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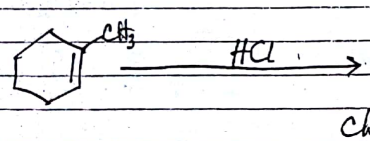
UNASE – MOCKS –01–
P525/1 – CHEMISTRY – 2019
MARKING GUIDE

(a) $Zn_{(s)}/Zn^{2+}_{(aq)} // MnO_{2(s)}/H^+_{(l)}/Mn_2O_{3(s)}/OH^-_{(aq)}/C_{(s)}$ or $Pt_{(s)}$ ✓ (01)

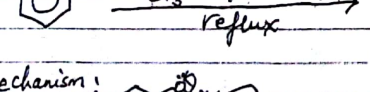
(b) $Zn_{(s)} + 2MnO_{2(s)} + H_2O_{(l)} \longrightarrow Zn^{2+}_{(aq)} + Mn_2O_{3(s)} + 2OH^-_{(aq)}$ ✓✓ (01½)

(c) Emf of cell reaction = +0.74 – −0.176 ✓
= (+)✓1.50V ✓ (01½)

(d) Reaction is feasible because Emf of cell is positive ✓ (01)
05

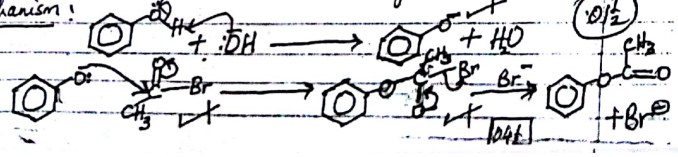
(i) 

Chloromethylcyclohexane (01½)

(ii) 

Phenylethanoate (01½)

Mechanism: (01½)



04

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3. (i) Purple solution turns colourless ✓ (0½)

$2MnO^-_{4(aq)} + 5SO_{2(g)} + 2H_2O_{(l)} \longrightarrow 2Mn^{2+}_{(aq)} + 5SO^{2-}_{4(aq)} + 4H^+_{(aq)}$ ✓✓ (01½)

(ii) purple solution turns brown ✓ (02)

$2MnO^-_{4(aq)} + 10I^-_{(aq)} + 16H^+_{(aq)} \longrightarrow 2Mn^{2+}_{(aq)} + 5I_{2(aq)} + 8H_2O_{(l)}$ ✓✓

04

4. (a) (i) $BrCH_2COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons BrCH_2COO^-_{(aq)} + H_3O^+_{(aq)}$ ✓✓ (01½)

accept $BrCH_2COOH_{(aq)} \rightleftharpoons BrCH_2COO^-_{(aq)} + H^+_{(aq)}$

(ii) $K_a = \dfrac{[BrCH_2COO^-][H^+]}{[BrCH_2COOH]}$ ✓ (02½)

(b) (i) $\Lambda^\circ_{BrCH_2COOH} = (\Lambda^\circ_{HNO_3} + \Lambda^\circ_{BrCH_2COONa}) - \Lambda^\circ_{NaNO_3}$ ✓

$\Lambda^\circ_{BrCH_2COOH} = 421 + 89.3 - 121.6$ ✓ (01½)
$= 388.7\ \Omega^{-1}cm^2mol^{-1}$ ✓

(ii) $\because K_a = \dfrac{C\alpha^2}{1-\alpha}$ ✓

$\alpha = \dfrac{\Lambda_{eff}}{\Lambda_\infty} = \dfrac{43.8}{388.7} = 0.113$ ✓

reject remains constant

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$$K_a = \frac{(0.113)^2 \times 0.11}{1 - 0.113} = \frac{1.2769 \times 10^{-3}}{0.887} \checkmark$$

$$K_a = 1.44 \times 10^{-3} \checkmark \quad (03\frac{1}{2})$$

6

5.

Complex ion	oxn state of Co	Name of complex ion
$[Co(NH_3)_4Cl]^+$	+2 ✓	chlorotetraammine cobalt(II) ion ✓
$[Cu(Br)_4(H_2O)_2]^{2-}$	+2 ✓	tetrabromodiaquacuprate(II) ion ✓
$[Zn(OH)_4]^{2-}$	+2 ✓	Tetrahydroxozincate(II) ion ✓

(04½)

b) Transition metal ions have a high charge density and can strongly attract lone pairs of electrons from the ligands. ✓
Transition metal atoms posses accessible vacant/empty 3d-orbitals that can accept and accomodate lone pairs of electrons from ligands. ✓

(02)

06½

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6 a) $CH_2=CH_2 \xrightarrow[\text{Warm (heat)}]{H_2O/H^+} CH_3CH_2OH \xrightarrow[\text{heat}]{Cr_2O_7^{2-}/H^+ \text{ (any oxidant)}} CH_3COOH$

$CH_3COOH \xrightarrow{PCl_5} CH_3COCl \xrightarrow{\text{Conc } NH_3,\ \text{reflux}} CH_3CONH_2$

$CH_3COOH \xrightarrow[\text{heat}]{(NH_4)_2CO_3} CH_3CONH_2$ (03)

b) $CH_3CHO \xrightarrow[\text{dry ether}]{LiAlH_4} CH_3CH_2OH$

$CH_3CHO \xrightarrow[\text{heat}]{MnO_4^-/H^+} CH_3COOH$

$CH_3COOH + CH_3CH_2OH \xrightarrow[\text{Warm}]{\text{Conc } H_2SO_4} CH_3COOCH_2CH_3$ (02½)

$CH_3CH_2OH \xrightarrow[\text{Warm or heat } 60°]{CH_3COOH/\text{Conc } H_2SO_4/\text{reflux } H^+}$

05½

7 (a) If a constraint is subjected to a system in equilibrium the system adjusts so as to nullify the effect imposed by the constraint. (01)

(b) (i) Equilibrium position shifts from the right (to the left). (0½ mrk)

(ii) Equilibrium position remain unaltered/unchanged reject remains constant (0½)

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(c) $K_p = \frac{P_{HI}^2}{P_{H_2} \cdot P_{I_2}}$ ✓

Let the number of moles of H_2 and I_2 that reacted = x

$\therefore 1.6 = 2x$

$x = 0.8$ moles ✓

At equilibrium;

No. of moles of H_2 = No. of moles of I_2 = $1 - 0.8 = 0.2$ ✓

Total No. of moles = $0.2 + 0.2 + 1.6 = 2.0$ ✓

$P_{HI} = \frac{1.6}{2} \times 10 = 8$ atm ✓

$P_{H_2} = P_{I_2} = \frac{0.2}{2} \times 10 = 1$ atm ✓

$K_p = \frac{8^2}{1 \times 1} = 64$ ✓ (03½) [05½]

8 (a) Silicon (IV) oxide adopts a giant covalent structure in which the silicon and oxygen atoms are tetrahedrally joined by strong covalent bond ✓ forming a solid three dimensional structure. ✓

Carbon dioxide exists as discrete covalent molecules ✓ with a simple molecular structures ✓ The molecules are held by weak Vandeqwaals forces ✓ Thus CO_2 is gas. (03)

(b) In water NH_4NO_3 dissociates to form ammonium and nitrate ions. ✓

-or $NH_4NO_{3(s)} + (aq) \rightleftharpoons NH_{4(aq)}^+ + NO_{3(aq)}^-$

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The ammonium ion hydrolyses ✓ forming ammonia and hydroxonium ions. This reduces ✓ the concentration of ammonium ions in solution so more salt dissolves to restore equilibrium

$NH_{4(aq)}^+ + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + H_3O_{(aq)}^+$ (02)

[05]

9) 50g of water dissolves 30g of Y ✓

1000g of water dissolves $\left(\frac{30 \times 1000}{50}\right)$ g of Y

= 600g ✓

6.2°c is the freezing point depression caused by 600g of Y ✓

1.86°c is the freezing point depression cause by

$\left(\frac{600}{6.2} \times 1.86\right)$ g of Y ✓ (03)

Relative molecular mass of Y = 180 ✓

density of Y = 1.91 g/cm³

Candidates should write correct statements ✓ reject use of formula but give only 1 mark for 180 //

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b) $(CH_2O)_n = 180$

$12n + 2n + 16n = 180$

$30n = 180$

$n = 6$ ✓ (01)

Molecular formula of Y is $C_6H_{12}O_6$ ✓

c) $C_6H_{12}O_6 \xrightarrow[15°C]{\text{yeast (enzyme zymase)}} 2CH_3CH_2OH + 2CO_2$ ✓

$CH_3CH_2OH \xrightarrow{Cr_2O_7^{2-}/H^+,\ heat} CH_3COOH$ ✓ (01½)

$CH_3Cl \xleftarrow{Cl_2/uv} CH_4 \xleftarrow[heat]{\text{sodalime}} CH_3COOH$ ✓ (excess)

5

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10 (i) Magnesium contributes two electrons per atom towards the electron cloud formation of a metallic bond whereas sodium contributes one electron per atom. (03)
Consequently magnesium forms stronger metallic bonds than sodium which require a greater amount of energy to break.

(ii) P_4 molecules of phosphorus have a lower molecular mass than the S_8 molecules of Sulphur.
As a result the Van-der-waals forces holding the P_4 molecules of phosphorus are relatively weaker than those holding S_8 molecules of Sulphur. (03)
Smaller amount of energy is required to break the Van der waals forces in phosphorus.

(iii) Silicon adopts a giant covalent structure in which each silicon atom is tetrahedrally joined to the other silicon atom by strong covalent bonds forming a three dimensional (Net work/structure) of bonds. (03)
A greater amount of energy is required to break the many covalent bonds in the lattice

TOTAL

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a) % by mass of Oxygen/O = 100 − (63.69 + 14.77 + 1.85)
reject O_2 = 19.69 ✓

	Pb	H	O	C
No of moles	63.69 / 207	1.85 / 1	19.69 / 16	14.77 / 12
n	0.31	1.85	1.23	1.23 ✓
Mole ratio	0.31 / 0.31 :	1.85 / 0.31 :	1.23 / 0.31 :	1.23 / 0.31 ✓
n	1 :	6 :	4 :	4 ✓

Empirical formula is $PbH_6O_4C_4$ ✓ (02½)

(b) $\Delta t_f = (0 - 0.14) = 0.14°C$ ✓

100g of water dissolve 2g of R ✓
1000g of water dissolve $\left(\frac{2}{100} \times 1000\right)$ g of R.
= 20g. ✓

0.14°C is the freezing pt depression caused by 20g of R ✓
1.86°C is the freezing pt depression caused by $\left(\frac{20}{0.14} \times 1.86\right)$ ✓
Molar mass of R = 265.7g ✓

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$(PbH_6O_4C_4)_n = 265.7$
$207n + 6n + 64n + 48n = 265.7$ ✓ (01½)
$n = 1$ ✓
Molecular formula of R is $PbH_6O_4C_4$ ✓

(c)(i) $(CH_3COO)_2Pb$ / Lead (II) ethanoate ½

(ii) $3(CH_3COO)_2Pb_{(s)} + 2FeCl_{3(aq)} \rightarrow 2(CH_3COO)_3Fe_{(aq)} + 3PbCl_{2(s)}$ ✓✓½ (09)

12 a(i)
$CH_{4(g)} + 4Cl_{2(g)} \xrightarrow{UV} CCl_{4(l)} + 4HCl_{(g)}$ ✓½
$CS_{2(l)} + 3Cl_{2(g)} \rightarrow CCl_{4(l)} + S_2Cl_{2(s)}$ (01½)
$CS_{2(l)} + 2Cl_{2(g)} \rightarrow CCl_{4(l)} + 2S_{(s)}$

(ii) $Pb_{(s)} + Cl_{2(g)} \rightarrow PbCl_{2(s)}$ ✓½ (01½)
$Pb(NO_3)_{2(aq)} + 2HCl_{(aq)} \rightarrow PbCl_{2(s)} + 2HNO_{3(aq)}$
$Pb_3O_{4(s)} + 8HCl_{(aq)} \rightarrow 3PbCl_{2(s)} + 4H_2O_{(l)} + Cl_{2(g)}$

(iii) $PbO_{2(s)} + 4HCl_{(aq)} \rightarrow PbCl_{4(l)} + 2H_2O_{(l)}$ ✓½ (01)

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(b) CCl_4 is thermally more stable than $PbCl_4$

$PbCl_4$ decomposes on heating to lead(II) chloride and Chlorine

$PbCl_{4(l)} \xrightarrow{heat} PbCl_{2(s)} + Cl_{2(g)}$ (02½)

(c) Pb^{4+} ion in lead(IV) chloride has a higher charge density than the Pb^{2+} ion in lead(II) chloride. Thus the Pb^{4+} ion strongly polarises the chloride anion making lead(IV) chloride more covalent than ionic. (02)

Pb^{2+} ions are less polarising than Pb^{4+}, thus $PbCl_2$ is more ionic than covalent. (09)

(13) (a) $CH_3C{\equiv}CH + Na/liq.NH_3 \xrightarrow{CH_3Br} CH_3C{\equiv}CCH_3$

Mechanism

$CH_3C{\equiv}CH + Na_{(s)}/liq.NH_3 \longrightarrow CH_3C{\equiv}C^-Na^+ + H$

$CH_3C{\equiv}C^-Na^+ \longrightarrow CH_3C{\equiv}C^- + Na^+$ (04)

$CH_3C{\equiv}C^- + CH_3Br \longrightarrow CH_3C{\equiv}CCH_3 + Br^-$

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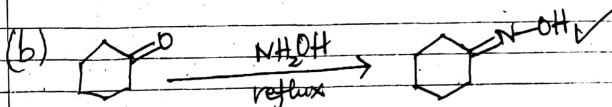
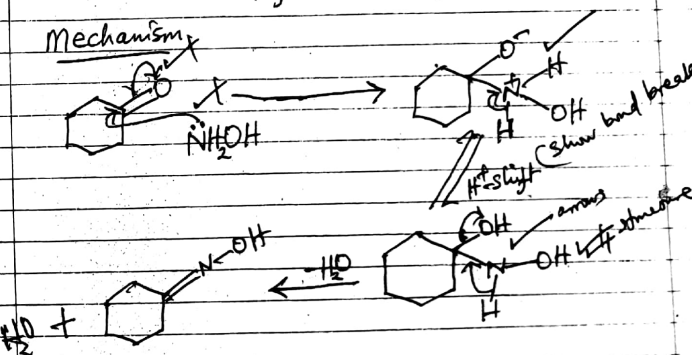
(b) 

Mechanism



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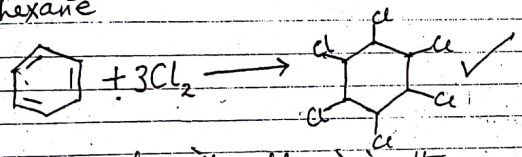
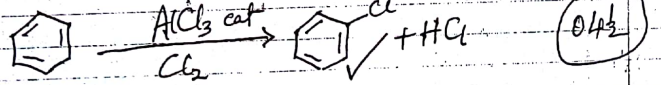
14. (a) Benzene reacts with chlorine in the presence of UV light to form 1,2,3,4,5,6-hexachlorocyclohexane ✓



Benzene reacts with chlorine in the presence of aluminium (III) chloride or iron (III) chloride as halogen carriers (catalyst) to chlorobenzene ✓



(04½)

(b) Chlorine reacts with hot concentrated / warm ✓ Sodium hydroxide to form sodium chloride, Sodium Chlorate(V) and water ✓

$3Cl_{2(g)} + 6OH^-_{(aq)} \longrightarrow 5Cl^-_{(aq)} + ClO^-_{3(aq)} + 3H_2O_{(l)}$ ✓✓

Chlorine reacts with cold dilute sodium hydroxide to form sodium chloride, water and sodium chlorate(I) ✓ (04)

$Cl_{2(g)} + 2OH^-_{(aq)} \longrightarrow Cl^-_{(aq)} + OCl^-_{(aq)} + H_2O_{(l)}$ ✓

09

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15. (a)(i) $Ag_2CO_{3(s)} + aq \rightleftharpoons 2Ag^+_{(aq)} + CO^{2-}_{3(aq)}$ ✓ (01)

(ii) $K_{sp} = [Ag^+]^2[CO_3^{2-}]$ ✓ (01)

(b)(i) Let $[CO_3^{2-}] = s$ ✓
$[Ag^+] = 2s$
$K_{sp} = (2s)^2 s$ ✓

$s = \sqrt[3]{\frac{8\times10^{-12}}{4}}$ ✓ (02)

$s = 1.26\times10^{-4}\ mol\,dm^{-3}$ ✓

(ii) Let new solubility in $0.1M\ K_2CO_3 = s'$ ✓
$[Ag^+] = 2s'$
$[CO_3^{2-}] = s' + 0.1$
Since $s' + 0.1 \approx 0.1$ because $s' \ll 0.1$ ✓
$\therefore [CO_3^{2-}] = 0.1$
$8\times10^{-12} = (2s')^2 \times 0.1 = 0.4s^2$ ✓
$s = 4.47\times10^{-6}$ ✓
Decrease in solubility due to potash $= (1.26\times10^{-4}) - (4.47\times10^{-6})$ ✓
$= 1.22\times10^{-4}$ mol

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RFM of $Ag_2CO_3 = (2\times108)+(12\times1)+(16\times3)$
$= 276$ ✓ (03)

Mass precipitated $= 1.22\times10^{-4}\times276$
$= 0.0334\,g$ ✓

(c) The solubility of silver carbonate increases because ammonia molecules react with silver ions in the saturated solution to form diamminesilver(I) ion which is a soluble complex ion. So more salt dissolves to restore the equilibrium (01½)

09

(16) Let the rate of diffusion of $Y = x$

(a)(i) $R_{O_2} = 1.3x$

$\frac{1.3x}{x} = \sqrt{\frac{M_{rY}}{32}}$ (02)

$M_{rY} = 54.08$

(ii) $C_nH_{2n-2} = 54.08$
$12n + 2n - 2 = 54.08$
$n = 4$

Molecular formula of Y is C_4H_6 (01½)

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(b) $CH_3CH_2C\equiv CH$ but-1-yne rej but-yne since the carbon position numbers

$CH_3C\equiv CCH_3$ but-2-yne (02)

(c)(i) Y is { But-1-yne or $CH_3CH_2C\equiv CH$ } (01)

(ii) $CH_3CH_2C\equiv CH \xrightarrow[\text{rej } H_2/Ni]{H_2/\text{Lindlar's cat}} CH_3CH_2CH=CH_2$

$CH_3CH_2CH=CH_2 \xrightarrow[\text{warm and wet}]{H^+/H_2O}$ (02½)

$CH_3CH_2\underset{OH}{CH}CH_3$

09

(17) (a)(i) Distribution law states that "If a solute in contact is dissolved in a pair of immiscible solvents it distributes itself between the two solvents irrespective of the amounts such that when equilibrium is reached the ratio of concentration of solute in the two solvents is a constant at constant temperature" (01)

(ii) – Solvents should be immiscible and should not be saturated by the solute (01)
– temperature should be constant (two conds.)

END

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(i) See graph overleaf
Axes labelled with units of any each at ½ mark = 01
Correctly plotted points = 01
Shape (line of best fit) = 01
03

(ii) Slope = $\frac{0.1405 - 0.075}{0.058 - 0.014}$ ✓ (01)
= 7.5 ✓
range (7.2 — 7.8)

(c) Let mass of succinic acid extracted = x ✓
Mass of acid left in aqueous layer = 18 − x ✓ (02½)

$K_D = \frac{[Acid]_E}{[acid]_W} = 7.5$

$7.5 = \frac{x/100}{18-x/1000} = \frac{x}{100} \times \frac{1000}{18-x}$ ✓ ✓

x = 1.469 ✓
Mass of acid left in aqueous layer = 18 − 1.469 ✓
= 16.531g

(d) Ion exchange chromatography, solvent extraction (½)

GRAPH OF [SUCCINIC ACID] IN ETHER AGAINST [SUCCINIC ACID] IN WATER

[SUCCINIC ACID] ether (Mol dm⁻³)

[SUCCINIC ACID] IN WATER (Mol dm⁻³)

0·01 0·02 0·03 0·04 0·05 0·06 0·07 0·08

18