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525/1

S6 CHEMISTRY

Exam 16

PAPER 1

DURATION: 2 HOUR 45 MINUTES

For Marking guide contact and consultations: Dr. Bbosa Science 0776 802709,

Instructions to candidates;

- *Answer **all questions in Section A** and **any six in Section B**.*
- *All questions must be answered in spaces provided.*
- *Illustrate your answers with equations where applicable.*
- *Molar gas constant, R=8.314jk^{-1}mol^{-1}*
- *Molar volume for a gas at s.t.p is 22400cm^{3}*
- *Standard temperature =273k*
- *Standard pressure =101325 Nm^{-2}*

SECTION A

Answer all questions from this section.

1. State the condition(s) and write equation for the reaction of aluminium and;
i) water (2marks)

Condition: **heat**

$2Al(s) + 6H_2O(l) \rightarrow 2Al(OH)_3(s) + 3H_2(g)$

ii) Iron (III) oxide (2marks)

Condition: **heat**

$2Al(s) + Fe_2O_3(s) \rightarrow 2Al_2O_3(s) + 2Fe(s)$

2. (a) State what is meant by the term ebullioscopic constant. (1mark)

Ebullioscopic constant is the elevation in boiling point caused by 1 mole of a solute dissolved in 1000g of a solvent.

b) 0.40g of camphor when dissolved in 33.5g of trichloromethane produces a solution boiling at 0.30^0C above the boiling point of pure solvent. Calculate the ebullioscopic constant of trichloromethane. (Molar mass of camphor = 155).
(3marks)

Boiling point elevation = 0.30^0C

Mass of camphor in 1000g of trichloromethane

33.5g of trichloromethane contain 0.4g of camphor

1000g of trichloromethane contain (0.4 x1000)/33.5 =11.94g

Ebullioscopic point constant Kb

11.94g of camphor causes boiling point elevation of 0.30g

155g of camphor causes boiling point elevation of (0.30 x 155)/11.94

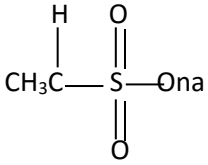
$= 3.9^0Cmol^{-1}kg^{-1}$

3. a) State what is observed and write equation for the reaction when;

i) Ethanal is mixed with a saturated solution of sodium bisulphite. (2marks)

Observation: **white crystals**

Equation:

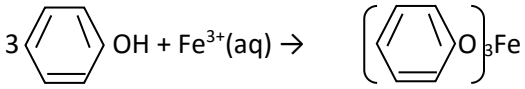
$CH_3CHO + NaHSO_3 \rightarrow$ 

ii) Neutral iron (III) chloride solution is added to aqueous solution of hydroxybenzene. (2marks)

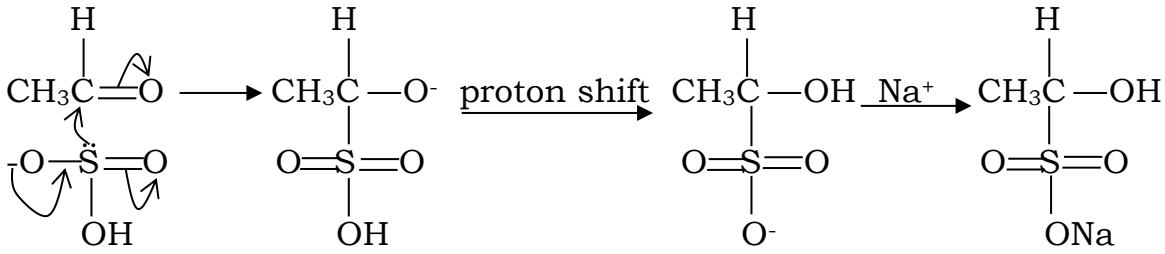
Observation;

Purple solution

Equation;



b) Write the mechanism for the reaction in a (i). (2 ½ marks)



4. (a) State what is meant by the term electrode potential. (1mark)

It is a potential difference set between a metal and a solution of metal ions

b) The electrode potential of some half cells are given below.

		(E^0/V)
$S_2O8_2^-(aq) + 2e$	$\longrightarrow$ $2SO_4^{2-}$ (aq)	+2.01
$I_2(aq) + 2e$	$\longrightarrow$ $2I^-$ (aq)	+0.54

Write;

i) The cell notation of cell formed when the half cells are combined.

(1mark)

Pt, $2I^-(aq)/I_2(aq)//S_2O_8^{2-}(aq)/SO_4^{2-}(aq)$, Pt

ii) Equation for the overall cell reaction. (1½ marks)

$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2\ SO_4^{2-}(aq) + I_2\ (aq)$

iii) Calculate the e.m.f of cell. (1mark)

$E_{cell} = E_{RHE} - E_{LHE}$

$= 2.01 - 0.54$

$= 1.47V$

iv) State whether the cell reaction is feasible or not. Give a reason for your answer. (1mark)

It is feasible because emf is positive

5. a) State two properties in which beryllium shows diagonal relationship with aluminum. (2marks)

- the react with sodium hydroxide

$Be\ (s) + 2OH^-(aq) \rightarrow BeO_2^{2-}(aq) + H_2(g)$

$2Al(s) + 2OH^-(aq) + 6H_2O(l) \rightarrow 2Al(OH)_4^-(aq) + 3H_2(g)$

- **do not react with nitric acid**
- **React with oxygen to form amphoteric oxides**

b) Write equations to illustrate the properties stated in (a) (3marks)

$Be\ (s) + 2OH^-(aq) \rightarrow BeO_2^{2-}(aq) + H_2(g)$

$2Al(s) + 2OH^-(aq) + 6H_2O(l) \rightarrow 2Al(OH)_4^-(aq) + 3H_2(g)$

$2Be\ (s) + O2(g) \rightarrow 2BeO(s)$

$BeO(s) + 2OH\text{-}(aq) \rightarrow BeO_2^{2-}(aq) + H_2O(l)$

$BeO(s) + 2H^+(aq) \rightarrow Be^{2+}(aq) + H_2O(l)$

6. State what would be observed and write equation for the reaction that takes place when

a) Chlorine gas is passed through a solution of potassium manganate(VI)

(2 ½ marks)

A green solution turns purple

$2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$

b) A few drops of hydrogen peroxide solution is added to acidified potassium dichromate(VI) solution. (2 ½ marks)

Blue solution formed

$Cr_2O_7^{2-}$ (aq) + $2H^+$ (aq) + $4H_2O_2$ (aq) → $2CrO(O_2)_2$ (aq) + $5H_2O$ (l)

7. Write equations to show how the following conversions can be effected.

(2½ marks)

a) $(CH_3)_2CHOH$ to $(CH_3)_3COH$

$(CH_3)_2CHOH \xrightarrow{PCl_5} (CH_3)_2CCl \xrightarrow{KCN} (CH_3)_2CHCN \xrightarrow{H^+(aq)}$

$(CH_3)_2CHCOOH \xrightarrow{LiAH_4,} (CH_3)_2CHCH_2OH \xrightarrow{Conc.\ H_2SO_4} (CH_3)_2C=CH_2$

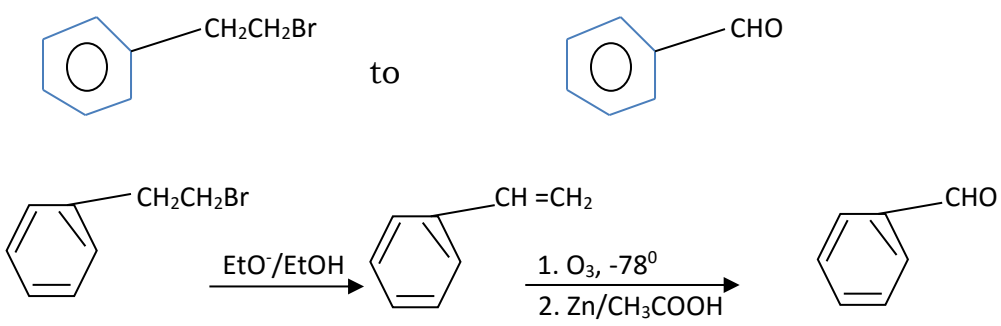
then

$(CH_3)_2C=CH_2 \xrightarrow{H_2O/H^+}$ $(CH_3)_2C(OH)-CH_3$

Or

$(CH_3)_2CHOH \xrightarrow{Cr_2O_7^{2-}/H^+} (CH_3)_2CO \xrightarrow{CH_3MgCl} (CH_3)_3C-OMgCl \xrightarrow{H^+(aq)} (CH_3)_3COH$

b)



8. 30cm^3 of a hydrocarbon Q was exploded with 200cm^3 of oxygen in excess. The volume of the residual gas on cooling to room temperature was found to be 155cm^3. When the residual gas was treated with concentrated potassium hydroxide solution, the volume reduced to 35cm^3.

a) Calculate the molecular formula of Q. (3marks)

volume of carbon dioxide produced = 155- 35 = 120cm^3

Volume of oxygen used 200- 35 = 165

Equation

$C_xH_y + (x + y/4)O_2 \rightarrow xCO2 + (y/2)H_2O$

Volume	30	165	120
Volume ratio	1	5.5	4

x = 4

(x + y/4) 5.5

y = 6

Molecular formula of Q = C_4H_6

b) Write the structures of all possible open chain isomers of Q. (1mark)

CH3CH2C≡CH but-1-yne

CH3C≡CCH3 but-2-yne

c) Q reacts with ammoniacal copper (I) chloride solution.

i) State what is observed. (1mark)

Red precipitate

ii) Write equation for the reaction that takes place. (1½ marks)

$CH_3CH_2C{\equiv}CH + Cu^+ \rightarrow CH_3CH_2C{\equiv}CCu\ (aq) + H^+(aq)$

9. The molar conductivity of a 0.093M solution of ethanoic acid at 25^0C is $5.34 \times 10^{-4}\ sm^2mol^{-1}$. The molar conductivity at infinite dilution of H^+ and CH_3COO^- ions are 3.51×10^{-2} and $0.4 \times 10^{-2} Sm^2mol^{-1}$ respectively. Calculate the;

i) molar conductivity of ethanoic acid at infinite dilution. (1½ marks)

$\Lambda_0 CH_3COOH = \lambda_0 CH_3COO^- + \lambda_0 H^+$

$= 0.4 \times 10^{-2} + 3.51 \times 10^{-2}$

$= 3.91 \times 10^{-2} Sm^2mol^{-1}$

ii) degree of dissociation , α of ethanoic acid. (1½ marks)

$\alpha = \Lambda_c / \Lambda_0$

$= 5.34 \times 10^{-4} / 3.91 \times 10^{-2}$

$=0.014$

iii) acid dissociation constant, Ka at 25^0C (1 ½ marks)

$Ka = \alpha^2 C = 0.014^2 \times 0.093$

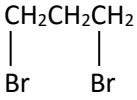
$= 1.8 \times 10^{-5} moldm^{-3}$

SECTION B

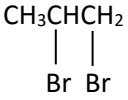
Attempt only **six** questions from this Section

10. a) An organic compound Z has a molecular formula $C_3H_6Br_2$.
Write down the structural formula and IUPAC names of all isomers of Z.

(3marks)



1,3-dibromopropane



1,2-dibromopropane

b) When Z was heated with sodium metal in ethanol a compound Y was formed. Y reacts with water in the presences of sulphuric acid and Mercurous sulphate at 60^0C to form a compound X. X does not react with Fehling's solution but forms an orange precipitate with Brady's reagent. Identify compound X, Y and Z.

(1½ marks)

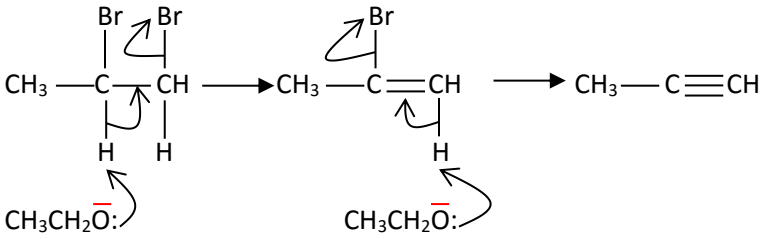
X -propanone

Y -propyne

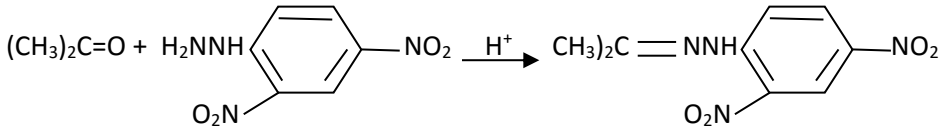
Z - 1,2-dibromopropane

c) Write the equation and suggest the mechanism for the reaction between
i) Z and sodium metal in ethanol.

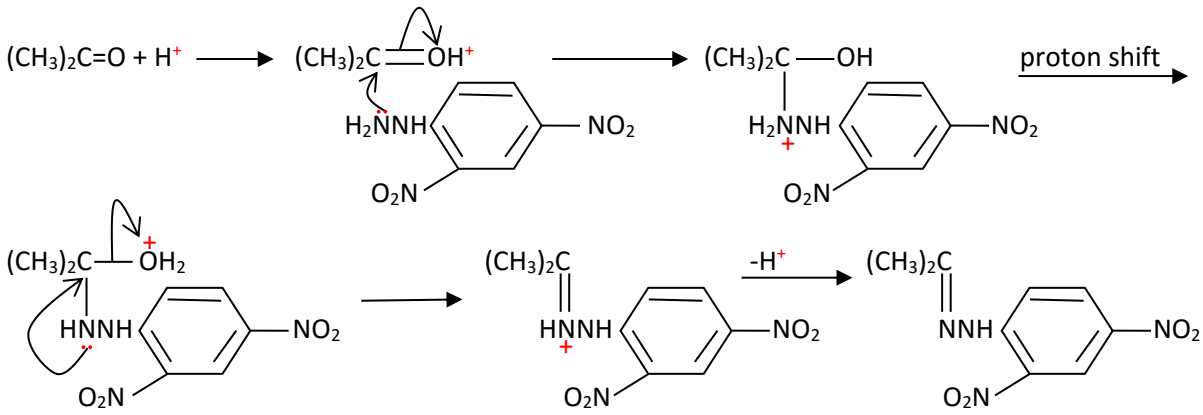
$2CH_3CH_2OH + 2Na \rightarrow CH_3CH_2ONa + H_2$ (g)



ii) X and Brady's reagent. (2 ½ marks)



Mechanism



11. Explain each of the following observations (Your answer should include balanced equations if any). (3marks each)

a) When hydrogen iodide is treated with concentrated sulphuric acid, iodine is liberated whereas when hydrogen chloride is similarly treated, chlorine is not evolved.

Solution

Iodide ion is a stronger reducing agent than chloride ion; it is oxidized by concentrated sulphuric acid to iodine

$2HI(g) + H_2SO_4\ (aq) \rightarrow I_2\ (aq) + 2H_2O(l) + SO_2(g)$

b) An aqueous solution of sodium sulphite has a pH greater than 7 whereas that of sodium hydrogen sulphite is less than 7.

Solution

Sulphate ions hydrolyze in water to produce hydroxide ions

$SO_3^{2-}(aq) + H_2O(l) \leftrightarrow HSO_3^-(aq) + OH^-(aq)$

Whereas hydrogen sulphate ions hydrolyze in water to produce hydrogen ions

$HSO_3^-(aq) \leftrightarrow SO_3^{2-}(aq)\ H^+(aq)$

c) When hydrogen sulphide is bubbled through an aqueous solution of iron(III) chloride a yellow precipitate is observed.

Solution

Iron (III) ions oxidize hydrogen sulphide to Sulphur

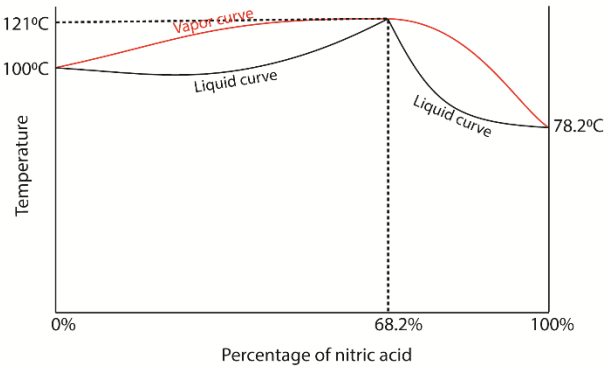
$Fe^{3+}(aq) + H_2S(g) \rightarrow 2Fe^{2+}(aq) + S(s) + 2H^+(aq)$

12. a) State Raoult's law as applied to binary liquid systems. (1mark)

States that the partial vapor pressure of a component of an ideal solution is proportional to its concentration

b) The mixture of water and nitric deviates negatively from Raoults law. The mixture form an azeotropic mixture at 68.2% nitric and boiling point 121^{0}C.

i) Sketch a labeled boiling point – composition diagram for the mixture above. (Bpts of HNO_3 and H_2O respectively are 78.2^{0}C and 100^{0}C at 760mmHg pressure.) (3marks)



ii) Describe briefly what happens when a mixture containing 50% nitric acid is distilled. (2½ marks)

The distillate is water while the residue is azeotrope

c) Explain why the mixture deviates negatively from Raoult's law.

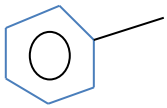
The adhesive forces between water and nitric acid molecules are stronger than the cohesive forces. This reduces the probability of molecules that escapes into vapour. The vapor pressure of the mixture lowers and the boiling point increase. The stronger adhesive forces are due to hydrogen bonds between water and nitric acid molecules.

d) Name one method of obtaining pure nitric acid from the azeotropic mixture. (1mark)

Pure nitric acid is distilled a from azeotrope containing concentrated sulphuric acid is added.

13. Name the reagents that can be used to distinguish between the following pair of organic compounds. In each case state what is observed when the compounds are separately treated with the reagent. (3marks)

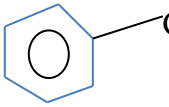
a)

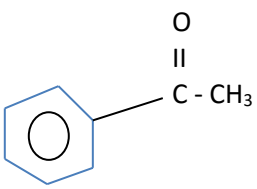
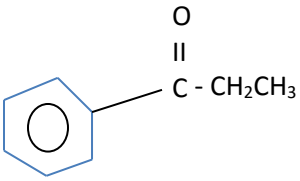


Reagent **Ammoniacal silver nitrate**

Observation

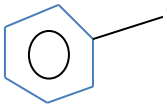
HCOOH forms silver mirror or black precipitate

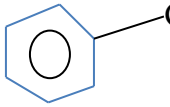


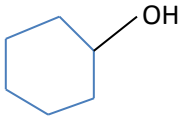
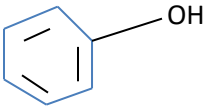
b)  and 

Reagent: solution of iodine in concentrated sodium hydroxide

Observations

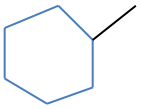
 $COCH_3$ forms yellow precipitate

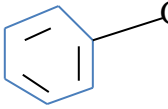
 $COCH_2CH_3$ no observable change

c)  and 

Reagent: neutral iron (III) chloride solution

Observations

 OH no observable change

 OH forms a purple solution

14. a) 0.111g of a vaporized sample of an organic compound R occupied 48.0cm^3 at 20^{0}C and 700mmHg pressure. Calculate the relative molecular mass of R.

From $\frac{PV}{T}$ = constant

$\frac{700\ x\ 48}{(273+20)} = \frac{760V}{273}$

V= 41.2cm^3

Formula mass of R

41.2cm^3 weight 0.111g

22400cm^3 weight RFM

RFM = $\frac{0.111\ x\ 22400}{41.2}$ = 60

b) R consists 59.9% carbon, 26.6% oxygen and the rest is hydrogen. Determine;

i) the empirical formula of R (2marks)

Percentage of hydrogen = 100 –(59.9 + 26.6) =13.5

Element	C	H	O
Percentage	59.9	13.5	26.6
RAM	12	1	16
Moles	5	13.5	1.6625
Mole ratio	3	8	1

Empirical formula of R = C_3H_8O

ii) the molecular formula of R (1½ marks)

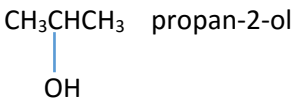
$[C_3H_8O]n = 60$

n = 1

molecular formula = C_3H_8O

c) Write down the structural formulae and give the IUPAC names of all isomers of R. (3marks)

$CH_3CH_2CH_2OH$ propan-1-ol



15. a) State two characteristic properties exhibited by manganese as a transition element.

- has variable oxidation states 2, 4, 7
- forms colored compounds MnO_4^- is purple
- has catalytic activity e.g. MnO_2 is a catalyst in decomposition of H_2O_2.
- froms complexes e.g. MnO_4^-

b) i) Write the electronic configuration of manganese. (½ mark)

Mn $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

ii) State the common oxidation states exhibited by manganese in its compounds. (1½ marks)

+2, +4, and +7.

c) i) Manganese (IV) oxide reacts with concentrated hydrochloric . Write the equation of reaction that takes place. (1½ marks)

$MnO_2(s) + 4HCl\ (aq) \rightarrow MnCl_2 + Cl_2(g) + 2H_2O(l)$

d) Lead(IV) oxide was added to an aqueous solution of manganese (II) chloride, followed by concentrated nitric acid. The mixture was then heated.

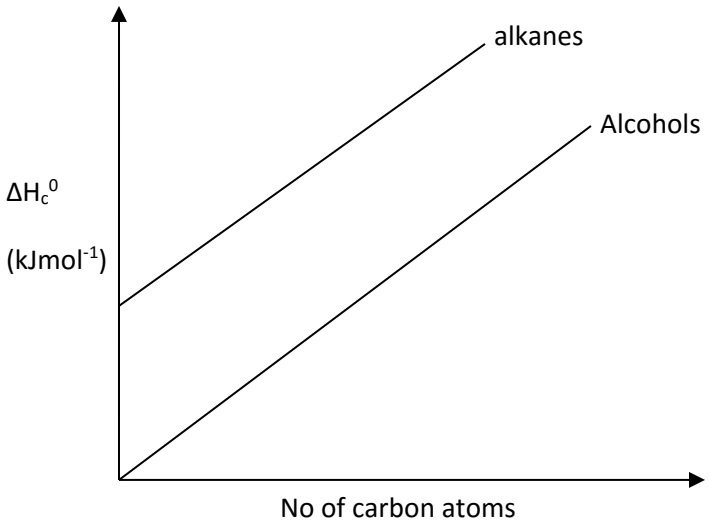
i) State what was observed. (1½ marks)

Purple color is formed

ii) Write equation of reaction that takes place. (1½ marks)

$2Mn^{2+}(aq) + 5PbO_2(s) + 4H^+(aq) \rightarrow 2MnO_4^-(aq) + 5Pb^{2+}(aq) + 2H_2O(l)$

16. a) The standard enthalpies of combustion of some straight chain alkanes and alcohols against number of carbon atoms is shown below.



i) Explain the shape of the graph(s)

Line graphs because compounds in the same homologous series differ from each other by a common group (CH_2)

ii) The graph for alcohol passes through the origin. Explain why this is so.

(1½ marks)

Because alcohols are partially oxidized, therefore, their enthalpy of combustion is lower than that of alkanes

iii) The graph for alkanes has an intercept. What is the significance of the intercept? (1 ½ marks)

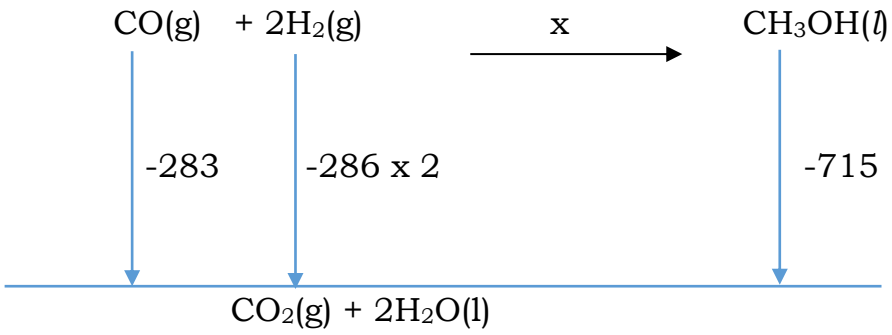
The enthalpy of combustion of alkane is higher than that of alcohols that are partially oxidized

b) Energy changes for some reactions are shown below;

	ΔHO/Kjmol^{-1}
i) $CO(g) + ½ O_2(g) \longrightarrow CO_2(g)$	-283
ii) $H_2(g) + ½ O_2(g) \longrightarrow H_2O(l)$	-286
iii) $CH_3OH(l) + {}^3/_2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$	-715

Calculate the enthalpy change for the reactions

$CO(g) + 2H_2(g) \longrightarrow CH_3OH(l)$ (3marks)



$-283 - 286 \times 2 = x - 715 =$

$x = -140 kJmol^{-1}$

Therefore, enthalpy of combustion of CH2OH = $-140 kJmol^{-1}$

17. a) Explain what is meant by the term complex ion. (1mark)

Complex ions are ions with a central metal ion bonded to one or more molecules or ions called ligands through dative bonds.

b) i) Some complex ions are given below. In each case state the coordination number and oxidation state of the central atom. (3marks)

Formulae of complex ion	**Coordination number**	**Oxidation state**
$CoCl_4^{2-}$	4	+2
$Fe(CN)_6^{3-}$	6	+3
$Ag(NH_3)_2^{+}$	2	1

ii) Explain why transition metals form complex ions.

- **They have high charge density to attract lone pairs of electrons from ligands**
- **The have vacant orbitals to accommodate lone pairs of electrons to form dative bonds**

c) In each case write equation catalyzed by the following ions/species.

(1 ½ marks @)

i) Vanadium pentoxide

$2SO_2(g) + O_2(g) \leftrightarrow 3SO_3(g)$ (in contact process)

ii) Manganese II ions

$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

END *