{2+}$ is 7360 cm^{-1} , the calculated value of Δ_0 in kJ mol^{-1} is _____
- The amount (in grams) of NaOH (MW = 40) required for complete neutralization of one mole of the following compound is _____



7. For the reaction, $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$, the equilibrium constant $K_p = 5.0$ at 207°C . If the partial pressures of SO_2 , O_2 and SO_3 are 1.0×10^{-3} , 0.20 and 1.0×10^{-4} , respectively, then the Gibbs free energy of the reaction ($\Delta_r G$) in kJ mol^{-1} at 207°C is _____ [Given : $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$].
8. In the given list, the total number of compounds that form a clear homogeneous solution on treatment with cold dilute H_2SO_4 is _____
 1-propyne
 cyclohexanone
 cyclohexane
 1-propene
 propane-1-amine
 propoxypropane
 tetrahydropyran
 ethyl butanoate
 pyridine
9. Two moles of an ideal gas is expanded isothermally and reversibly from 5 to 1 bar at 298K . The change in the entropy (in JK^{-1}) of the system is _____
10. The pK_a values of H_3PO_4 are 2.12, 7.21 and 12.67. The pH of a phosphate buffer containing $0.2\text{M NaH}_2\text{PO}_4$ and $0.1 \text{ M Na}_2\text{HPO}_4$ is _____

Q. 11 - Q. 20 carry two marks each.

11. The ionic radii of Cs^+ and Cl^- ions are 181 and 167 pm, respectively. The Born exponents for the He, Ne, Ar, Kr and Xe configuration are 5, 7, 9, 10 and 12 respectively. If the value of $\frac{A\text{Ne}^2}{4\pi\epsilon_0}$ is $2.45 \times 10^{-4} \text{ Jm}$, the lattice energy (in kJ mol^{-1}) of CsCl according to Born-Landé equation is _____
12. A $2.5 \times 10^{-4} \text{ M}$ solution of a complex exhibits an absorption maximum at 625 nm with an absorbance of 0.90 when measured in a cuvette with a path length of 1.5 cm. The absorbance of $1.5 \times 10^{-3} \text{ M}$ solution of the same complex recorded in a cuvette with a path length of 0.2 cm is _____
13. The total number of compounds (shown below) that form phenylhydrazone derivatives under acidic conditions is _____



14. The standard reduction potentials of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and Fe^{2+}/Fe couples are 0.77 and -0.44 V respectively. The standard reduction potential (in V) for the Fe^{3+}/Fe couple is _____
15. The number of possible monoalkylated products formed in the Friedel-Crafts reaction of anisole with 2-chloro-3-methylbutane in the presence of anhydrous AlCl_3 at 50°C is _____
16. In an ideal monoatomic gas, the speed of sound is given by $\sqrt{\frac{5RT}{3M}}$. If the speed of sound in argon at 25°C is 1245 km h^{-1} , the root mean square velocity in m s^{-1} is _____
17. A wood specimen containing ^{14}C taken from an ancient palace showed 24 counts in 3 minutes per gram of carbon in a detector. However, a fresh wood showed 52 counts in 2 minutes per gram of carbon. Assuming no background signal in the detector and half life of ^{14}C as 5730 years, the age (in year) of the wood specimen is _____
18. The magnetic field (in Tesla) required for flipping a ^1H nucleus in an NMR spectrometer operating at 400 MHz is _____ [Given : $\gamma = 2.67 \times 10^8 \text{ T}^{-1}\text{s}^{-1}$, $\pi = 3.14$]
19. For a reaction, the rate constant at 25°C is doubled when the temperature is raised to 45°C . The activation energy (in kJ mol^{-1}) of the reaction is _____ [Given : $\ln 2 = 0.693$]
20. When a perfect monolayer of stearic acid is formed at the air-water interface, each molecule of stearic acid (MW = 284, density = 0.94 g cm^{-3}) occupies an area of 20 \AA^2 . The length (in \AA) of the molecule is _____

