



R.K.

GROUP OF COLLEGE

Behind Kalwar Police Station, Kalwar, Jaipur (Raj.)



ASSIGNMENT

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B.A. / B.Sc. / B.Com.

ASSIGNMENT WORK / MIDTERM TEST

Session 20 - 20

Semester III

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Roll No. **Enrollment No.**

Year **Semester** III

1. (a) Explain the following the large size of s-block elements do not form 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) disproportionation rxn

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 electrophilic addition rxn 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 $\left(\frac{dE}{dT}\right)_{\text{for ideal gas}}$
 (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 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.



These solutions are paramagnetic 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 conduct heat well.

Ans-3 (a) Frost Diagram:-

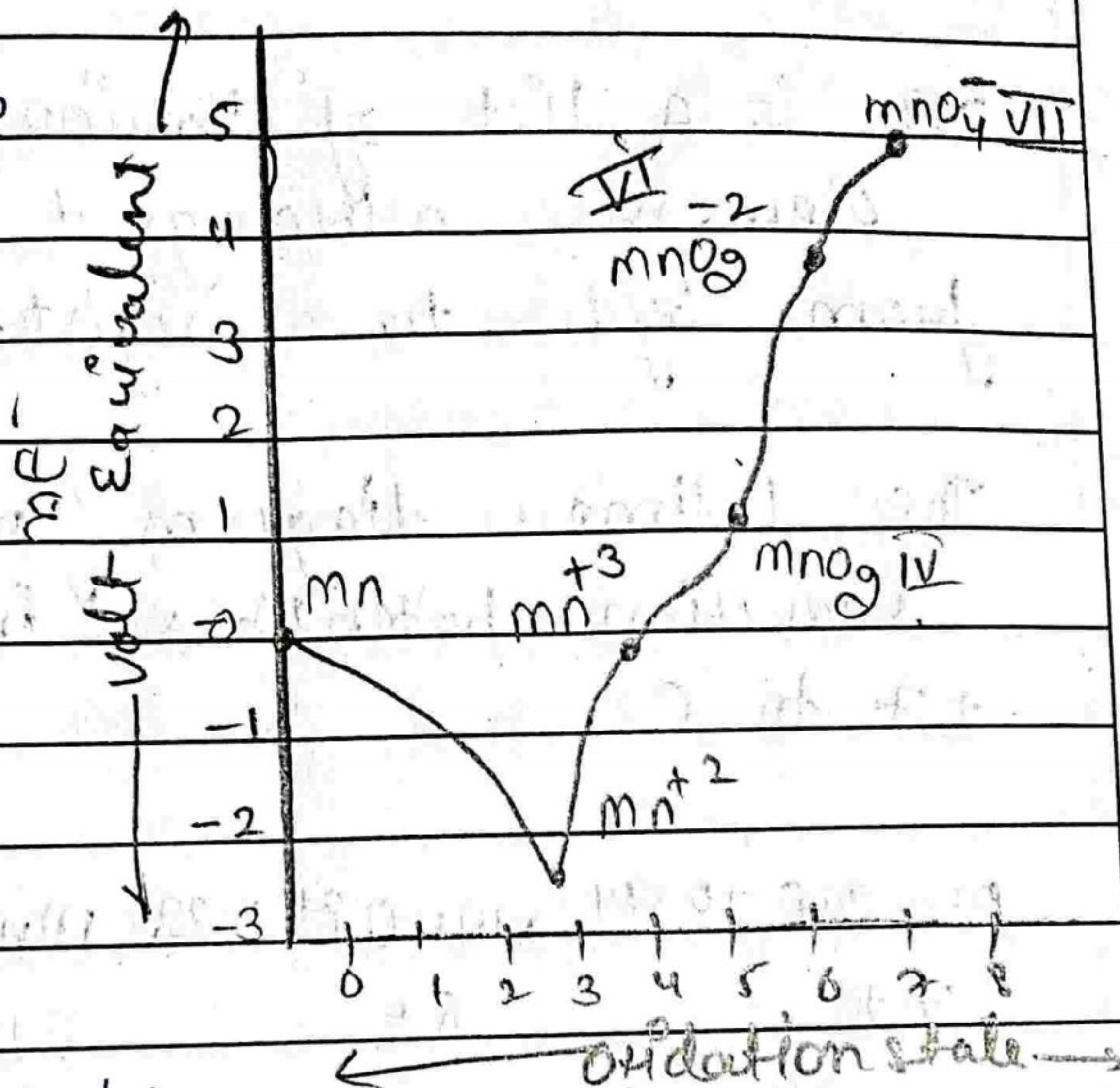
This diagram explain the stability of the oxidation states of an element.

Author is Atwater Frost (Scientist)

$$\Delta G^\circ = -nF \epsilon^\circ$$

Volt Equivalent

Standard Reduction potential Values



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

The zero oxidation state is assigned as $nF\epsilon^\circ$ value of zero.

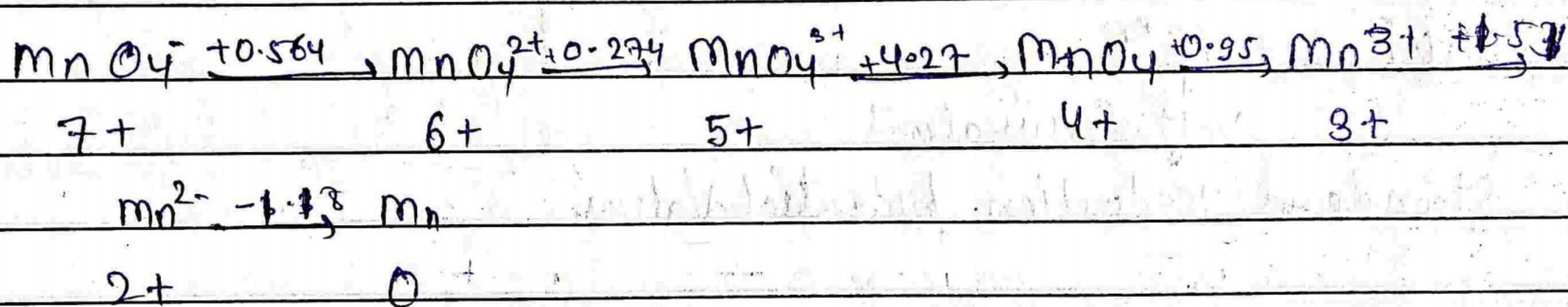
Contains the same information as in a Latimer diagram, but graphically shows stability and oxidizing power.

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

(b) Latimer Diagram $\rightarrow$

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.



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

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

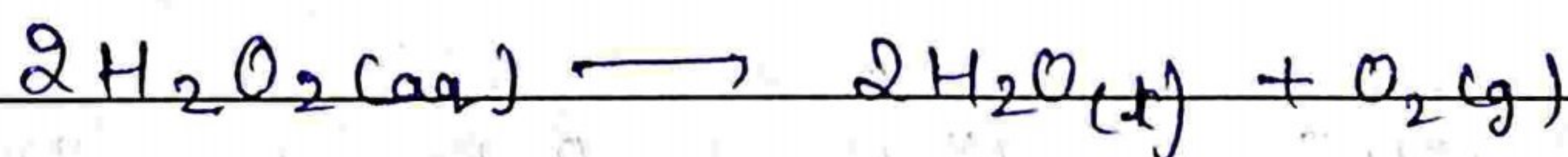
For the three electron reduction of MnO_4^- (aq) to MnO_2 (s),

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

(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 rxⁿ are known as disproportionation rxⁿ.

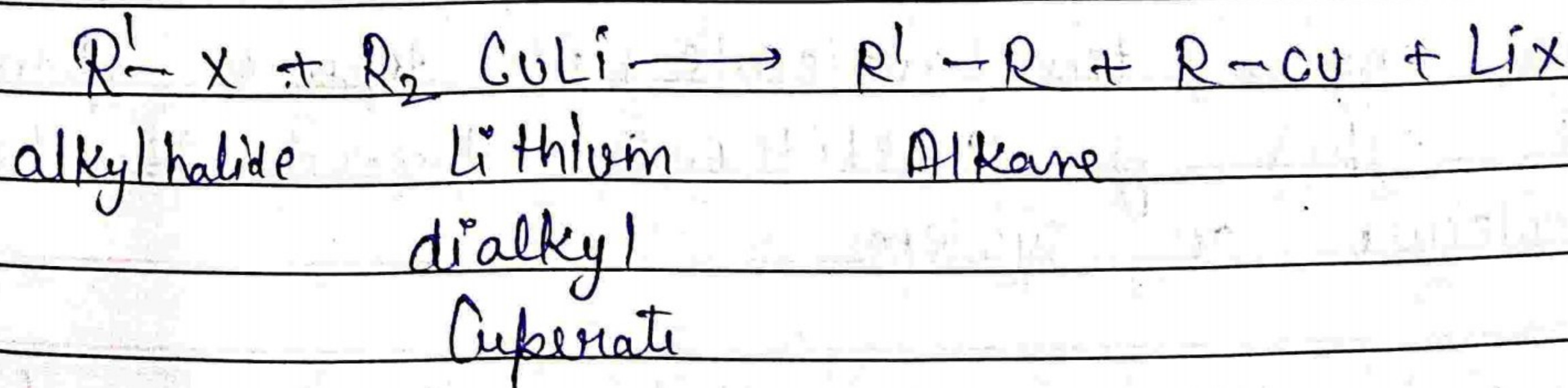
Ex! - Decomposition reaction of H₂O₂

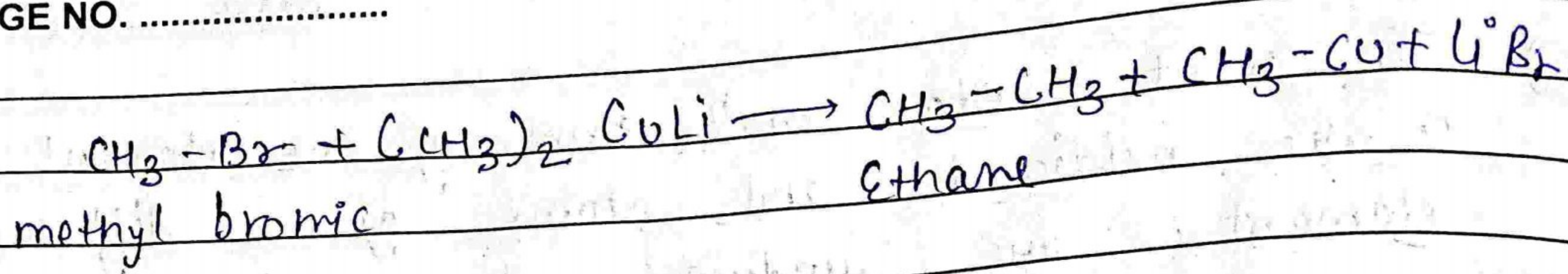


The decomposition rxⁿ of hydrogen peroxide produces oxygen and water.

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.





Mechanism $\rightarrow$ It involves following steps

Step 1 $\rightarrow$ Rxn of Alkyl halide with Lithium metal

$$\text{R-X} + \text{Li-Li} \longrightarrow \text{R-Li} + \text{LiX}$$

Step 2 $\rightarrow$ Rxn of R-Li with CuI

$$2\text{R-Li} + \text{CuI} \longrightarrow \text{R}_2\text{CuLi} + \text{LiI}$$

Step 3 $\rightarrow$ Rxn of Lithium dialkyl Cuperate with other alkyl halide.

$$\text{R}_2\text{CuLi} + \text{R}'\text{-X} \longrightarrow \text{R}'\text{-R} + \text{R-Cu} + \text{LiX}$$

Alkane

(b) DIELS - ALDER REACTION -

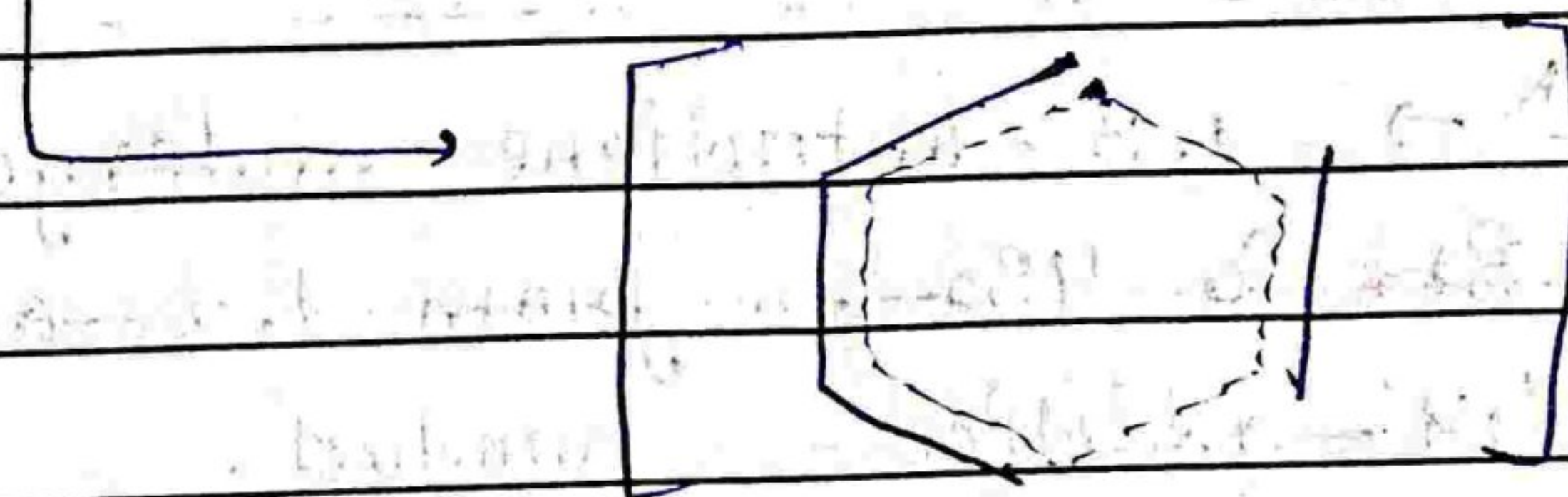
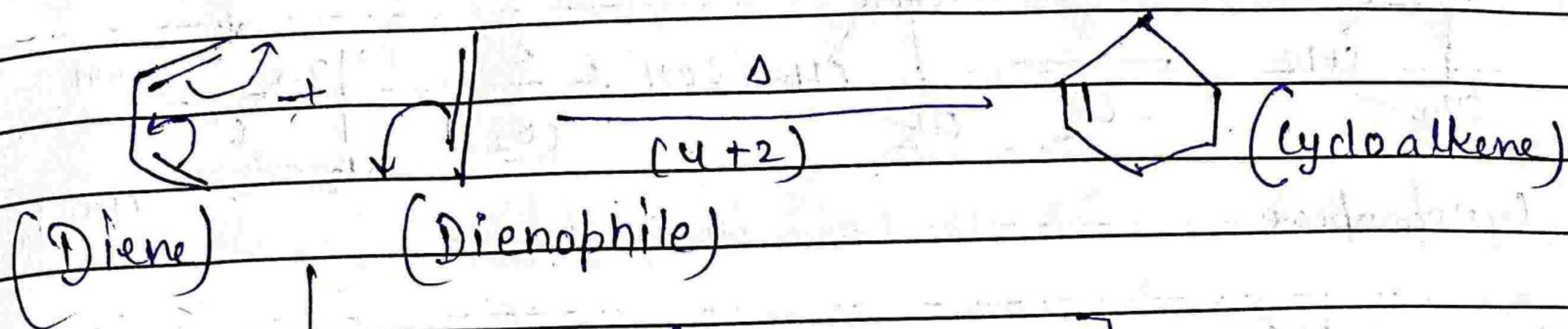
$\rightarrow$ (4+2) Cyclo addition Rxn

$\rightarrow$ Thermally Allowed

$\rightarrow$ In Diels - alder rxn HOMO and LUMO is provided by any system / molecule, it depends upon the types of substituent attached to the molecule or system.

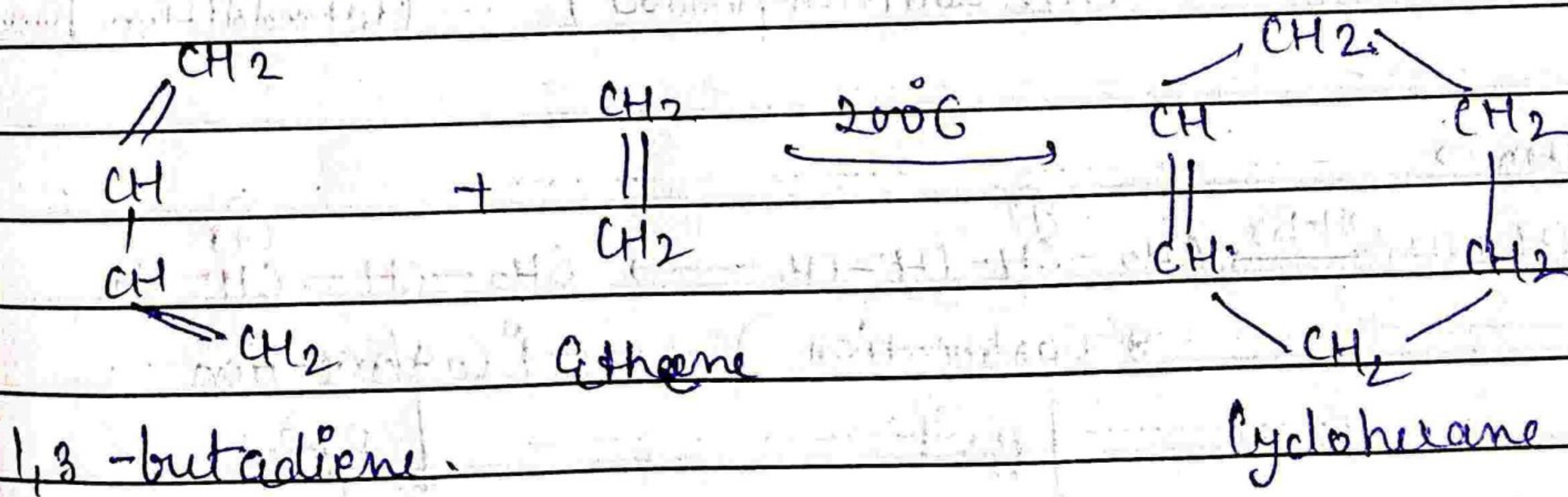
$\rightarrow$ Generally HOMO is provided by the Diene and LUMO by the dienophile.

→ Diels - Alder rxⁿ are stereospecific

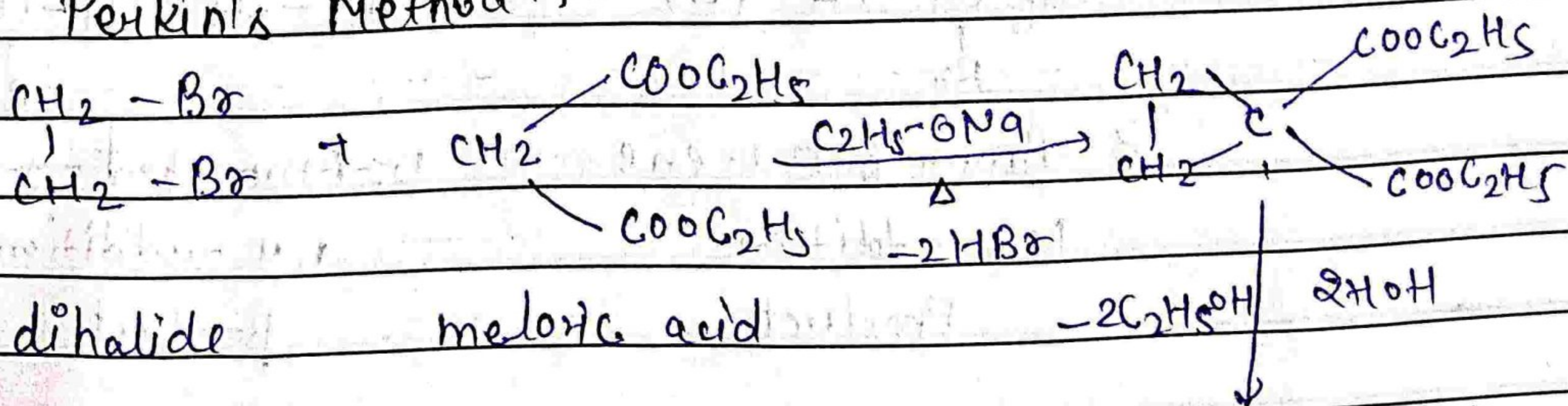


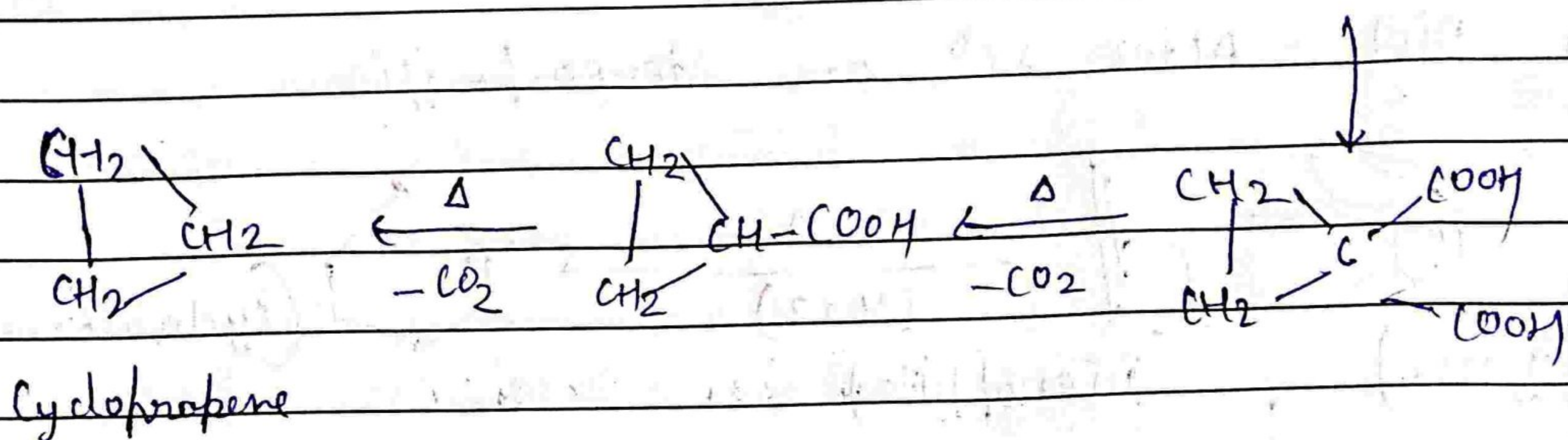
6-membered cyclic T.S.

In this rxⁿ, a Conjugated diene ($4\pi e^-$ system) and a Compound containing a double bond ($2\pi e^-$ system) reacts to form an adduct.



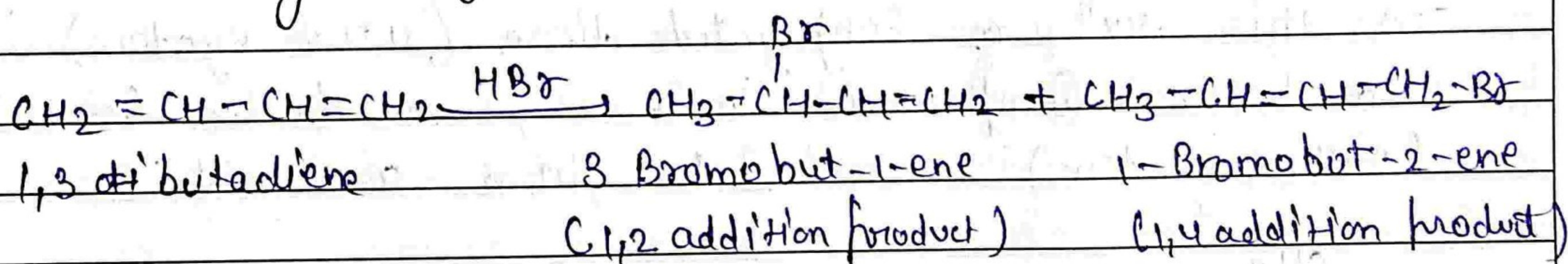
(c) Perkin's Method →



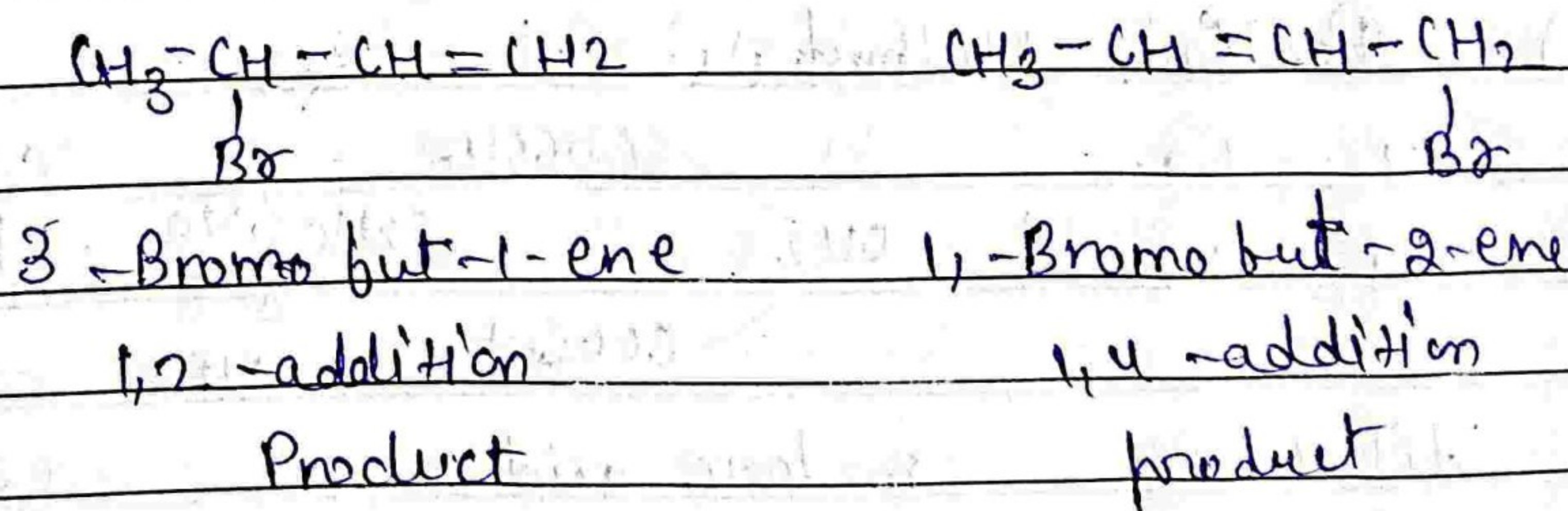
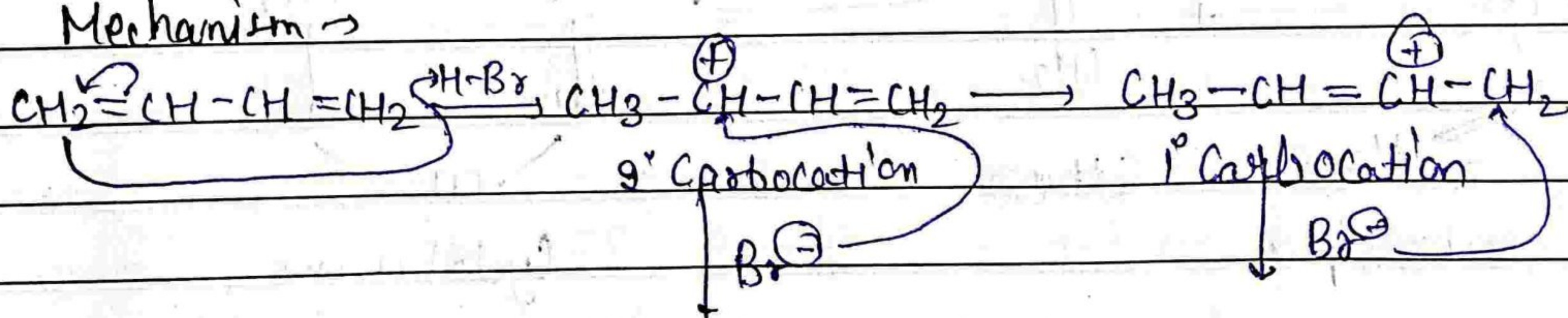


(d) Addition $\text{R}^{\text{H}} \rightarrow$ 1,3-butadiene undergoes addition $2x^n$ with Br_2 & HBr to form 1,2 addition product & 1,4-addition product.

Addition of Halogen Acids $\rightarrow$



Mechanism $\rightarrow$



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

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

Since, $PV = RT$ (from ideal gas eqⁿ)

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

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

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

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

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

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

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

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

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

(b) During isothermal expansion of an ideal gas

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

we know that,

$$H = E + PV$$

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

$$\Rightarrow \Delta H = \Delta E + n(\Delta RT)$$

$$\therefore \Delta H = \Delta E + nRT = 0 + 0 = 0$$

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

(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.

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

E depends on T, V

$$E = \int T, V$$

T = Constant

So, E = Constant

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

(D) Heat of Combustion

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

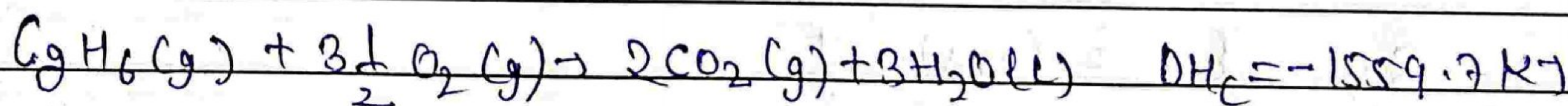
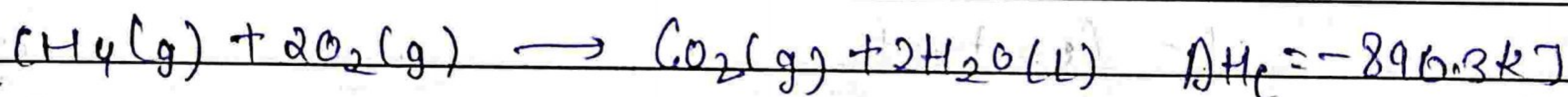
The change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen.

Application of the Heat of Combustion:-

(1) Calculation of heat of formation.

(2) Calorific value of foods and fuels

(3) Deciding constitution.



(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.

(2) Calorific Value of foods and fuels:-

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

It is expressed in cal g^{-1} or kJ 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 .

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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 = 200 g

- C_p of water = 4.18 J/g°C

- Temperature increase = 5°C

Amount of ethanol used:-

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

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Energy generated

$$4.184 \text{ J/g}^\circ\text{C} \times 200 \text{ g} \times 55^\circ\text{C} = 40602.4 \text{ J} =$$

$$46.024 \text{ kJ}$$

molar heat of Combustion:-

$$\frac{46.024 \text{ kJ}}{0.0336 \text{ mol}} = 1370 \text{ kJ/mol}$$

