### **CHEMISTRY**

Q. 1. Which one of the following is the correct statement?

i. Chlorides of both beryllium and aluminium have bridged chloride structures in solid phase.

ii. B<sub>2</sub>H<sub>6</sub>.2NH<sub>3</sub> is known as 'inorganic benzene'.

iii. Boric acid is a protonic acid.

iv. Beryllium exhibits coordination number of six.

**Sol:** Becl<sub>2</sub> and Alcl<sub>3</sub> both have bridged structure in solid phase.

B<sub>3</sub>N<sub>3</sub> H<sub>6</sub> is known as inorganic benzene.

Boric acid is Lewis acid.

Beryllium exhibits coordination number of 4

: Correct answer is (1)

The treatment of  $CH_3M_gX$  with  $CH3C \equiv C - H$  produce

Sol:

$$CII_3Mg\ X + CII_3 - C = C - II$$
  
 $\rightarrow CII_4 \uparrow + CII_3 - C = C\ Mg\ X$   
: Correct answer is (2)

**Q. 3.** The correct decreasing order of priority for the functional groups of organic compounds in the IUPAC system of nomenclature is

i. 
$$-CHO$$
,  $-COOH$ ,  $-SO_3H$ ,  $-CONH_2$ 

$$CONH_2 - CHO$$
,  $-SO_3H - COOH$ ,
$$-COOH$$
,  $-SO_3H$ ,  $-CONH_2 - CHO$ ,
iii.  $-SO_3H$ ,  $-COOH$ ,  $-CONH_2 - CHO$ ,

**Sol:** The correct decreasing order of priority for the functional group of organic compounds in the IUPAC system of nomenclature is:

$$-CO_2H$$
,  $-SO_3H$ ,  $-CONH_2$ ,  $-CHO$ .

: Correct answer is (3)

**Q. 4.** The pK<sub>a</sub> of a weak acid, HA is 4.80. The pK<sub>b</sub> of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be

- i. 7.01
- ii. 9.22
- iii. 9.58
- iv. 4.79

Sol:

$$BOH + HA \leftrightarrow B^{+} + A^{-} + H_{2}O$$

$$p^{H} - \frac{1}{2}pk_{w} + \frac{1}{2}pk_{z} - \frac{1}{2}pk_{o}$$

$$= \frac{1}{2} (14 + 4.80 - 4.78) = 7.01$$

:. Correct answer is (1)

Q. 5. The hydrocarbon which can react with sodium in liquid ammonia is

$$CH_3CH = CHCH_3$$

$$CH_3CH_2C \equiv CCH_2CH_3$$

$$CH_3CH_2C \equiv CCH_2CH_2CH_3$$

$$CH_3CH_2C \equiv CH$$

Sol:

$$CH_3UH_2C\equiv CH+Na~(in~liquid~NH_3) \rightarrow$$

$$CH_3CH_2C\equiv C^-\ Na^-+\frac{1}{2}\ H_2\ \uparrow$$

\* Correct answer is (4)

Q. 6.

Given  $E^{\rm C}_{c^{s+}/\sigma}=-0.72V$ ,  $E^{\rm C}_{Fe^{s+}/Fe}=-0.42V$ . The potential for the cell  $Cr\mid Cr^{3+}$  (0.1M)  $\mid\mid Fe^{2+}$  (0.01 M)  $\mid Fe$  is

- i. -0.339 V
- ii. -0.26 V
- iii. 0.26 V

Sol:

$$2 Cr(s) + 3Fe^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Fe(s)$$
  
The potential for the cell  
=  $E^0_{Fe^{3+}/Fe} - E^0_{O^{3+}/O}$ 

$$-\frac{0.059}{6} \log \frac{\left[Cr^{3+}\right]^2}{\left[Fe^{2+}\right]^3}$$

$$= -0.42 - (-0.720) - \frac{0.059}{6} \log \frac{(0.1)^2}{(0.01)^2}$$

$$= 0.3 - 0.039 = 0.26V$$
.

:. Correct answer is (3)

- **Q. 7.** Amount of oxalic acid present in a solution can be determined by its titration with KMnO<sub>4</sub>solution in the presence of H<sub>2</sub>SO<sub>4</sub>. The titration gives unsatisfactory result when carried out in the presence of HCl, because HCl
  - i. reduces permanganate to Mn<sup>2+</sup>.
  - ii. oxidises oxalic acid to carbon dioxide and water.
  - iii. gets oxidised by oxalic acid to chlorine.
  - iv. furnishes H<sup>+</sup> ions in addition to those from oxalic acid.

**Sol:** KMnO<sub>4</sub>can oxidise HCl along with oxalic acid into Cl<sub>2</sub> and itself gets reduced to Mn<sup>2+</sup>.

## : Correct answer is (1)

- **Q. 8.** Among the following substituted silanes the one which will give rise to cross linked silicone polymer on hydrolysis is
  - i. R<sub>2</sub>SiCl<sub>2</sub>
  - ii. R<sub>3</sub>SiCl
  - iii. R<sub>4</sub>Si
  - iv. RSiCl<sub>3</sub>

# Cross linked silicon polymer.

- Correct answer is (4)
- Q. 9. Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below:

$$\frac{1}{2}\operatorname{Cl}_2(g) \xrightarrow{\frac{1}{2}\Delta_{diss}H^{\Theta}} \operatorname{Cl}(g) \xrightarrow{\Delta_{eg}H^{\Theta}} \operatorname{Cl}^-(g) \xrightarrow{\frac{1}{2}\Delta_{hyd}H^{\Theta}} \operatorname{Cl}^-(aq)$$

The energy involved in the conversion of

$$\frac{1}{2} \operatorname{Cl}_2(g) \text{ to } \operatorname{Cl}^-(aq)$$
 (using the data,  $\Delta_{\text{diss}} H_{\text{Cl}_2}^{\Theta} = 240 \text{ kJ mol}^{-1}$ ,  $\Delta_{\text{eg}} H_{\text{Cl}}^{\Theta} = -349 \text{ kJ mol}^{-1}$ ,  $\Delta_{\text{hyd}} H_{\text{Cl}^-} = -381 \text{ kJ mol}^{-1}$ ) will be

- i. -850 kJ mol<sup>-1</sup>
- ii. +120 kJ mol<sup>-1</sup>
- iii. +152 kJ mol<sup>-1</sup>
- iv.  $-610 \text{ kJ mol}^{-1}$

Energy involved =

$$= \frac{1}{2} (240) + (-349) + (-381)$$
$$= 120 - 730$$
$$= -610 \text{ KJ mol}^{-1}$$

: Correct answer is (4)

**Q. 10.** Which of the following factors is of no significance for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly?

- i. Metal sulphides are less stable than the corresponding oxides.
- ii. CO<sub>2</sub>is more volatile than CS<sub>2</sub>.
- iii. Metal sulphides are thermodynamically more stable than CS<sub>2</sub>.
- iv. CO<sub>2</sub>is thermodynamically more stable than CS<sub>2</sub>.

Sol:

$$2 MS + C \rightarrow 2 M + CS_2 + \Delta$$
$$2 MO + C \rightarrow 2M + CO_2 - \Delta$$

Hence, CO<sub>2</sub> is more stable than CS<sub>2</sub> while Ms are more stable than MO.

: Correct answer is (1)

Q. 11. Four species are listed below:

$$HCO_3^-$$

$$H_3O^-$$

Which one of the following is the correct sequence of their acid strength?

$$(1) \ (i) < (iii) < (ii) < (iv) (2) \ (iii) < (i) < (iv) < (ii) (3) \ (iv) < (ii) < (iii) < (i) (4) \ (ii) < (iii) < (iv) < (iv)$$

Sol: The increasing order of acidic strength is

$$HCO_3^- < HSO_4^- < H_3O^- < HSO_4^- F$$

$$i\,e.\,(i)\,<\!(iii\,)<\!(ii)\,<\!(i\nu)$$

Q. 12. Which one of the following constitutes a group of the isoelectronic species?

$$CN^{-}$$
,  $N^{2}$ ,  $C_{2}^{-2}$ ,  $C_{2}^{-2}$ 

$$_{\rm ii.}$$
  $N^2$ ,  $O_2^-$ ,  $NO^+$ ,  $CO$ 

$$C_2^{-2}$$
,  $C_2^{-2}$ ,  $CO$ ,  $NO$ 

$$_{\rm iv.}$$
  $NO^+, C_2^{-2}, CN^-, N_2$ 

Sol: Isoelectronic species have same number of electrons

 $NO^+$ ,  $C_2^{2-}$ ,  $CN^-$  and  $N_2$  each have 14 electrons.

: Correct answer is (4)

Q. 13. Phenol, when it first reacts with concentrated sulphuric acid and then with concentrated nitric acid, gives

- i. p-nitrophenol
- ii. nitrobenzene
- iii. 2,4,6-trinitrobenzene
- iv. o-nitrophenol

Sol:

$$\begin{array}{c}
OH \\
OH \\
SO_3H \\
HNO_3
\end{array}$$

$$\begin{array}{c}
OH \\
NO_2
\end{array}$$

As, temperature is not mentioned, 0- mitrophenol is the only stable product.

: Correct answer is (4)

**Q. 14.** The ionization enthalpy of hydrogen atom is  $1.312 \times 10^6$  J mol<sup>-1</sup>. The energy required to excite the electron in the atom from n = 1 to n = 2 is

- $_{\rm i.}$  7.56 × 10<sup>5</sup> J mol<sup>-1</sup>
- $^{"}_{ii}$  9.84 × 10<sup>5</sup> J mol<sup>-1</sup>
- $_{\rm iii.}$  8 51×10<sup>5</sup> J mol<sup>-1</sup>
- $_{\rm iv.}^{\rm iv.}$  6.56 × 10<sup>5</sup> J  $mol^{-1}$

$$E_2 = \frac{-1.312 \times 10^6 \times (1)^2}{(2)2} = -3.28 \times 10^5 \text{ J mcl}^{-1}$$

$$E_1 = -1.312 \times 10^6 \ J \ mol^{-1}$$

: Correct answer is (2)

Q. 15. The organic chloro compound, which shows complete stereochemical inversion during a S<sub>N</sub>2 reaction, is

- i. (CH<sub>3</sub>)<sub>2</sub>CHCl
- ii. CH<sub>3</sub>Cl
- iii. (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>CHCl
- iv. (CH<sub>3</sub>)<sub>3</sub>CCI

**Sol:** Primary halides show inversion during  $S_N2$  reaction more than secondary while secondary show more than tertiary.

# : correct answer is (2)

**Q. 16.** Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotized and then heated with cuprous bromide. The reaction mixture so formed contains

- i. mixture of o-; and p-bromoanilines
- ii. mixture of o- and m-bromotoluenes
- iii. mixture of o- and p-bromotoluenes
- iv. mixture of o- and p-dibromobenzenes

Sol:

$$\begin{array}{c} CH_{3} \\ Conc. \ H_{2}SO_{4} \\ Conc. \ HNO_{3} \\ \end{array} \begin{array}{c} CH_{3} \\ + \\ CH_{3} \\ \end{array} \begin{array}{c} CH_{3} \\ NH_{2} \\ \end{array} \begin{array}{c} CH_{3} \\ NNO_{2} / HCI \\ \end{array} \begin{array}{c} CH_{3} \\ N_{2}CI \\ CH_{3} \\ \end{array} \begin{array}{c} CH_{3} \\ CU_{2}Br_{2} \Delta \\ \end{array} \begin{array}{c} CH_{3} \\ + \\ CH_{3} \\ \end{array} \begin{array}{c} CH_{3} \\ N_{2}CI \\ \end{array} \begin{array}{c} CH_{3} \\ CU_{2}Br_{2} \Delta \\ \end{array} \begin{array}{c} CH_{3} \\ CH_{3} CH_{3}$$

# :. Correct answer is (3)

Q. 17. In the following sequence of reactions, the alkene affords the compound 'B'

$$CH_3CH = CHCH_3 \xrightarrow{G_3} A \xrightarrow{B_so} B$$
 
$$Zn$$

The compound B is

i. CH<sub>3</sub>CH<sub>2</sub>COCH<sub>3</sub>

ii. CH₃CHO

iii. CH<sub>3</sub>CH<sub>2</sub>CHO

iv. CH<sub>3</sub>COCH<sub>3</sub>

Sol:

$$CH_3-CH=CH-CH_3 \xrightarrow{O_3} CH_3-CH \xrightarrow{CH_3-CH_3} CH-CH_3 \xrightarrow{Z_{10}/H_2O} 2CH_3CHO + H_2O + Z_{10}CHO +$$

Correct answer is (2)

Q. 18. Which one of the following pairs of species have the same bond order?

$$O_2^-$$
 and  $CN^-$ 

$$_{\rm iii.}^{\circ\circ}$$
  $CN^-$  and  $NO^+$ 

$$_{iv.}$$
  $CN^-$  and  $CN^+$ 

**Sol:** The species which have the same number of total electrons will have the same bond order. CN<sup>-</sup> and NO<sup>+</sup> each have 14 electrons and they will have same bond order.

### :. Correct answer is (3)

**Q. 19.** At  $80^{\circ}$ C, the vapour pressure of pure liquid 'A' is 520 mm Hg and that of pure liquid 'B' is 1000 mm Hg. If a mixture solution of 'A' and 'B' boils at  $80^{\circ}$ C and 1 atm pressure, the amount of 'A' in the mixture is (1 atm = 760 mm Hg)

i. 48 mol percent

ii. 50 mol percent

iii. 52 mol percent

iv. 34 mol percent

Let amount of A in the mixture be  $\times_A & B$  be  $\times_B$ .

$$P_T = 760 = P_A^0 \times_A + P_B^0 \times_B$$
  
or,  $760 = 520 \times_A + 1000 (1 - \times_A)$ 

$$or$$
,  $480 \times_{A} = 240$ 

or, 
$$X_A = \frac{1}{2}$$
 or 50 molpercent.

: Correct answer is (2)

 $\frac{1}{2}~A\to 2B$  Q. 20. For a reaction , rate of disappearance of 'A' is related to the rate of appearance of 'B' by the expression

i. 
$$-\frac{d\left[A\right]}{dt} = \frac{d\left[B\right]}{dt}$$

$$-\frac{d\left[A\right]}{dt} = 4\frac{d\left[B\right]}{dt}$$

$$-\frac{d\left[A\right]}{dt} = \frac{1}{2}\frac{d\left[B\right]}{dt}$$

$$-\frac{d\left[A\right]}{dt} = \frac{1}{4}\frac{d\left[B\right]}{dt}$$

$$-\frac{d\left[A\right]}{dt} = \frac{1}{4}\frac{d\left[B\right]}{dt}$$

Sol:

Rate of reaction with respect to  $A = \frac{-2d\left[A\right]}{dt}$ 

Rate of reaction with respect to  $B = \frac{1}{2} \frac{d[B]}{dt}$ 

$$-\frac{2d[A]}{dt} = \frac{1}{2} \cdot \frac{d[B]}{dt}$$

$$\Rightarrow \frac{d[A]}{dt} = \frac{1}{4} \cdot \frac{d[B]}{dt}$$

:. Correct answer is (4)

Q. 21. The equilibrium constants  $K_{p1}$  and  $K_{p2}$  for the reactions  $X \leftrightarrow 2Y$  and  $Z \leftrightarrow P + \mathcal{Q}$  respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal then the ratio of total pressures at these equilibria is

- i. 1:3
- ii. 1:9
- iii. 1:36
- iv. 1:1

#### Sol:

Let initial moles of X be a and that of Z be b.

$$X \Leftrightarrow 2Y$$

$$a(1-\alpha) = 2a\alpha$$

Moles at equilibriu m.

$$\therefore K_{P1} = \frac{(2a \alpha)^2 P_{P1}}{a (1-\alpha) a (1+\alpha)}$$
 (i)

$$Z \Leftrightarrow P + Q$$

$$b(1-\alpha)$$
  $b\alpha$   $B\alpha$ 

Moles at equilibrium

$$\therefore K_{P2} = \frac{(b\alpha)^2 P_{P2}}{B(1-\alpha)b(1+\alpha)}$$
 (ii)

$$\therefore \frac{K_{P1}}{K_{P2}} = \frac{4 P_{P1}}{P_{P2}} = \frac{1}{9}$$

$$\therefore \frac{P_{T1}}{P_{T2}} = \frac{1}{36}$$

:. Correct answer is (3)

- **Q. 22.** In context with the industrial preparation of hydrogen from water gas  $(CO + H_2)$ , which of the following is the correct statement?
  - i. H<sub>2</sub> is removed through occlusion with Pd.
  - ii. CO is oxidised to CO<sub>2</sub> with steam in the presence of a catalyst followed by absorption of CO<sub>2</sub>in alkali.
  - iii. CO and H2are fractionally separated using differences in their densities.
  - iv.  $\,$  CO is removed by absorption in aqueous  $Cu_2Cl_2$  solution.

### Sol:

$$\underbrace{CO + H_2}_{\textit{Watergas}} + H_2O \xrightarrow{\textit{catadyst}} CO_2 + 2H_2$$

$$\frac{2\ NaOH}{(alkali)} \rightarrow Na_2CO_3 + H_2O$$

: Correct answer is (2)