



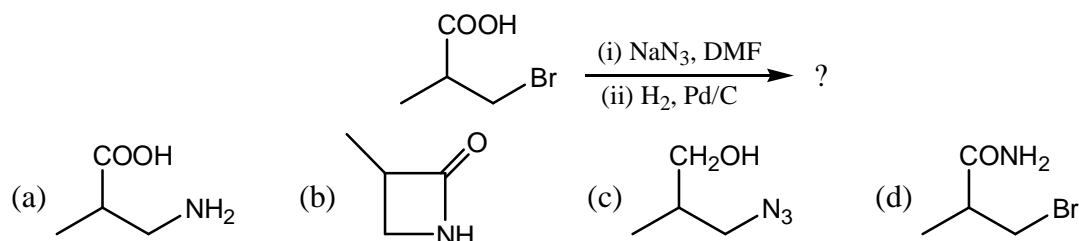
IIT JAM CHEMISTRY-CY 2015

Question Paper

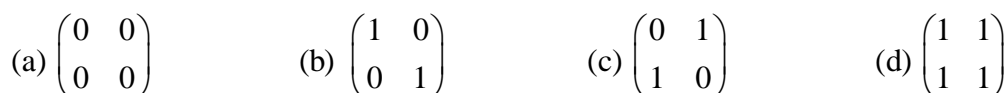
SECTION-A : MCQ

1. 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)  $\Delta_t > \Delta_0$

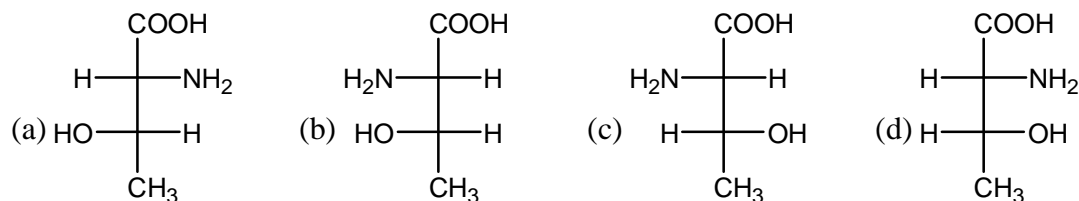
2. The major product formed in the following reaction is



3. Which one of the following is an identity matrix?



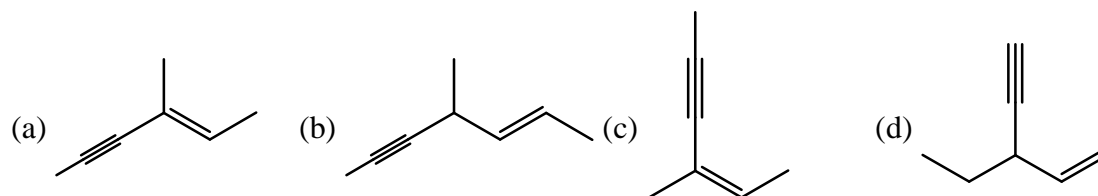
4. The structure of (2S, 3R)-2-amino-3-hydroxy butanoic acid is



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



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



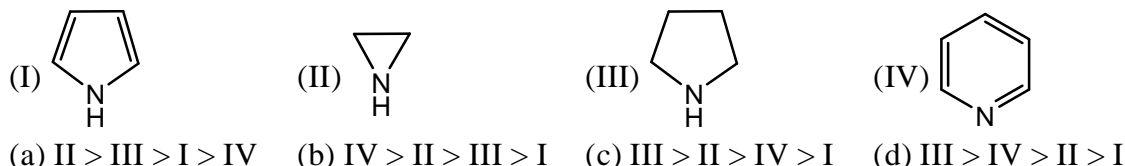
8. Low-spin iron (III) centre is present in



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)  $H_2SO_3F^+$

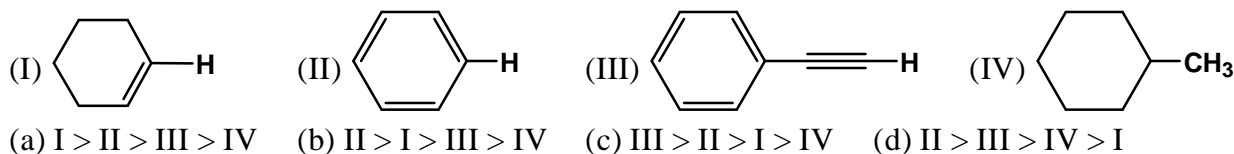
11. The correct order of the pKa values for the conjugate acids of heterocyclic compounds given below is



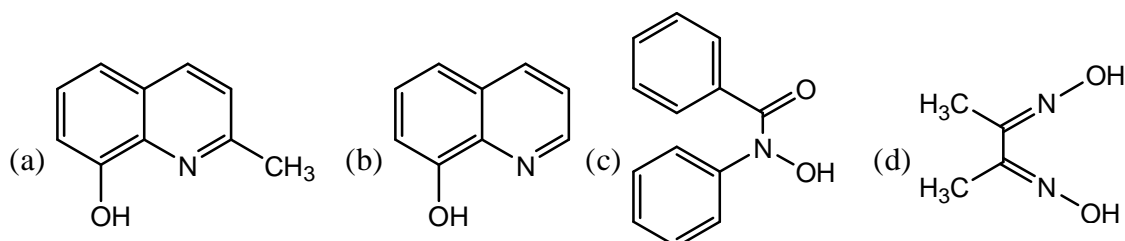
12. The species having trigonal pyramidal shape is  
 (a)  $NO_3^-$  (b)  $CO_3^{2-}$  (c)  $BrF_3$  (d)  $SO_3^{2-}$

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 ( $\delta$ ) for the indicated hydrogens (in bold) in the following compounds is

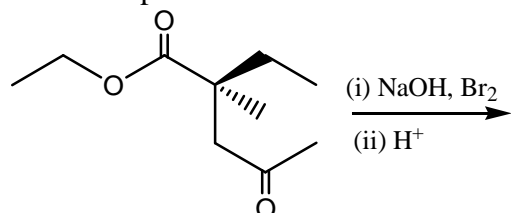


15. The reagent 'oxine' commonly used in analytical chemistry is



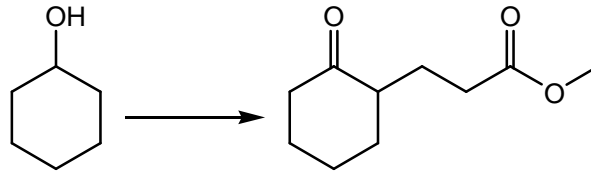
16. The correct statement about ionization potential (IP) is  
 (a) non-metallic character of an element decreases as teh IP increases  
 (b) IP decreases down the group in the periodic table  
 (c) second IP of Ca is larger than second IP of K  
 (d) IP decreases on going from left to right in the periodic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

17. The set of products formed in the following reaction is

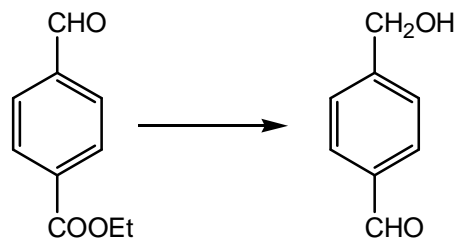


- (a)  $CHBr_3$  and a racemic acid (b)  $CHBr_3$  and a chiral acid  
 (c)  $CHBr_3$  and a racemic ester (d)  $CH_2Br_2$  and a chiral ester

18. The normal spinel among the following mixed metal-oxides is  
 (a)  $\text{CoFe}_2\text{O}_4$  (b)  $\text{NiFe}_2\text{O}_4$  (c)  $\text{CuFe}_2\text{O}_4$  (d)  $\text{ZnFe}_2\text{O}_4$
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

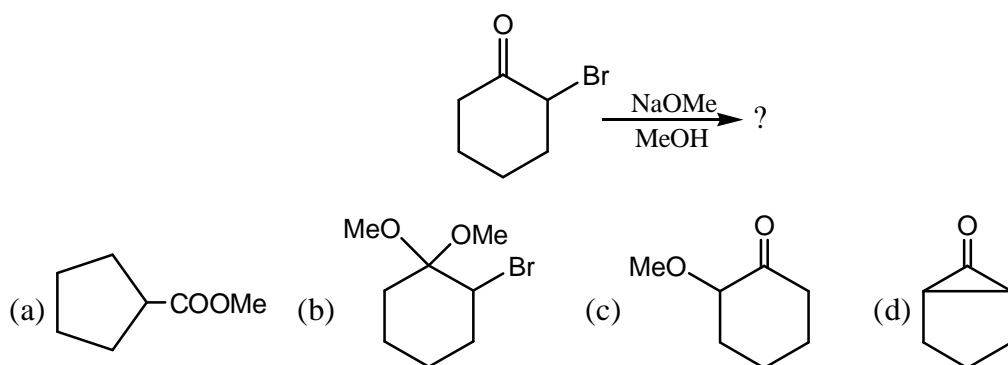


- (a) (i)  $\text{CrO}_3$ ; (ii) acrylonitrile; (iii)  $\text{H}_3\text{O}^+$   
 (b) (i)  $\text{O}_2$ ; (ii) methyl acrylate  
 (c) (i)  $\text{CrO}_3$ ; (ii)  $\text{NaOMe/MeOH}$ , methyl acrylate; (iii)  $\text{H}_3\text{O}^+$   
 (d) (i)  $\text{H}_2\text{O}$ ; (ii) methyl acrylate.
21. The concentration of  $\text{K}^+$  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  $25^\circ\text{C}$ , the solubility product ( $K_{\text{sp}}$ ) of  $\text{CaF}_2$  in water is  $3.2 \times 10^{-11}$ . The solubility (in mole per kg of water) of the salt at the same temperature (ignore ion pairing) is  
 (a)  $4.0 \times 10^{-6}$  (b)  $3.2 \times 10^{-4}$  (c)  $2.5 \times 10^{-4}$  (d)  $2.0 \times 10^{-4}$
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



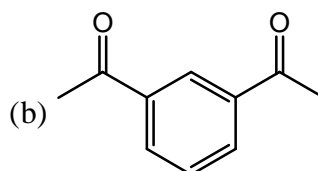
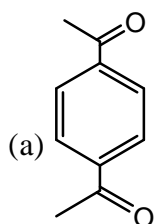
- (a) (i)  $\text{NaBH}_4$ ; (ii)  $\text{H}_3\text{O}^+$   
 (b) (i)  $\text{LiAlH}_4$ ; (ii)  $\text{H}_3\text{O}^+$   
 (c) (i)  $\text{HOCH}_2\text{CH}_2\text{OH}$ ,  $\text{H}^+$ ; (ii)  $\text{LiAlH}_4$ ; (iii)  $\text{H}_3\text{O}^+$   
 (d) (i)  $\text{HSCH}_2\text{CH}_2\text{SH}$ ,  $\text{H}^+$ ; (ii)  $\text{LiAlH}_4$ ; (iii)  $\text{H}_3\text{O}^+$
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)  $\Delta U < 0$ ,  $q = 0$ ,  $w < 0$

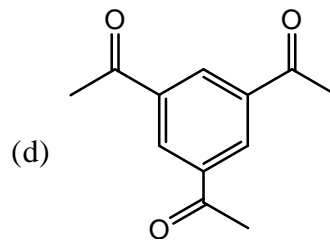
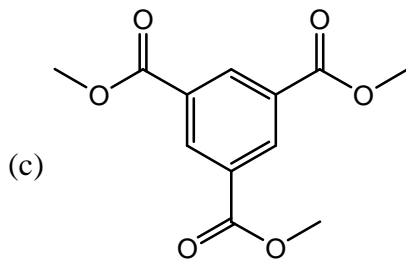
27. The kinetics of the reaction  $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$  in liquid bromine medium was measured independently for three different initial concentrations of  $\text{N}_2\text{O}_5$  : 0.11, 0.07 and 0.05 mol L<sup>-1</sup>. The half-life of the reaction was found 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 S<sub>N</sub>Ar reaction?  
 (i) Follows second order kinetics  
 (ii)  $K_H/K_D > 1$   
 (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<sub>2</sub>H<sub>2</sub> 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



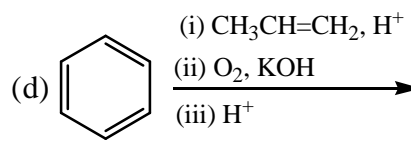
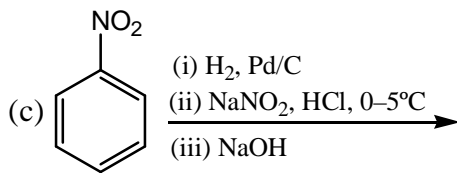
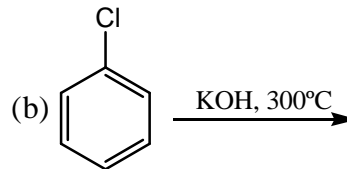
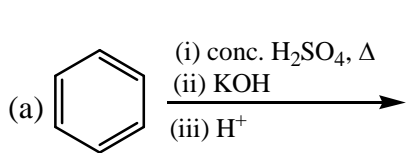
### SECTION-B : MSQ

1. If  $\hat{x} = xX$  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  $\text{Rb}^+$ ,  $\text{Kr}$  and  $\text{Br}^-$  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 <sup>1</sup>H NMR and a strong IR band at ~ 1690 cm<sup>-1</sup>.





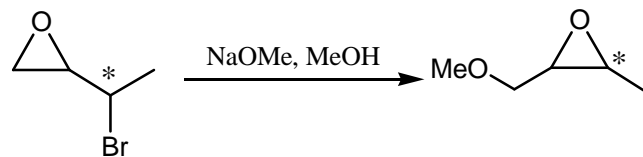
5. The reaction(s) which give(s) phenol is/are



6. At what angle(s) of incidence, X-rays of wavelength  $5.0\text{\AA}$  will produce diffracted beam from the (110) planes in a simple cubic lattice with  $a = 10\text{\AA}$ ?

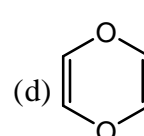
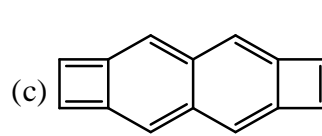
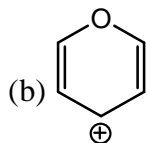
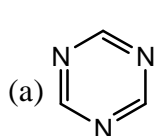
- (a)  $6.8^\circ$  (b)  $10.2^\circ$  (c)  $20.7^\circ$  (d)  $45.0^\circ$

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?

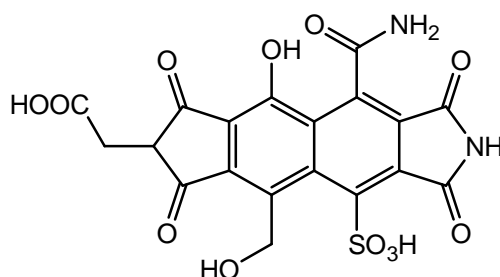
- (a) Back-bonding weakens the double bond of the alkene  
 (b)  $\sigma$ -bonding and back-bonding synergistically strengthen metal-alkene interaction  
 (c) Electron-withdrawing substituents on alkene reduce back-bonding  
 (d)  $\pi$ -acidic co-ligands on metal strengthen back-bonding

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)  $\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$

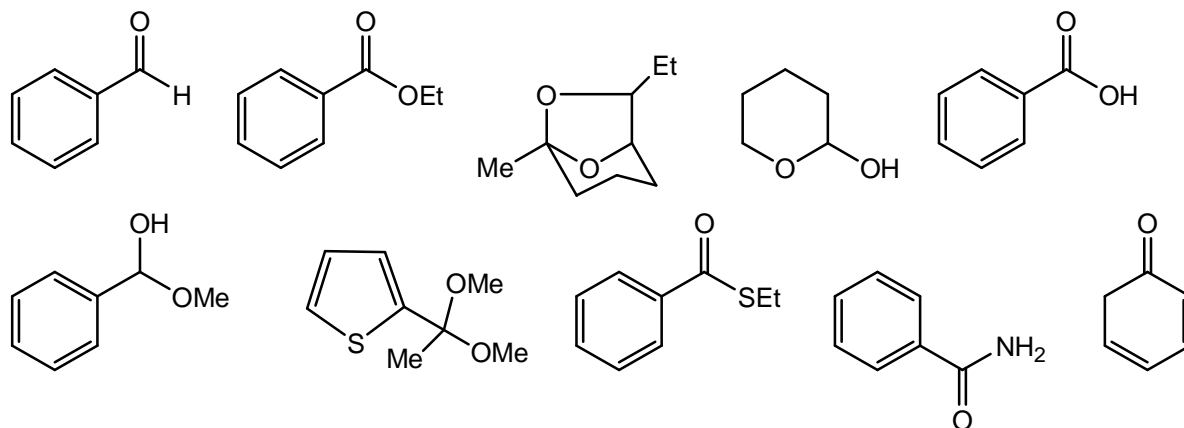
## SECTION-C : NAT

- 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  $7360 \text{ cm}^{-1}$ , the calculated value of  $\Delta_0$  in  $\text{kJ mol}^{-1}$  is \_\_\_\_\_
- The amount (in grams) of NaOH (MW = 40) required for complete neutralization of one mole of the following compound is \_\_\_\_\_



- For the reaction,  $2SO_2 + O_2 \rightleftharpoons 2SO_3$ , the equilibrium constant  $K_p = 5.0$  at  $207^\circ\text{C}$ . If the partial pressures of  $SO_2$ ,  $O_2$  and  $SO_3$  are  $1.0 \times 10^{-3}$ ,  $0.20$  and  $1.0 \times 10^{-4}$ , respectively, then the Gibbs free energy of the reaction ( $\Delta_r G$ ) in  $\text{kJ mol}^{-1}$  at  $207^\circ\text{C}$  is \_\_\_\_\_ [Given :  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ]
- 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
- Two moles of an ideal gas is expanded isothermally and reversibly from 5 to 1 bar at 298K. The change in the entropy (in  $\text{JK}^{-1}$ ) of the system is \_\_\_\_\_
- The  $pK_a$  values of  $H_3PO_4$  are 2.12, 7.21 and 12.67. The pH of a phosphate buffer containing 0.2M  $NaH_2PO_4$  and 0.1 M  $Na_2HPO_4$  is \_\_\_\_\_

11. The ionic radii of  $\text{Cs}^+$  and  $\text{Cl}^-$  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  $\text{kJ mol}^{-1}$ ) 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  $\text{Fe}^{2+}/\text{Fe}$  couples are 0.77 and  $-0.44 \text{ V}$  respectively. The standard reduction potential (in V) for the  $\text{Fe}^{3+}/\text{Fe}$  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  $\text{AlCl}_3$  at  $50^\circ\text{C}$  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  $25^\circ\text{C}$  is  $1245 \text{ km h}^{-1}$ , the root mean square velocity in  $\text{m s}^{-1}$  is \_\_\_\_\_
17. A wood specimen containing  $^{14}\text{C}$  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  $^{14}\text{C}$  as 5730 years, the age (in year) of the wood specimen is \_\_\_\_\_
18. The magnetic field (in Tesla) required for flipping a  $^1\text{H}$  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  $25^\circ\text{C}$  is doubled when the temperature is raised to  $45^\circ\text{C}$ . The activation energy (in  $\text{kJ mol}^{-1}$ ) 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 ( $\text{MW} = 284$ , density =  $0.94 \text{ g cm}^{-3}$ ) occupies an area of  $20 \text{ \AA}^2$ . The length (in  $\text{\AA}$ ) of the molecule is \_\_\_\_\_