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ASSIGNMENT WORK / MIDTERM TEST

Session 20 .... - 20 ....

Semester III^rd ....

Name of Student Radha Yadav .... **Father's Name** GyanSingh Yadav

Roll No. .... **Enrollment No.** ....

Year .... **Semester** III^rd ....

.1 (a) Explain the following the large size of s-block elements do not from complexes. Explain the reason.
(b) why Alkali metal in liquid ammonia to give blue solutions and conductor of electricity.

.2 Explain the following
(a) frost diagram (b) latimer diagram (c) disproportion Rx?

.3 write short note on-
(a) Corey house reaction
(b) Diel Alder Reaction.
(c) Preparation of cycloalkanes by Perkin method.
(d) 1,2 and 1,4 electrophillic addition rx^n on conjugated dienes.

Q.4 (a) Derive the expression work done is 2.303 log $\frac{V_2}{V_1}$ in Isothermal reversible process
(b) Prove that $\Delta H = 0$ for Ideal gas at isothermal explain
(c) According to thermodynamics prove that $\left(\frac{dE}{dV}\right)_T$ for ideal gas.
(d) Define Heat of Combustion and its application and How to find experimental value of heat of Combustion.

Ans-1 (a) Alkali metals are large in size and they have less charge i.e. +1. That is why they a have ~~less~~ charge very weak tendency ~~to~~ form complexes.

Complexation tendency is observed in cations of high charge and small size besides this vacant orbitals of suitable energy level should be available.

Thus complexation of large size of s-block elements do not occur.

So complexation tendency of second group elements will be more than that of first group elements.

(b) Alkali metals easily dissolve in liquid ammonia to form blue coloured solution in dilution due to the ionisation of alkali metal atom into ammoniated metal ion and ammoniated electron.

$M(s) + (x+y) NH_3 \rightarrow [M(NH_3)_x]^+ + [e^- (NH_3)_y]^-$

This solutions are paramagnectic due to the presence of unpaired electrons and are reducing in nature.

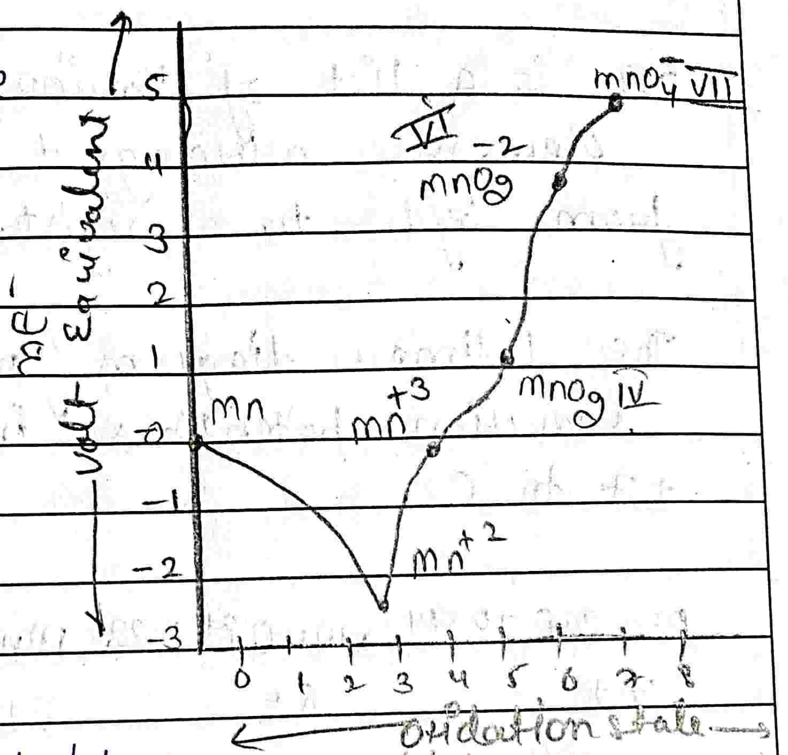
Due to the presence of a single electron that can be easily removed from the Valence Shell, alkali metals act as very good Conductors of heat and electricity.

Conductivity increases from Li to Cs

Alkali metals due to its low ionisation energy and high metallic character Conducts heat well.

Ans-3 (a) Frost Diagram:-

This diagram explain the stability of the oxidation states of an element.



Author is Atwater Frost (Scientist)

$\because \Delta G^\circ = -nE^*F$

↓ Volt Equivalent

↓ Standard Reduction potential Values

In a frost diagram, we plot $\Delta G^\circ/F$ $(=nE^\circ)$ vs. oxidation number.

The zero oxidation state is assigned as nE° value of zero.

Contain the same information as in a latimer diagram, but graphically shows stability and oxidising power.

Stable and unstable oxidation states can be easily identified in the plot.

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(b) Latimer Diagram →

It is a list of various oxidation states of an element arranged in descending order from left to right.

The latimer diagram for Mn illustrates its standard reduction potentials in oxidation states from +7 to 0.

$$\underset{7+}{MnO_4^-} \xrightarrow{+0.564} \underset{6+}{MnO_4^{2-}} \xrightarrow{+0.274} \underset{5+}{MnO_4^{3-}} \xrightarrow{+4.27} \underset{4+}{MnO_2} \xrightarrow{+0.95} \underset{3+}{Mn^{3+}} \xrightarrow{+1.51}$$

$$\underset{2+}{Mn^{2+}} \xrightarrow{-1.18} \underset{0}{Mn}$$

for the 5 electron reduction of MnO_4^- to Mn^{2+}, we write

$$E^\circ = \frac{1(0.564) + 1(0.274) + 1(4.27) + 1(0.95) + 1(1.51)}{5} = +1.51\,V$$

For the three electron reduction of $MnO_4^-(aq)$ to $MnO_2(s)$,

$$E^\circ = \frac{1(0.564) + 1(0.274) + 1(4.27)}{3} = +1.70\,V$$

(c) In most redox rxn atoms of one element are oxidized and atoms of a different element are reduced.

In some redox rxn a single substance can be both oxidized and reduced. These are known as disproportionation rxn.

Ex:- Decomposition reaction of H_2O_2

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

The decomposition rxn of hydrogen peroxide produces oxygen and water.

Ans-3 (a) Corey-House Synthesis-

The rxn which involve treatment of alkyl halide with dialkyl Cuperate to form alkane is known as Corey house synthesis.

$$\underset{\text{alkyl halide}}{R'-X} + \underset{\text{Lithium dialkyl Cuperate}}{R_2CuLi} \longrightarrow \underset{\text{Alkane}}{R'-R} + R-Cu + LiX$$

$CH_3-Br + (CH_3)_2CuLi \longrightarrow CH_3-CH_3 + CH_3-Cu + LiBr$

methyl bromic — Ethane

Mechanism → It involves following steps

step 1 → Rx^n of Alkyl halide with Lithium metal

$R-X + Li-Li \longrightarrow R-Li + LiX$

step 2 → Rx^n of R-Li with CuI

$2R-Li + CuI \longrightarrow R_2CuLi + LiI$

step 3 → Rx^n of lithium dialkyl Cuperate with other alkyl halide.

$R_2CuLi + R'-X \longrightarrow R'-R + R-Cu + LiX$

Alkane

(b) DIELS - ALDER REATION -

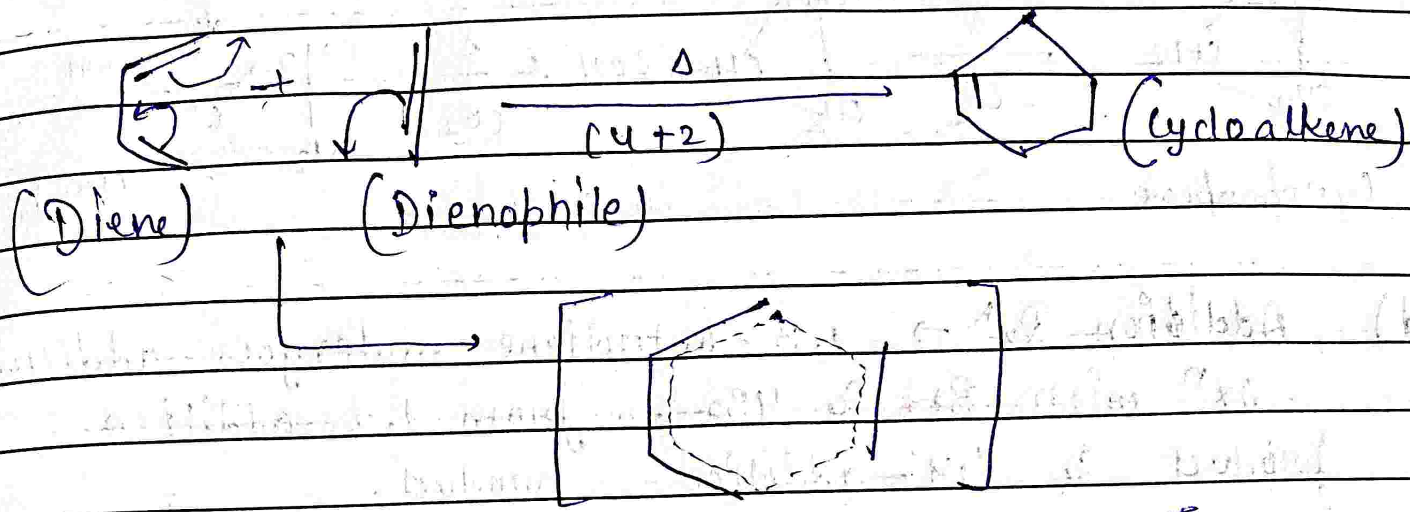
→ (4+2) (cyclo addition Rx^n)

→ Thermally Allowed

→ In Diels - alder rx^n Homo and Lumo is provided by any system / molecule, it depends upon the types of substituent attached to the molecule or system.

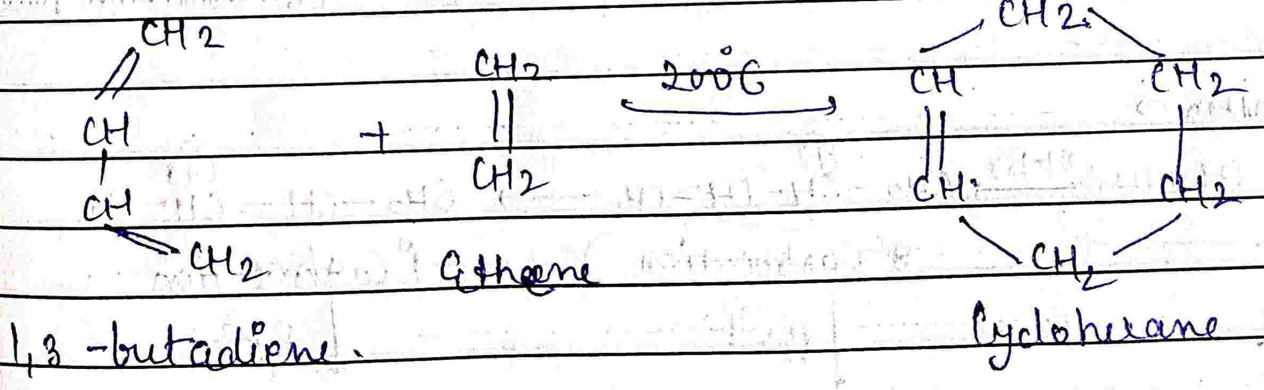
→ Generally HOMO is provided by the Diene and Lumo by the dienophile.

→ Diels - Alder rx^n are stereospecific

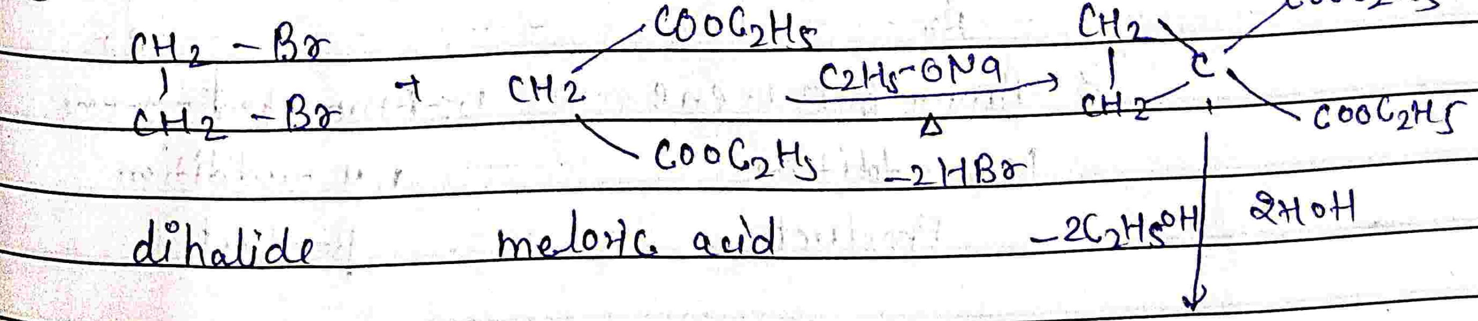


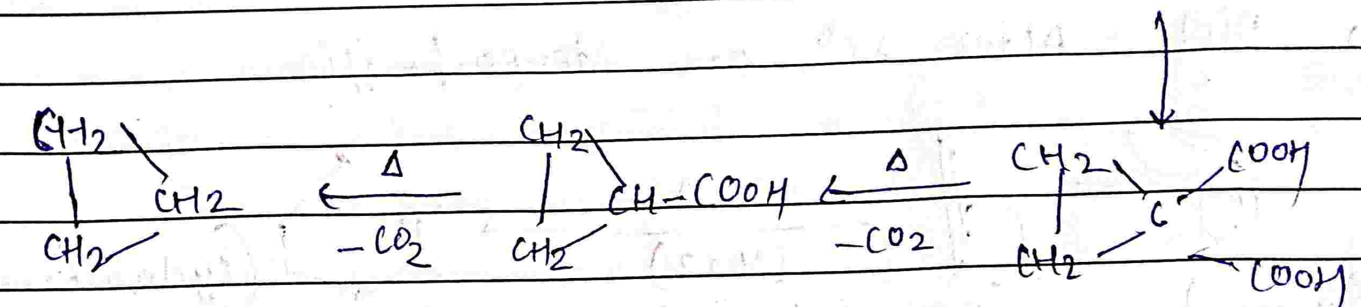
6-membered cyclic T.S.

In this rx^n, a conjugated diene ($4\pi e^-$ system) and a compound containing a double bond ($2\pi e^-$ system) reacts to form an adduct.



(c) Perkin's Method →





Cyclopropene

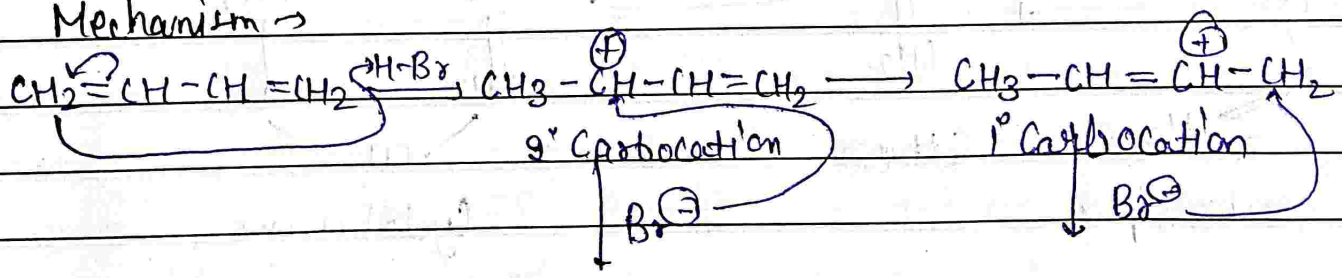
(d) Addition Rx^n → 1,3-butadiene undergoes addition rx^n with Br_2 & HBr to from 1,2 addition product & 1,4-addition product.

Addition of Halogen Acids →

$CH_2=CH-CH=CH_2 \xrightarrow{HBr} CH_3-\underset{}{\overset{Br}{C}}H-CH=CH_2 + CH_3-CH=CH-CH_2-Br$

1,3 di butadiene — 3 Bromobut-1-ene (1,2 addition product) — 1-Bromobut-2-ene (1,4 addition product)

Mechanism →



$CH_3-\underset{Br}{CH}-CH=CH_2$ — $CH_3-CH=CH-\underset{Br}{CH_2}$

3-Bromo but-1-ene, 1,2-addition Product — 1,-Bromo but-2-ene, 1,4-addition product

Ans-4 (a) Isothermal reversible expansion for ideal gas

$$W = \int_{V_1}^{V_2} P\,dV$$

Since, $PV = RT$ (from ideal gas eqn)

$$P = \frac{RT}{V}$$

$$W = \int_{V_1}^{V_2} \frac{RT}{V}\,dv$$

$$W = RT \int_{V_1}^{V_2} \frac{dv}{V}$$

$$\left(\because \int \frac{dx}{x} = \log_e x \right)$$

$$W = RT \log_e V \Big|_{V_1}^{V_2}$$

$$W = RT \left[\log_e V_2 - \log_e V_1 \right]$$

$$W = RT \log_e \frac{V_2}{V_1}$$

$\left[\because \log m - \log n = \log \frac{m}{n}\right]$

$w = 2.3026\, RT \log_{10} \left(\frac{V_2}{V_1}\right)$

(b) During isothermal expansion of an ideal gas

$\Delta T = 0, \Delta E = 0$

we know that,

$H = E + PV$

$\Rightarrow \Delta H = \Delta E + \Delta (PV)$

$\Rightarrow \Delta H = \Delta E + \Delta (nRT)$

$\therefore \Delta H = \Delta E + nR\Delta T = 0 + 0 = 0$

change in enthalpy is zero, means its enthalpy remains same or uneffected.

(C) For an ideal gas, the value of $\left(\frac{dE}{dV}\right)$ is zero because the internal energy, i.e

Kinetic energy of gas depends only on temperature.

For ideal Gas - $\left(\frac{dE}{dV}\right)_T$

E depends on T, V

$E = f(T, V)$

T = Constant

So, E = Constant

so $\left(\frac{dE}{dV}\right)_T = 0$

(D) Heat of Combustion

The Heat of Combustion of a substance is defined as:-

The change in enthalpy of a system when one mole of the substances is completely burnt in excess of air or oxygen.

Application of the Heat of Combustion:-

(1) Calculation of heat of formation.

(2) Calorific value of foods and fuels

(3) Deciding constitution.

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \quad \Delta H_c = -890.3 kJ$

$C_2H_6(g) + 3\frac{1}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta H_c = -1559.7 kJ$

(1) Calculation of Heat of formation →

Since the heats of combustion of organic compounds can be determined with considerable ease, these are employed to calculate their heats of formation.

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(2) Calorific Value of foods and fuels:-

- The amount of heat produced in Calories (or joules) when one gram of a substances is completely burnt.

It is expressed in cal g^{-1} or k Cal g^{-1} or KJ g^{-1}

Heats of Combustion are usually determined by burning a known amount of the material in a bomb Calorimeter with an excess of oxygen.

By measuring the temperature changes, the heat of Combustion Can be determined.

A 1.55 gram sample of ethanol is burned and produced a temperature increase of 55°C

Teacher's Signature.....................

in 200 grams of water,

Calculate the molar heat of Combustion.

- mass of ethanol = 1.55 g
- Molar mass of ethanol = 46.1 g/mol
- mass of water = 200g
- C_p water = 4.18 J/g°C
- Temperature increase = 57°C

Amount of ethanol used:-

$$\frac{1.55\ g}{46.1\ g/mol} = 0.0336\ mol$$

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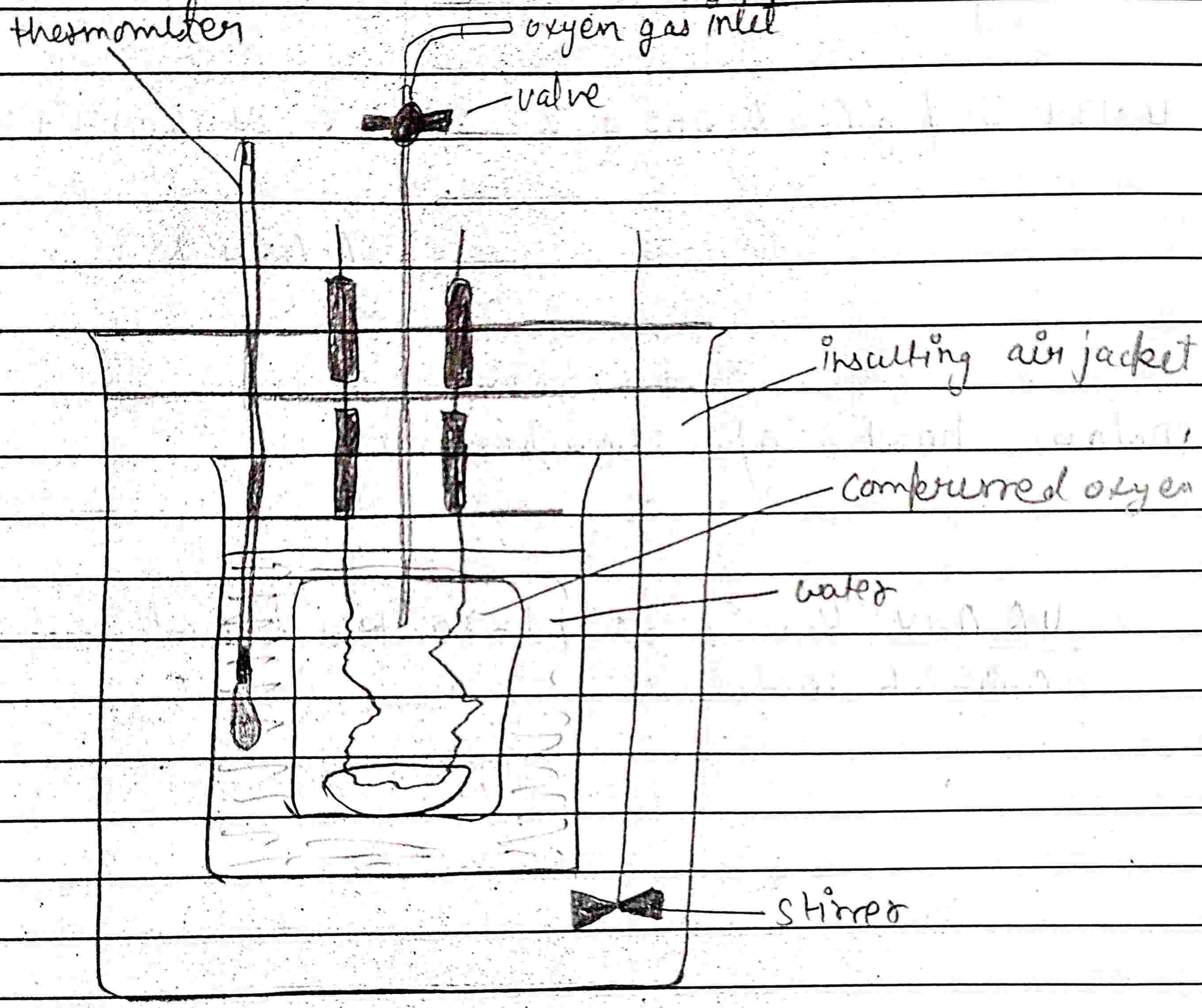
Energy generated

4.184 J / g°C x 200 g x 55°C = 46024 J = 46.024 KJ

molar heat of Combustion:-

$$\frac{46.024\ KJ}{0.0336\ mol} = 1370\ KJ/mol$$


thermometer
oxyen gas inlet
valve
insulting air jacket
comperurred oxyen
water
stirrer