IITJEE 2013

PART A –CHEMISTRY

1. An unknown alcohol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism:
    (1) tertiary alcohol by S_N1
    (2) secondary alcohol by S_N2
    (3) tertiary alcohol by S_N2
    (4) secondary alcohol by S_N1

Sol. **(1)**
Reaction proceeds through carbocation formation as 3^0 carbocation is highly stable, hence reaction proceeds through S_N1 with 3^0 alcohol.
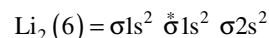
2. The first ionization potential of Na is 5.1 eV. The value of electron gain enthalpy of Na^+ will be:
    (1) -5.1 eV
    (3) -10.2 eV
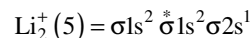   (3) $+2.55$ eV
    (4) -2.55 eV

Sol. **(1)**
$Na \underset{\Delta H=-5.1eV}{\overset{\Delta H=+5.1eV}{\rightleftharpoons}} Na^+ + e^-$, here the backward reaction releases same amount of energy and known as Electron gain enthalpy.

3. Stability of the species Li_2, Li_2^- and Li_2^+ increases in the order of:
    (1) $Li_2^- < Li_2^+ < Li_2$
    (3) $Li_2 < Li_2^- < Li_2^+$
    (3) $Li_2^- < Li_2 < Li_2^+$
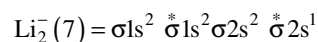   (4) $Li_2 < Li_2^+ < Li_2^-$

Sol. **(1)**
$$Li_2(6) = \sigma 1s^2 \; \overset{*}{\sigma} 1s^2 \; \sigma 2s^2$$
$$B.O. = \frac{4-2}{2} = 1$$
$$Li_2^+(5) = \sigma 1s^2 \; \overset{*}{\sigma} 1s^2 \sigma 2s^1$$
$$B.O. = \frac{3-2}{2} = 0.5$$
$$Li_2^-(7) = \sigma 1s^2 \; \overset{*}{\sigma} 1s^2 \sigma 2s^2 \; \overset{*}{\sigma} 2s^1$$
$$B.O. = \frac{4-3}{2} = 0.5$$
Li_2^+ is more stable than Li_2^- because Li_2^- has more numbers of antibonding electrons.

4. The molarity of a solution obtained by mixing 750 mL of 0.5 (M) HCl with 250 mL of 2(M)HCl will be:
    (1) 1.00 M
    (2) 1.75 M
    (3) 0.975 M
    (4) 0.875 M

Sol. **(4)**
$M_1V_1 + M_2V_2 = MV$
$$M = \frac{M_1V_1 + M_2V_2}{V} = \frac{0.5 \times 750 + 2 \times 250}{1000}$$
M = 0.875

5. Which of the following is the wrong statement?
    (1) O_3 molecule is bent
    (2) Ozone is violet-black in solid state
    (3) Ozone is diamagnetic gas
    (4) ONCl and ONO^- are not isoelectronic

Sol. **(All the options are correct statements)**
(1) Correct, as $O\overset{O}{\diagdown\diagup}O$ is bent.

(2) Correct, as ozone is violet-black solid.
(3) Correct, as ozone is diamagnetic.
(4) Correct, as ONCl = 32 electrons and ONO⁻ = 24 electron hence are not isoelectronic.
All options are correct statements.

6. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest $E^0_{M^{3+}/M^{2+}}$ value?

(1) Mn(Z = 25) (2) Fe(Z = 26)
(3) Co(Z = 27) (4) Cr(Z = 24)

Sol. **(3)**

$$E^0_{Mn^{+3}/Mn^{+2}} = 1.57 \text{ V}$$

$$E^0_{Fe^{+3}/Fe^{+2}} = 0.77 \text{ V}$$

$$E^0_{Co^{+3}/Co^{+2}} = 1.97 \text{ V}$$

$$E^0_{Cr^{+3}/Cr^{+2}} = -0.41 \text{ V}$$

7. A solution of (–) –1 – chloro –1 – phenylethane is toluene racemises slowly in the presence of a small amount of SbCl₅, due to the formation of :

(1) carbene (2) carbocation
(3) free radical (4) carbanion

Sol. **(2)**

8. The coagulating power of electrolytes having ions Na^+, Al^{3+} and Ba^{2+} for arsenic sulphide sol increases in the order:

(1) $Na^+ < Ba^{2+} < Al^{3+}$ (2) $Ba^{2+} < Na^+ < Al^{3+}$
(3) $Al^{3+} < Na^+ < Ba^{2+}$ (4) $Al^{3+} < Ba^{2+} < Na^+$

Sol. **(1)**
As_2S_3 is an anionic sol (negative sol) hence coagulation will depend upon coagulating power of cation, which is directly proportional to the valency of cation (Hardy-Schulze rule).

9. How many litres of water must be added to 1 litre of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2?

(1) 0.9 L (2) 2.0 L
(3) 9.0 L (4) 0.1 L

Sol. **(3)**
Initial pH = 1, i.e. [H⁺] = 0.1 mole/litre
New pH = 2, i.e. [H⁺] = 0.01 mole/litre
In case of dilution: $M_1V_1 = M_2V_2$
$0.1 \times 1 = 0.01 \times V_2$
V_2 = 10 litre.
Volume of water added = 9 litre.

10. Which one of the following molecules is expected to exhibit diamagnetic behaviour?

(1) N_2 (2) O_2
(3) S_2 (4) C_2

Sol. **(1) & (4) both are correct answers.**
$N_2 \rightarrow$ Diamagnetic
$O_2 \rightarrow$ Paramagnetic
$S_2 \rightarrow$ Paramagnetic

$C_2 \rightarrow$ Diamagnetic

11. Which of the following arrangements does **not** represent the correct order of the property stated against it ?
(1) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$: ionic size
(2) $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$: stability in aqueous solution
(3) $Sc < Ti < Cr < Mn$: number of oxidation states
(4) $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$: paramagnetic behaviour

Sol. **(2) & (4) both are correct answers)**
The exothermic hydration enthalpies of the given trivalent cations are:
$Sc^{+3} = 3960$ kJ/mole
$Fe^{+3} = 4429$ kJ/mole
$Co^{+3} = 4653$ kJ/mole
$Cr^{+3} = 4563$ kJ/mole
Hence Sc^{+3} is least hydrated; so least stable (not most stable)
Fe^{+2} contains 4 unpaired electrons where as Mn^{+2} contains 5 unpaired electrons hence (4) is incorrect.

12. Experimentally it was found that a metal oxide has formula $M_{0.98}O$. Metal M, is present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M^{3+} would be:
(1) 4.08%   (2) 6.05%
(3) 5.08%   (4) 7.01%

Sol. **(1)**
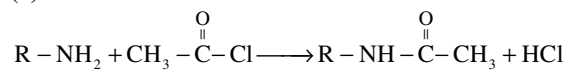Metal oxide = $M_{0.98}O$
If 'x' ions of M are in +3 state, then
$3x + (0.98 - x) \times 2 = 2$
$x = 0.04$

So the percentage of metal in +3 state would be $\dfrac{0.04}{0.98} \times 100 = 4.08\%$

13. A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is:
(1) 5   (2) 4
(3) 6   (4) 2

Sol. **(1)**

$$R - NH_2 + CH_3 - \overset{\overset{O}{\|}}{C} - Cl \longrightarrow R - NH - \overset{\overset{O}{\|}}{C} - CH_3 + HCl$$

Each $CH_3 - \overset{\overset{O}{\|}}{C}$ addition increases the molecular wt. by 42.
Total increase in m.wt. = 390 – 180 = 210
Then number of NH_2 groups $= \dfrac{210}{42} = 5$

14. Given
$E^0_{Cr^{3+}/Cr} = -0.74$ V; $E^0_{MnO_4^-/Mn^{2+}} = 1.51$ V
$E^0_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V; $E^0_{Cl/Cl^-} = 1.36$ V
Based on the data given above, strongest oxidising agent will be:
(1) Cr^{3+} (2) Mn^{2+}
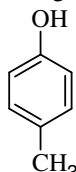(3) MnO_4^- (4) Cl^-

Sol. **(3)**
As per data mentioned
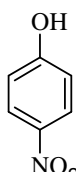MnO_4^- is strongest oxidising agent as it has maximum SRP value.

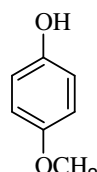15.   Arrange the following compounds in order of decreasing acidity:
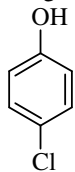
(I)   (II)   (III)   (IV)

(1) I > II > III > IV
(3) IV > III > I > II
(2) III > I > II > IV
(4) II > IV > I > III

Sol.   **(2)**
Correct order of acidic strength is III > I > II > IV

16.   The rate of a reaction doubles when its temperature changes from 300K to 310K. Activation energy of such a reaction will be:
($R = 8.314\ JK^{-1}\ mol^{-1}$ and $\log 2 = 0.301$)
(1) $48.6\ kJ\ mol^{-1}$
(3) $60.5\ kJ\ mol^{-1}$
(2) $58.5\ kJ\ mol^{-1}$
(4) $53.6\ kJ\ mol^{-1}$

Sol.   **(4)**
As per Arrhenius equation:

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$2.303 \log 2 = -\frac{E_a}{8.314}\left(\frac{1}{310} - \frac{1}{300}\right)$$

$\Rightarrow E_a = 53.6\ kJ/mole$

17.   Synthesis of each molecule of glucose in photosynthesis involves:
(1) 10 molecules of ATP
(3) 6 molecules of ATP
(2) 8 molecules of ATP
(4) 18 molecules of ATP

Sol.   **(4)**

$$12H_2O + 12NADP + 18ADP \xrightarrow{\text{Light reaction}} 6O_2 + 18ATP + 12NADPH$$

$$6CO_2 + 12NADPH + 18ATP \xrightarrow{\text{Dark reaction}} C_6H_{12}O_6 + 12NADP + 18ADP + 6H_2O$$

Net reaction: $6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$

18.   Which of the following complex species is not expected to exhibit optical isomerism?

(1) $\left[Co(en)_2 Cl_2\right]^+$
(2) $\left[Co(NH_3)_3 Cl_3\right]$

(3) $\left[Co(en)(NH_3)_2 Cl_2\right]^+$
(4) $\left[Co(en)_3\right]^{3+}$

Sol.   **(2)**
$[Co(NH_3)_3Cl_3]$ exists in two forms (facial and meridonial)

facial   meridonial

Both of these forms are achiral. Hence, $[Co(NH_3)_3Cl_3]$ does not show optical isomerism.

19. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0^0C. As it does so, it absorbs 208J of heat. The values of q and w for the process will be: (R = 8.314 J/mol K) (ℓ n 7.5 = 2.01)

(1) q = – 208 J, w = – 208 J   (2) q = – 208 J, w = + 208 J

(3) q = + 208 J, w = + 208 J   (4) q = + 208 J, w = – 208 J

Sol. **(4)**

Process is isothermal reversible expansion, hence $\Delta U = 0$.

$\therefore$ q = –W

As q = +208 J

Hence W = –208 J

20. A gaseous hydrocarbon gives upon combustion 0.72 g of water and 3.08 g of CO_2. The empirical formula of the hydrocarbon is:

(1) C_3H_4 (2) C_6H_5

(3) C_7H_8 (4) C_2H_4

Sol. **(3)**

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$$

Weight (g)   3.08 g   0.72 g

moles   0.07   0.04

$$\frac{x}{y/2} = \frac{0.07}{0.04}$$

$$\Rightarrow \frac{x}{y} = \frac{7}{8}$$

21. The order of stability of the following carbocations:

$$\overset{\oplus}{C}H_2$$

$$H_2C=CH-\overset{\oplus}{C}H_2 \; ; \; H_3C-CH_2-\overset{\oplus}{C}H_2 \; ;$$
$$\text{I} \qquad\qquad\qquad \text{II}$$

III

is:

(1) II > III > I   (2) I > II > III

(3) III > I > II   (4) III > II > I

Sol. **(3)**

Order of stability is III > I > II.

(Stability ∝ extent of delocalization)

22. Which of the following represents the correct order of increasing first ionization enthalpy for Ca, Ba, S, Se and Ar?
(1) S < Se < Ca < Ba < Ar
(2) Ba < Ca < Se < S < Ar
(3) Ca < Ba < S < Se < Ar
(4) Ca < S < Ba < Se < Ar

Sol. **(2)**
Increasing order of first ionization enthalpy is
Ba < Ca < Se < S < Ar

23. For gaseous state, if most probable speed is denoated by C*, average speed by $\overline{C}$ and mean square speed by C, then for a large number of molecules the ratios of these speeds are:
(1) $C^* : \overline{C} : C = 1.128 : 1.225 : 1$
(2) $C^* : \overline{C} : C = 1 : 1.128 : 1.225$
(3) $C^* : \overline{C} : C = 1 : 1.125 : 1.128$
(4) $C^* : \overline{C} : C = 1.225 : 1.128 : 1$

Sol. **(2)**
$$C^* = \sqrt{\frac{2RT}{M}}, \ \overline{C} = \sqrt{\frac{8RT}{\pi M}}, \ C = \sqrt{\frac{3RT}{M}}$$

24. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was:
(1) Methylamine
(2) Ammonia
(3) Phosgene
(4) Methylisocyanate

Sol. **(4)**
It was methyl isocyanate (CH_3NCO)

25. Consider the following reaction:

$$xMnO_4^- + yC_2O_4^{2-} + zH^+ \longrightarrow xMn^{2+} + 2yCO_2 + \frac{z}{2}H_2O$$
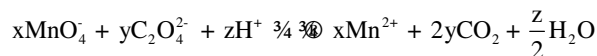
The values of x, y and z in the reaction are, respectively:
(1) 2, 5 and 8
(2) 2, 5 and 16
(3) 5, 2 and 8
(4) 5, 2 and 16

Sol. **(2)**
$$2MnO_4^- + 5C_2O_4^{-2} + 16H^+ \longrightarrow 2Mn^{+2} + 10CO_2 + 8H_2O$$
x = 2, y = 5, z = 16

26. Which of the following exists as covalent crystals in the solid state?
(1) Silicon
(2) Sulphur
(3) Phosphorous
(4) Iodine

Sol. **(1)**
Silicon (Si) – covalent solid
Sulphur (S_8) – molecular solid
Phosphorous (P_4) – Molecular solid
Iodine (I_2) – Molecular solid

27. Compound (A), C_8H_9Br, gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives a acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A).

(1)

(2)

(3)

(4)

Sol. **(3)**

$+$ AgBr $\downarrow$
(pale yellow)

pthalic anhydride
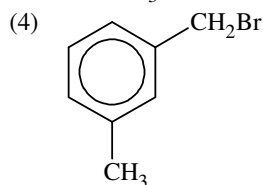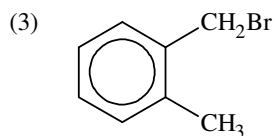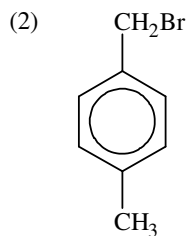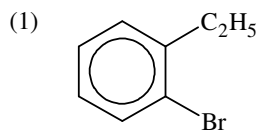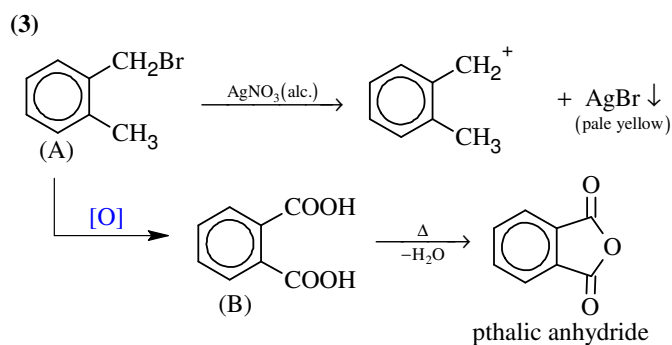
28. Energy of an electron is given by $E = -2.178 \times 10^{-18} J \left(\dfrac{Z^2}{n^2} \right)$. Wavelength of light required to excite an

electron in an hydrogen atom from level $n = 1$ to $n = 2$ will be
$(h = 6.62 \times 10^{-34}$ Js and $c = 3.0 \times 10^8$ ms$^{-1})$
(1) 2.816×10^{-7} m
(2) 6.500×10^{-7} m
(3) 8.500×10^{-7} m
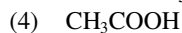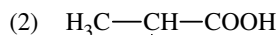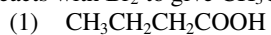(4) 1.214×10^{-7} m

Sol. **(4)**

$$E = \frac{hc}{\lambda} = 2.178 \times 10^{-18} \times Z^2 \left[\frac{1}{1^2} - \frac{1}{2^2} \right]$$
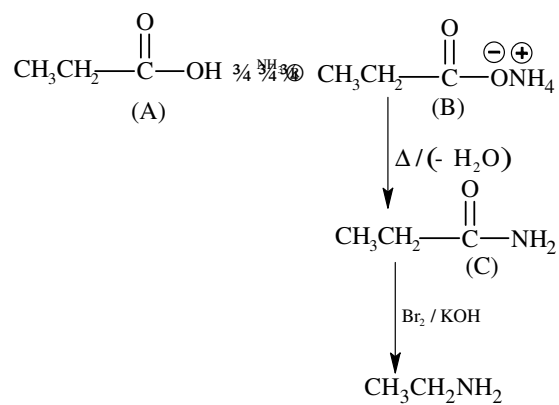
$$\Rightarrow \quad \lambda = 1.214 \times 10^{-7}\, m$$

29. An organic compound A upon reacting with NH_3 gives B. On heating B gives C. C in presence of KOH reacts with Br_2 to give $CH_3CH_2NH_2$. A is
(1) $CH_3CH_2CH_2COOH$
(2) $H_3C-CH-COOH$ with CH_3 substituent
(3) CH_3CH_2COOH
(4) CH_3COOH

Sol. **(3)**

$$CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow{NH_3} CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\ominus}{O}N\overset{\oplus}{H_4}$$

(A)　　　　　　　　　　　(B)

$$\downarrow \Delta/(-\ H_2O)$$

$$CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$$

(C)

$$\downarrow Br_2\ /\ KOH$$

$$CH_3CH_2NH_2$$

30. In which of the following pairs of molecules/ions, both the species are not likely to exist?

(1) H_2^-, He_2^{2-} 　　　　　　　　(2) H_2^{2+}, He_2

(3) H_2^-, He_2^{2+} 　　　　　　　　(4) H_2^+, He_2^{2-}

Sol. **(2)**

Bond order of H_2^{2+} and He_2 is zero, thus their existence is not possible.