

# JAM – 2013 – Chemistry



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Attempt ALL the questions. Q.1 – Q.10 Multiple Choice Question (MCQ), carry TWO marks each (for each wrong answer: -0.66). 1. The most polar compound among the following is: (a) SF<sub>4</sub> (d)  $SO_3$ (b)  $BF_3$ (c)  $XeF_4$ 2. Which one of the following order of the carbonates is **CORRECT** for their decomposition temperature? BaCO3  $> CaCO_3 > SrCO_3 > MgCO_3$ (a)  $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$ (b)  $MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$ (c)  $MgCO_3 > CaCO_3 > BaCO_3 > SrCO_3$ (d) The CORRECT order of CO vibrational stretching frequency in the following 3. complexes is  $(PCl_3)_3Mo(CO)_3$  $(PF_3)_3Mo(CO)_3$  ${P(OMe)_3}_3Mo(CO)_3$ Ш Ι II (a) I < II < III (b) III < II < I (c) II < I < III (d) III < I < II Among the following, the ligand that **BEST** stabilizes low oxidation state of 4. tungsten (W) is (b) NH<sub>3</sub> (c) CO (d) F<sup>-</sup> (a)  $H_2O$ The function  $y = x \exp(-x^2)$  has a minimum at  $x = -\frac{1}{\sqrt{2}}$ . The second derivative 5. 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)  $-\sqrt{2} \exp\left(-\frac{1}{2}\right)$ For a particular reaction at constant temperature, a plot of inverse of reactant 6. concentration  $\left(\frac{1}{|A|}\right)$  versus time is a straight line with a slope of 4.0 ×  $10^{-2}$  L mol<sup>-1</sup> s<sup>-1</sup>. 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.

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

#### 8. The product of the following reaction is



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



#### 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.

Attempt ALL the questions. Q.11 – Q.20 (fill in the blank questions) carry three marks each (No Negative Mark).

- 11. The reaction of anhydrous FeCl<sub>2</sub> with sodium-pentadienyl in ether gives an airstable 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<sub>8</sub> 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<sup>solid</sup> and P<sup>liq</sup> 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,

$$\varphi(\mathbf{r}, \theta, \phi) = \sin \theta \cos \phi \left(\frac{2\mathbf{r}}{a_0} - \left(\frac{\mathbf{r}}{a_0}\right)^2\right) \exp\left(-\frac{\mathbf{r}}{a_0}\right),$$

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  $30^\circ$ . The density of the crystal is \_\_\_\_\_ g cm<sup>-3</sup>.

[Avogadro number,  $N_A = 6.02 \times 10^{23}$ ]

- $MnO_{4}^{-}(aq) + Zn(s) + H_{3}O^{+}(aq) \rightarrow Mn^{2+}(aq) + Zn^{2+}(aq) + H_{2}O(\ell)$ 17. For the above reaction if the equilibrium constant at 298 K is represented by 10<sup>X</sup>, then the value of X is [Given: The standard cell potential  $E^0 = 2.4$  V and  $\frac{2.303RT}{F} = 0.06V$  at 298 K]
- 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<sup>-1</sup>. [Given: The energies (kcal mol<sup>-1</sup>) for H/CH<sub>3</sub> eclipsing = 1.8, CH<sub>3</sub>/CH<sub>3</sub> eclipsing = 2.9 and  $CH_3/CH_3$  gauche = 0.9]
- 19. The number of peaks or signals in <sup>1</sup>H-NMR of N,N-dimethylformamide (DMF) at 25 °C is \_ -CADEN
- 20.

### calixene

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

Attempt ALL the questions. Questions 21 30 (subjective questions) carry five marks each.

A mixture of C<sub>3</sub>H<sub>8</sub> and oxygen in 1L closed vessel has an internal pressure of 21. 4 atm at 100 °C. When the mixture is ignited, the reaction produces CO<sub>2</sub>(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.

$$2\mathrm{H}_2(\mathbf{g}) + \mathrm{O}_2(\mathbf{g}) \longrightarrow 2\mathrm{H}_2\mathrm{O}(\ell)$$

 $\Delta U$  for the above reaction is 550 kJ. Assuming ideal gas behaviour for H<sub>2</sub> and **O**<sub>2</sub>, calculate the value of  $\Delta$ **H**.

constant,  $R = 0.082 L atm mol^{-1} K^{-1} =$ The of [Given: value gas 8.314 mol<sup>-1</sup>K<sup>-1</sup>. 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 GATE & JAM

Given at 298 K,

$$\begin{split} H_2S(aq) + H_2O(liq) & \leftrightarrows H_3O^+(aq) + HS^-(aq) \\ MS(s) + H_2O(liq) & \rightleftharpoons M^{2+}(aq) + HS^-(aq) + OH(aq) \\ \end{split} \qquad \begin{array}{l} K = 10^{-7} \\ K = 5 \times 10^{-19} \\ \end{array}$$

- 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, oxyhemocyanin, 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 ( $\epsilon$ ) of CuSO<sub>4</sub>. 5H<sub>2</sub>O in L M<sup>-1</sup>cm<sup>-1</sup>. When 25 mL of the above solution is titrated against Na<sub>2</sub>EDTA (aq) solution, it consumes 50 mL of Na<sub>2</sub>EDTA (aq) solution. Calculate the concentration of Na<sub>2</sub>EDTA (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<sup>-</sup> is an ambidentate ligand.
- 27. Write the structures of **A** to **E** in the following reaction sequence:



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

$$\begin{array}{c} O \\ \hline \end{array} \end{array} \xrightarrow{PPh_3.Me_3SiCl} F \xrightarrow{i. n-BuLi, HCHO} G \xrightarrow{KOH} H \\ \hline isomerization \end{array} \xrightarrow{I} DiBAL-H \\ (1 equiv) \end{array}$$

- DiBAL-H = Diisobutylaluminium hydride
- 29. Propose a mechanism for the following reaction. Show stepwise correct reactive intermediates.



### <u>Answer Key</u>

Q.No	Ans	E E	Q.No	Ans
1.	а		11.	Ferricinium cation
2.	b		12.	VO > MnO > CaO
3.	b		13.	Square antiprismatic
4.	С		14.	3:2
5.	а		15.	2
6.	С		16.	$3.985 \text{ g cm}^{-3}$
7.	С		17.	400
8.	d		18.	4.7 Kcal/mol
9.	d		19.	Three
10.	а		20.	

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