IIT-JAM 2013 Chemistry

INSTRUCTIONS:

- **Questions 1-10 (Objective questions) carry <u>two</u> marks each, questions 11-20 (fill in the blank questions) carry <u>three</u> marks each and questions 21-30 (descriptive questions) carry <u>five</u> marks each.**
- **The marking scheme for the objective type question, is as follows:**
  (a) For each correct answer, you will be anwarded 2 (Two) marks.
  (b) For each wrong answer, you will be awarded –0.5 (Negative half) mark.
  (c) Multiple answers to a question will be treated as a wrong answer.
  (d) For each un-attempted question, you will be awarded 0(Zero) marks.
  (e) Negative marks for objective part will be carried over to total marks.
- **There is no negative marking for fill in the blank questions.**

Objective Questions

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) $(PF_3)_3Mo(CO)_3$ (II) $(PCl_3)_3Mo(CO)_3$ (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 stablizes low oxidation state of tungsten (W) is
   (a) H_2O (b) NH_3 (c) CO (d) F^-

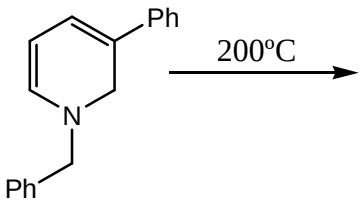
5. The function $y = x\exp\left(-x^2\right)$ has a minimum at $x = -\frac{1}{\sqrt{2}}$. The second derivative of the function at the minimum is

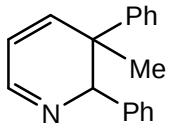
   (a) $2\sqrt{2}\exp\left(-\frac{1}{2}\right)$ (b) $-2\sqrt{2}\exp\left(-\frac{1}{2}\right)$ (c) 0 (d) $-\sqrt{2}\exp\left(-\frac{1}{2}\right)$

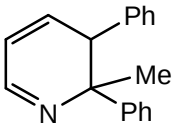
6. For a particular reaction at constant temperature, a plot of inverse of reactant concentration $\left(\frac{1}{[A]}\right)$ versus time is a straight line with a slope of 4.0×10^{-2} L mol^{-1} s^{-1}. The time required (in seconds) for 1.0 M of reactant to decrease to 0.25 M is:
   (a) 18.8 (b) 34.7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

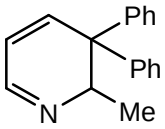
7. For a physisorption process, which one of the following statements is NOT correct?
   (a) There are van der Waals interactions between the adsorbate and the adsorbent.
   (b) The process predominates at low temperature.
   (c) The process cannot proceed beyond a monolayer
   (d) The process is reversible.

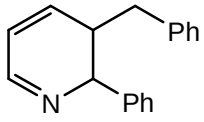
8. The product of the following reaction is



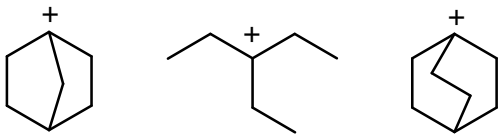
(a) 

(b) 

(c) 

(d) 

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



(I) **(II)** **(III)**

(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 occuring 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 interhalide IF_8^- is .....

14. The vapour pressures of solid and liquid chlorine are given by

$$\log_e P^{solid} = 24 - \frac{3900}{T} \text{ and } \log_e P^{liq} = 18 - \frac{2600}{T}$$

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 .....

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 .....

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 Å appears at an angle of 30°. The density of the crystal is ..... $g\ cm^{-3}$. [Avogadro number, $N_A = 6.02\times10^{23}$]

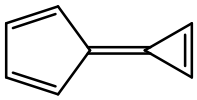
17. $MnO_4^-(aq) + Zn(s) + H_3O^+(aq) \rightarrow Mn^{2+}(aq) + Zn^{2+}(aq) + H_2O(\ell)$

For the above reaction if the equilibrium constant at 298 K is represented by 10^X, then the value of X is .....

[Given: The standard cell potential $E^0 = 2.4V$ and $\frac{2.303RT}{F} = 0.06V$ at 298K]

18. The rotational energy barrier between the most stable and the least stable conformations of 2, 3-dimethylbutane along C2–C3 bond is .....kcal mol^{-1}.
[Given: 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 ^1H NMR of N, N-dimethylformamide (DMF) at 25°C is .....

20. 

calixene

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

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 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

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$$

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 = 0.082L atm $mol^{-1}K^{-1}$ = 8.314 $mol^{-1}K^{-1}$.
[Given: The volume of 1 mole of liquid water is 18 mL under the above reaction condition]

23. At 298K, calculate the solubility of metal sulfide, 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,

$H_2S(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$ $\quad K = 10^{-7}$

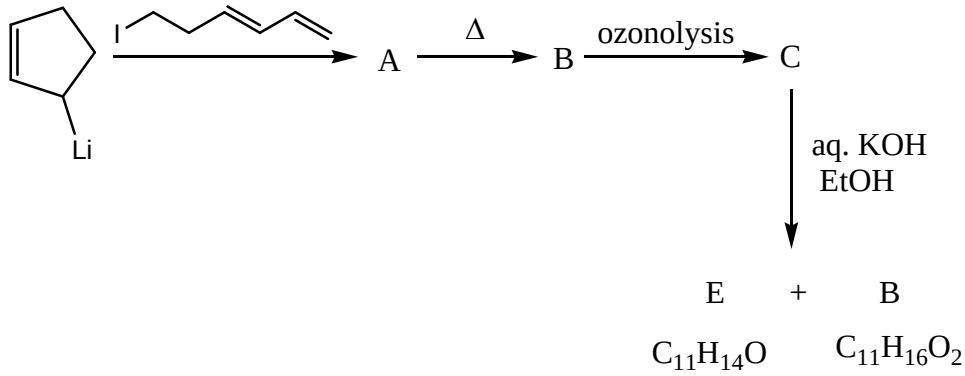
$MS(s) + H_2O(\ell) \rightleftharpoons M^{2+}(aq) + HS^-(aq) + OH^-(aq)$ $\quad K = 5 \times 10^{-19}$

24. For each of the following metallo-proteins identify the metal-ion at the active-site and the function of the proteins:
deoxy-hemoglobin, deoxy-myoglobin, oxy-hemocyanin, cytochrome-c and carbonic anhydrase.

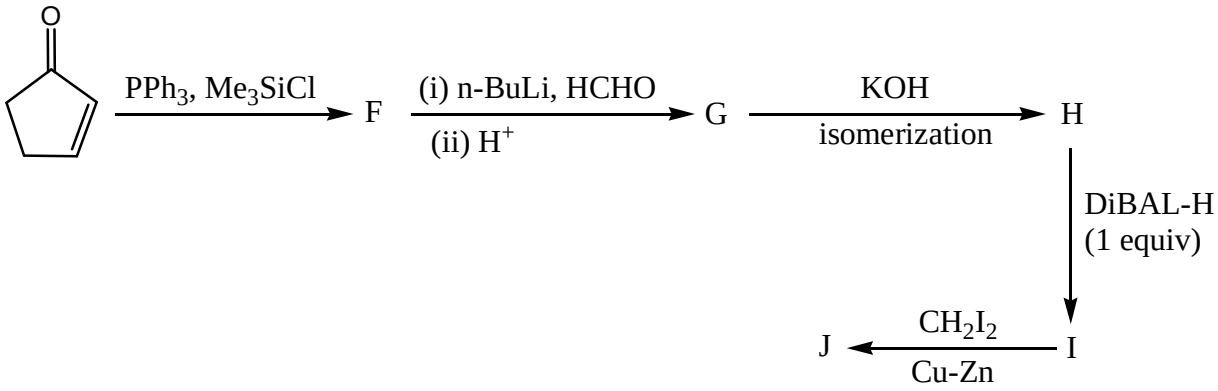
25. A solution containing 250 ppm of $CuSO_4.5H_2O$ (formula weight = 250) has an absorbance of 0.1 measured in 1 cm cell at 600 nm. Calculate the molar absorptivity (ε) of $CuSO_4.5H_2O$ in L $M^{-1}cm^{-1}$. When 25 mL of Na_2EDTA (aq) solution is titrated against Na_2EDTA (aq) solution, it consumes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

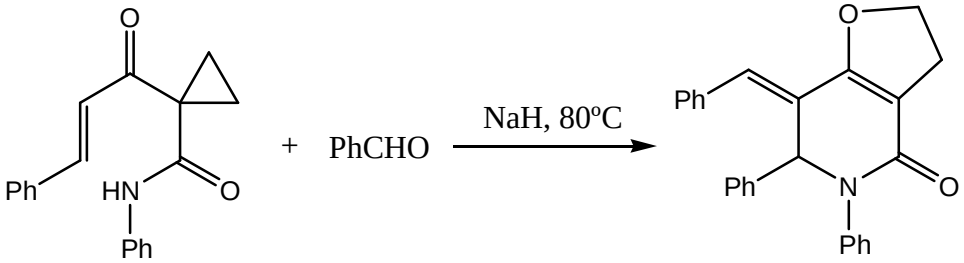


28. Write the structures of F to J in the following reaction scheme:



[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.