Prepared by:
Dr. Ambika Kumar
Asst. Prof. in Chemistry
Dept. of Chemistry
B. N. College Bhagalpur
Contact No. 7542811733
e-mail ID: kumarabika.1115@gmail.com

Department of Chemistry, B. N. College Bhagalpur

http://bncollegebgp.ac.in/

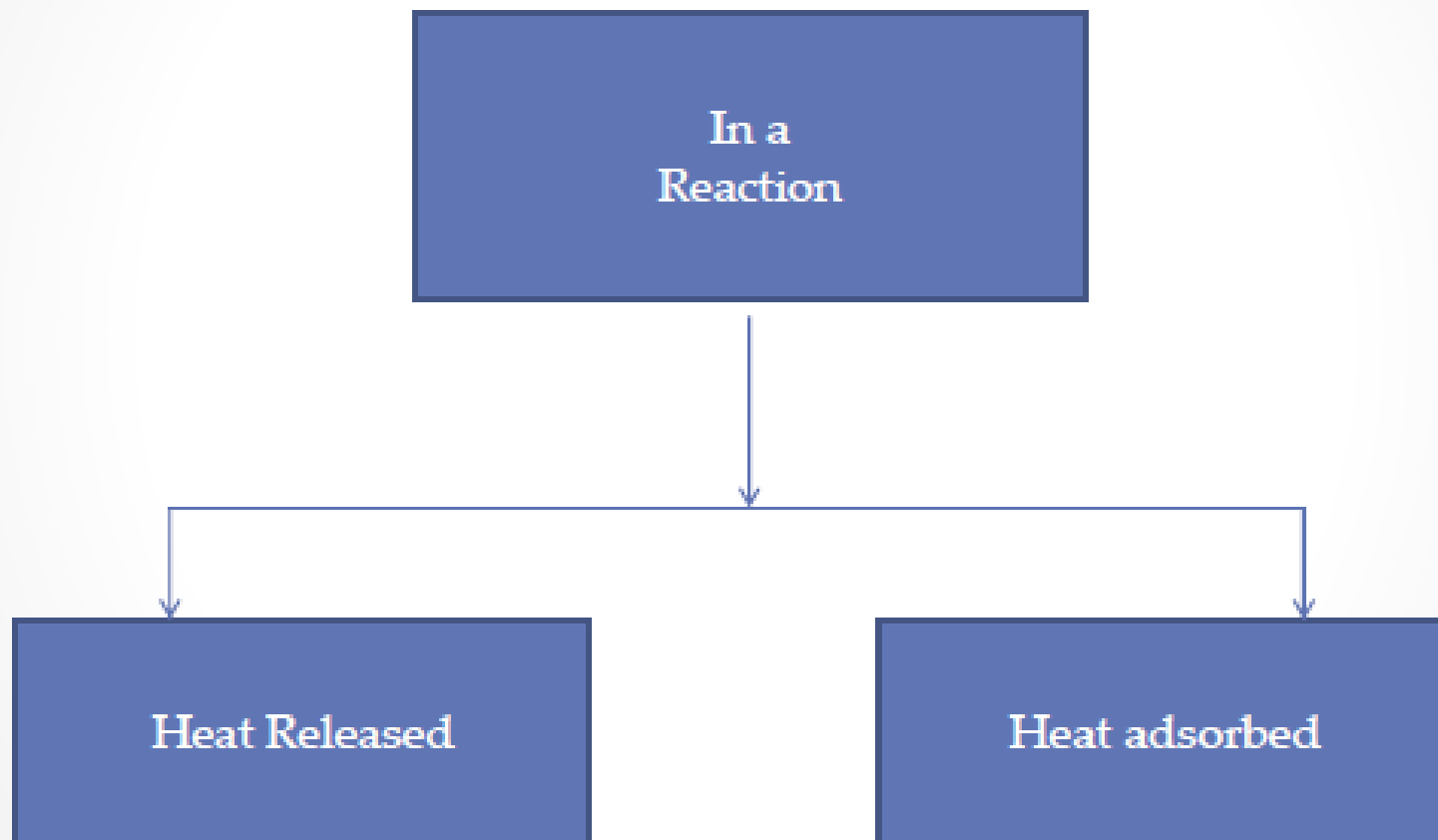# Thermochemistry

What is Thermochemistry ?

Thermochemistry is the study of
the energy and heat associated
with chemical reactions and/or physical
transformations. A reaction may release
or absorb energy, and a phase change may
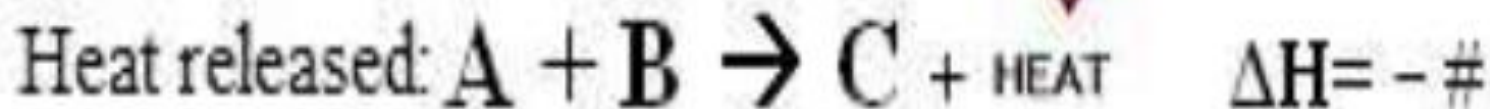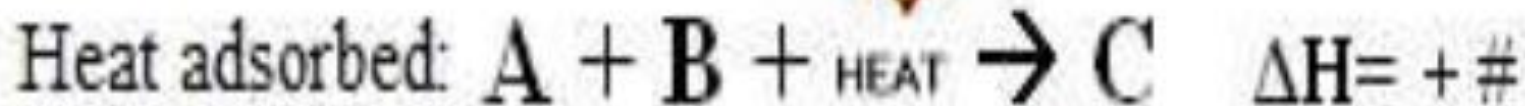do the same, such as
in melting and boiling.

Origin of Heat of Reaction

In a chemical reaction, the amount of heat that must be added or removed in order to keep all of the substances present at the same temperature. Some reactions will release energy and some reactions will adsorb energy and the energy will work here is Heat.
Whenever a chemical reaction will occur, it will release heat or will adsorb heat.

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So, We can get two different types of Heat of Reaction.

In a
Reaction

Heat Released

Heat adsorbed

Heat adsorbed: $A + B + \text{HEAT} \rightarrow C$ $\Delta H = +\#$

Heat released: $A + B \rightarrow C + \text{HEAT}$ $\Delta H = -\#$

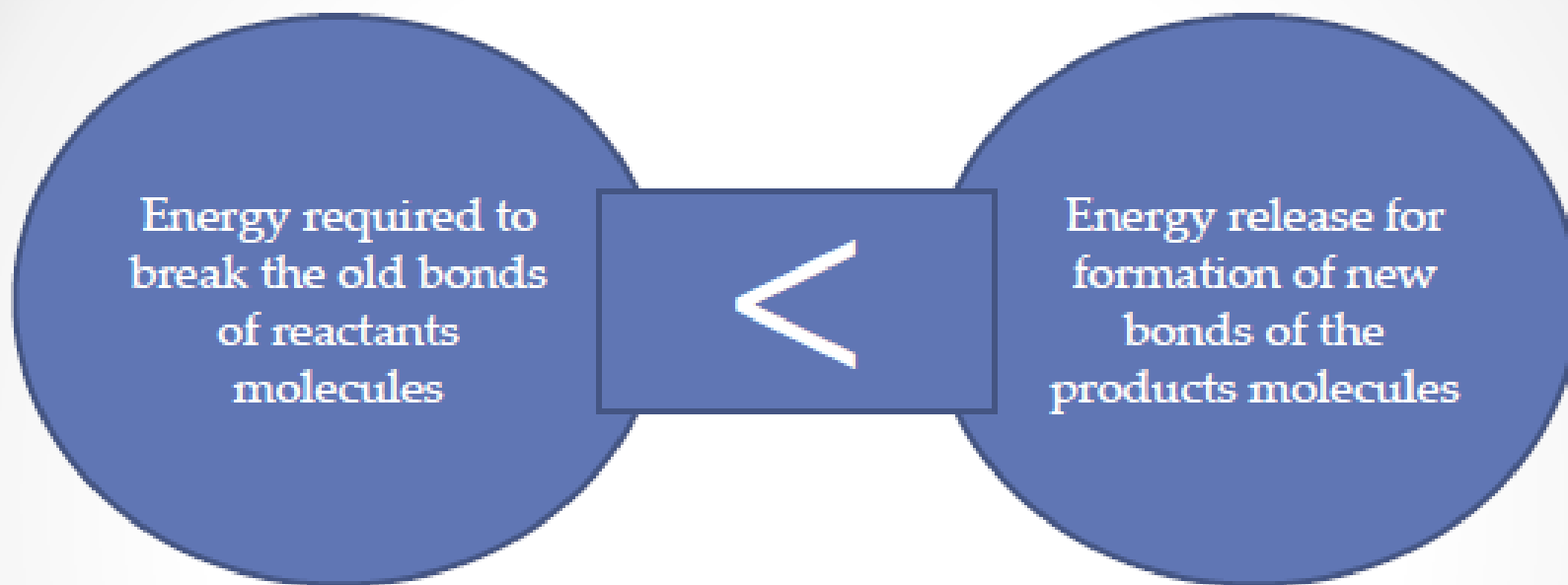Dept. of Chem.B. N. College BGP_ Dr. Ambika Kr.
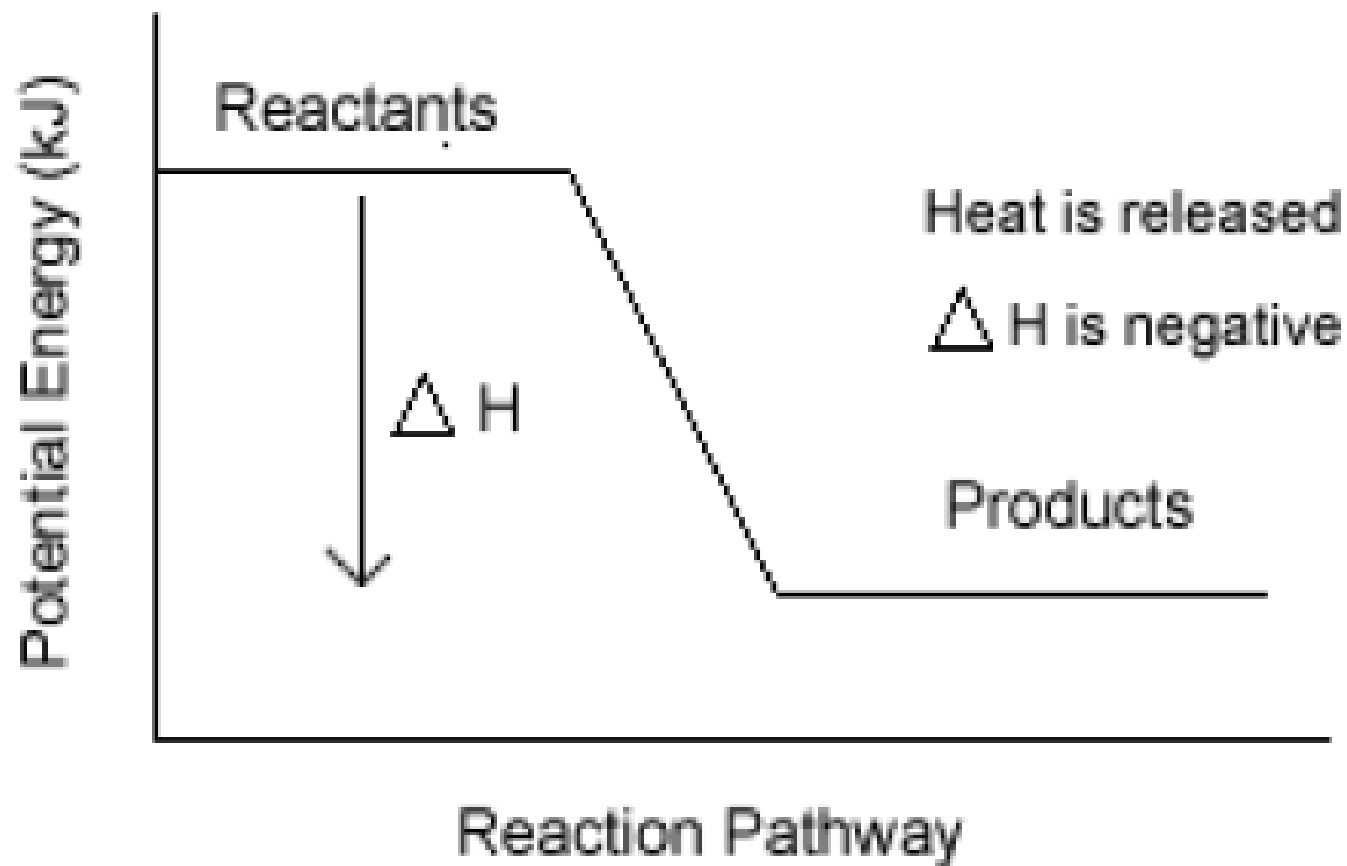
Exothermic Reaction

Many reactions release energy in the form of heat, light, or sound. These are exothermic reactions.
In a chemical reaction, the amount of energy required to break the old bonds of the reactants is lower than amount of energy released for formation of new bonds of the products and thereby heat is transferred from system to surrounding is referred to as Exothermic reaction.

Energy required to break the old bonds of reactants molecules **<** Energy release for formation of new bonds of the products molecules

System → Heat transfer → Surrounding

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EXOTHERMIC REACTION

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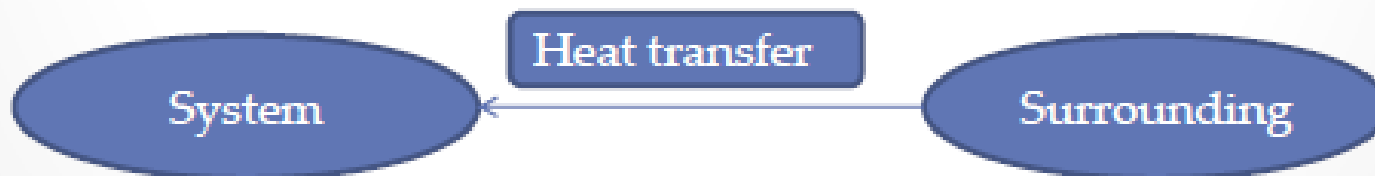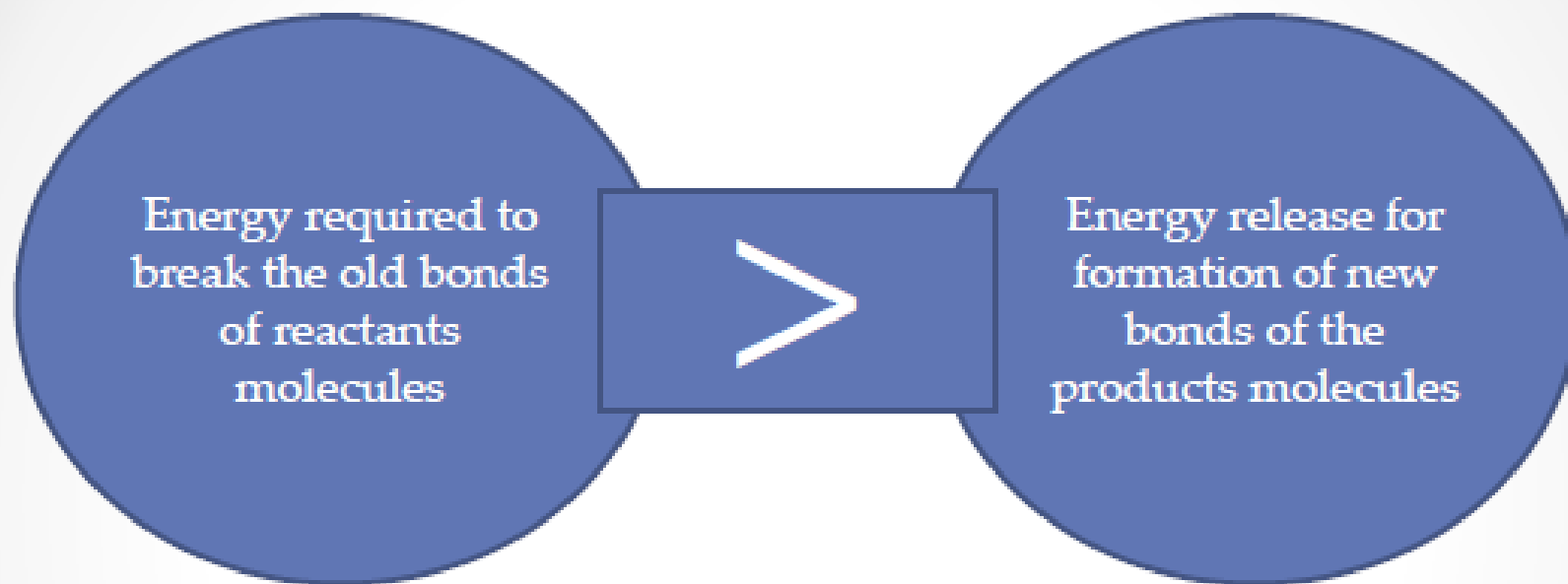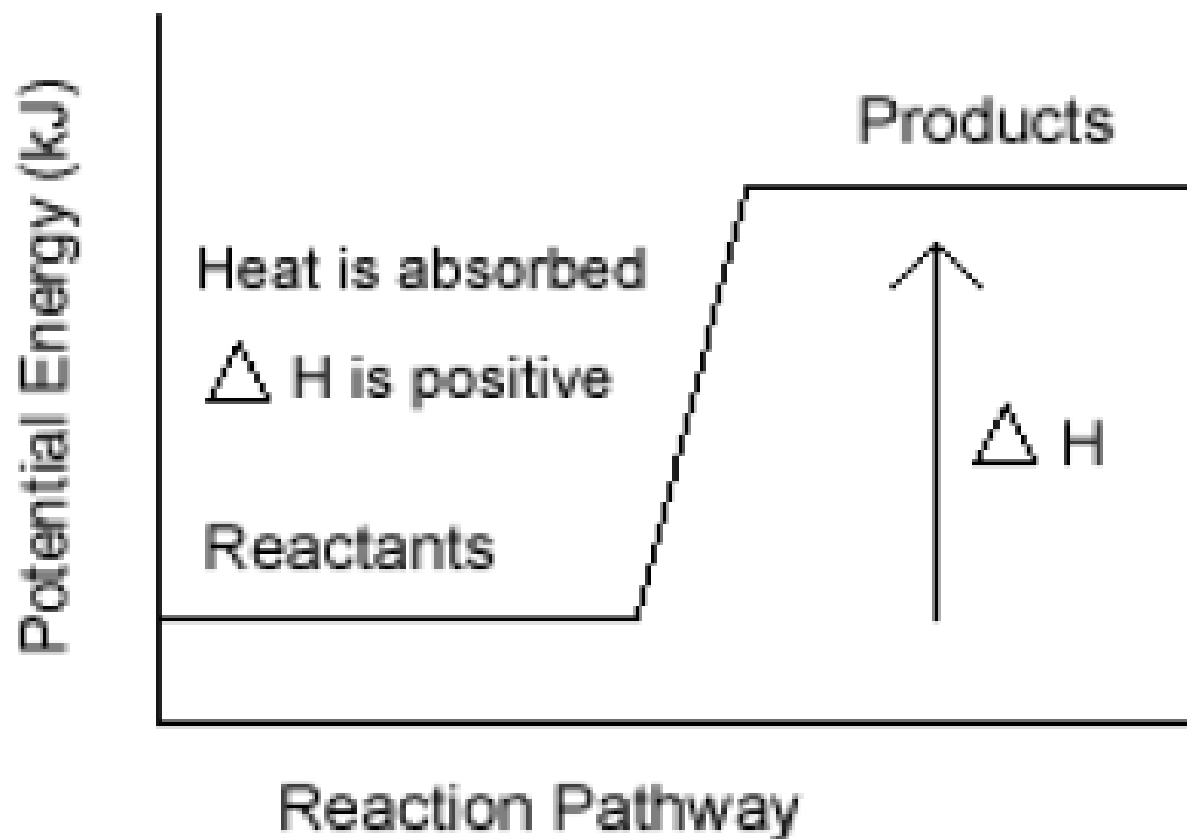
Endothermic Reaction

An endothermic reaction is any chemical reaction that absorbs heat from its environment.

In a chemical reaction, the amount of energy required to break the old bonds of the reactants is higher than amount of energy released for formation of new bonds of the products and thereby heat is penetrated from surrounding to system is referred to as Exothermic reaction.

Energy required to break the old bonds of reactants molecules

>

Energy release for formation of new bonds of the products molecules

Heat transfer

System

Surrounding

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ENDOTHERMIC REACTION

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Graphical representation of Exothermic and Endothermic reactions

A graph is scatted out putting time or rate of reaction or reaction coordination along x axis against energy or heat along y axis. Let A and B two reactants produce C and D two products by a reaction.
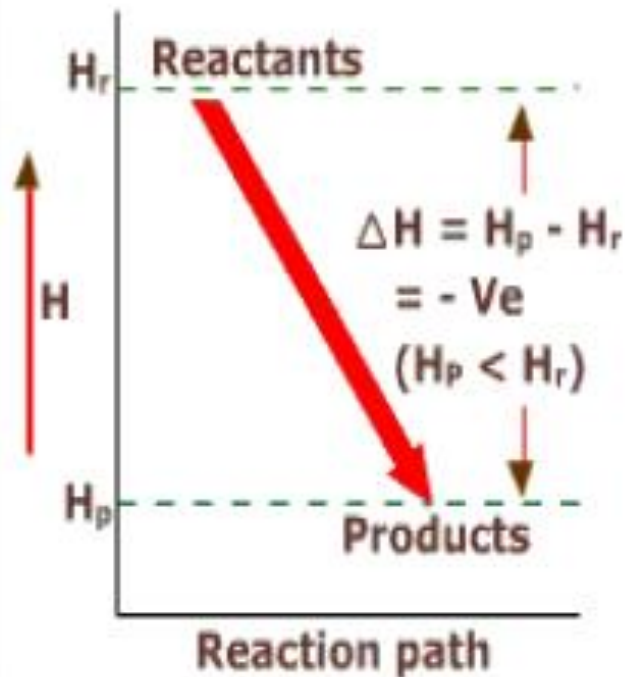
If the reaction release heat then it will be exothermic reaction and if the reaction adsorb heat then it will be endothermic reaction.

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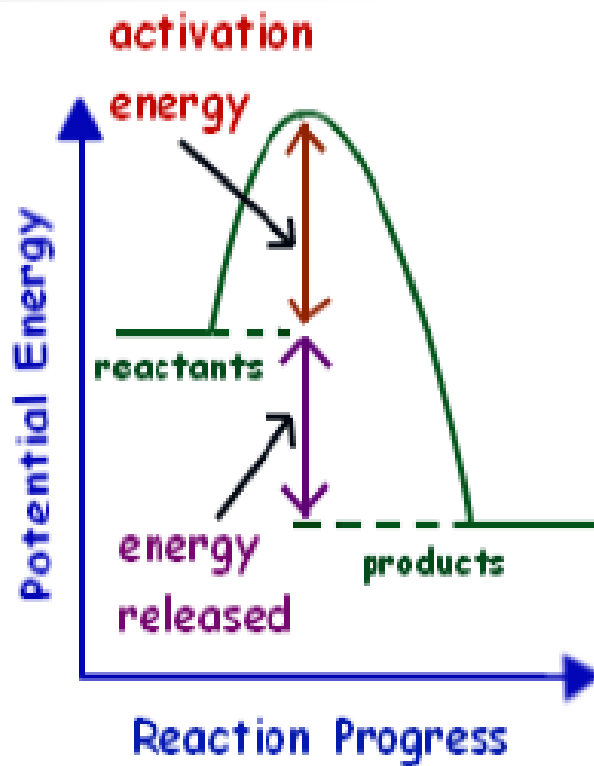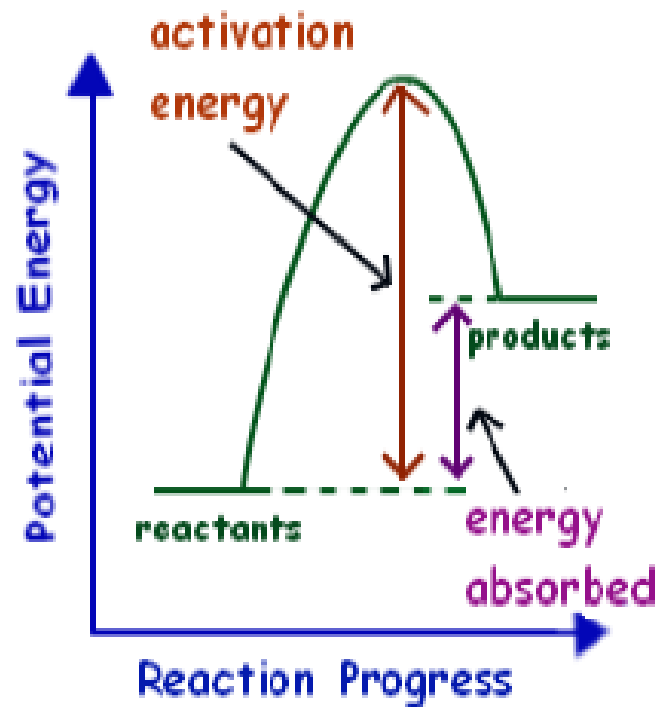
(a) Enthalpy change during an Exothermic reaction
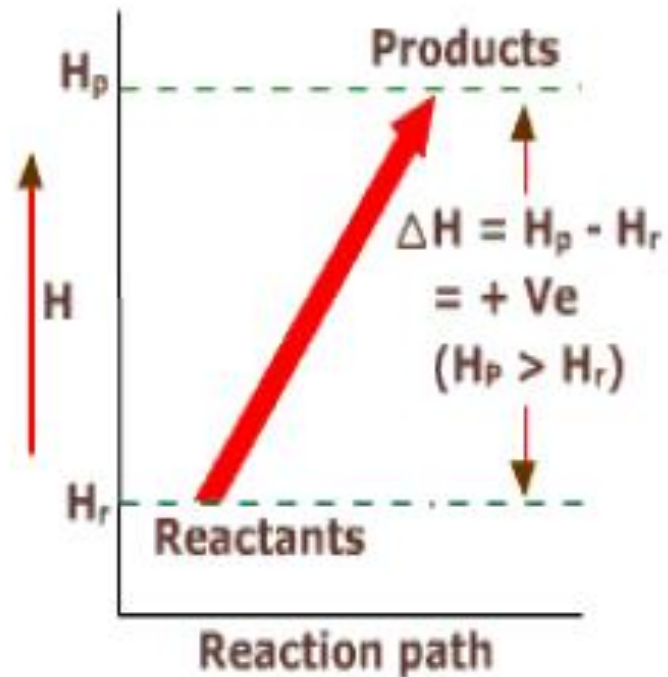
(b) Enthalpy change during Endothermic reaction

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Different type of heat reactions

There are four different types of heat reactions. Those are:

- Heat of formation
- Heat of decomposition
- Heat of combustion
- Enthalpy or Heat of Neutralisation

Heat of Formation

The heat of formation of a compound may be defined as the quality of heat change during the formation of one mole of a substance from this constituent elements.
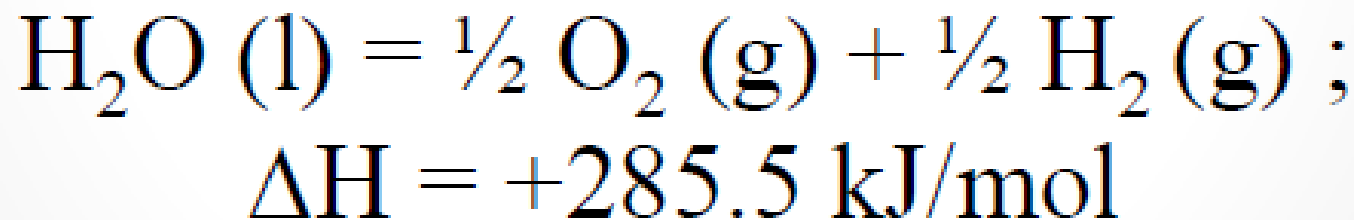
For example, the standard enthalpy of formation of carbon dioxide would be the enthalpy of the following reaction under the conditions above:

$$C_{(s,graphite)} + O_{2(g)} \rightarrow CO_{2(g)} \; ; \; \Delta H_f = -393.5 \text{ kJ/mol}$$

Imp: Here all elements are written in their standard states, and one mole of product is formed. This is true for all enthalpies of formation.
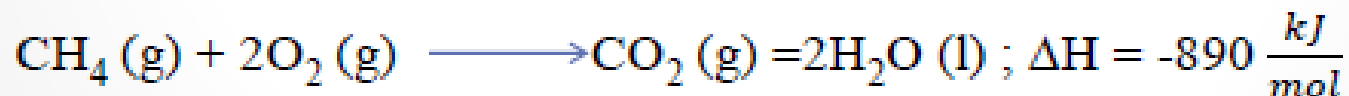
Heat of Decomposition

The amount of heat required to decompose 1 mole of a substance to its constituent elements is called Heat of Decomposition.

$$H_2O \,(l) = \tfrac{1}{2}\, O_2\,(g) + \tfrac{1}{2}\, H_2\,(g)\,;$$
$$\Delta H = +285.5 \text{ kJ/mol}$$

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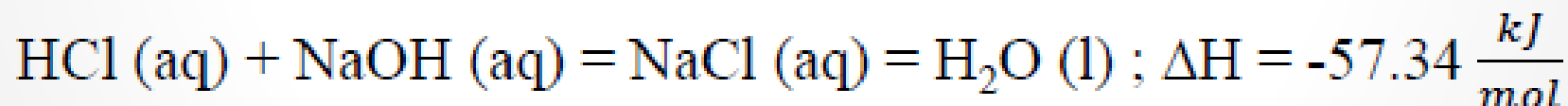
Heat of Combustion

The heat of combustion of a compound or an element is defined as the amount of heat evolved, when 1 mole of a substance is burnt completely in oxygen at a given temperature at 1 atm. Pressure.

$$CH_4 \text{ (g)} + 2O_2 \text{ (g)} \longrightarrow CO_2 \text{ (g)} = 2H_2O \text{ (l)} ; \Delta H = -890 \frac{kJ}{mol}$$

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Enthalpy or Heat of Neutralisation

Heat of Neutralisation is defined as the change of heat or enthalpy during the formation of one mole of water by the neutralisation reaction of required amounts of an acid and a base.

$$HCl\ (aq) + NaOH\ (aq) = NaCl\ (aq) = H_2O\ (l) \; ; \; \Delta H = -57.34 \frac{kJ}{mol}$$

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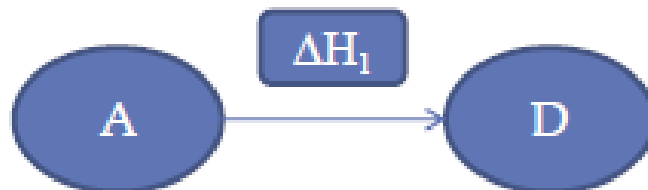# Hess's Law

If a reaction can take place by more then one routes the overall change in enthalpy is the same whichever route is followed.

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Illustration of Hess's Law

Let us assume that a reactant A gives product D directly by a single step and its change of enthalpy is ΔH_1.
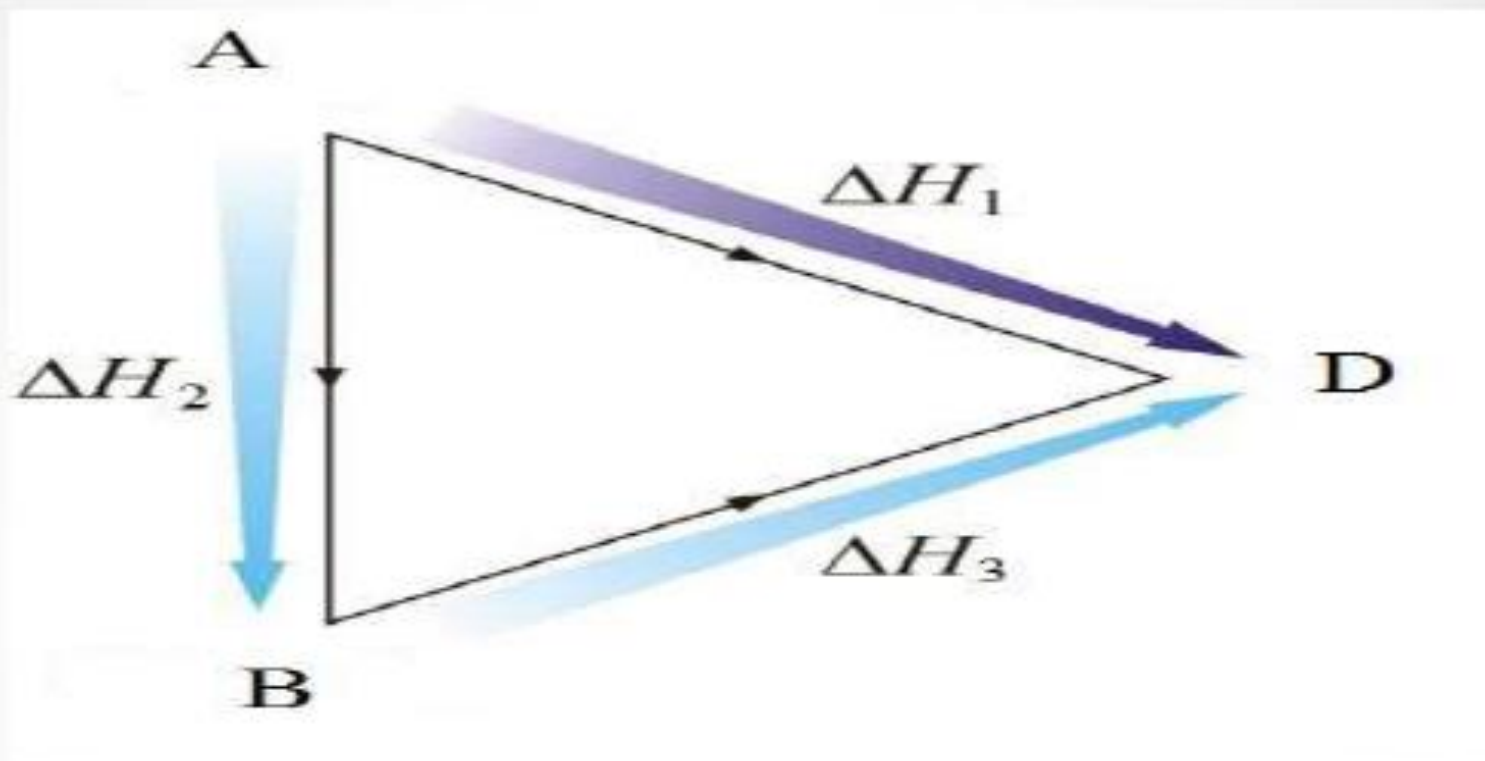
A → D with ΔH_1

Now the same reactant A produce D into two steps. First A is converted into B with an enthalpy change ΔH_2 and in the 2nd step intermediate product B is converted in to D with enthalpy change ΔH_3.

ΔH_2

A → B

ΔH_3

B → D

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According to the Hess's law, we get

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

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It follows also that the standard enthalpy change for the reaction D→A is -ΔH and for A→D is + ΔH.

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Application of Hess's law

- Hess's law used for,

- To calculate heat of formation, combustion, neutralization, ionization etc

- To calculate the heat of reaction which may not take place normally or directly.

- To calculate heat of extremely slow or fast reactions.

- To calculate enthalpies of reactants and product.

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Kirchhoff's Law

Kirchhoff's Law describes the **enthalpy of a reaction's variation with temperature changes**. In general, enthalpy of any substance increases with temperature, which means both the products and the reactants' enthalpies increase. **The overall enthalpy of the reaction will change if the increase in the enthalpy of products and reactants is different.**

At constant pressure, the heat capacity is equal to change in enthalpy divided by the change in temperature:

$$c_p = \frac{\Delta H}{\Delta T}$$

Therefore, if the heat capacities do not vary with temperature then the change in enthalpy is a function of the difference in temperature and heat capacities. The amount that the enthalpy changes by is proportional to the product of temperature change and change in heat capacities of products and reactants. Hence, enthalpy at a particular temperature can be calculated using integrated form of above equation (i):

$$H_{T_f} = H_{T_i} + \int_{T_i}^{T_f} c_p dT$$

Where
➢ c_p is the heat capacity (assumed constant)
➢ H_{T1} and H_{T2} are the enthalpies at the respective temperatures
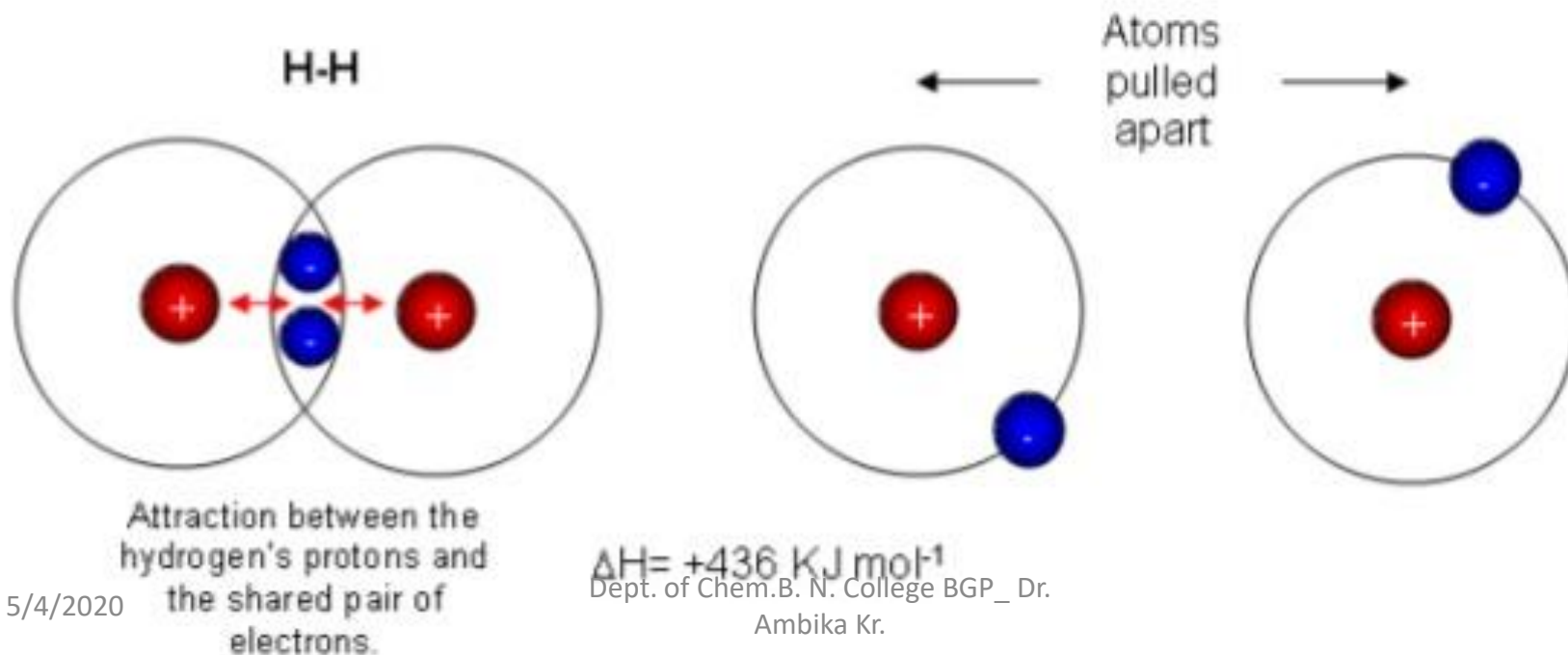
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If the heat capacity is temperature independent over the temperature range (between T_i and T_f), then Equation 1. can be expressed as:

$$H_{T_f} = H_{T_i} + c_p(T_f - T_i)$$

Note: Above equation is applicable for small temperature differences **(< 100 K),** As for higher temperature, c_p may also not remain constant.

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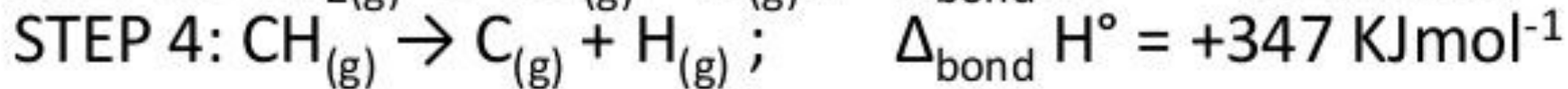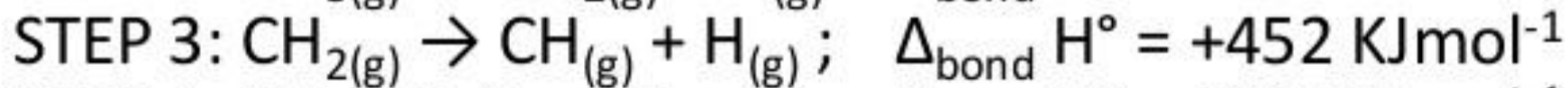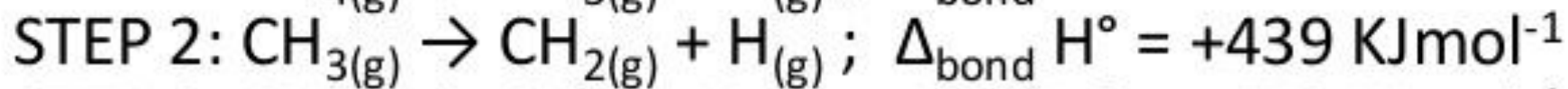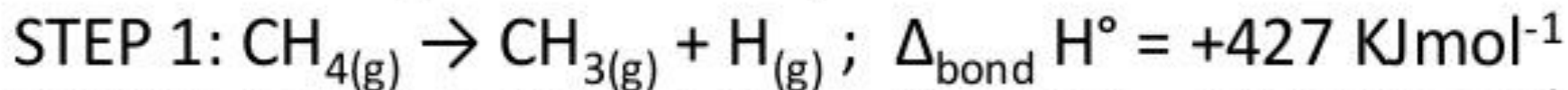
Bond Enthalpy or Bond energy

- **Amount of heat require to break 1 mole of particular covalent bonds of gaseous molecule forming free gaseous atoms or radicals at constant temperature and pressure.**

H-H

Atoms pulled apart

Attraction between the hydrogen's protons and the shared pair of electrons.

$\Delta H = +436 \, KJ \, mol^{-1}$

Bond dissociation enthalpy

Amount of energy require to break 1 mole of of a particular bond of a particular polyatomic gaseous molecules forming free gaseous atoms and radicals at constant temperature and pressure.

STEP 1: $CH_{4(g)} \rightarrow CH_{3(g)} + H_{(g)}$; $\Delta_{bond} H° = +427$ KJmol^{-1}
STEP 2: $CH_{3(g)} \rightarrow CH_{2(g)} + H_{(g)}$; $\Delta_{bond} H° = +439$ KJmol^{-1}
STEP 3: $CH_{2(g)} \rightarrow CH_{(g)} + H_{(g)}$; $\Delta_{bond} H° = +452$ KJmol^{-1}
STEP 4: $CH_{(g)} \rightarrow C_{(g)} + H_{(g)}$; $\Delta_{bond} H° = +347$ KJmol^{-1}

Average bond enthalpy $\Delta_{C-H}H° = ¼ (\Delta_a H°)$
$= ¼ (1665$ KJmol$^{-1})$
$= 416$ KJmol^{-1}

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