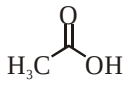
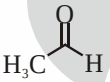
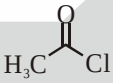
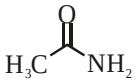
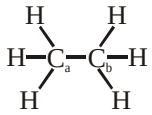
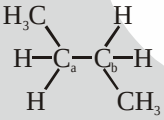
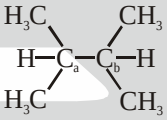
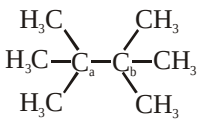
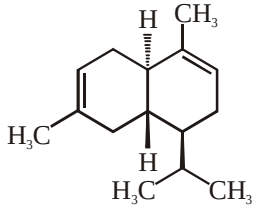
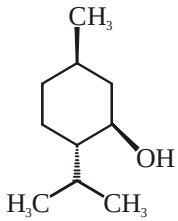
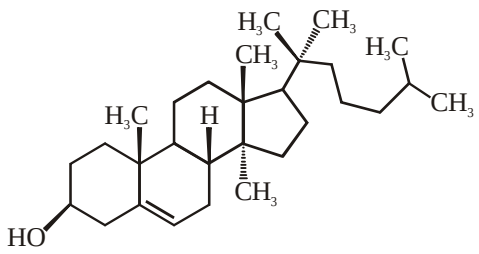
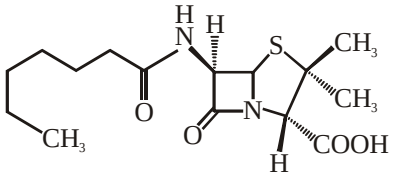
PAPER : IIT-JAM 2014

CHEMISTRY-CY

- **PART-I consists of 35 objective type questions. The first ten question carry ONE marks each and the rest of the objective questions carry TWO marks each. There will be negative marks for wrong answers. For each 1 mark question the negative mark will be 1/3 and for each 2 mark question it will be 2/3.**
- **PART-II consists of 8 descriptive type questions each carrying FIVE marks.**

PART-I : OBJECTIVE QUESTIONS

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

1. For square matrices M and N, if MN = M and NM = N, then:
   (a) $M^2 = M$ and $N^2 = N$ (b) $N^2 \neq N$ and $M^2 = M$
   (c) $M^2 \neq M$ and $N^2 \neq N$ (d) $M^2 \neq M$ and $N^2 = N$
2. The energy of an electron in a hydrogenic atom with nuclear charge Z varies as:
   (a) Z (b) Z^2 (c) 1/Z (d) $1/Z^2$
3. The carbonyl stretching frequency ($\nu_{C=O}$) is highest for:
   (a)  (b)  (c)  (d) 
4. The homolytic breaking of the $C_a - C_b$ bond is easiest in:
   (a)  (b)  (c)  (d) 
5. Tollen's test will be negative for:
   (a) Glucose (b) Mannose (c) Sucrose (d) Galactose
6. Which one among the following is a sesquiterpene?
   (a)  (b) 
   (c)  (d) 

7. The predicted geometry of TeF_4 by **VSEPR theory** is:
(a) Octahedral (b) Square planar (c) Tetrahedral (d) Trigonal bipyramidal

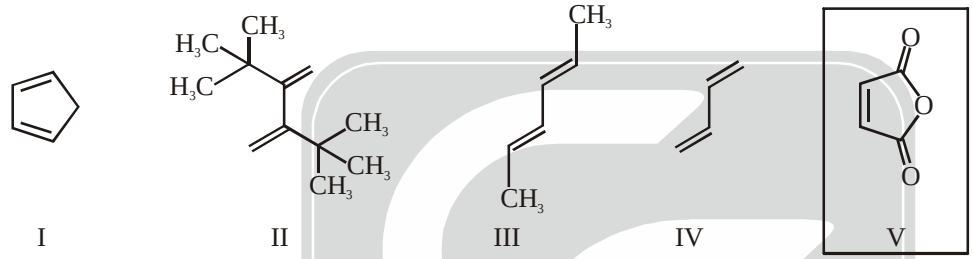
8. Among the following, the isoelectronic pair is:
(a) NO and CO (b) O_2^- (superoxide anion) and NO^-
(c) NO^+ and CO (d) O_2^- (superoxide anion) and NO^+

9. The metal ion of an enzyme involved in hydration of CO_2 is:
(a) Cu(II) (b) Fe(II) (c) Mg(II) (d) Zn(II)

10. Among the following, the element having maximum inert pair effect is:
[Given : Atomic number of Ge = 30, Pb = 82, Si = 14 and Sn = 50]
(a) Ge (b) Pb (c) Si (d) Sn

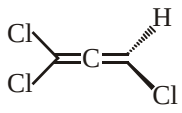
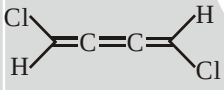
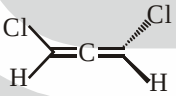
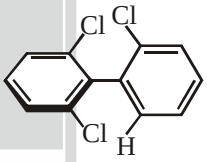
Q.11 - Q.35 carry two marks each:

11. The reactivity of compounds I-IV with maleic anhydride (V) follows the order:

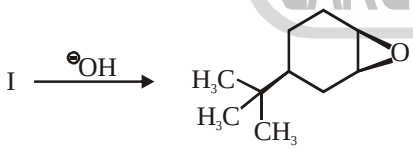


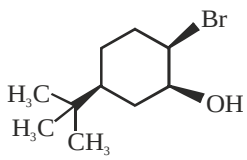
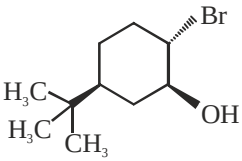
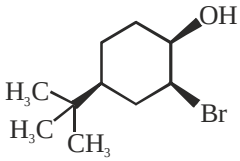
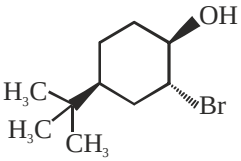
(a) I < II < III < IV (b) II < IV < III < I
(c) II < I < III < IV (d) II < I < IV < III

12. Which one among the following molecules is chiral?

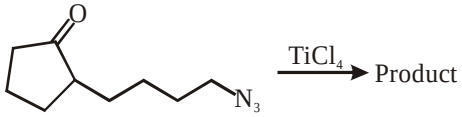
(a)  (b)  (c)  (d) 

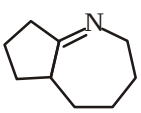
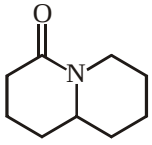
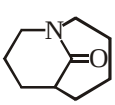
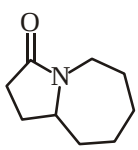
13. Identify the starting material I in the given reaction.



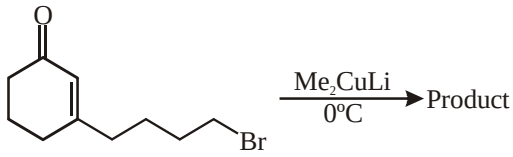
(a)  (b)  (c)  (d) 

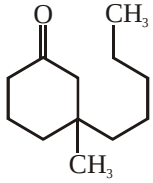
14. The major product for the following reaction is:

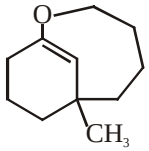


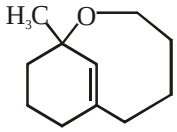
(a)  (b)  (c)  (d) 

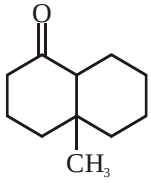
15. The structure of the major product in the following reaction is:



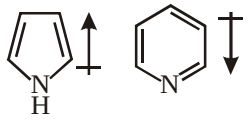
(a) 

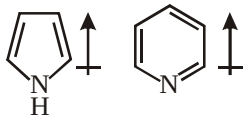
(b) 

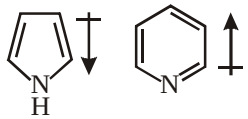
(c) 

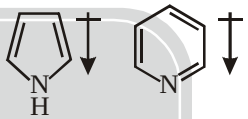
(d) 

16. The correct orientation of dipoles in pyrrole and pyridine is:

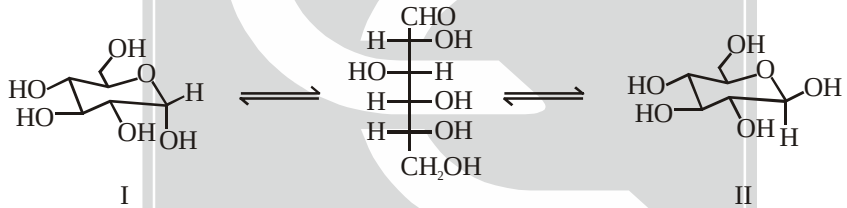
(a) 

(b) 

(c) 

(d) 

17. Specific rotations of freshly prepared aqueous solutions of I and II are +112 and +18.7, respectively. On standing the optical rotation of aqueous solution of I slowly decreases to give a final value of +52.7 due to equilibration with II. Under this state of equilibrium, what is the ratio II : I?

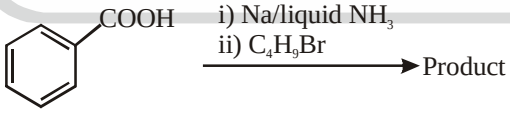


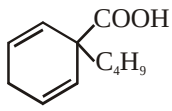
I
$[\alpha]_D^{25} = +112$

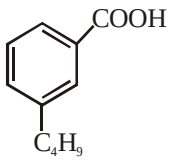
II
$[\alpha]_D^{25} = +18.7$

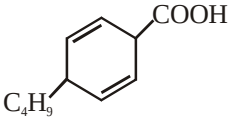
(a) 0.57 (b) 1.00 (c) 1.75 (d) 5.9

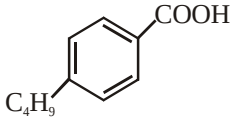
18. The major product formed in the following reaction is:



(a) 

(b) 

(c) 

(d) 

19. In boron neutron capture therapy, the initial boron isotope used and the particle generated after neutron capture respectively are:

(a) ^{11}B and α particle (b) ^{10}B and α particle

(c) ^{11}B and β particle (d) ^{10}B and β particle

20. The number of α and β particle(s), generated in the following radioactive decay process, are:

$$^{238}_{92}U \rightarrow {}^{234}_{92}U$$

(a) one α and two β particles (b) two α and one β particles

(c) one α and four β particles (d) no α and four β particles

21. In the measurement of hardness of water by complexometric titration, identify P and Q in the following equation.

$[P]^-$ + $[H_2Y]^{2-}$ → $[Q]^{2-}$ + $[HIn]^{2-}$ + H^+

red colourless colourless blue

(a) P = MgY, Q = MgIn (b) $P = MgY_2$, $Q = MgIn_2$

(c) $P = MgIn_2$, $Q = MgY_2$ (d) P = MgIn, Q = MgY

22. An aqueous solution of haemoglobin has a molar absorptivity value of 18,600 L mol^{-1} cm^{-1} for an absorbance value of 0.1 at 540 nm (Given : cell thickness = 1cm). The concentration (in μM) of the haemoglobin solution is:

(a) 0.537 (b) 5.37 (c) 53.7 (d) 537.0

23. The electronic transitions responsible for the colour of $K_2Cr_2O_7$ and porphine in their solid state respectively are:

(a) $d \rightarrow d; \pi \rightarrow \pi^*$ (b) $M \rightarrow L$ charge transfer; $\pi \rightarrow \pi^*$

(c) $L \rightarrow M$ charge transfer; $\pi \rightarrow \pi^*$ (d) $L \rightarrow M$ charge transfer; $d \rightarrow d$

24. The correct order of M–C(M = Ti, V, Cr and Mn) bond stretching frequency is:
(Given: Atomic number of Ti = 22, V = 23, Cr = 24 and Mn = 25)

(a) $[V(CO)_6]^- < Cr(CO)_6 < [Mn(CO)_6]^+ < [Ti(CO)_6]^{2-}$

(b) $[Ti(CO)_6]^{2-} < [V(CO)_6]^- < Cr(CO)_6 < [Mn(CO)_6]^+$

(c) $[Mn(CO)_6]^+ < Cr(CO)_6 < [V(CO)_6]^- < [Ti(CO)_6]^{2-}$

(d) $[Mn(CO)_6]^+ < [V(CO)_6]^- < Cr(CO)_6 < [Ti(CO)_6]^{2-}$

25. For the following reactions, the metal complexes X and Y are:

(i) $Ni(s) \xrightarrow[1\ atm\ /\ 25^oC]{CO(g)} X$ (ii) $FeCl_2 \xrightarrow{2NaC_5H_5} Y$

(a) X = $Ni(CO)_4$; Y = $Fe(\eta^5\text{-}C_5H_5)_2$ (b) X = $Ni(CO)_4$; Y = $Fe(\eta^1\text{-}C_5H_5)_2$

(c) X = $Ni(CO)_5$; Y = $Fe(\eta^5\text{-}C_5H_5)_2$ (d) X = $Ni(CO)_6$; Y = $Fe(\eta^1\text{-}C_5H_5)_2$

26. The correct order of crystal field strength is : (Given: en = ethylenediamine)

(a) $Cl^- < H_2O <$ en $< (\eta^5\text{-}C_5H_5)^-$ (b) $H_2O < Cl^- < (\eta^5\text{-}C_5H_5)^- <$ en

(c) $H_2O < (\eta^5\text{-}C_5H_5)^- <$ en $< Cl^-$ (d) en $< Cl^- < H_2O < (\eta^5\text{-}C_5H_5)^-$

27. The carbon-oxygen bond in an organic compound absorbs electromagnetic radiation of frequency 6×10^{13} Hz. This frequency corresponds to the region:

(a) Infrared (b) Microwave (c) Ultraviolet (d) Visible

28. According to the equipartition principle of energy, the molar heat capacity at constant volume for $CO_2(g)$, $SO_2(g)$ and $H_2O(g)$ follows the trend:

(a) $CO_2 = SO_2 = H_2O$ (b) $CO_2 > SO_2 = H_2O$

(c) $H_2O > SO_2 = CO_2$ (d) $CO_2 = SO_2 > H_2O$

29. $\left[\frac{-h^2}{(8\pi^2 m)}\frac{d^2}{dx^2}+\frac{h^2\alpha^2x^2}{(2\pi^2 m)}\right]\exp(-\alpha x^2) = C\frac{h^2}{(4\pi^2)}\exp(-\alpha x^2)$, where h, π, m and α are constants. Then C is:

(a) $2\alpha/m$ (b) $\alpha/2m$ (c) α/m (d) α^2/m

30. Among Ar, NH_4Cl, HF and HCl, the strength of interatomic / intermolecular forces follows the order:
(a) $NH_4Cl > HF > HCl > Ar$ (b) $HF > HCl > Ar > NH_4Cl$
(c) $HCl > Ar > NH_4Cl > HF$ (d) $Ar > NH_4Cl > HF > HCl$

31. The number of degrees of freedom in the homogeneous liquid region of a two component system with a eutectic point, at one atmosphere pressure, is:
(a) 0 (b) 1 (c) 2 (d) 3

32. The ionic strength of 0.1 M aqueous solution of $Fe_2(SO_4)_3$ is:
(a) 0.1 M (b) 0.65 M (c) 1.3 M (d) 1.5 M

33. If the transport number of Na^+ is 0.463 (dilute solution of NaCl in methanol), the transport number of H^+ (dilute solution of HCl in methanol) is:

(Given, Λ^∞ (NaCl in methanol) = 96.9 ohm^{-1} cm^2 mol^{-1} and Λ^∞ (HCl in methanol) = 192 ohm^{-1} cm^2 mol^{-1})
(a) 0.27 (b) 0.46 (c) 0.54 (d) 0.73

34. Charcoal (1 gram) of surface area 100 m^2 per gram, absorbs 60mg of acetic acid from an aqueous solution at 25ºC and 1 atmosphere pressure. The number of moles of acetic acid adsorbed per cm^2 of charcoal surface is:
(a) 10^{-2} (b) 10^{-6} (c) 10^{-5} (d) 10^{-9}

35. The change in entropy for the following transformations is respectively: (+ indicates increase, – indicates decrease and 0 indicates no change)

(i) $SO_2Cl_2(g) \xrightarrow{\Delta} SO_2(g) + Cl_2(g)$

(ii) $nCH_2 = CH_2(g) \xrightarrow{\text{Catalyst}} \left[-CH_2-CH_2-\right]_n(s)$

(iii) $I_2(s) \xrightarrow[\text{1 atmosphere}]{\Delta} I_2(v)$

(iv) Adiabatic reversible expansion of an ideal gas
(a) +, –, 0, + (b) +, –, 0, 0 (c) –, +, +, 0 (d) +, –, +, 0

PART-II: DESCRIPTIVE QUESTIONS

Q.36 – Q.43 carry five marks each.

36. Using crystal field theory (CFT), for the $[Co(NH_3)_6]^{3+}$ ion
(a) draw the d-orbital splitting including their orbital labels (designations) and show their electron occupancy.
(b) calculate the crystal field stabilization energy (ignore pairing energy) and spin-only magnetic moment values. (Given : atomic number of Co = 27).

37. (a) Write the correct order of lattice energy for LiX, X = F, Cl, Br and I.

(b) A first order reflection from (111) plane is observed for LiX with $2\theta = 24.6^o$ (X-ray of wavelength 1.54Å). Assuming LiX to be a cubic crystal system, calculate the length of the side of the unit cell in Å.

38. For the reaction:

$2NO + 2H_2 \xrightarrow{700^oC} N_2 + 2H_2O$

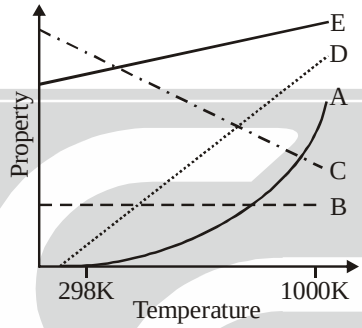
(i) Write the expression for the rate of the reaction in terms of the change in concentrations of NO and H_2O.

(ii) Given the following data for the above reaction, find the order of the reaction with respect to (a) NO and (b) H_2 and the rate constant of the reaction along with the proper unit.

	$[NO]_{t=0}(\text{mol dm}^{-3})$	$[H_2]_{t=0}(\text{mol dm}^{-3})$	Intial rate $(\text{mol dm}^{-3}\text{s}^{-1})$
Experiment 1	0.025	0.01	2.4×10^{-6}
Experiment 2	0.025	0.005	1.2×10^{-6}
Experiment 3	0.0125	0.01	0.6×10^{-6}

39. The vapour pressure of benzene is 5333 Pa at 7.6ºC and 53330 Pa at 60.6ºC. Calculate the heat of vapourization of benzene and the normal boiling point of benzene.

40. The following graph represents the dependence of certain properties I to V (given below) as a function of temperature.



Property

I The enthalpy change of a gas phase reaction in which the sum of the number of moles of products is greater than the sum of the number of moles of reactants

II The osmotic pressure of an ideal solution at a given concentration

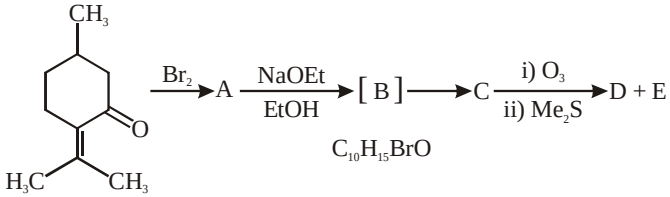
III The standard Gibbs free energy of formation of metal oxides

IV The molar heat capacity at constant volume for a an ideal gas, as predicted by the equipartition of energy

V The rate constant of a reaction with E_a = 100 kJ mol^{-1}

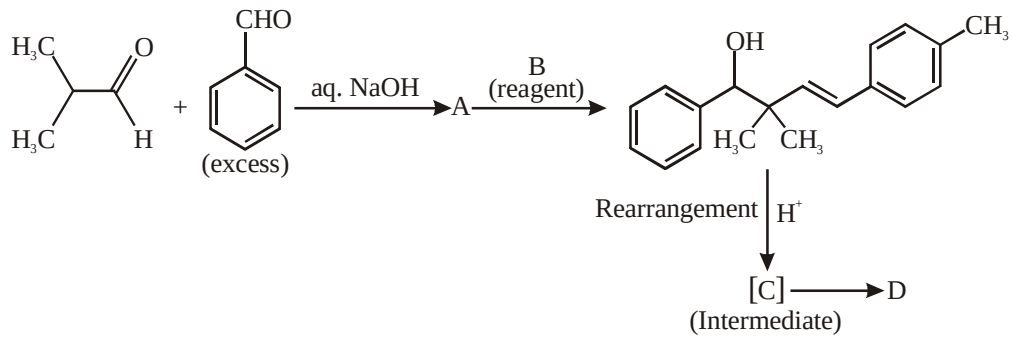
The lines / curves A, B, C, D and E corresponding to the appropriate property are:

41. Draw the structures A-E for the given transformation:



(+)-pulegone

42. In the reaction sequence given below, draw the structures of A, C, D and reagent B.



43. (a) How many ^1H NMR signals are expected for 2-chlorobut-2-ene? (ignore spin-spin coupling)
(b) Write down the iron containing chemical species, E, F and G in the following reactions.