IIT JAM 2013

1. The most polar compound among the following is:
(a) SF_4 (b) BF_3 (c) XeF_4 (d) SO_3

2. Which one of the following order of the carbonates is correct for their decomposition temperature?
(a) $BaCO_3 > CaCO_3 > SrCO_3 > MgCO_3$ (b) $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$
(c) $MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$ (d) $MgCO_3 > CaCO_3 > BaCO_3 > SrCO_3$

3. The CORRECT order of CO vibrational stretching frequency in the following complexes is
(I) $(PF_3)_3$ Mo $(CO)_3$ (II) $(PCl_3)_3$ Mo$(CO)_3$ (III) $\{P(OMe)_3\}_3Mo(CO)_3$
(a) I < II < III (b) III < II < I (c) II < I < III (d) III < I < II

4. Among the following, the ligand that BEST stabilizes low oxidation state of tungsten (W) is
(a) H_2O (b) NH_3 (c) CO (d) F^-

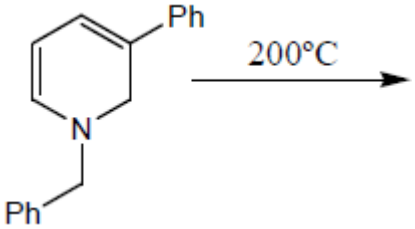
5. The function $y = x \exp(-x^2)$ has a minimum at $x = -\frac{1}{\sqrt{2}}$. The second derivative of the function at the minimum is
(a) $2\sqrt{2}\exp\left(-\frac{1}{2}\right)$ (b) $-2\sqrt{2}\exp\left(-\frac{1}{\sqrt{2}}\right)$
(c) 0 (d) $-\sqrt{2}\exp\left(-\frac{1}{2}\right)$

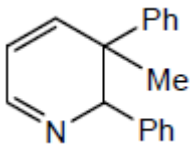
6. For a particular reaction at constant temperature, a plot of inverse of reactant concentration $\left(\frac{1}{[A]}\right)$ versus time is a straight line with a slope of 4.0×10^{-2} L mol^{-1} s^{-1}. the time required (in seconds) for 1.0 M of reactant to decrease to 0.25 M is
(a) 18.8 (b) 34.7 (c) 75.0 (d) 187.5

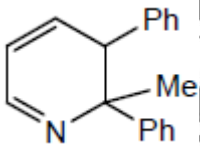
7. For a physisorption process, which one of the following statements is **NOT** correct?
(a) There are van der Waal's interactions between the adsorbate and the adsorbent.
(b) The process predominates at low temperature.

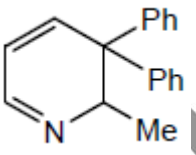
(c) The process cannot proceed beyond a monolayer.
(d) The process is reversible.

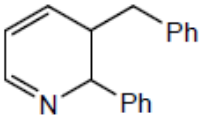
8. The product of the following reaction is



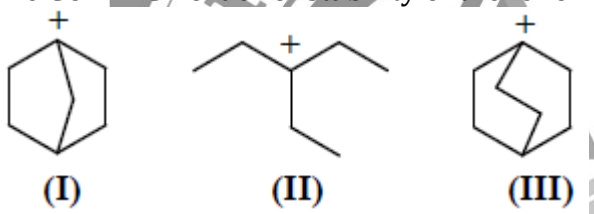
(a) 

(b) 

(c) 

(d) 

9. The CORRECT order of stability of the following carbonium ions is



(a) II > I > III (b) III > II > I (c) I > III > II (d) II > III > I

10. Which one of the following statements is CORRECT?
(a) Naturally occurring DNA has B-configuration.
(b) Nucleic acids are derived from proteins.
(c) Proteins store genetic information
(d) Vitamins generally act as enzymes.

Fill in the blank questions.

11. The reaction of anhydrous $FeCl_2$ with sodium-pentadienyl in ether gives an air-stable diamagnetic orange solid, which on oxidation gives an air-sensitive paramagnetic blue-green compound in solution. The blue-green compound is ……

12. CaO, VO and MnO have octahedral coordination of the metal ions in a rock-salt structure. The correct increasing order of their lattice enthalpies is ……..

13. The shape of the inter-halide IF_8^- is ……

14. The vapour pressures of solid and liquid chlorine are given by: $\log_e P^{solid} = 24 - \frac{3900}{T}$ and $\log_e P^{liq} = 18 - \frac{2600}{T}$, where P_{solid} and P_{liq} are the vapour pressures (in Torr) of solid and liquid chlorine near the triple point, respectively and T is the absolute temperature. The ratio of the slope of the solid-gas curve to the slope of the liquid-gas curve at the triple point in the P-T diagram is _____ (Fill in the blanks)

15. For unnormalized wave-function, $\psi(r,\theta,\phi) = \sin\theta\cos\phi\left(\frac{2r}{a_0} - \left(\frac{r}{a_0}\right)^2\right)\exp\left(-\frac{r}{a_0}\right)$, the number of radial node(s) is _____ *(Fill in the blanks)*

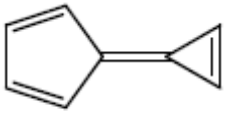
16. A hypothetical element (atomic weight = 300) crystallizes in a simple cubic lattice. For this crystal, the first order X-ray diffraction with wavelength of 5 $\overset{0}{A}$ appears at an angle of 30°C. The density of the crystal is _____ g cm^{-3}. [Avogadro number, $N_A = 6.02 \times 10^{23}$] *(Fill in the blanks)*

17. $MnO_4^-(aq) + Zn(s) + H_3O^+(aq) \rightarrow Mn^{2+}(aq) + Zn^+(aq) + H_2O(l)$
For the above reaction if the equilibrium constant at 298 K is represented by 10x, then the value of x is _____ [Given: The standard cell potential $E^0 = 2.4V$ and $\frac{2.303}{F} = 0.06$ V at 298 K]

18. The rotational energy barrier between the most stable and the least stable conformations of 2, 3-dimethylbutane along C_2 –C_3 boind is …….. kcal mol^{-1},
[Give: The energies (kcal mol^{-1}) for H/CH_3 eclipsing = 1.8, CH_3/CH_3 eclipsing = 2.9 and CH_3/CH_3 gauche = 0.9]

19. The number of peaks or signals in ^{1}H NMR of N, N-dimethylformamide (DMF) at 25^{o}C is is ……

20. Calixene is a polar hydrocarbon with a high dipole moment. The most stable dipolar canonical structure is ……..



calixene

Descriptive Questions

21. A mixture of C_3H_8 and oxygen in 1L closed vessel has an internal pressure of 4 atm at 100°C. When the mixture is ignited, the reaction produces $CO_2(g)$ and $H_2O(g)$ until all the oxygen is consumed. After the reaction, pressure of the vessel is 4.2 atm at the same temperature. Calculate the weight of oxygen present before the reaction. [Gas constant, R = 0.082 L atm mol^{-1} K^{-1}]

22. The following reaction is carried out at 1 atm and 300 K. $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ ΔU for the above reaction is 550 kJ. Assuming ideal gas behaviour for H_2 and O_2, calculate the value of ΔH. The value of gas constant, R = 0.082 L atm mol^{-1} K^{-1} = 8.314 J mol^{-1} K^{-1}.
[Given: The volume of 1 mol of liquid water is 18 mL under the above reaction condition]

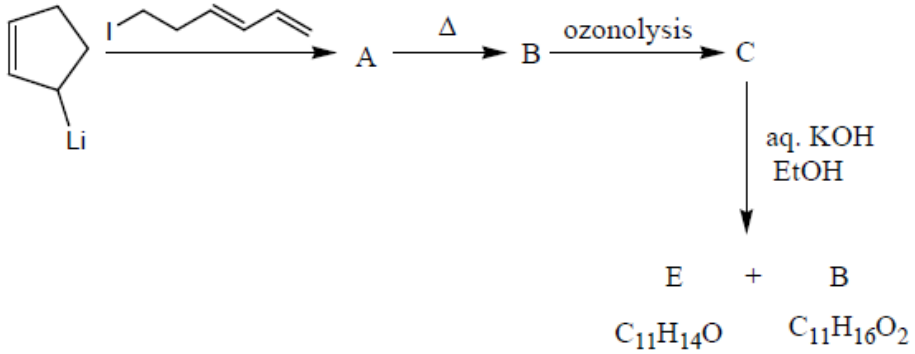
23. At 298 K, calculate the solubility of metal sulphide, MS(s), in a saturated solution of H_2S where the concentration of H_2S and pH are maintained at 0.1 M and 3.0, respectively. Given at 298 K,
$H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$ $K = 10^{-7}$
$MS(s) + H_2O(l) \rightleftharpoons M^{2+}(aq) + HS^-(aq) + {}^-OH(aq)$ $K = 5 \times 10^{-19}$

24. A solution containing 250 ppm of $CuSO_4.5H_2O$ (formula weight = 250) has an absorbance of 0.1 measured in 1 cm cell at 600 nm. Calculate the molar absorptivity (ε) of $CuSO_4.5H_2O$ in L M^{-1} cm^{-1}. When 25 mL of the above solution is titrated against $Na_2EDTA(aq)$ solution, it consumes 50 mL of $Na_2EDTA(aq)$ solution. Calculate the concentration of Na_2EDTA (aq) solution in moles L^{-1}.

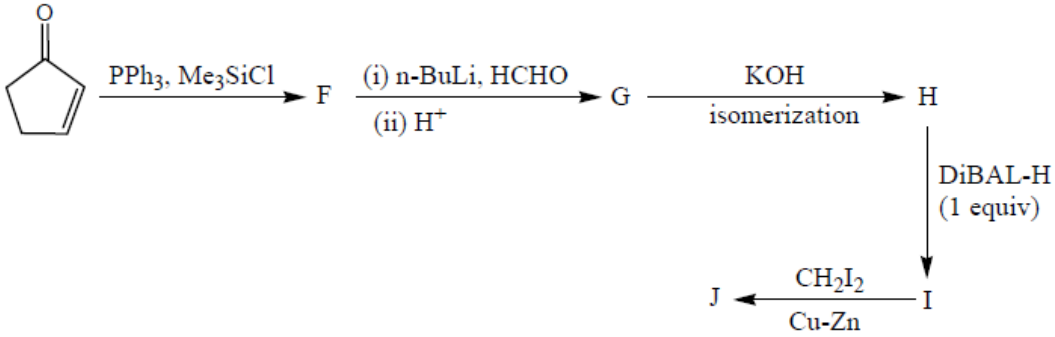
25. A solution containing 250 ppm of CuSO4.5H2O (formula weight = 250) has an absorbance of 0.1 measured in 1 cm cell at 600 nm. Calculate the molar absorptivity $(\in)$ of $CuSO4.5H_2O$ in L $M^{-1}cm^{-1}$. When 25 mL of Na_2EDTA (aq) solution is titrated against Na_2EDTA (aq) solution, it consumes at 50 mL of Na2EDTA(aq) solution. Calculate the concentration of $Na_2EDTA(aq)$ solution in moles L^{-1}.

26. Assume the complex $[Ni(PPh_3)_2(SCN)_2]$ is paramagnetic. The analogous complex of Pd(II) is diamagnetic. Draw all the probable isomers for both the complexes considering SCN– is an ambidentate ligand.

27. Write the structures of A to E in the following reaction sequence:

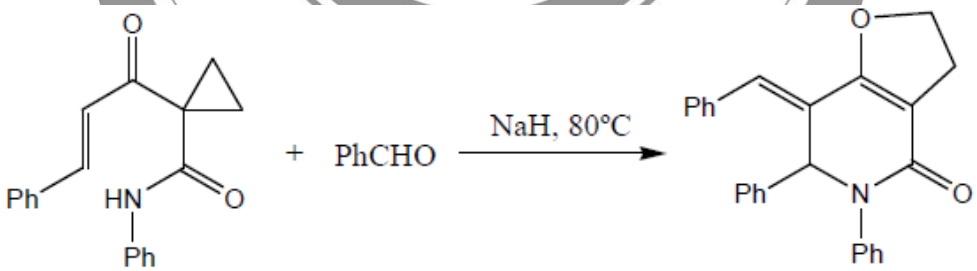


28. Write the structures of F to J in the following reaction scheme:



[DiBAL–H = diisobutylaluminium hydride]

29. Propose a mechanism for the following reaction. Show stepwise correct reactive intermediates



30. Complete the following reaction sequence and write structures of K to O.