IIT-JEE 2003 Mains Questions & Solutions - Chemistry

(The questions are based on memory)

Break-up of questions:

Physical	Inorganic	Organic
8	4	8

1. Write the balanced chemical reactions involved in the extraction of lead from Galena. Mention oxidation state of lead in litharge. **[2]**

Sol. The reactions involved in the extraction of lead from galena (PbS) are

$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$

$PbS + 2O_2 \longrightarrow PbSO_4$

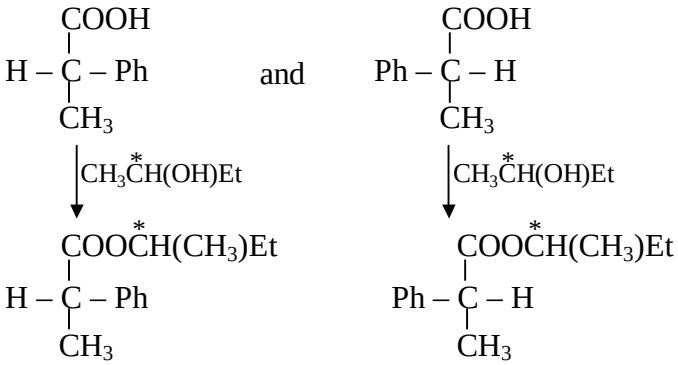
$2PbO + PbS \longrightarrow 3Pb + SO_2$

$PbSO_4 + PbS \longrightarrow 2Pb + 2SO_2$

Oxidation state of lead in litharge (PbO) is +2.

2. (±)2–phenylpropanoic acid on treatment with (+) 2–butanol gives (A) and (B). Deduce their structures and also establish stereochemical relation between them. **[2]**

Sol. The two stereoisomers of 2–phenylpropanoic acid in the racemic mixture are



(A) (B)

(A) and (B) are diastereomers.

3. Find the molarity of water. Given: $\rho = 1000\ kg/m^3$ **[2]**

Sol. Let us consider 1 litre of water.

$\therefore$ Number of moles of solute present in 1 litre = $\frac{1000}{18}$ = 55.56 M

4. Name the Hetrogenous catalyst used in the polymerization of ethylene.

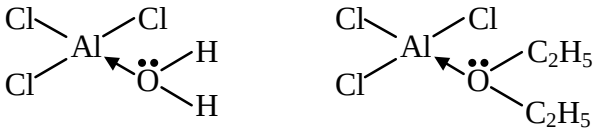
[2]

Sol. Zeigler Natta catalyst is a mixture of trialkyl aluminium and titanium tetrachloride which is used for the polymerization of ethylene.

5. Which of the two, anhydrous or hydrated $AlCl_3$ is more soluble in diethyl ether? Justify using the concepts of bonding in not more than 2 or 3 sentences.

[2]

Sol. Anhydrous $AlCl_3$ is more soluble in diethyl ether as the oxygen atom of the ether donates its pair of electrons to the vacant orbital of electron deficient aluminium of $AlCl_3$ through the formation of coordinate bond. But in case of hydrated $AlCl_3$ aluminium is not electron deficient as oxygen atom of water molecule has already donated its pair of electrons to meet the electron deficiency of aluminium.

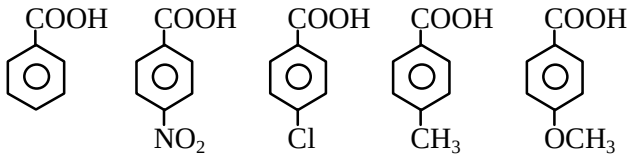


6. Match the following with their K_a values

Benzoic acid	4.2×10^{-5}
p–nitrobenzoic acid	3.3×10^{-5}
p–chlorobenzoic acid	6.4×10^{-5}
p–methylbenzoic acid	36.2×10^{-5}
p–methoxybenzoic acid	10.2×10^{-5}

[2]

Sol.



The correct order of acetic strength would be 2 > 3 > 1 > 4 > 5.
Therefore, the correct matching

Benzoic acid	6.4×10^{-5}
p–nitrobenzoic acid	36.2×10^{-5}
p–chlorobenzoic acid	10.2×10^{-5}
p–methylbenzoic acid	4.2×10^{-5}
p–methoxybenzoic acid	3.3×10^{-5}

7. The wavelength corresponding to maximum energy for hydrogen is 91.2 nm. Find the corresponding wavelength for He^+ ion.

[2]

Sol. For Maximum energy $n_1 = 1$ and $n_2 = \infty$

For H atom:

$$\frac{1}{\lambda_H} = R_H Z^2 \left(\frac{1}{1^2} - \frac{1}{\infty^2} \right)$$

$$\frac{1}{\lambda_H} = R_H Z_H^2 \qquad \ldots(i)$$

For He^+ ion:

$$\frac{1}{\lambda_{He^+}} = R_{He} \times Z_{He^+}^2 \qquad \ldots(ii)$$

Dividing equation (i) by (ii), we get

$$\frac{\lambda_{He^+}}{\lambda_H} = \frac{R_H Z_H^2}{R_{He^+} Z_{He^+}^2} \qquad (R_H = R_{He^+})$$

$$\lambda_{He^+} = \frac{\lambda_H}{4} = \mathbf{22.8\ nm}.$$

8.

$HOOC - (CH_2)_2 - \underset{\displaystyle NH_2}{\underset{|}{CH}} - COOH \quad ; \quad NH_2 - (CH_2)_4 - \underset{\displaystyle NH_2}{\underset{|}{CH}} - COOH$

Find the structure of possible two dipeptides. **[2]**

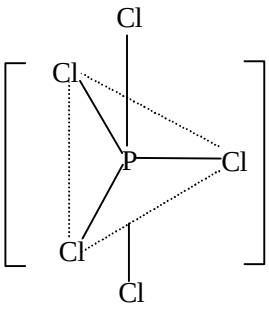
Sol. The structures of two possible dipeptides are

$$HOOC - (CH_2)_2 - \underset{\displaystyle \overset{\oplus}{N}H_3}{\underset{|}{CH}} - CO - NH - \underset{\displaystyle COO^-}{\underset{|}{CH}} - (CH_2)_4 - NH_2$$

$$HOOC - (CH_2)_2 - \underset{\displaystyle COO^-}{\underset{|}{CH}} - NH - CO - \underset{\displaystyle \overset{\oplus}{N}H_3}{\underset{|}{CH}} - (CH_2)_4 - NH_2$$

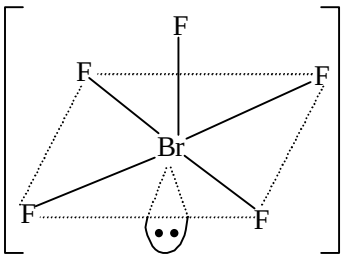
9. Using VSEPR theory deduce the structures of PCl_5 and BrF_5. **[2]**

Sol. **PCl_5:**



Triangular bipyramidal

BrF_5:



Square pyramidal

10. The average velocity of a gas is 400 m s^{-1}, find the rms velocity of the gas.

[2]

Sol. $C_{av} = \sqrt{\frac{8RT}{\pi M}}$ …(i)

$C_{rms} = \sqrt{\frac{3RT}{M}}$ …(ii)

$\therefore \quad \frac{C_{rms}}{C_{av}} = \sqrt{\frac{3RT}{M} \times \frac{\pi M}{8RT}} = \sqrt{\frac{3\pi}{8}}$

$\therefore \quad C_{rms} = \sqrt{\frac{3\pi}{8}} \times C_{av}$

$= \sqrt{\frac{3 \times 3.14}{8}} \times 400 = \mathbf{434.05\ ms^{-1}}$

11. (a) Will pH value of water be same at temperature 25°C and 4°C. Justify in not more than 2 or 3 sentences.

[2]

(b) Two students make Daniel cells in laboratory. They take $ZnSO_4$ from common stock with Cu as positive electrode. The emf of one cell is 0.03 V more than the other. The concentration of $CuSO_4$ in cell of higher emf is 0.5 M. Find the concentration of $CuSO_4$ in second cell.

Given: $\frac{2.3\ RT}{F} = 0.06\,V$

[2]

Sol.(a) pH of solution depends upon H^+ ion concentration, which depends on K_w which is a function of temperature. Therefore, change in temperature brings a change in pH value for given sample of water.

(b) Let the emf of 1st cell be *x* volt.
Emf of 2nd cell = (*x* + 0.03) V
$[Cu^{2+}]$ in 2nd cell = 0.5 M
$[Cu^{2+}]$ in 1st cell = ?

$E_1 = E_1^o - \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]_1}$

$E_2 = E_1^o - \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]_2}$

$E_2 - E_1 = E_1^o - \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]_2} - E_1^o + \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]_1}$

$$x + 0.03 - x = \frac{2.303RT}{2F}\left[\log\frac{[Zn^{2+}]}{[Cu^{2+}]_1} - \log\frac{[Zn^{2+}]}{[Cu^{2+}]_2}\right]$$

$$0.03 = 0.03\left[\log\frac{[Zn^{2+}]}{[Cu^{2+}]_1} \times \frac{[Cu^{2+}]_2}{[Zn^{2+}]}\right]$$

$$1 = \log\frac{[Cu^{2+}]_2}{[Cu^{2+}]_1}$$

$$1 = \log\frac{0.5}{[Cu^{2+}]_1}$$

$[Cu^{2+}]_1$ = **0.05 M**

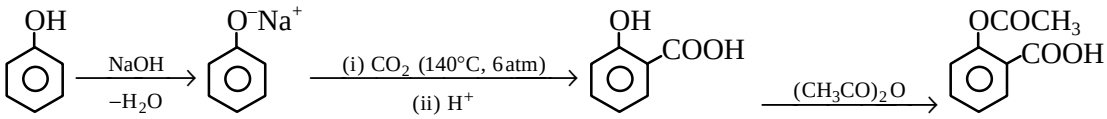
12. Carry out the following conversions.

(i) Phenol to Aspirin

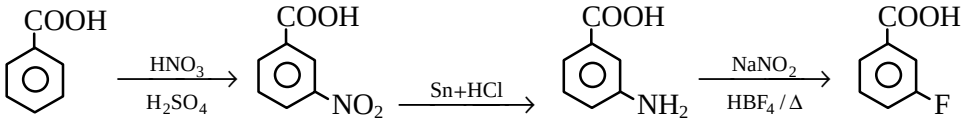
(ii) Benzoic acid to meta–fluorobenzoic acid in not more than three steps.

[4]

Sol.(i)



(ii)

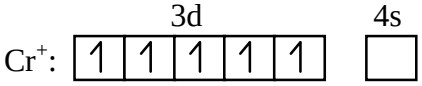


13. Write the IUPAC name of the compound $K_2[Cr(NO)(CN)_4(NH_3)]$. Spin magnetic moment of the complex, μ = 1.73 BM. Give the structure of anion.

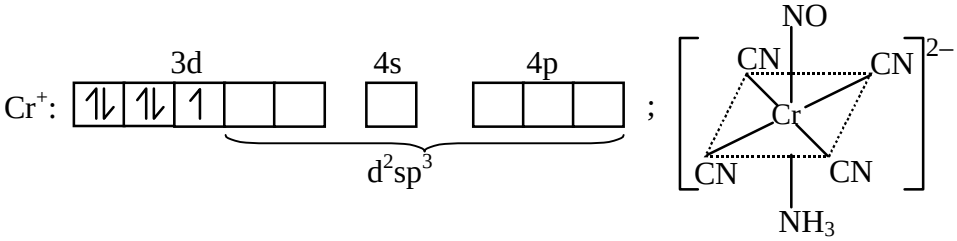
[4]

Sol. The spin magnetic moment, μ of the complex is 1.73 BM. It means that nucleus of the complex, chromium ion has one unpaired electron. So the ligand NO is unit positively charged.

IUPAC name: Potassium amminetetracyanonitrosoniumchromate (I).



Electronic configuration of Cr^+ under the influence of strong field ligand CN^- is



So,

Hybridization: d^2sp^3
Shape: Octahedral

14. A salt mixture consists of a yellow solid (A) and a colourless solid (B). The aqueous solution of the mixture

(i) On passing H_2S, we get a black precipitate of (C), which dissolves only in aqua regia. On extraction and reaction with $SnCl_2$ a grayish white precipitate is obtained.

(ii) On treatment with ammonium hydroxide a reddish brown precipitate (D) is obtained.

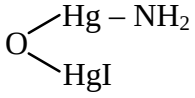
The sodium extract of the solution gives the following tests

(i) On reaction with $AgNO_3$ it gives a yellow precipitate which is insoluble in NH_3.

(ii) On shaking with $FeCl_3$ and CCl_4 a violet colouration in CCl_4 layer is obtained.

Mixture on performing flame test gives lilac colour. Identify the compounds (A), (B), (C) and (D).

[4]

Sol. (A): HgI_2 (B): KI (C): HgS (D): 

15. (a) For He molecule C_v value is 3/2 R, independent of temperature. But for H_2 at very low temperature 3/2 R, at moderate temperature 5/2 R and at higher temperature > 5/2 R. Explain the temperature dependence and justify.

[2]

(b) Consider the three solvents of identical molar masses. Match their boiling point with their K_b values:

Solvents	Boiling point	K_b values
X	100°C	0.92
Y	27°C	0.63
Z	283°C	0.53

[2]

Sol.(a) Helium molecule is monoatomic so it has just three degrees of freedom corresponding to the three translational motion at all temperature and hence C_v value is always 3/2 R.

Hydrogen molecule is diatomic whose atoms are not rigidly held so they vibrate about a well defined average separation. For hydrogen molecule we have rotational and vibrational motion both besides translational motion. These two additional contributions increase its total heat capacity. Contribution from vibrational motion is not appreciable at low temperature but increases from 0 to R on raising temperature.

(b) Higher value of K_b of a solvent suggests larger polarity of solvent molecules which in turn implies higher boiling point due to dipole–dipole interaction. Therefore, the correct order of K_b values of the three given solvents is

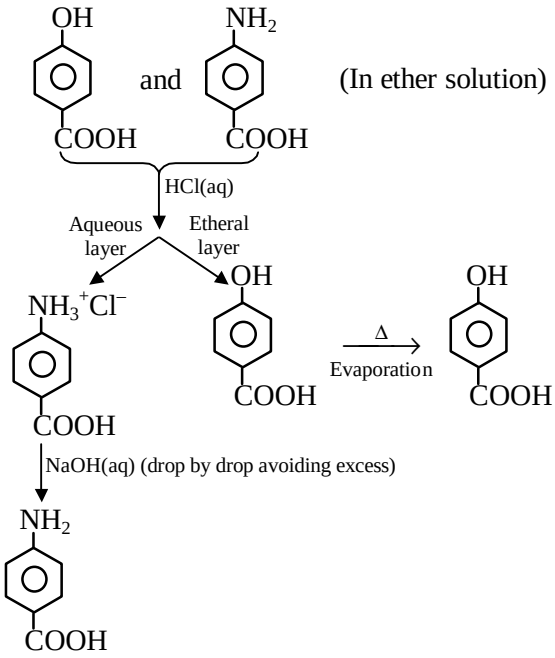
Solvents Boiling point K_b values

X	100°C	0.63
Y	27°C	0.53
Z	283°C	0.92

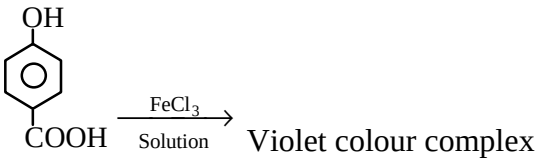
16. You have an ether solution containing 4–hydroxybenzoic acid and 4–aminobenzoic acid. Explain how will you separate the two in not more than 3 steps. Give confirmatory tests with reagents and conditions for functional groups of each.

[4]

Sol.

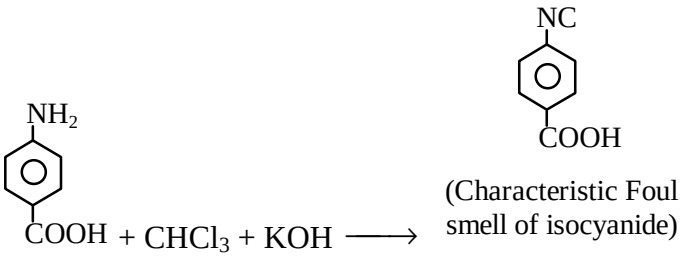


Test of Phenolic group:



Violet colour complex

Test of 1°–amino group:



(Characteristic Foul smell of isocyanide)

Test of Carboxylic group:

$$-COOH \xrightarrow{NaHCO_3} CO_2\uparrow \xrightarrow[\text{lime water}]{\text{With effervesence}} \text{Milky solution}$$

17. (A), $C_6H_{12} \xrightarrow{HCl}$ (B), $C_6H_{13}Cl$ + (C), $C_6H_{13}Cl$

(B) $\xrightarrow{\text{Alcoholic KOH}}$ (D) (an isomer of (A))

(D) $\xrightarrow{\text{Ozonolysis}}$ (E) (Positive iodoform and negative Fehling's solution test)

(A) $\xrightarrow{\text{Ozonolysis}}$ (F) + (G) (Positive Tollen's test for both)

(F) + (G) $\xrightarrow{\text{conc. NaOH}}$ HCOONa + A primary alcohol

Identify the compounds (A) to (D).

[4]

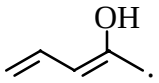
Sol. (A): $CH_2 = CH - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - CH_3$ (B): $CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{C}}}H - \underset{\displaystyle CH_3}{\overset{\displaystyle Cl}{\overset{|}{\underset{|}{C}}}} - CH_3$

(C): $CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle Cl}{\overset{|}{\underset{|}{C}}}}H - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - CH_3$ (D): $CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{C}}} = C - CH_3$

(E): $CH_3 - \overset{\displaystyle O}{\overset{\|}{C}} - CH_3$ (F): $CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{C}}} - CHO$ (G): HCHO

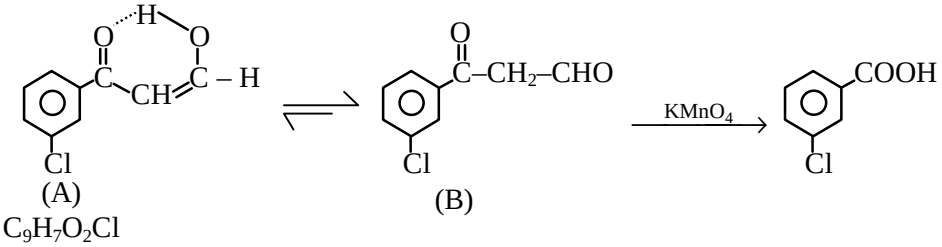
18. (a) A compound $C_9H_7O_2Cl$ exists predominantly in enol form (A) and also in keto form (B). On oxidation with $KMnO_4$ it gives m–chlorobenzoic acid as one of the products. Identify the compounds (A) and (B).

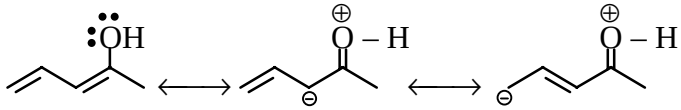
[2]

(b) Draw the resonating structures of  .

[2]

Sol.(a)



(b) 

19. (a) Marbles of diameter 10 mm are to be put in a square area of side 40 mm so that their centers are within this area. Find the maximum number of marbles per unit area and deduce an expression for calculating it.

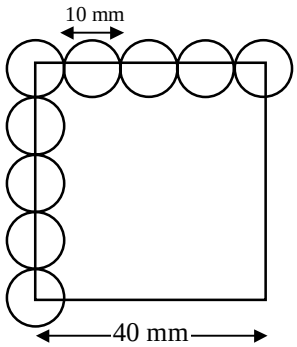
[2]

(b) In a solution of 100 ml 0.5 M acetic acid, one g of active charcoal is added, which adsorbs acetic acid. It is found that the concentration of acetic acid becomes 0.49 M. If surface area of charcoal is 3.01×10^2 m^2, calculate the area occupied by single acetic acid molecule on surface of charcoal.

[2]

Sol.(a)

Side of a square = 40 mm
Diameter of a marbles = 10 mm
Number of marbles along an edge of the square with their centers within the square is equal to 5.
Maximum number of marbles per unit area $= 5 \times 5 = 25$



(b) Number of moles of acetic acid in 100 ml before adding charcoal = 0.05
Number of moles of acetic acid in 100 ml after adding charcoal = 0.049
Number of moles of acetic acid adsorbed on the surface of charcoal = 0.001
Number of molecules of acetic acid adsorbed on the surface of charcoal
$= 0.001 \times 6.02 \times 10^{23} = 6.02 \times 10^{20}$
Surface area of charcoal = 3.01×10^2 m^2
Area occupied by single acetic acid molecule on the surface of charcoal

$$= \frac{3.01 \times 10^2}{6.02 \times 10^{20}} = 5 \times 10^{-19}\ m^2$$

20. $Na_2CO_3 \xrightarrow{SO_2} (A) \xrightarrow{Na_2CO_3} (B) \xrightarrow[Sulphur/\Delta]{Elemental} (C) \xrightarrow{I_2} (D)$

Identify the compounds (A), (B), (C), (D) and give oxidation state of sulphur in each compound.

[4]

Sol. (A): $\overset{+4}{NaHSO_3}$ (B): $\overset{+4}{Na_2SO_3}$ (C): $\overset{+2}{Na_2S_2O_3}$ (D): $\overset{+2.5}{Na_2S_4O_6}$