Std-XI science- Lecture-30

Unit 6:

THERMODYNAMICS

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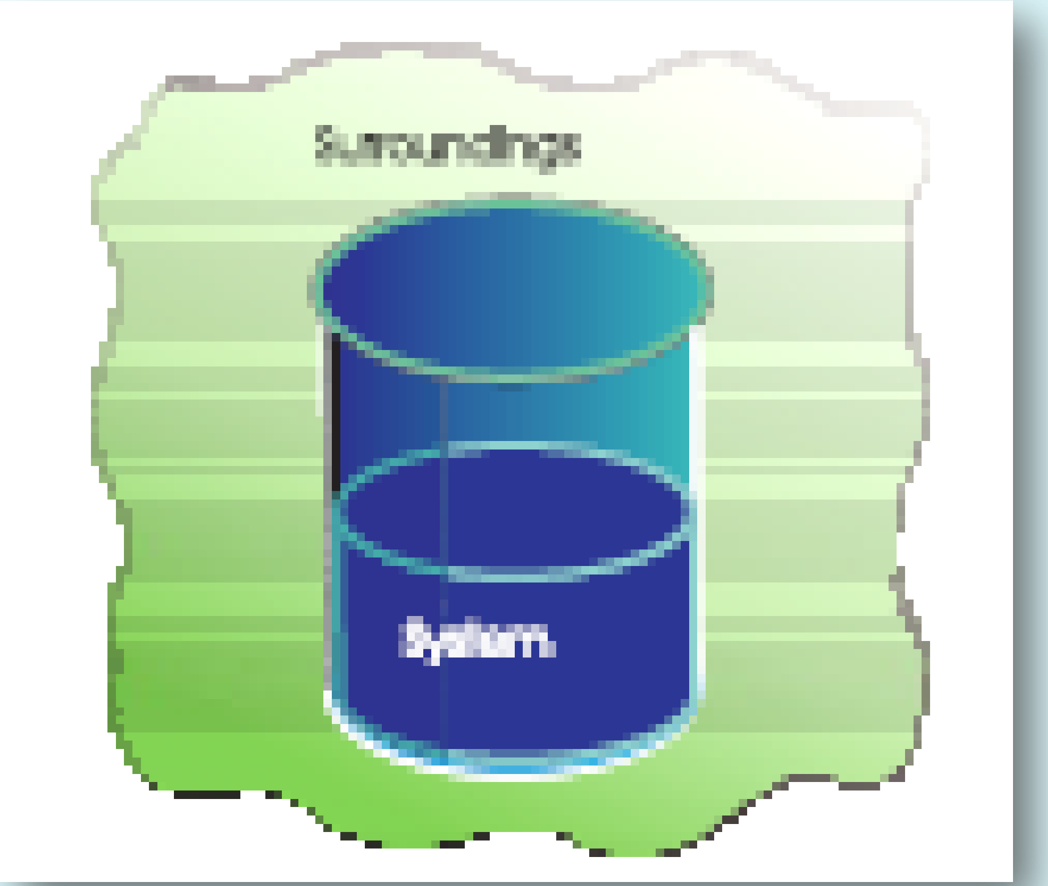
What is THERMODYNAMICS ????

- *How do we determine the energy changes involved in a chemical reaction/process? Will it occur or not?*

- *What drives a chemical reaction/process?*

- *To what extent do the chemical reactions proceed?*

System and the surroundings



The System and the Surroundings

- A **system in thermodynamics refers to that** part of universe in which observations are made and remaining universe constitutes the **surroundings.**
- **The surroundings include** everything other than the system.
- System and the surroundings together constitute the universe .
- **The universe** = The system + The surroundings

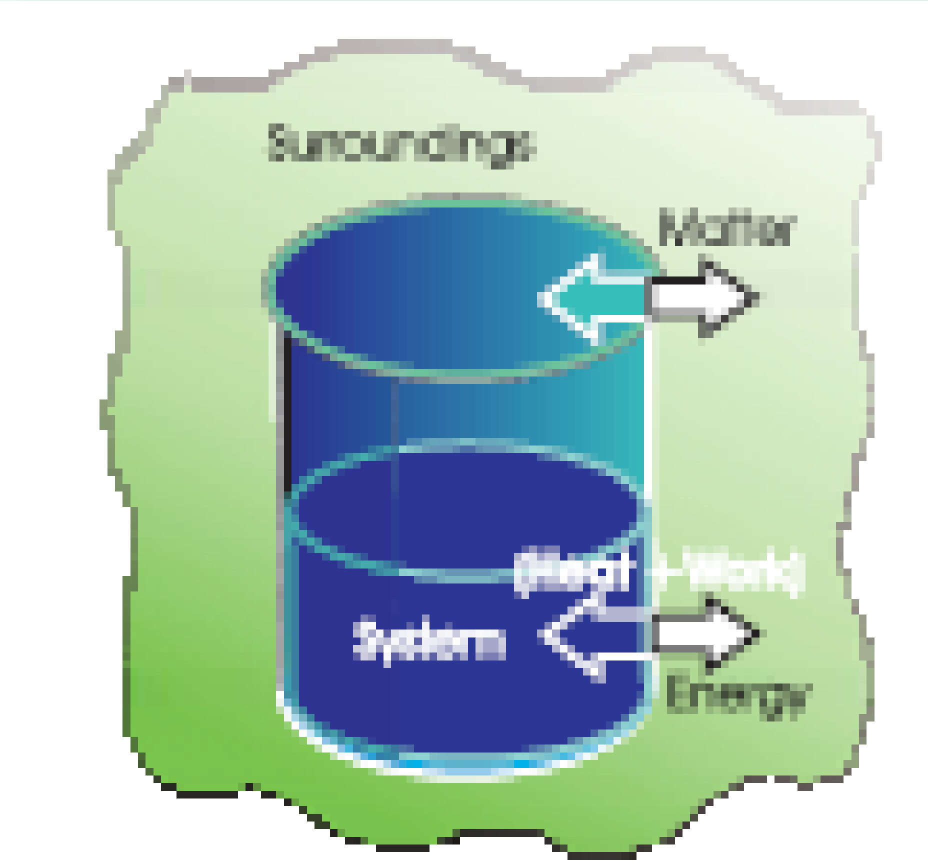
Boundary

- It is necessary to think of the system as separated from the surroundings by some sort of wall which may be real or imaginary.
- The wall that separates the system from the surroundings is called **boundary.**

Types of the System

1. **Open System**
2. **Closed System**
3. **Isolated System**

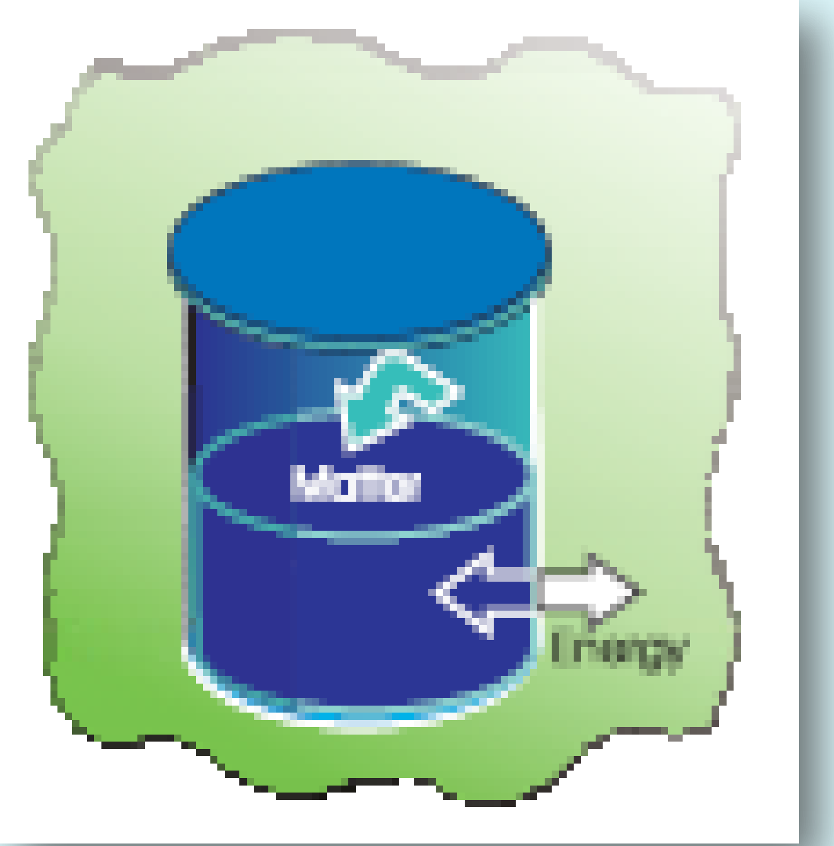
Open System



Open System

- In an open system, there is **exchange** of **energy** and **matter** between system and surroundings
- The presence of reactants in an open beaker is an example of an open system*.
- Here the boundary is an imaginary surface enclosing the beaker and reactants.

Closed System



Closed System

- In a closed system, there is no exchange of **matter,** but **exchange** of **energy** is possible between system and the surroundings
- The presence of reactants in a closed vessel made of conducting material e.g., copper or steel is an example of a closed system.

Isolated System

Isolated System

- In an isolated system, there is **no** exchange of **energy** or **matter** between the **system** and the **surroundings**

- The presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system.

The State of the System

- The system must be described in order to make any useful calculations by specifying quantitatively each of the properties such as its pressure (p), *volume* (V), *and temperature* (T) *as well as the composition of the system.*

- In thermodynamics, a different and much simpler concept of the state of a system is introduced.

State functions

- We specify the state of the system by **state functions or state variables.**
- The **state of a thermodynamic system is** described by its measurable or macroscopic (bulk) properties.
- We can describe the state of a gas by quoting its pressure (*p*), *volume* (*V*), temperature (*T*), *amount* (*n*) *etc.*
- *Variables like p, V, T are called* ***state variables or state*** **functions**

The Internal Energy , *U*

- A quantity which represents the total energy of the system.
- It may be chemical, electrical, mechanical or any other type of energy, the sum of all these is the energy of the system.

The Internal Energy , *U*

- In thermodynamics, we call it the **internal energy**, ***U*** *of the system, which may* change, when

- heat passes into or out of the system,

- work is done on or by the system,

- matter enters or leaves the system.

The Internal Energy as a State Function

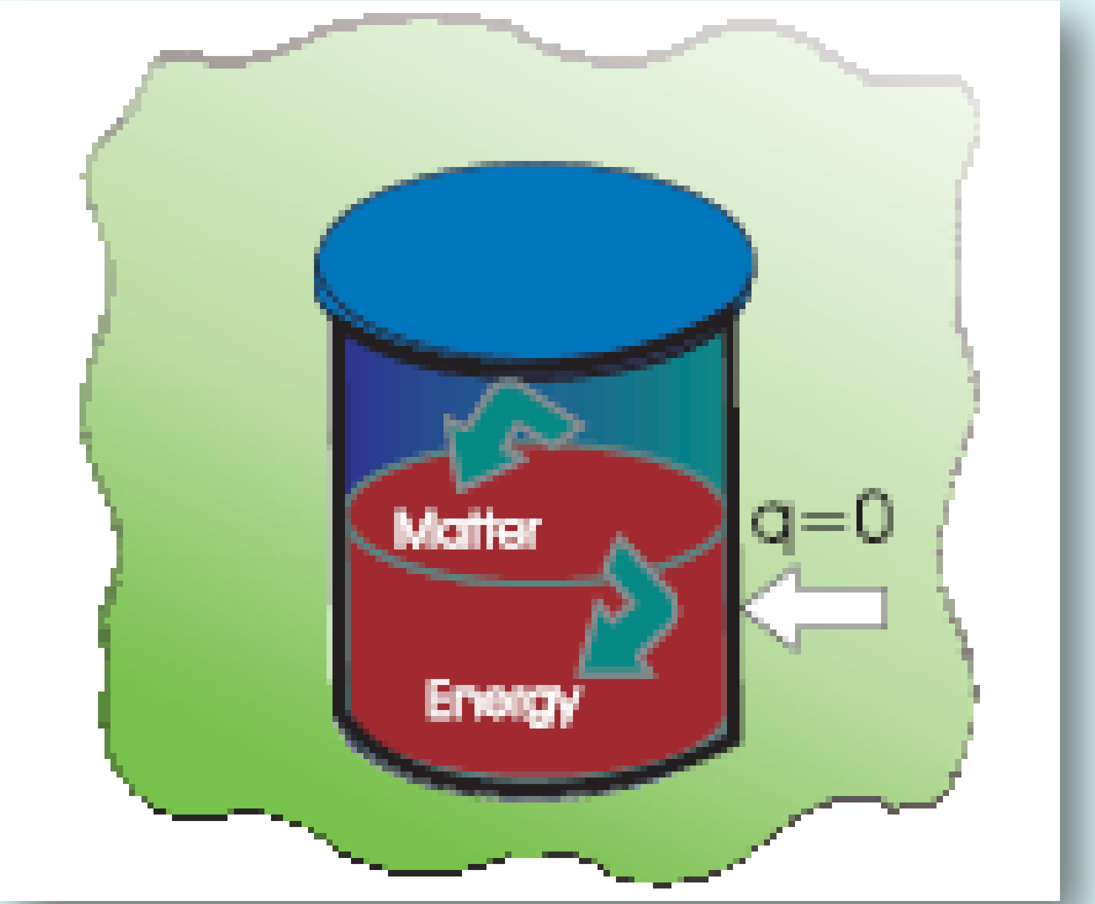
- $\Delta U = U2 - U1 = W_{ad}$
- **Since Internal Energy change depends only on final & initial state of a system & not on how that state is achieved therefore**
- Internal energy, ***U***, *of the system* is a state function.

Change in Internal energy

- Change in internal energy can be carried out by doing **work**.

- Change the internal energy of a system can also be obtained by transfer of **heat** from the surroundings to the system or vice-versa without expenditure of work.

Adiabatic process



Adiabatic process

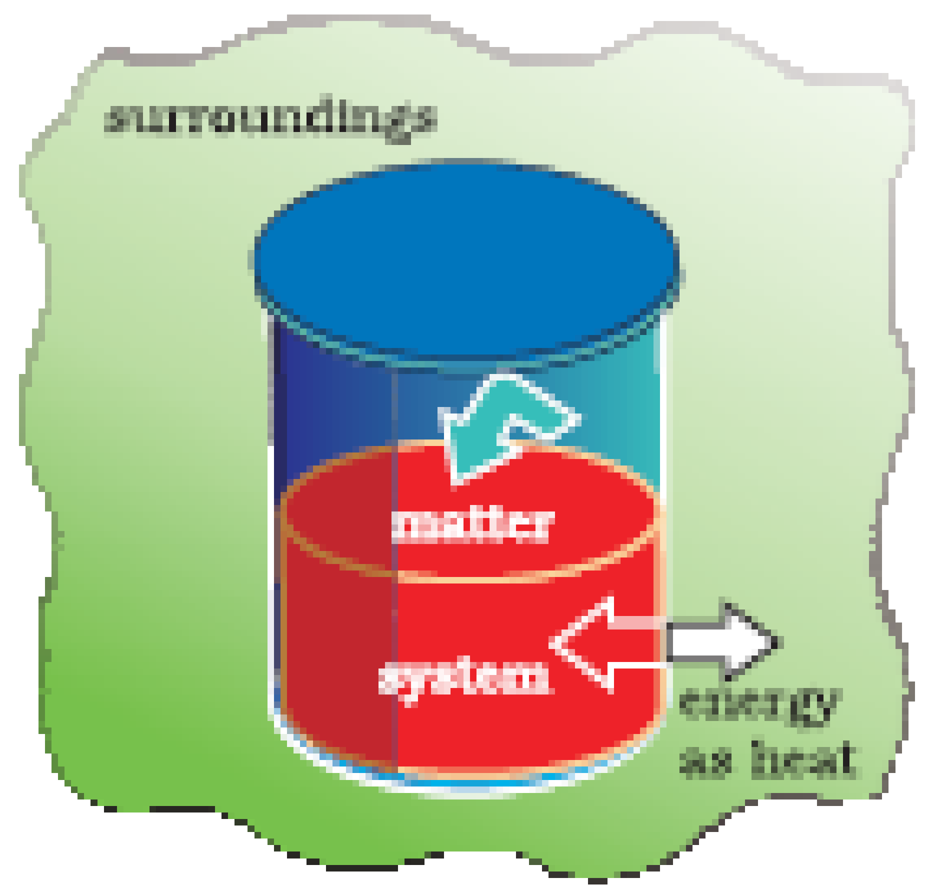
- Adiabatic process is a process in which there is no transfer of heat between the system and surrounding.
- Here, the wall separating the system and the surroundings is called the adiabatic wall

Work (w)

- The positive sign expresses that w_{ad} is **positive** when work is done **on the system.**

- Similarly, if the work is done **by the system,** w_{ad} will be **negative**.

Heat



Heat (q)

- *The* ***q*** *is* ***positive****, when heat is transferred from the surroundings to the system and*
- ***q*** *is* ***negative*** *when heat is transferred from system to the surroundings.*

First law of thermodynamics

The equation $\Delta U = q + w$

- Is mathematical statement of the **first law of thermodynamics, which states that**
- ***The energy of an isolated system is constant.***
- It is commonly stated as the law of conservation of energy i.e., ***energy can neither be created nor be destroyed.***

Enthalpy, *H*

- The enthalpy H *[Greek word enthalpien, to warm or heat content] is defined as* $\mathbf{H = U + pV}$ **…….1**
- For finite changes at constant pressure, we can write equation ***1*** as $\Delta H = \Delta U + \Delta pV$
- Since p *is constant, we can write* $\Delta H = \Delta U + p\Delta V$
- Remember $\Delta H = q_p$, *heat absorbed by the* system at constant pressure.

Enthalpy, *H*

- ***ΔH is negative for exothermic reactions*** **which evolve heat during the reaction and**

- ***ΔH is positive for endothermic reactions*** **which absorb heat from the surroundings.**

Extensive and Intensive Properties

- In thermodynamics, a distinction is made between extensive properties and intensive properties.
- An **extensive property is a** property whose value depends on the quantity or size of matter present in the system.
- For example, mass, volume, internal energy, enthalpy, heat capacity, etc. are extensive properties.

Extensive and Intensive Properties

- Those properties which do not depend on the quantity or size of matter present are known as **intensive properties.**

- **For example** temperature, density, pressure etc. are intensive properties.

Standard enthalpy of reactions

- Enthalpy of a reaction depends on the conditions under which a reaction is carried out.
- It is, therefore, necessary that we must specify some standard conditions.
- **The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.**

Standard state

- **The standard state of a substance at a specified temperature is its pure form at 1 bar.**
- **For example, the standard state of liquid** ethanol at 298 K is pure liquid ethanol at 1 bar;
- Standard state of solid iron at 500 K is pure iron at 1 bar.
- Usually data are taken at 298 K.
- Standard conditions are denoted by adding the superscript ^{o} *to the symbol* ΔH*, e.g.,* $\boldsymbol{\Delta H}^{o}$

Enthalpy changes during phase transformations

1. **Standard enthalpy of fusion or molar enthalpy of fusion,**

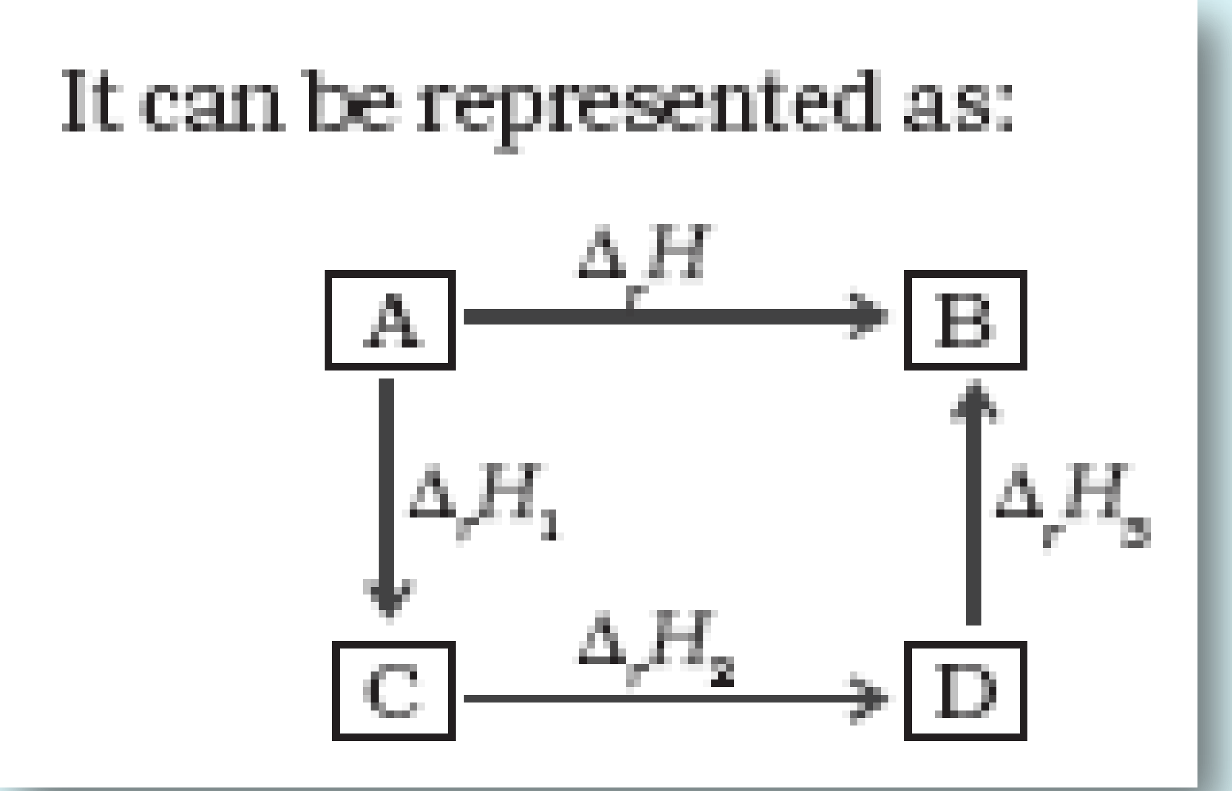
- ***The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called standard enthalpy of fusion or molar enthalpy of fusion,*** $\Delta_{fus}H^{o}$.

2. **Standard enthalpy of vaporization or molar enthalpy of vaporization,**
3. **Standard enthalpy of sublimation,**

Standard enthalpy of formation

- **The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation** *(also known as reference states)* **is called Standard Molar Enthalpy of Formation.**
- **Its symbol is $\Delta_f H^o$,**

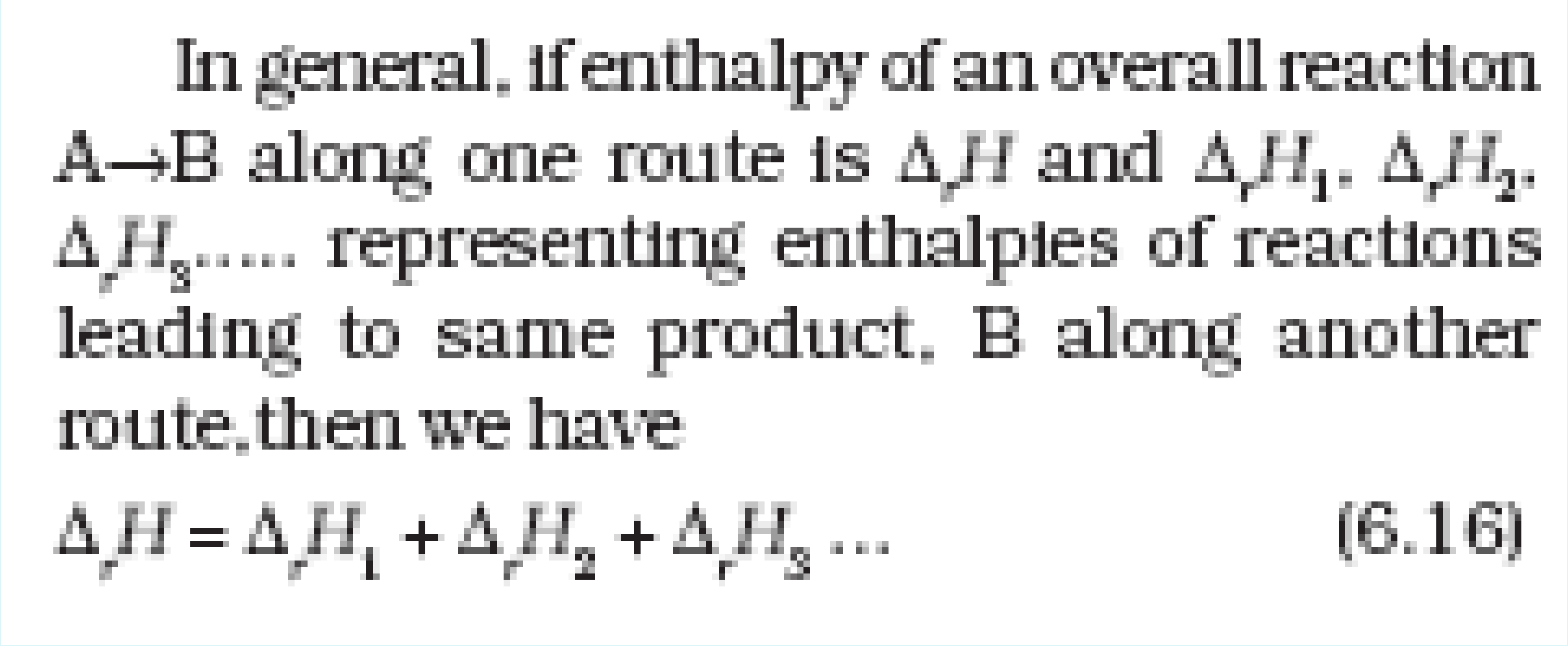
Hessís Law of Constant Heat Summation



It can be represented as:

$$\begin{tikzcd} A \arrow[r, "\Delta_r H"] \arrow[d, "\Delta_r H_1"] & B \\ C \arrow[r, "\Delta_r H_2"] & D \arrow[u, "\Delta_r H_3"'] \end{tikzcd}$$

Hessís Law of Constant Heat Summation



In general, if enthalpy of an overall reaction A→B along one route is $\Delta_r H$ and $\Delta_r H_1$, $\Delta_r H_2$, $\Delta_r H_3$..... representing enthalpies of reactions leading to same product, B along another route, then we have

$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 \ldots \qquad (6.16)$$

Hessís Law of Constant Heat Summation

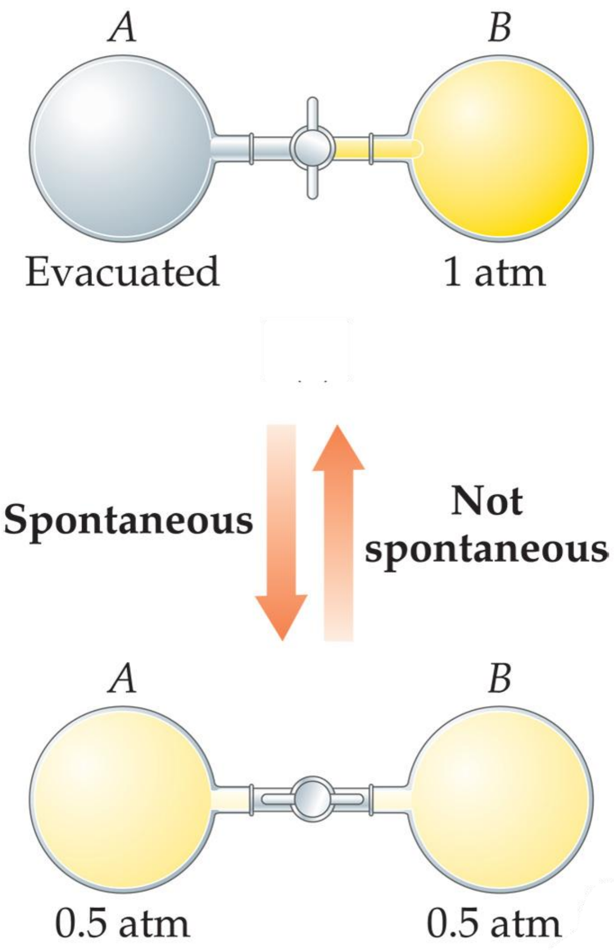
- **If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature.**

ENTHALPIES FOR DIFFERENT TYPES OF REACTIONS

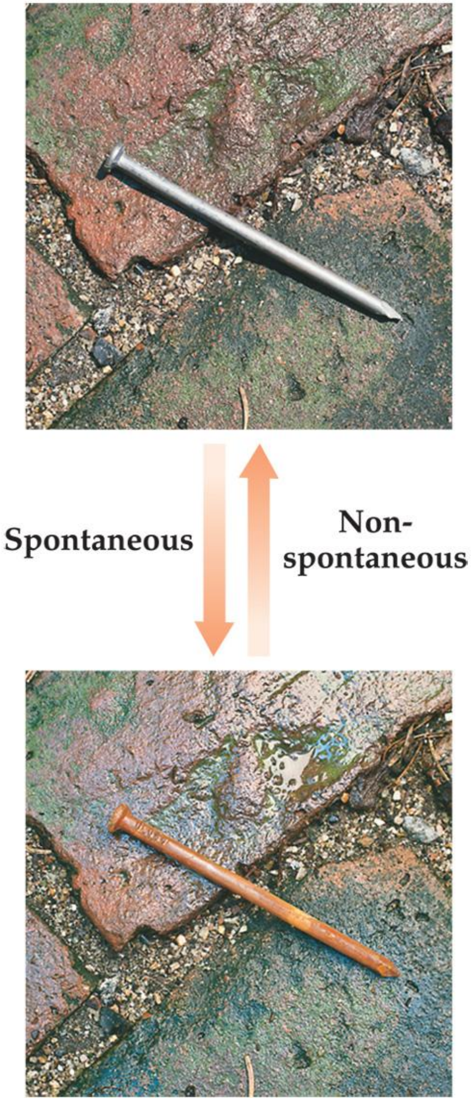
- ***Standard enthalpy of combustion***
- ***Enthalpy of atomization***
- ***Bond Enthalpy***
- ***Enthalpy of Solution***
- ***Lattice Enthalpy***

Spontaneous Processes

- Spontaneous processes are those that can proceed without any outside intervention.
- The gas in vessel *B* will spontaneously effuse into vessel *A*, but once the gas is in both vessels, it will *not* spontaneously



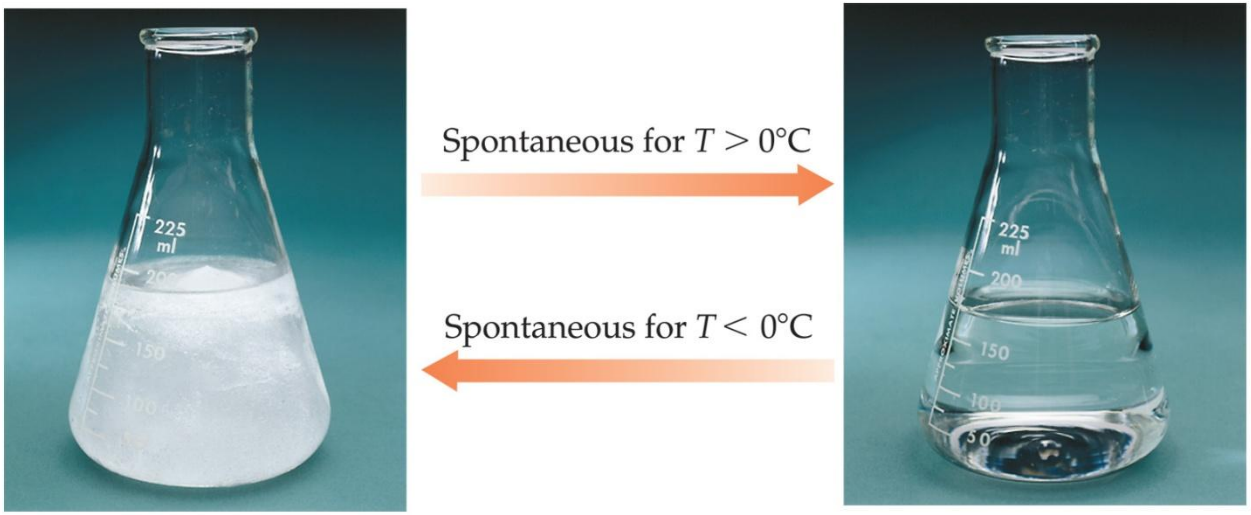
Spontaneous Processes



Processes that are spontaneous in one direction are non spontaneous in the reverse direction.

Spontaneous Processes

- Processes that are spontaneous at one temperature may be non-spontaneous at other temperatures.
- Above 0°C it is spontaneous for ice to melt.
- Below 0°C the reverse process is spontaneous.



SPONTANEITY

- We may summarise it as follows:

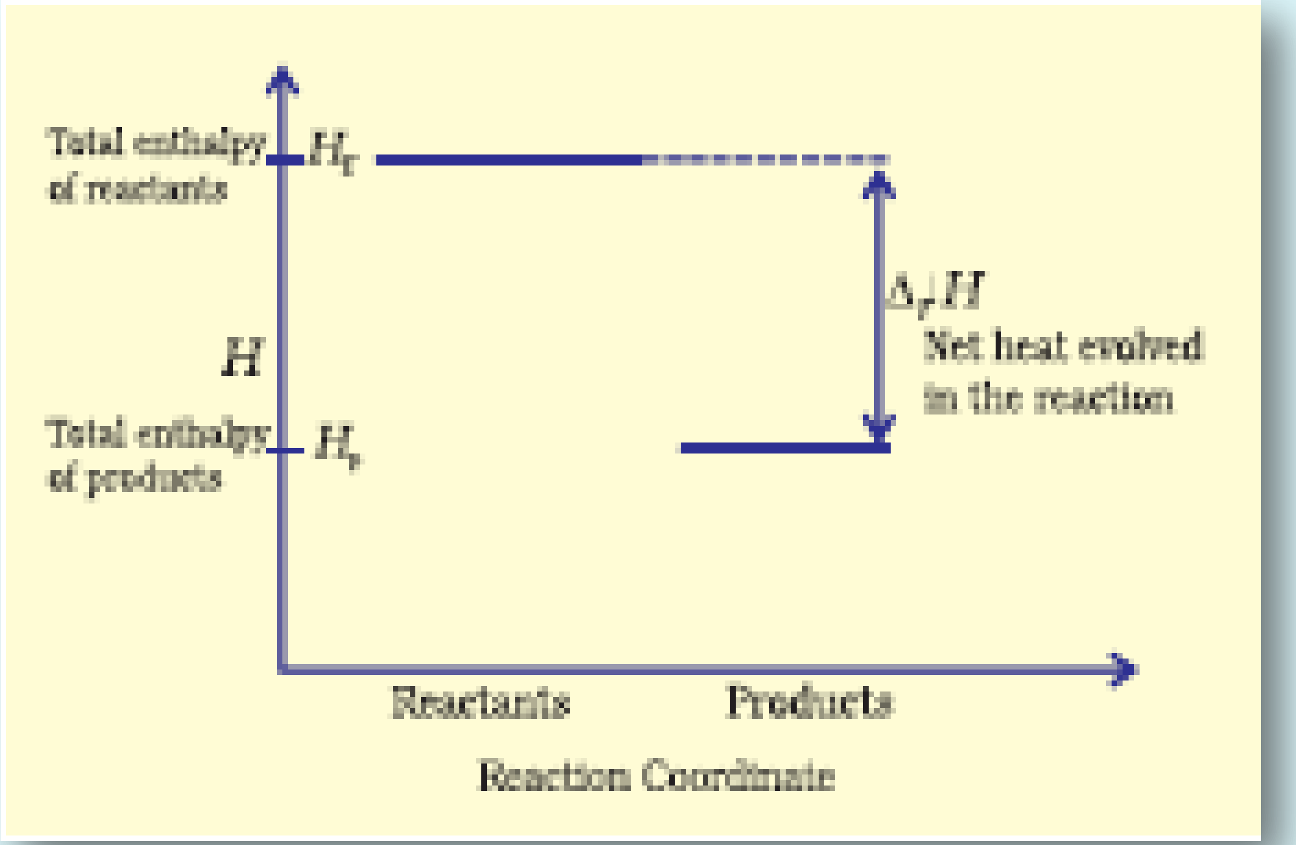
- ***A spontaneous process is an irreversible process and may only be reversed by some external agency.***

- So spontaneity means *having the potential to proceed without the assistance of external agency.*

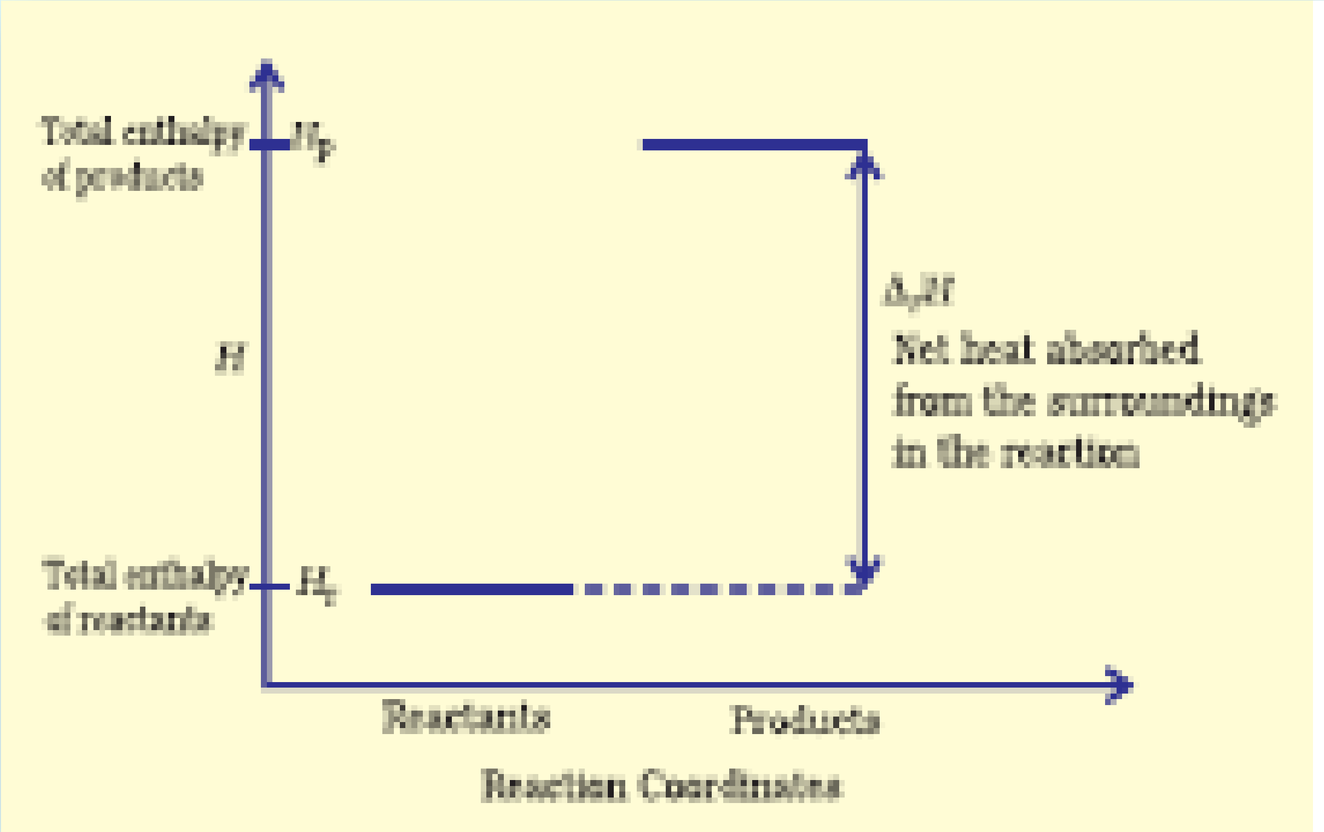
criterion for spontaneity ?

- ***(a) Is decrease in enthalpy a criterion for spontaneity ?***
- Ans ???
- No

Enthalpy diagram for exothermic reactions



Enthalpy diagram for endothermic reactions



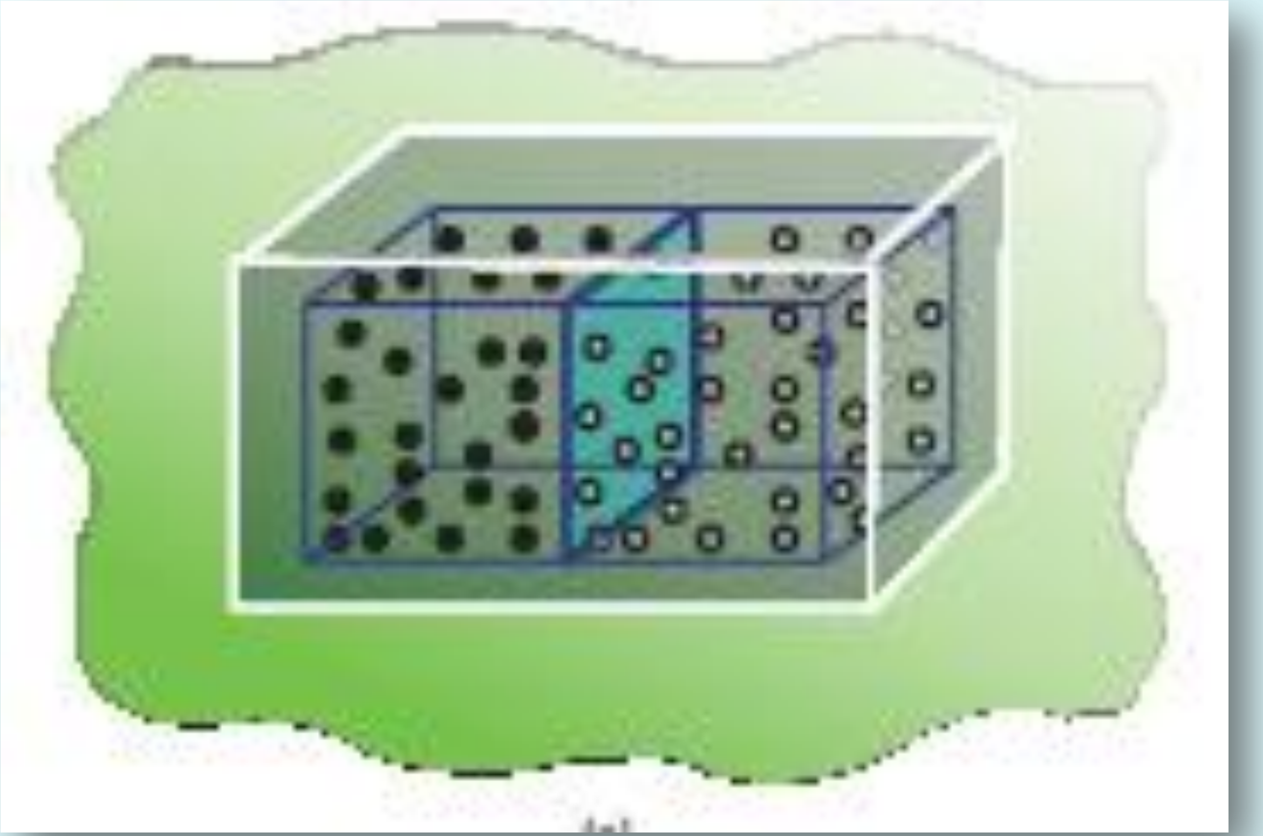
Enthalpy Change for Chemical reactions

Exothermic reactions	Endothermic reactions
$\Delta H = Hp - Hr$	$\Delta H = Hp - Hr$
ΔH = -ve	ΔH = +ve
$Hp < Hr$	$Hp > Hr$

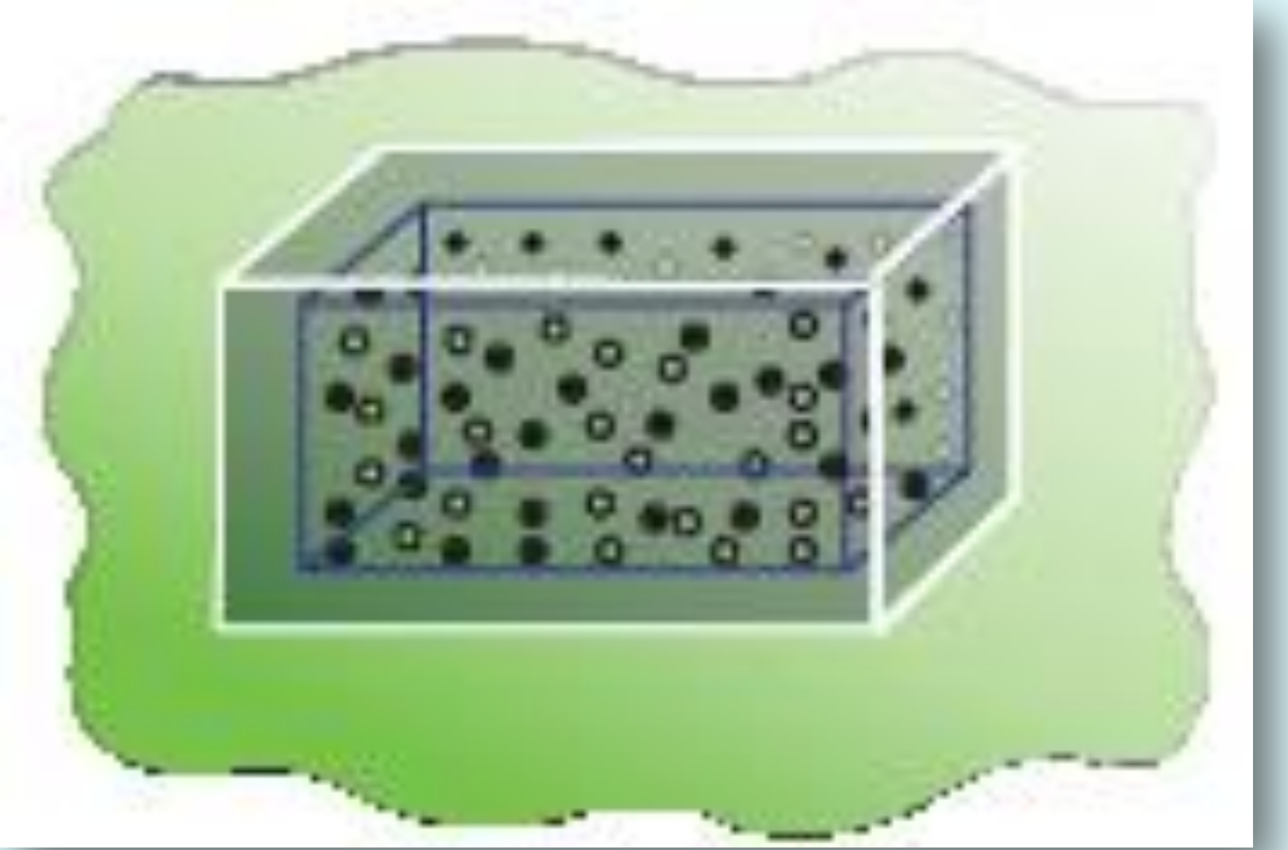
Entropy S

- Entropy can be thought of as a measure of the randomness of a system.
- It is related to the various modes of motion in molecules.

Diffusion of two gases



Diffusion of two gases



Entropy

- Like total energy, *E*, and enthalpy, *H*, entropy is a state function.
- Therefore,

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

Gibbs Free Energy

All chemical systems tend naturally toward states of minimum Gibbs free energy

$$G = H - TS$$

Where:

G = Gibbs Free Energy

H = Enthalpy (heat content)

T = Temperature in Kelvins

S = Entropy (can think of as randomness)

$$\Delta G = \Delta H - T \Delta S$$

Gibbs free energy is a measure of chemical energy

Change in Gibbs Free Energy

- ΔG *gives a criteria for spontaneity at* constant pressure and temperature.
- (i) If ΔG *is negative (< 0), the process is* spontaneous.
- (ii) If ΔG *is positive (> 0), the process is non* spontaneous

GIBBS ENERGY CHANGE AND EQUILIBRIUM

- The criterion for equilibrium
    - **A+B** → **C+D**; is
- $\Delta_r G = 0$
- Gibbs energy for a reaction in which all reactants and products are in standard state, $\Delta_r G^o$ *is related to the equilibrium constant of* the reaction as follows:
- $0 = \Delta_r G^o + RT \ln K$
- or $\Delta_r G^o = -RT \ln K$
- or $\Delta_r G^o = -2.303\, RT \log K$

Thank you

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