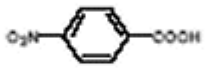
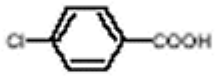
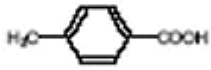
Chemistry

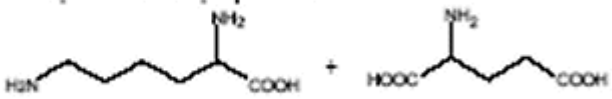
Time: 2 hours ***Marks: 60***

[10 × 2 = 20]

1. Calculate the molarity of water if its density is 1000 kg/m^3.
2. The average velocity of gas molecules is 400 m/sec. Calculate its rms velocity at the same temperature.
3. Write down the heterogeneous catalyst involved in the polymerisation of ethylene.
4. Which one is more soluble in diethyl ether anhydrous $AlCl_3$ or hydrous $AlCl_3$? Explain in terms of bonding.
5. Using VSEPR theory, draw the shape of PCl_5 and BrF_5.
6. A racemic mixture of (±) 2–phenyl propanoic acid on esterification with (+) 2–butanol gives two esters. Mention the stereochemistry of the two esters produced.
7. Wavelength of high energy transition of H-atoms is 91.2nm. Calculate the corresponding wavelength of He atoms.
8. Match the K_a values

		K_a
a)	Benzoic acid	3.3×10^{-5}
b)		6.3×10^{-5}
c)		30.6×10^{-5}
d)		6.4×10^{-5}
e)		4.2×10^{-5}

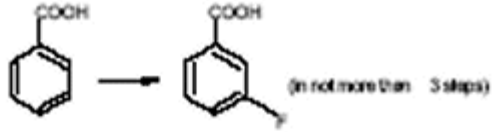
9. Write down reactions involved in the extraction of Pb. What is the oxidation number of lead in litharge?
10. Following two amino acids lionise and glutamine form dipeptide linkage. What are two possible dipeptides?

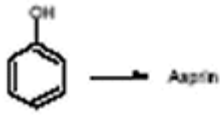


[10 × 4 = 40]

11. a) You are given marbles of diameter 10 mm. They are to be placed such that their centres are lying in a square bound by four lines each of length 40 mm. What will be the arrangements of marbles in a plane so that maximum number of marbles can be placed inside the area? Sketch the diagram and derive expression for the number of molecules per unit area.
    b) 1 gm of charcoal adsorbs 100 ml 0.5 M CH_3COOH to form a monolayer, and thereby the molarity of CH_3COOH reduces to 0.49. Calculate the surface area of the charcoal adsorbed by each molecule of acetic acid. Surface area of charcoal = 3.01×10^2 m^2/gm.
12. a) Will the pH of water be same at 4°C and 25°C? Explain.
    b) Two students use same stock solution of $ZnSO_4$ and a solution of $CuSO_4$. The emf of one cell is 0.03 V higher than the other. The conc. of $CuSO_4$ in the cell with higher emf value is 0.5 M. Find out the conc. of $CuSO_4$ in the other cell (2.203 RT/F = 0.06).

13. Convert

a) 

b) 

14. There is a solution of p–hydroxy benzoic acid and p–amino benzoic acid. Discuss one method by which we can separate them and also write down the confirmatory tests of the functional groups present.

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

$B \xrightarrow{\text{alc. KOH}} D$ (isomer of A)

$D \xrightarrow{\text{ozonolysis}} E$ (it gives negative test with Fehling solution but responds to iodoform test).

$A \xrightarrow{\text{Ozonolysis}} F + G$ (both give positive Tollen's test but do not give iodoform test).

$F + G \xrightarrow{\text{conc. NaOH}} HCOONa +$ a primary alcohol

Identify from A to G.

16. Identify the following:

$$Na_2CO_3 \xrightarrow{SO_2} A \xrightarrow{Na_2CO_3} B \xrightarrow[\Delta]{\text{Elemental S}} C \xrightarrow{I_2} D$$

Also mention the oxidation state of S in all the compounds.

17. Write the IUPAC nomenclature of the given complex along with its hybridisation and structure.

$K_2[Cr(NO)(NH_3)(CN)_4]$, μ = 1.73 BM

18. A mixture consists A (yellow solid) and B (colourless solid) which gives lilac colour in flame.

a) Mixture gives black precipitate C on passing $H_2S_{(g)}$.

b) C is soluble in aqua–regia and on evaporation of aqua–regia and adding $SnCl_2$ gives greyish black precipitate D.

The salt solution with NH_4OH gives a brown precipitate.

i) The sodium extract of the salt with $CCl_4/FeCl_3$ gives a violet layer.

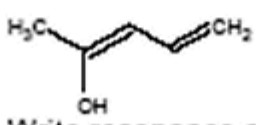
ii) The sodium extract gives yellow precipitate with $AgNO_3$ solution which is insoluble in NH_3.

Identify A and B, and the precipitates C and D.

19. a) Match the following if the molecular weights of X, Y and Z are same.

	Boiling Point	K_b
X	100	0.68
Y	27	0.53
Z	253	0.98

b) C_v value of He is always 3R/2 but C_v value of H_2 is 3R/2 at low temperature and 5R/2 at moderate temperature and more than 5R/2 at higher temperature explain in two to three lines.

20. a) 

Write resonance structure of the given compound.

b) Compound A of molecular formula $C_3H_7O_2Cl$ exists in ketoform and predominantly in enolic form 'B'. On oxidation with $KMnO_4$, 'A' gives m-chlorobenzoic acid.

Chemistry Solutions

1. 1 litre water = 1kg i.e. 1000 g water ($\because$ d = 1000 kg/m^3)

$$\equiv \frac{1000}{18} = 55.55 \text{ moles of water}$$

So, molarity of water = 55.55M

2. $C_{rms} = \sqrt{\frac{3RT}{M}}, C_{av} = \sqrt{\frac{8RT}{\pi M}}$

$$\frac{C_{rms}}{C_{av}} = \sqrt{\frac{3RT}{M}} \times \sqrt{\frac{\pi M}{8RT}} = \sqrt{\frac{3\pi}{8}} = 1.085$$

$C_{rms} = 1.085 \times C_{av}$

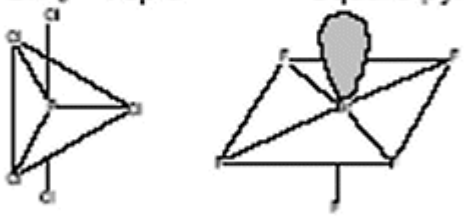
$= 1.085 \times 400$

$= 434 \text{ ms}^{-1}$

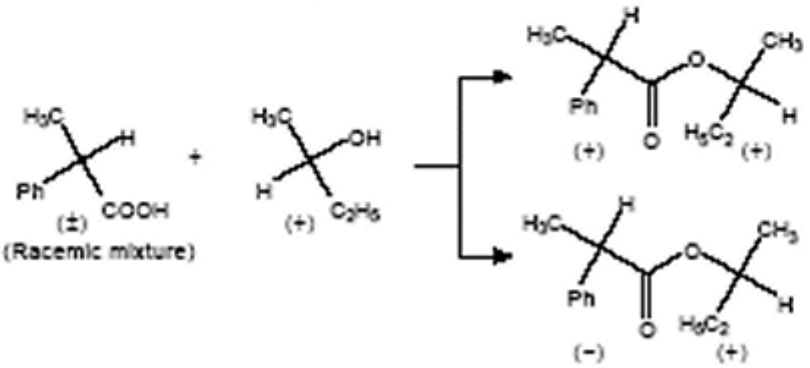
3. Ziggler Natta catalyst ($R_3Al + TiCl_4$)

4. Oxygen atom of diethyl ether by donation of its lone pair to vacant 3p orbitals of Al in anhydrous $AlCl_3$ solvates it more compared to hydrous $AlCl_3$.

5. PCl_5 : sp^3d Trigonal bipyramid
BrF_5 : sp^3d^2 Square pyramidal



6.



The bonds attached to the chiral carbon in both the molecules are not broken during the esterification reaction. (+) Acid reacts with (+) alcohol to give an (++) ester while (–) acid reacts with (+) alcohol to give (+ –) ester. These two esters are diastereoisomers.

$$\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\frac{\lambda_{He}}{\lambda_H} = \frac{Z_H^2}{Z_{He}^2} = \frac{1}{4}$$

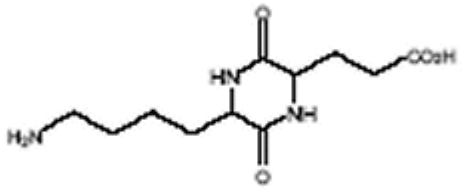
So, $\lambda_{He} = \frac{1}{4} \times 91.2 = 22.8$ nm

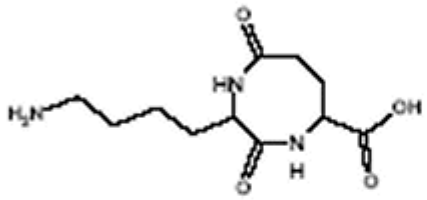
8.

		K_a value
a)	Benzoic acid	6.3×10^{-5}
b)	p–NO_2– C_6H_4– COOH	30.6×10^{-5}
c)	p–Cl – C_6H_4– COOH	6.4×10^{-5}
d)	p–CH_3–C_6H_4 – COOH	4.3×10^{-5}
e)	p–OCH_3– C_6H_4 – COOH	3.3×10^{-5}

9. $2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$
$PbS + 2O_2 \longrightarrow PbSO_4$
$PbS + 2PbO \longrightarrow 3Pb + SO_2$
$PbS + PbSO_4 \longrightarrow 2Pb + 2SO_2$
Oxidation number of Pb in litharge (PbO) is +2.

10.





11. a) Area of quadrilateral = $2\frac{1}{2} \times a \times a \times \sin\theta = a^2 \times \sin\theta$
Where a = length of the side of the quadrilateral
To have the maximum area, i.e. $\sin\theta = 1$
or $\theta = 90°$. In other words, the quadrilateral must be a square
Area of square = $4 \times 4 = 16$ cm^2
Again to have the maximum no. of spheres the packing must be hcp
Maximum no. of sphere s= 18 (see fig. 2)
Area = 16 sq. cm

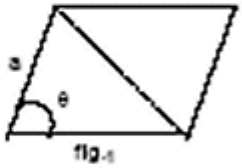
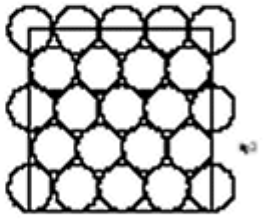


fig-1



$\therefore$ No. of spheres per cm^2 = $\frac{18}{16} = 1.125$

b) No. of m mole of CH_3COOH initially taken = $100 \times 0.5 = 50$
Since concentration reduces to 0.49 M
$\therefore$ Final no. of m mole of CH_3COOH = $100 \times 0.49 = 49$
$\therefore$ No. of m mole of CH_3COOH get adsorbed
= 50 – 49 = 1
$\therefore$ No. of molecules of CH_3COOH get adsorbed = 6.02×10^{20}
Since 1g charcoal has area = 3.01×10^2 m^2
$\because$ 6.02×10^{20} molecules of acetic acid gets adsorbed in 3.01×10^2 m^2 area

$\therefore$ 1 molecule of acetic acid gets adsorbed = $\frac{3.01 \times 10^2}{6.02 \times 10^{20}} = \frac{1}{2} \times 10^{-18} = 5 \times 10^{-19}$ m^2

12. a) At 25°C: $K_w = 10^{-14}$ $pK_w = 14$ $\therefore$ pH + pOH = 14
Pure water being neutral, pH = pOH = 7

$Zn \mid Zn^{2+}(C_1) \parallel Cu^{2+}(C = ?) \mid Cu, \quad E_{cell} = E_1$

$Zn \mid Zn^{2+}(C_2) \parallel Cu^{2+}(C = 0.5\ M) \mid Cu \quad E_{cell} = E_2$ where $E_2 > E_1$

From question

$E_2 - E_1 = 0.03$ and $C_2 = C_1$

The cell reaction is $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$, $Q = \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$

So, $E_{cell} = E^0_{cell} - \dfrac{0.06}{2}\log\dfrac{[Zn^{2+}]}{[Cu^{2+}]}$

Thus, $E_1 = E^0_{cell} - \dfrac{0.06}{2}\log\dfrac{C_1}{C}$

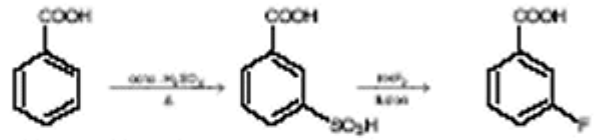
$E_2 = E^0_{cell} - \dfrac{0.06}{2}\log\dfrac{C_2}{0.5}$

So, $E_2 - E_1 = \dfrac{0.06}{2}\left[\log\dfrac{C_2}{C}\times\dfrac{0.5}{C_1}\right] \Rightarrow 0.03 = \dfrac{0.06}{2}\log\dfrac{0.5}{C} \Rightarrow$

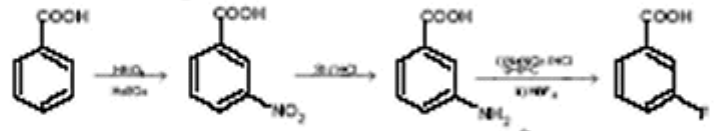
$\log\dfrac{0.5}{C} = 1$

$C = 0.05$ M

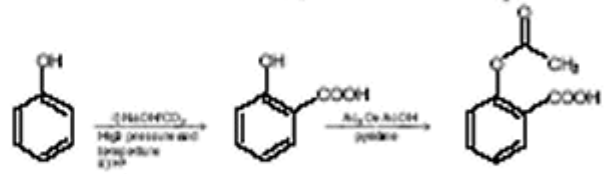
13. a)



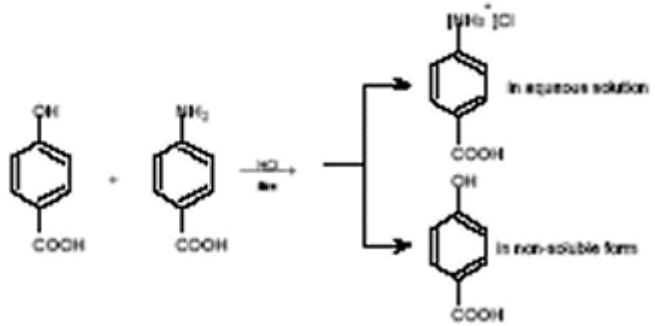
Alternatively

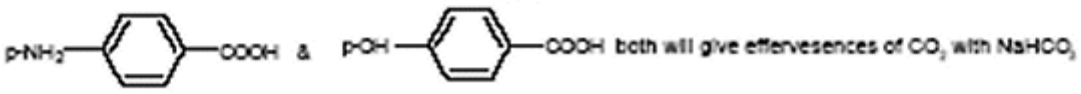


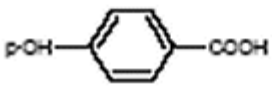
b)



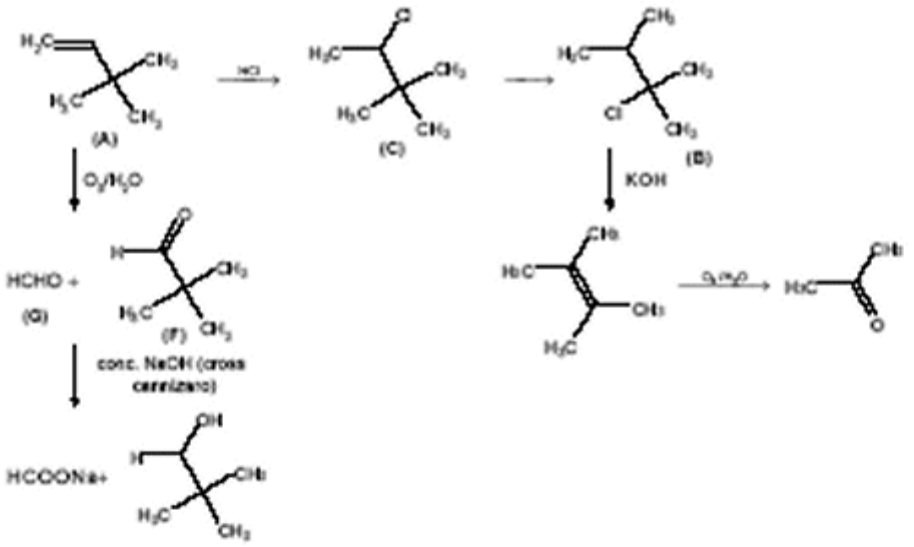
14.







15.



16. $Na_2CO_3 + 2SO_2 + H_2O \longrightarrow \underset{(A)}{2NaHSO_3} + CO_2$

$2NaHSO_3 + Na_2CO_3 \longrightarrow \underset{(B)}{2Na_2SO_3} + H_2O + CO_2$

$Na_2SO_3 + S \longrightarrow \underset{(C)}{2Na_2S_2O_3}$

$2Na_2S_2O_3 + I_2 \longrightarrow \underset{(D)}{2Na_2S_4O_6} + 2NaI$

Oxidation states of 'S' are
in (A) and (B) (+4)
in (C) (+6, –2)
in (D) (+5, 0)

17. Potassiumamminetetracyano(C)nitrosoniumchromium(I)
Cr is in + 1 state and d^2sp^3 hybridisation

$\mu = \sqrt{n(n+2)} = \sqrt{3} = 1.73$ B.M.

18. [A = KI, B = HgI_2]

$HgI_2 + H_2S \longrightarrow HgS + 2HI$

$HgI_2 \xrightarrow{\text{aqua-regia}} HgCl_2$

$HgCl_2 + SnCl_2 \longrightarrow \underset{\text{(greyish black)}}{Hg\downarrow} + SnCl_4$

$2KI + HgI_2 \longrightarrow \underset{\text{orange}}{K_2[HgI_4]}$; $2K_2HgI_4 + NH_3 + 3KOH \longrightarrow \underset{\text{Iodide of Millon's base}}{[HgOHgNH_2]} + 7KI + 2H_2O$

$Na_2CO_3 + HgI_2 \longrightarrow Hg\downarrow + NaI + CO_2 + O_2\uparrow$

$NaI + Fe^{3+} \longrightarrow \underset{(CCl_4 \text{ layer violet})}{I_2} + Na^+ + Fe^{2+}$

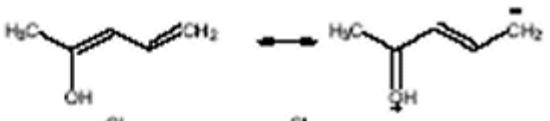
$AgNO_3 + I^- \longrightarrow \underset{\text{(insoluble in } NH_3)}{\underset{\text{Yellow}}{AgI}}$

19. a) $K_b = \dfrac{RT_b^2}{1000\, l_v} = \dfrac{RT_b^2M}{1000\Delta H_v} = \dfrac{RT_bM}{1000\Delta S}$ $\left[\because l_v = \dfrac{\Delta H_v}{M}\right]$

A change from liquid to vapour at boiling point is accompanied by increase in disorderness and hence increase in entropy. However, since a vapour is highly disordered state the difference of the extent of disorderness between vapour

R/2 = 3R/2. Hydrogen molecule is diatomic. However, at low temperature rotational and vibrational contribution are also zero so C_v is 3R/2. At moderate temperature rotational contribution (C = 2× R/2) also becomes dominant and at even higher temperature vibrational contribution (1 × R) also becomes significant.

20. a)



b)