

## Chemical thermodynamics

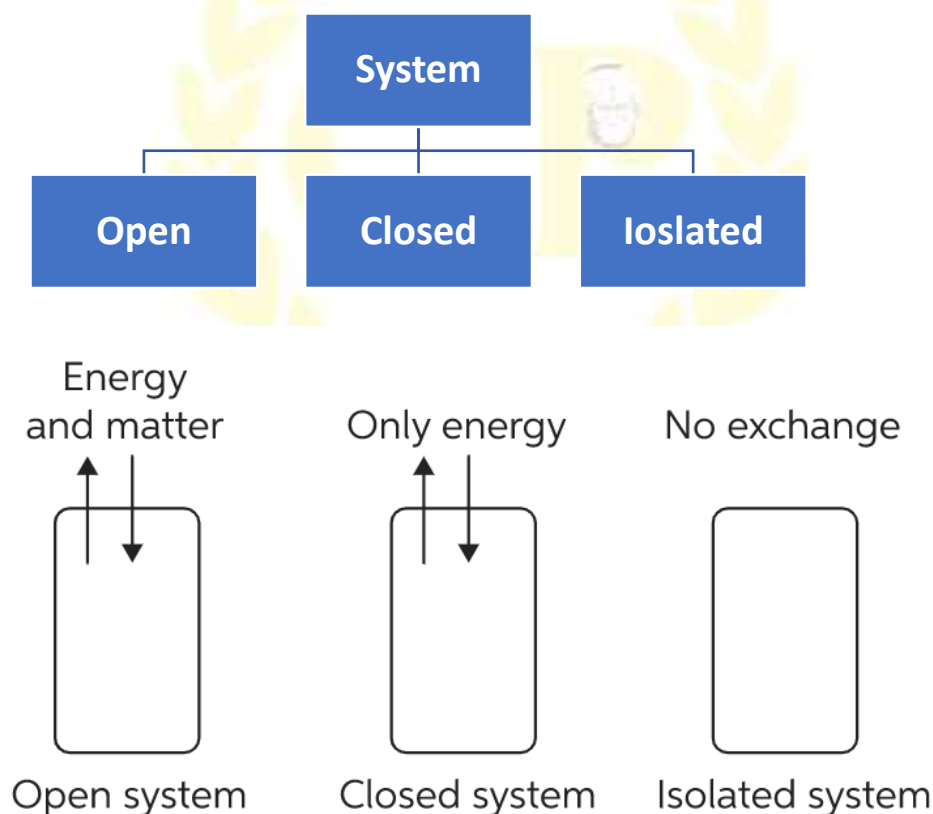
The branch of physical chemistry which deals with the flow of heat between system and surrounding and correlates the heat energy with work and other form of energies is known as thermodynamics.

### Thermodynamic terms:

#### The system and the surroundings-

- A part of universe which is selected for investigation is called system and rest part of universe is called surroundings.
- System and surrounding are separated by real or imaginary boundary.
- The Universe = system + surrounding

#### Types of the system



#### 1. Open System –

- In an open system there is exchange of energy and matter between the system and the surroundings

- The reactants present in an open beaker is an example of an open system. Other examples: Cup of tea, river, pond, test tube reaction without a cork.

## 2. Closed System –

- In a closed system exchange of matter does not take place, but exchange of energy is possible between the system and the surroundings.
- The presence of reactants in a closed vessel made of conducting material like copper or steel is an example of a closed system.
- Examples: Greenhouse system, condensation, distillation, etc.

## 3. Isolated System –

- In an isolated system there is no any exchange of energy or matter between the system and the surroundings.
- Example: Thermo flask.

## The state of the system –

- The system and the state of the system by state functions need to be described before and after the change.
- We can describe the state of a gas by its pressure (p), volume (V), temperature (T), amount (n) etc.
- Pressure (p), volume (V) and temperature (T) are called state variables or state functions because their values depend upon the state of the system.

## The internal energy as a state function –

- The energy of a system is known as internal energy. It is denoted by **U**.
- Internal energy is characteristic of the state of a system.
- It may change when heat passes into or out of the system or work is done on or by the system, or matter enters or leaves the system.

## Work

- The change in internal energy is calculated by doing work. If we a system taken as a thermos flask containing water; so no exchange of heat between the system and surroundings through its boundary and this type of system is known as adiabatic.

- **Adiabatic system**- A process in which no transfer of heat between the system and surroundings and heat of the system remains constant is known as an adiabatic process. The wall separating the system and the surroundings is called the adiabatic wall.
- The change in the internal energy of the system by doing some work on the system. Let the initial state of the system is state A and its temperature is  $T_A$ . The internal energy of the system in state A is  $U_A$ . The state of the system can be changed by two different ways.

One way: We do some mechanical work, say 1 kJ, by rotating a set of small paddles and thereby churning water. Let us consider the new state named B state and its temperature is  $T_B$ . It is found that  $T_B > T_A$  and the change in temperature ( $\Delta T$ ):

$$\Delta T = T_B - T_A$$

Let's take the internal energy of the system in state B as  $U_B$  and the change in internal energy as:

$$\Delta U = U_B - U_A$$

Second way: We now do an equal amount (1kJ) electrical work with the help of an immersion rod and note down the temperature change. We find that the change in temperature is same as in the earlier case which is  $T_B - T_A$ .

- In 1840-50 J. P. Joule stated that a given amount of work done on the system irrespective of path, produced the same change of state, as measured by the change in the temperature of the system.
- The adiabatic work ( $W_{ad}$ ) required to bring about a change in state is equal to the difference between the value of  $U$  in one state and that in another state i.e. change in internal energy ( $\Delta U$ ) is as follows:

$$\Delta U = U_2 - U_1 = W_{ad}$$

- According to the IUPAC the +ve sign expresses that  $W_{ad}$  is +ve when work is done on the system and the internal energy of system will increase.
- If the work is done by the system then  $W_{ad}$  will be negative because the internal energy of the system will decrease.

- The volume of water in a pond is a state function, because change in volume of its water is independent of the route by which water is filled by rain or by tube well in the pond.

## Heat

- The internal energy of a system can be changed by transfer of heat from the surroundings to the system or vice-versa without expenditure of any work.
- This exchange of energy is a result of temperature difference, is called heat. It is denoted by **q**.
- The change in temperature by transfer of heat through thermally conducting walls instead of adiabatic walls. If we take water at temperature  $T_A$  in a container having thermally conducting walls which are made up of copper and enclose it in a huge heat reservoir at temperature,  $T_B$ .
- The heat absorbed by the system is **q**. It can be measured in terms of temperature difference  $=T_B - T_A$ .
- In this case change in internal energy, when no work is done at constant volume.

$$\Delta U = q$$

- According to IUPAC the **q** is positive, when heat is transferred from the surroundings to the system and the internal energy of the system increases.
- **q** is -ve when heat is transferred from system to the surroundings resulting in decrease of the internal energy of the system.

## The general case

- The general case in which a change in state is made both by transfer of heat and by doing work.
- The change in internal energy is as follows:

$$\Delta U = q + w$$

It is mathematical statement of the first law of thermodynamics, according to that 'The energy of an isolated system is constant'.

- It is generally known as the law of conservation of energy which states - energy can neither be created nor be destroyed.
- If there is no transfer of energy as heat or as work means in isolated system. Then  $w = 0$ ,  $q = 0$  and  $\Delta U = 0$ .

## Applications

- Many chemical reactions involve the generation of gases capable of doing mechanical work or generating heat.

### 1. Work –

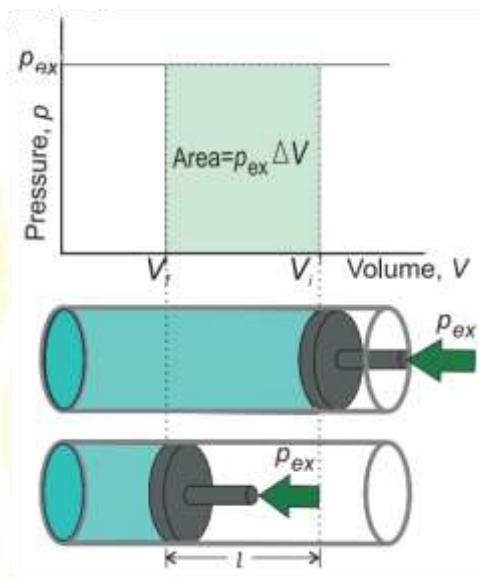


Figure: Work done on an ideal gas in a cylinder when it is compressed by a constant external pressure,  $p_{ex}$  (in single step) is equal to the shaded area.

- To understand pressure-volume work, let us consider a cylinder which contains one mole of an ideal gas which is fitted with a frictionless piston.
- The pressure of the gas inside is  $p$  and total volume of gas is  $V_i$ . If external pressure is  $p_{ex}$  and  $p_{ex} > p$ , piston is moved inward till  $p = p_{ex}$ .
- Suppose this change is achieved in a single step and the final volume be  $V_f$ . Suppose during this compression piston moves to a distance  $l$  and the cross-sectional area of the piston is  $A$ . Then

$$\text{Volume change} = l \times A = \Delta V = (V_f - V_i)$$

- As we know pressure =  $\frac{\text{Force}}{\text{Area}}$
- The force on the piston =  $p_{ex} \cdot A$

- By movement of the piston  $w$  is the work done on the system then-

$$w = \text{force} \times \text{distance} = p_{\text{ex}} \cdot A \cdot l$$

$$= p_{\text{ex}} \cdot (-\Delta V) = - p_{\text{ex}} \cdot \Delta V = - p_{\text{ex}} (V_f - V_i)$$

The -ve sign of this expression is required to obtain conventional sign for  $w$ , which will be +ve. This indicates that when compression occurs, work is done on the system.

Here  $(V_f - V_i)$  will be -ve and -ve multiplied by -ve become positive. The sign obtained for the work will be +ve.

- If the pressure is not constant at every stage of compression, but changes in number of finite steps, work done on the gas will be equal to  $-\sum p \Delta V$

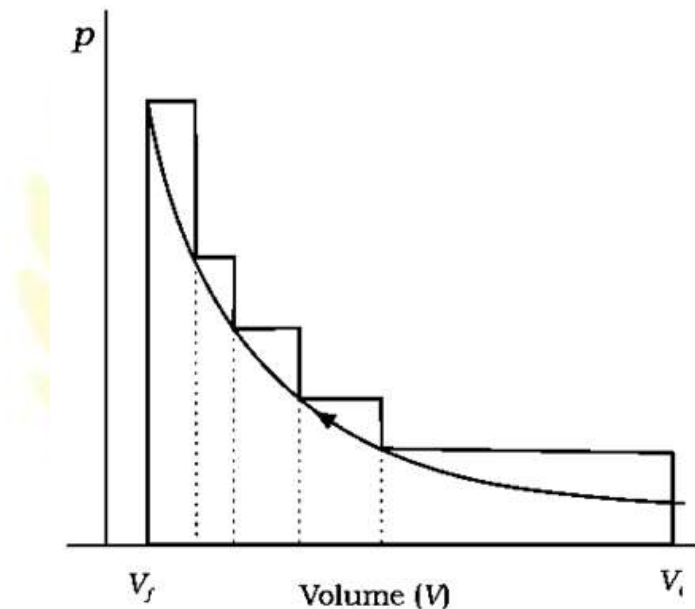


Figure:  $pV$ -plot when pressure is not constant and changes in finite steps during compression from initial volume,  $V_i$  to final volume,  $V_f$ .

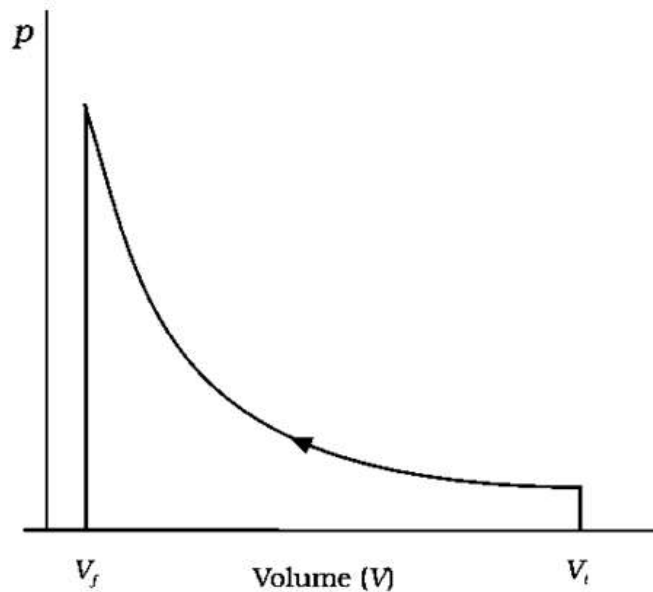


Figure: pV-plot when pressure is not constant and changes in infinite steps (reversible conditions) during compression from initial volume,  $V_i$  to final volume,  $V_f$ .

- If the pressure is not constant and changes during the process such that it is always greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount which is  $dV$ .
- In such a case we can calculate the work done on the gas by –

$$w = - \int_{V_i}^{V_f} p_{ex} dV$$

Here,  $p_{ex} = (p_{in} + dp)$  at each stage in case of compression.

- In an expansion process under similar conditions, the external pressure is always less than the pressure of the system which is  $p_{ex} = (p_{in} - dp)$ .
- In general case we can write,  $p_{ex} = (p_{in} + dp)$ . Such processes are called reversible processes.
- A process or change is said to be reversible, if a change is brought out in such a way that the process could be reversed at any moment by an infinitesimal change.
- A reversible process proceeds slowly by a series of equilibrium states such that system and the surroundings are always in approximate equilibrium with each other.

- We can relate work to internal pressure of the system under reversible conditions:

$$w_{rev} = - \int_{V_i}^{V_f} p_{ex} dV = - \int_{V_i}^{V_f} (p_{in} \pm dp) dV$$

- As  $dp \times dV$  is very small so

$$w_{rev} = - \int_{V_i}^{V_f} p_{in} dV$$

- The pressure of the gas can be expressed in terms of its volume through gas equation. For  $n$  mol of an ideal gas :

$$pV = nRT$$

$$p = \frac{nRT}{V}$$

- At constant temperature means isothermal process -

$$w_{rev} = - \int_{V_i}^{V_f} nRT \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$

$$= - 2.303 nRT \log \frac{V_f}{V_i}$$

- **Free expansion:** Expansion of a gas in vacuum ( $p_{ex} = 0$ ) is called free expansion. There is no work is done during free expansion of an ideal gas whether the process is reversible or irreversible.

- Let us substitute  $w = - p_{ex} \Delta V$  in equation

$$\Delta U = q + w$$

$$\Delta U = q - p_{ex} \Delta V$$

If the process is carried out at constant volume then  $\Delta V = 0$

$$\Delta U = q_v$$

Here  $q_v$  denotes that heat is supplied at constant volume.

### Isothermal and free expansion of an ideal gas



- For isothermal expansion of an ideal gas into vacuum;  $w = 0$  since  $p_{\text{ex}} = 0$ .
- Joule determined it experimentally that  $q = 0$ ; so the  $\Delta U = 0$
- $\Delta U = q + w$  can be expressed for isothermal irreversible and reversible changes as follows:

1. For isothermal irreversible change

$$q = -w = p_{\text{ex}} (V_f - V_i)$$

2. For isothermal reversible change

$$q = -w = nRT \ln \frac{V_f}{V_i}$$

$$q = 2.303 nRT \ln \frac{V_f}{V_i}$$

3. For adiabatic change  $q=0$ , so

$$\Delta U = w_{\text{ad}}$$

## 2. Enthalpy, H

### (a) A useful new state function-

- The heat absorbed at constant volume is equal to change in the internal energy ( $\Delta U$ ). Which is :

$$\Delta U = q_v$$

- But most of chemical reactions are not carried out at constant volume, but in flasks or test tubes under constant atmospheric pressure. We can write equation as follows

$$\Delta U = q_p - p\Delta V$$

At constant pressure, where  $q_p$  is heat absorbed by the system and  $p\Delta V$  represent expansion work done by the system.

- Let us denote the initial state by subscript 1 and final state by 2. Now the above equation can be as follows:

$$U_2 - U_1 = q_p - p(V_2 - V_1)$$

On the rearrangement –

$$q_p = (U_2 + pV_2) - (U_1 + pV_1)$$

- The enthalpy **H** [Greek word enthalpien] is expressed as follows:

$$H = U + pV$$

$$q_p = H_2 - H_1 = \Delta H$$

- H is a state function because it depends on p, V and U all of which are state functions. q is a path dependent function.
- $\Delta H$  is independent of path. Thus, qp is also independent of path.
- For limited changes at constant pressure, we can write –

$$\Delta H = \Delta U + p\Delta V$$

- $\Delta H$  is -ve for exothermic reactions which evolve heat during the reaction and  $\Delta H$  is +ve for endothermic reactions which absorb heat from the surroundings.
- At constant volume,  $\Delta V=0$ ,  $\Delta U= q_v$  then

$$\Delta H = \Delta U = q_v$$

- The  $(\Delta H - \Delta U)$  is significant only for gases.
- Let's consider a reaction involving gases:  
 $V_A$  = the total volume of the gaseous reactants  
 $V_B$  = the total volume of the gaseous products  
 $n_A$  = the number of moles of gaseous reactants  
 $n_B$  = the number of moles of gaseous products, all at constant pressure and temperature.

Then by using the ideal gas law–

$$pV_A = n_A RT$$

$$pV_B = n_B RT$$

$$pV_B - pV_A = n_B RT - n_A RT = (n_B - n_A)RT$$

$$p(V_B - V_A) = (n_B - n_A)RT$$

$$p\Delta V = \Delta n_g RT$$

Here,  $\Delta n_g = n_P - n_R$  (number of moles of gaseous products minus the number of moles of gaseous reactants).

- By substituting the value of  $p\Delta V$

$$\Delta H = \Delta U + \Delta n_g RT$$

## (b) Extensive and intensive properties –

- Properties which are not depend on the amount of the substance called intensive properties. Examples: temperature, pressure, density, boiling point, melting point, etc.
- Properties which are depend upon amount of the substance called extensive properties. For example: volume, mass, force, surface area etc.
- Molar properties ( $\chi_m$ ) –  
It is the value of an extensive property  $\chi$  of the system for 1 mol of the substance. If  $n$  is the amount of matter then –

$$\chi_m = \frac{\chi}{n}$$

It is independent of the amount of matter.

## (c) Heat capacity

- To measure the heat transferred to a system the term heat capacity is coined. There is a rise in temperature of the system in case of heat absorption by system.
- The heat transferred is proportional to the increase in temperature.

$$q = \text{coeff} \times \Delta T$$

- The coefficient depends on nature, composition and size of the system.

$$q = C \times \Delta T$$

Here  $C$  = Heat capacity

- By this formula we can measure the heat supplied by monitoring the temperature rise, only if we know the heat capacity.
- $C$  is proportional to amount of the substance.
- The **molar heat capacity** of a substance is as follows:

$$C_m = \frac{C}{N}$$

It is the heat capacity for one mole of the substance and it is the quantity of heat needed to raise the temperature of one mole by one degree Celsius or one kelvin.

- The **specific heat capacity** is the quantity of heat required to raise the temperature of one unit mass of a substance by one degree Celsius or one kelvin.

- For finding out the heat( $q$ ) required to raise the temperatures of a sample the formula is:

$$q = c \times m \times \Delta T$$

#### (d) The relationship between $C_p$ and $C_v$ for an ideal gas

- The heat capacity ( $C$ ) at constant volume is denoted by  $C_v$  and at constant pressure this is denoted by  $C_p$ .
- The heat ( $q$ ) at constant volume as

$$q_v = C_v \Delta T = \Delta U$$

At constant pressure  $q_p = C_p \Delta T = \Delta H$

- **The difference between  $C_p$  and  $C_v$ :**

For a mole of an ideal gas

$$\Delta H = \Delta U + \Delta(pV)$$

$$\Delta H = \Delta U + \Delta(RT)$$

$$\Delta H = \Delta U + R\Delta T$$

On putting the values of  $\Delta H$  and  $\Delta U$ :

$$C_p \Delta T = C_v \Delta T + R\Delta T$$

$$C_p = C_v + R$$

$$C_p - C_v = R$$

#### Measurement of $\Delta H$ and $\Delta U$ : Calorimetry

- Measurement of  $\Delta H$  and  $\Delta U$  is done by :
  1. At constant volume ( $q_v$ )
  2. At constant pressure ( $q_p$ )

##### (a) $\Delta U$ Measurement:

- For chemical reactions the heat absorbed at constant volume is measured in a bomb calorimeter.

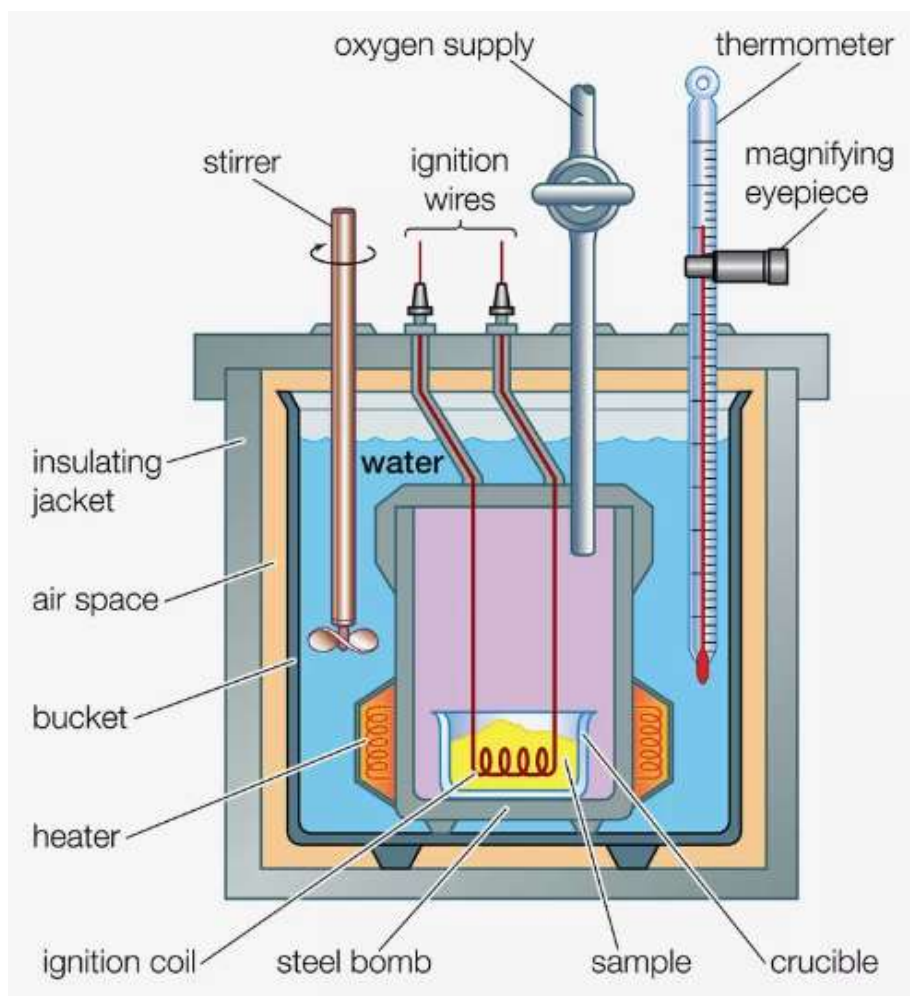


Figure: Bomb calorimeter

- In a bomb calorimeter a steel vessel is immersed in a water bath to make sure that no heat is lost to the surroundings.
- A combustible substance is burnt in pure O<sub>2</sub> supplied in the steel bomb. The whole device is called calorimeter.
- Heat evolved during the reaction gets transferred to the water present around the bomb and temperature is measured.
- Since the bomb calorimeter is sealed, its volume does not change; so the energy changes associated with reactions are measured at constant volume.
- There is no work is done as the reaction is carried out at constant volume in the bomb calorimeter.
- Temperature change of the calorimeter produced by the completed reaction is then converted to q<sub>v</sub>, by using the known heat capacity of the calorimeter.
- The formula is:

$$q = c \times m \times \Delta T = C \Delta T$$

## (b) $\Delta H$ Measurement

- Measurement of heat change at constant pressure can be done in a calorimeter.
- As we know that  $\Delta H = q_p$  and the heat absorbed or evolved,  $q_p$  at constant pressure is also called the heat of reaction or enthalpy of reaction,  $\Delta_r H$ .
- In an exothermic reaction heat is released and it transfers to the surroundings. The  $q_p$  will be -ve and  $\Delta_r H$  will also be -ve.
- In an endothermic reaction heat is absorbed,  $q_p$  is +ve and  $\Delta_r H$  will be +ve.

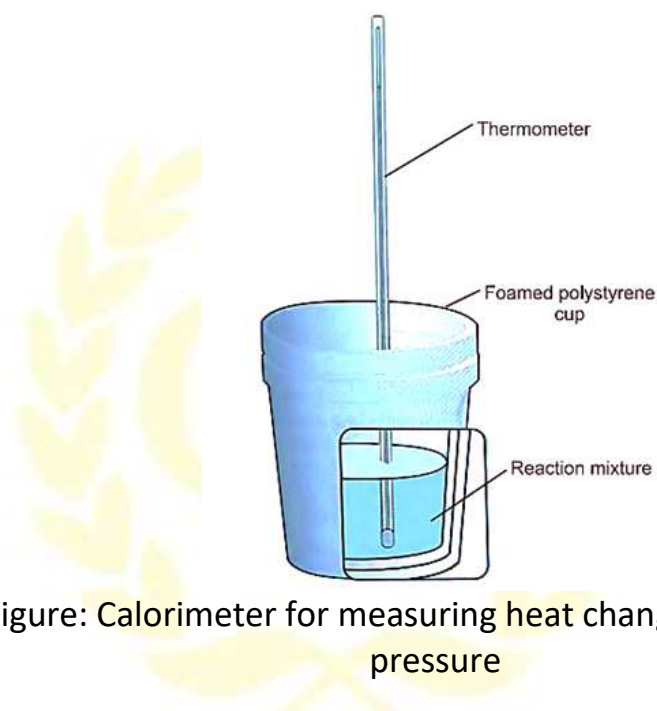
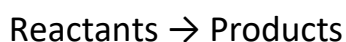


Figure: Calorimeter for measuring heat changes at constant pressure

### Enthalpy change, $\Delta_r H$ of a reaction – reaction enthalpy

- In chemical reaction reactants are converted into products and is represented by-



- The enthalpy change associated to a reaction is called the reaction enthalpy. The enthalpy change of a chemical reaction is denoted by the symbol  $\Delta_r H$ .

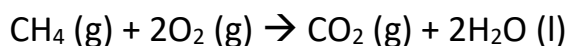
**$\Delta_r H = (\text{sum of enthalpies of products}) - (\text{sum of enthalpies of reactants})$**

$$= \sum_i a_i H_{\text{products}} - \sum_i b_i H_{\text{reactants}}$$

Here  $\sum$  = summation

$a_i$  and  $b_i$  = Stoichiometric coefficient of the products and reactants respectively.

- For example:



$$\Delta_r H = \sum_i a_i H_{\text{Products}} - \sum_i b_i H_{\text{Reactants}}$$

$$= [H_m(\text{CO}_2, \text{g}) + 2H_m(\text{H}_2\text{O}, \text{l})] - [H_m(\text{CH}_4, \text{g}) + 2H_m(\text{O}_2, \text{g})]$$

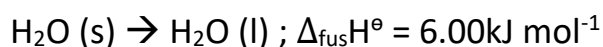
Here  $H_m$  = Molar enthalpy.

### (a) Standard enthalpy of reactions:

- The standard enthalpy of reaction is defined as the enthalpy change for a reaction when all the participating substances are present in their standard states.
- The standard state of a substance is its pure form at 1 bar at a specified temperature.
- 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.
- Standard conditions are denoted by adding the superscript  $\ominus$  to the symbol  $\Delta H$  i.e.  $\Delta H^\ominus$ .

### (b) Enthalpy changes during phase transformation:

- 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,  $\Delta_{\text{fus}}H^\ominus$ .
- Phase transformations also involves energy changes. For example, Ice requires heat for melting; this melting takes place at constant pressure and during the phase change, temperature remains constant throughout.



Here  $\Delta_{\text{fus}}H^\ominus$  = enthalpy of fusion in standard state.

If water freezes then process is reversed and equal amount of heat is transferred to the surroundings.

- Since, melting of a solid is endothermic therefore all enthalpies of fusion are positive. Water requires heat for evaporation, its boiling point is  $T_b$  at constant pressure.

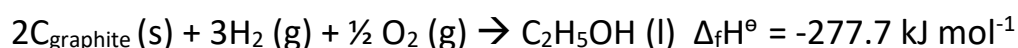
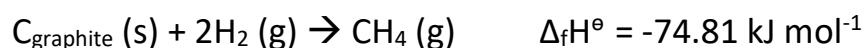


Here  $\Delta_{\text{vap}}H^\ominus$  = standard enthalpy of vaporization.

- Amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure is called its standard enthalpy of vaporization or molar enthalpy of vaporization,  $\Delta_{\text{vap}}H^\ominus$ .
- 
- **Standard enthalpy of sublimation** ( $\Delta_{\text{sub}}H^\ominus$ ) is the change in enthalpy when one mole of a solid substance sublimates at a constant temperature and under standard pressure i.e. 1bar.
- Sublimation is defined as the direct conversion of a solid into its vapour form. Solid  $\text{CO}_2$  or dry ice sublimates at 195K with  $\Delta_{\text{sub}}H^\ominus = 25.2 \text{ kJ mol}^{-1}$ ; naphthalene sublimates slowly and for this  $\Delta_{\text{sub}}H^\ominus = 73.0 \text{ kJ mol}^{-1}$ .
- The enthalpy change depends on the strength of the intermolecular interactions occurring during the phase transformation. Example: strong H-bonds between water molecules hold them tightly in liquid phase.

### (c) 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 is called Standard molar enthalpy of formation. Its symbol is  $\Delta_f H^\ominus$ . Here f shows that 1 mole of the compound has been formed in its standard state from its elements in their most stable states of aggregation.
- The condition for most stable state of aggregation is  $25^\circ\text{C}$  temperature and 1 bar pressure.
- For example, some reactions with standard molar enthalpies of formation are as follows-

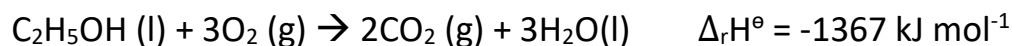


- Standard molar enthalpy of formation,  $\Delta_f H^\ominus$  is considered as a special case of  $\Delta_r H^\ominus$ , where one mole of a compound is formed from its constituent elements, as in above three equations, one mol of water, methane and ethanol is formed.



#### (d) Thermodynamic equations:

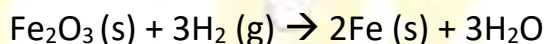
- A balanced chemical equation with the value of its  $\Delta_r H$  is called a thermochemical equation.
- For example:



In above reaction combustion of liquid ethanol at constant temperature and pressure take place.

Conventions regarding thermo- chemical equations:

1. In a balanced thermo-chemical equation, the coefficients is the number of moles of reactants and products involved in the reaction.
  2. The numerical value of  $\Delta_r H^\circ$  refers to the number of moles of substances specified by an equation. Standard enthalpy changes  $\Delta_r H^\circ$  have units as  $\text{kJ mol}^{-1}$ .
- To describe it lets take a reaction:



$$\Delta_f H^\circ (\text{H}_2\text{O}) (\text{l}) = -285.83 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ (\text{Fe}_2\text{O}_3) (\text{s}) = -824.2 \text{ kJ mol}^{-1}$$

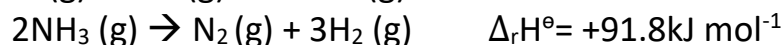
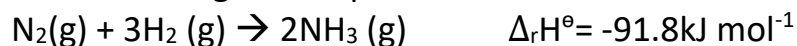
$$\Delta_f H^\circ (\text{Fe}) (\text{g}) = 0 \text{ and } \Delta_f H^\circ (\text{H}_2) (\text{g}) = 0$$

$$\Delta_r H_1^\circ = 3(-285.83 \text{ kJ mol}^{-1}) - 1(-824.2 \text{ kJ mol}^{-1})$$

$$= (-857.5 + 824.2) \text{ kJ mol}^{-1}$$

$$= -33.3 \text{ kJ mol}^{-1}$$

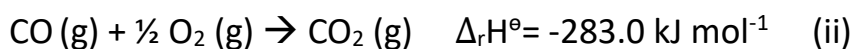
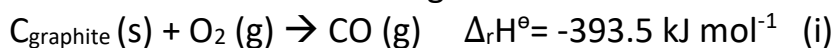
3. When a chemical equation is reversed, the value of  $\Delta_r H^\circ$  is reversed in sign. Example:



#### (e) Hess's law of constant heat summation:

- If a reaction completed 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.
- Let's consider the enthalpy change for the reaction:  
 $\text{C}_{\text{graphite}} (\text{s}) + \frac{1}{2} \text{O}_2 (\text{g}) \rightarrow \text{CO} (\text{g}) \quad \Delta_r H^\circ = ?$

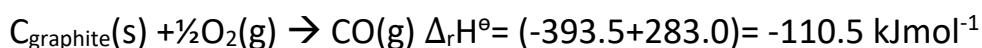
Let us consider the following reactions:



On combining the above two reactions:

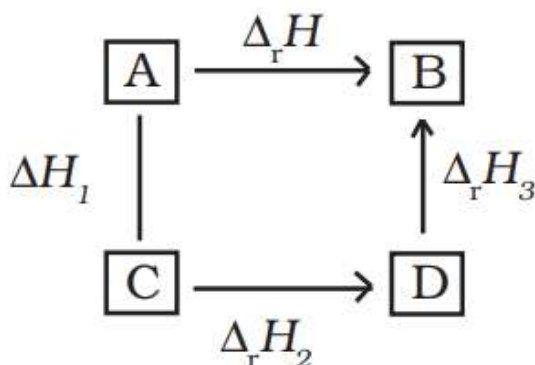


After adding (i) and (iii)



- If enthalpy of an overall reaction  $\text{A} \rightarrow \text{B}$  is  $\Delta_r H$  and  $\Delta_r H_1, \Delta_r H_2, \Delta_r H_3, \dots$  representing enthalpies of reactions leading to same product from another route, then we have

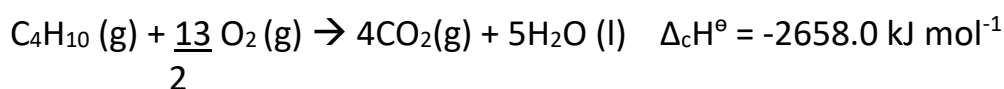
$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3, \dots$  it can be represented as



### Enthalpies for different types of reactions:

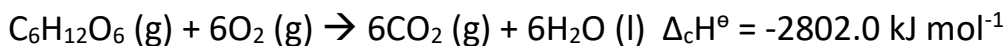
#### (A) Standard enthalpy of combustion ( $\Delta_c H^\ominus$ ) –

- Combustion reactions are exothermic in nature. These reactions are important in industry, rocketry.
- Standard enthalpy of combustion is can be defined as the enthalpy change per mole of a substance when the substance undergoes the combustion.
- All the reactants and products are in their standard states at the specified temperature.
- Cooking gas in cylinders contains majorly butane ( $\text{C}_4\text{H}_{10}$ ). Complete combustion of one mole of butane release 2658 kJ of heat. The chemical reaction is as follows:



- The combustion of glucose release 2802.0 kJ/mol of heat. The chemical equation is as follows :

- 



- Human body also generates energy from food by the same process as combustion, though the final products are produced after a series of complex bio-chemical reactions involving enzymes.

- 

### (B) Enthalpy of atomization ( $\Delta_a H^\ominus$ ) –

- In case of atomization of  $\text{H}_2$  gas-



- The H-atoms are formed by breaking the H–H bonds in dihydrogen. The enthalpy change in this process is known as enthalpy of atomization ( $\Delta_a H^\ominus$ ).
- It is the enthalpy change on breaking one mole of bonds to obtain atoms in the gas phase.
- In diatomic molecules the enthalpy of atomization is also the bond dissociation enthalpy.

### (C) Bond Enthalpy ( $\Delta_{\text{bond}} H^\ominus$ )

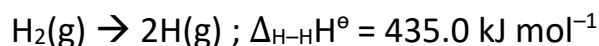
- The making and breaking of chemical bonds take place in a chemical reaction.
- The Energy is desired to break a bond and energy is released due to bond formation is known as bond enthalpy. It is possible to correlate heat of reaction to changes in energy associated with breaking and making of chemical bonds.
- The enthalpy changes associated with chemical bonds there are two different terms are used in thermodynamics which are as follows:

1. Bond dissociation enthalpy
2. Mean bond enthalpy

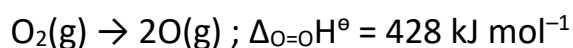
These terms with reference to diatomic and polyatomic molecules as follows:

#### 1. Diatomic molecules -

- The bonds in one mole of H<sub>2</sub> gas are broken:



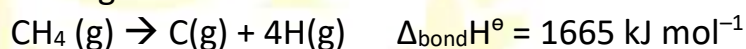
- The enthalpy change ( $\Delta\text{H}$ ) involved in this process is the bond dissociation enthalpy of H–H bond.
- When one mole of covalent bonds of a gaseous covalent compound is broken to form products in the gas phase; the bond dissociation enthalpy is the change in enthalpy.
- Example:



- In polyatomic molecules the bond dissociation enthalpy is different for different bonds within the same molecule.

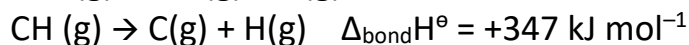
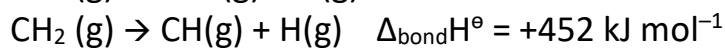
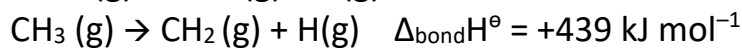
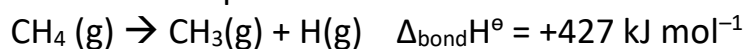
## 2. Polyatomic Molecules:

- In polyatomic molecule like CH<sub>4</sub>. The overall thermochemical equation for methane atomization reaction is given below:



In CH<sub>4</sub>, all four C – H bonds are identical in bond length and energy.

The energies required to break the C – H bonds in each successive step is different:



- It is the mean bond enthalpy of C-H bond.
- Example: in CH<sub>4</sub> the  $\Delta_{\text{C-H}}\text{H}^\ominus$  is as follows:

$$\Delta_{\text{C-H}}\text{H}^\ominus = \frac{1}{4} (\Delta_{\text{a}}\text{H}^\ominus) = \frac{1}{4} (1665 \text{ kJ mol}^{-1}) = 416 \text{ kJ mol}^{-1}$$

- We can predict the enthalpy of a reaction in gas phase, if we know different bond enthalpies.
- In gas phase reactions the standard enthalpy of reaction is related to bond enthalpies of the reactants and products as follows:

$$\Delta_r H^\ominus = \sum \text{bond enthalpies}_{\text{reactants}} - \sum \text{bond enthalpies}_{\text{products}}$$

Table: Some mean single bond enthalpies in  $\text{kJ mol}^{-1}$  at 298K

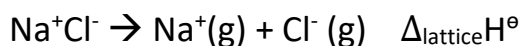
H	C	N	O	F	Si	P	S	Cl	Br	I	
435.8	414	389	464	569	293	318	339	431	368	297	H
	347	293	351	439	289	264	259	330	276	238	C
		159	201	272	-	209	-	201	243	-	N
			138	184	368	351	-	205	-	201	O
				155	540	490	197	255	197	-	F
					176	213	289	360	289	213	Si
						213	272	331	272	213	P
							213	251	213	-	S
								243	218	209	Cl
									192	180	Br
										151	I

Table: Mean Multiple Bond Enthalpies in  $\text{kJ mol}^{-1}$  at 298 K

N=N	418	C≡O	1070
N≡N	946	O=O	498
C=N	615	C=C	611
C≡N	891	C≡C	837

### (D) Lattice Enthalpy

- Enthalpy change due to dissociation of one mole of an ionic compound into its ions in gaseous state is known as lattice enthalpy.



- Lattice enthalpy is determined by Born-Haber Cycle. In case NaCl lattice enthalpy is as follows:

1. Sublimation of sodium metal

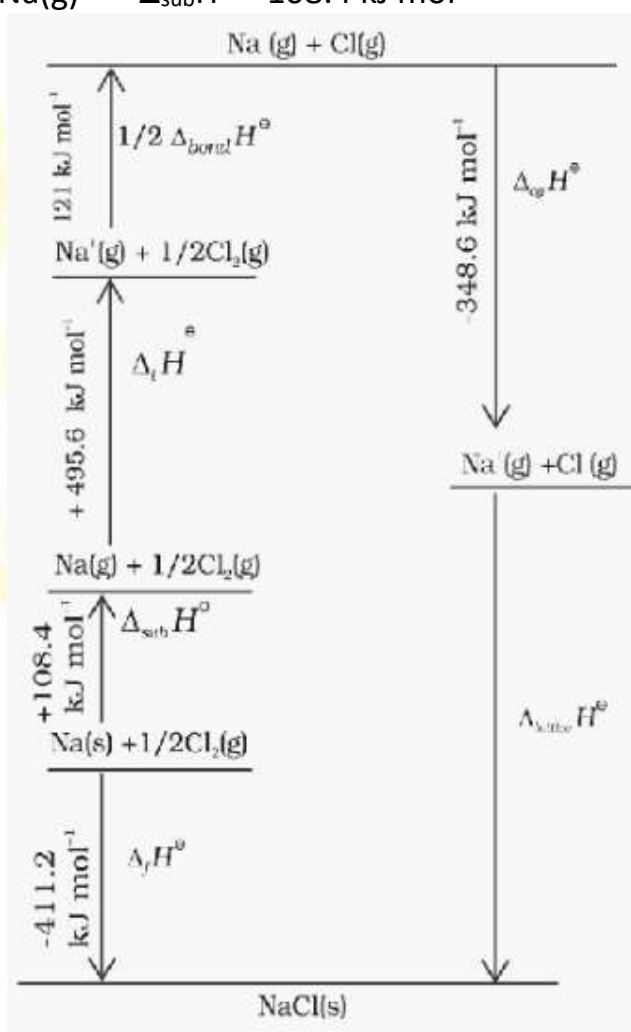
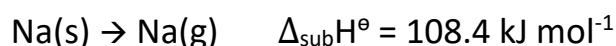
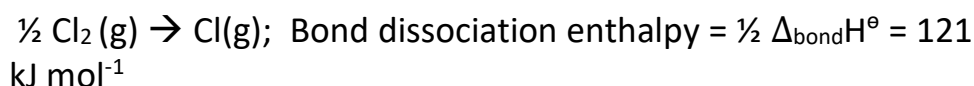


Figure: Enthalpy diagram for lattice enthalpy of NaCl

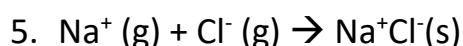
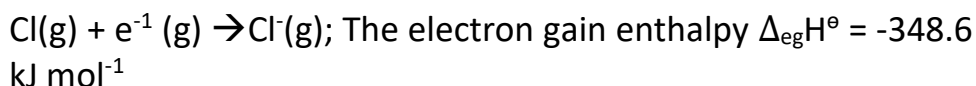
2. The ionization of sodium atoms



3. The dissociation of chlorine



4. The electron gained by chlorine atoms



- The sum of the enthalpy changes round a cycle is zero. On applying Hess's law:

$$\Delta_{\text{lattice}}\text{H}^\ominus = 411.2 + 108.4 + 121 + 496 - 348.6$$

$$\Delta_{\text{lattice}}\text{H}^\ominus = + 788\text{kJ}$$

- For  $\text{NaCl} (\text{s}) \rightarrow \text{Na}^{+}(\text{g}) + \text{Cl}^{-}(\text{g})$   
Internal energy is smaller by  $2RT$  (because  $\Delta n_g = 2$ ) and internal energy =  $+ 783 \text{ kJ mol}^{-1}$
- Enthalpy of solution:

$$\Delta_{\text{sol}}\text{H}^\ominus = \Delta_{\text{lattice}}\text{H}^\ominus + \Delta_{\text{hyd}}\text{H}^\ominus$$

For 1 mol of  $\text{NaCl} (\text{s})$

Lattice enthalpy =  $+788\text{kJ mol}^{-1}$

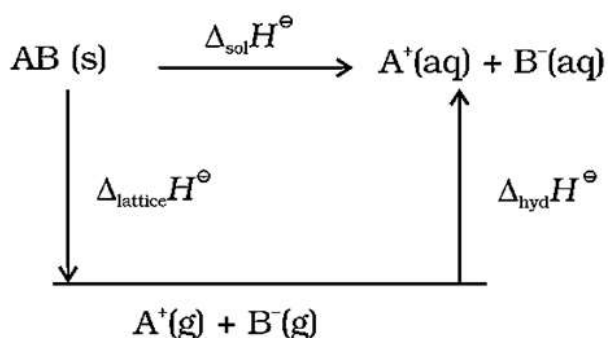
Enthalpy of hydration,  $\Delta_{\text{hyd}}\text{H}^\ominus = -784 \text{ kJ mol}^{-1}$

$$\Delta_{\text{sol}}\text{H}^\ominus = + 788 \text{ kJ mol}^{-1} - 784 \text{ kJ mol}^{-1} = + 4\text{kJ mol}^{-1}$$

The dissolution of  $\text{NaCl}(\text{s})$  is done by very little heat change.

### (E) Enthalpy of solution ( $\Delta_{\text{sol}}\text{H}^\ominus$ )`

- Enthalpy change due to desolatingss 1 mole of a substance in a specified amount of solvent is known as enthalpy of a solution.
- An ionic compound on dissolving in a solvent, the ions leave their ordered positions on the crystal lattice.
- They become free in solution. Solvation of these ions occurs in solution. In a diagram below shown this process for AB compound which is ionic in nature:

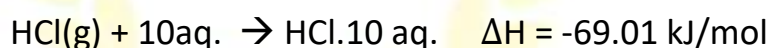


- The enthalpy of solution of AB(s) is as follows:  

$$\Delta_{\text{sol}}H^\ominus = \Delta_{\text{lattice}}H^\ominus + \Delta_{\text{hyd}}H^\ominus$$
- The enthalpy of solution for most ionic compounds is +ve. Dissociation process is endothermic in nature.

#### (F) Enthalpy of dilution:

- The enthalpy of dilution of a solution is the heat withdrawn from the surroundings when additional solvent is added to the solution.
- It is dependent on the original concentration of the solution and the amount of the solvent added.
- The enthalpy of solution is the enthalpy change associated with addition of a specified amount of solute to the specified amount of solvent at constant temperature and pressure.
- Enthalpy change for dissolving 1 mole of gaseous HCl in 10 mol of water can be represented by the following equation:



- Enthalpy change in above reaction:
  - Set-1  $\text{HCl (g)} + 25\text{aq.} \rightarrow \text{HCl.25aq.} \quad \Delta H = -72.03 \text{ kJ/mol}$
  - Set-2  $\text{HCl (g)} + 40\text{aq.} \rightarrow \text{HCl.40aq.} \quad \Delta H = -72.79 \text{ kJ/mol}$
  - Set-3  $\text{HCl (g)} + \infty \text{ aq.} \rightarrow \text{HCl.}\infty\text{aq.} \quad \Delta H = -72.03 \text{ kJ/mol}$

- The values of  $\Delta H$  show the dependence of the enthalpy of solution on amount of solvent.
- On adding more solvent, the enthalpy of solution approaches a limiting value which is the value in infinitely dilute solution.
- In case of HCl the value of  $\Delta H$  :  
Subtract set-1 from set-2



$$\text{Enthalpy of dilution } (\Delta H) = [-72.79 - (-72.03)] \text{ kJ/mol} = -0.76 \text{ kJ/mol}$$

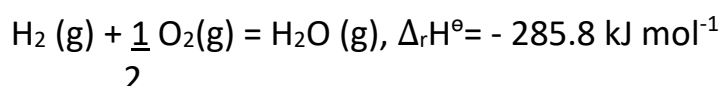
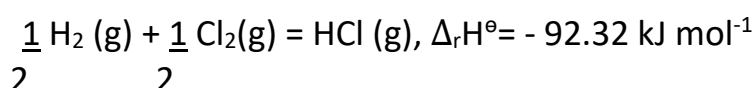
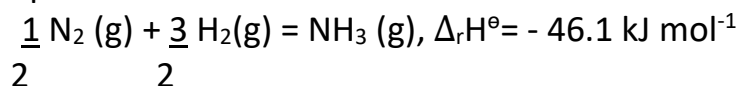


## Spontaneity

- A spontaneous process is an irreversible process and can only be reversed by an external agency.

1. Is decrease in entropy a criterion for spontaneity?

- A chemical reaction is spontaneous in a given direction due to decrease in energy. Example: In exothermic reactions-



- The decrease in enthalpy in passing from reactants to products for any exothermic reaction on an enthalpy diagram as shown below:

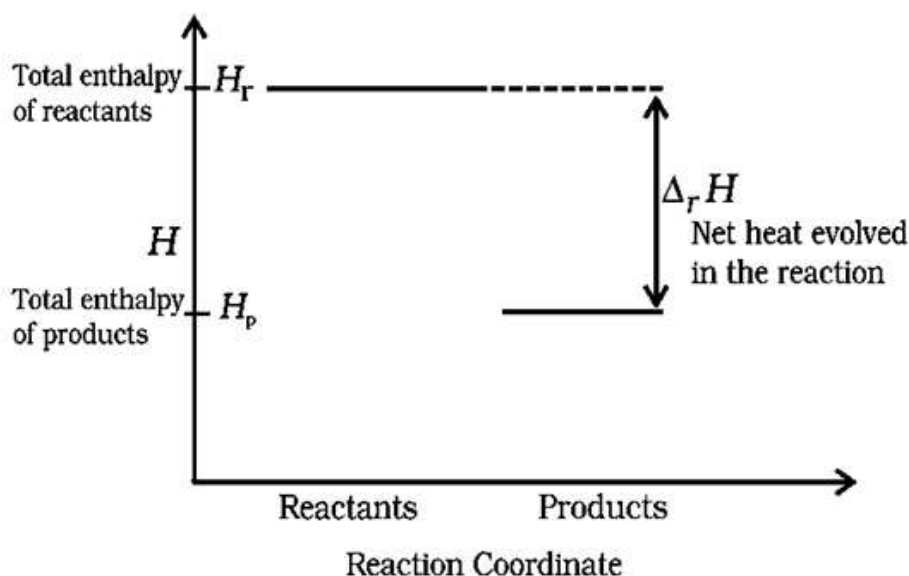
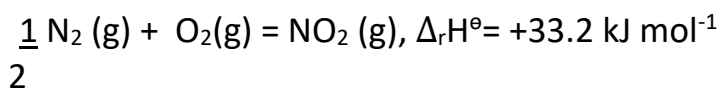


Figure: Enthalpy diagram for exothermic reactions

- In case of endothermic reactions:



- The increase in enthalpy can be represented on an enthalpy diagram as shown below:

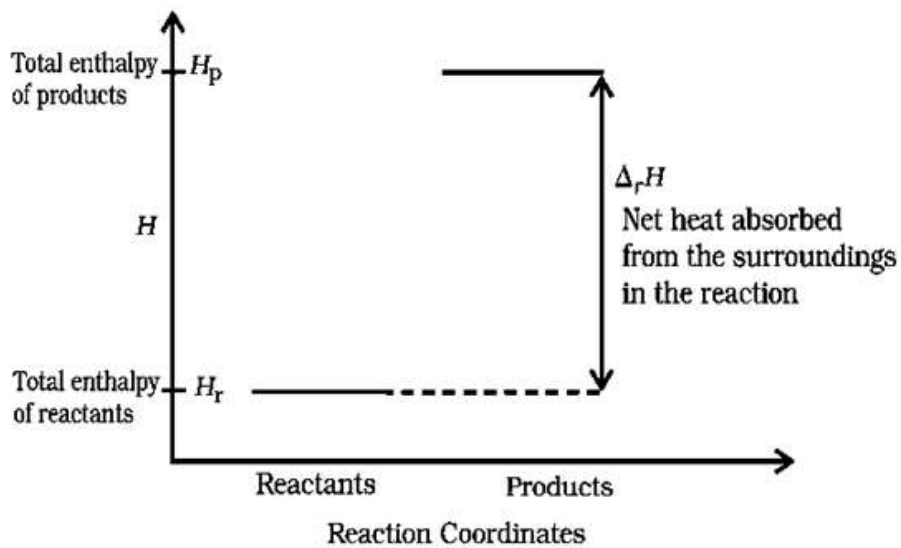


Figure: Enthalpy diagram for endothermic reactions

## 2. Entropy and spontaneity

- In case of the condition  $\Delta H = 0$  means there is no change in enthalpy, but still the process is spontaneous.
- If we consider diffusion of two gases into each other in a closed container. Both gases are denoted by dots one is white and other is black in color. They are separated by a movable partition. When partition is removed both gases diffuse into each other slowly.

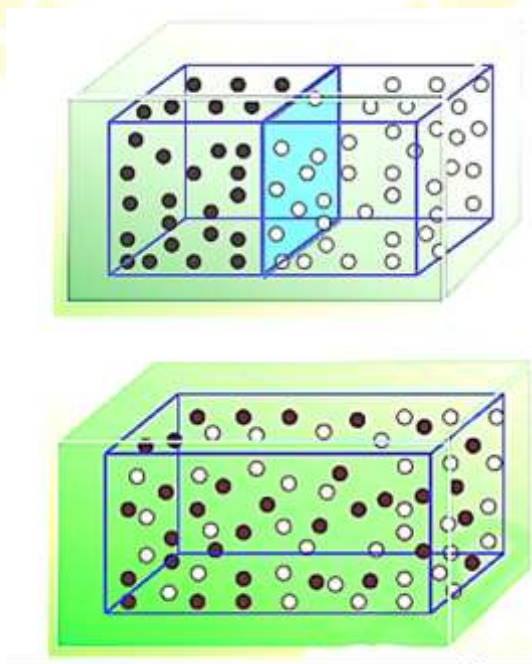


Figure: Diffusion of gases

- After removing the partition the disturbance in the container is increased. We can say that in an isolated system, there is always a tendency for the system energy to become more disordered.
- A thermodynamic term entropy, it is the randomness or disorderness of a system. It is denoted by symbol **S**.
- When heat is supplied to a system, the gaseous molecule increase motion due to this randomness generate in system. We can say the entropy of the system increased.
- Temperature is the measure of average chaotic or random motion of particles in the system.
- Entropy change ( $\Delta S$ ) can be defined as:

$$\Delta S = \frac{q_{rev}}{T}$$

Here q = heat

T= Temperature

- The total entropy change for the system and surroundings of a spontaneous process is as follows:

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surr} > 0$$

- When a system is in equilibrium, the entropy is maximum, and the change in entropy is  $\Delta S = 0$ .
- The change in entropy of a reversible process:

$$\Delta S_{sys} = \frac{q_{sys,rev}}{T}$$

### 3. Gibbs energy and spontaneity

- Gibbs energy (G) is a state function also an extensive property.
- The Gibbs energy is as follows:

$$(G) = H - TS$$

- The change in Gibbs energy for a system is  $\Delta G_{sys}$ :

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} - S_{sys}\Delta T$$

- At constant temperature:

$$\Delta T = 0, \text{ so}$$

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$

Or

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

- It is known as Gibbs equation.

- As we know that

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}}$$

- At thermal equilibrium the temperature of system is equal to the surroundings temperature. The entropy change of surroundings is as follows:

$$\Delta S_{\text{surr}} = \frac{\Delta H_{\text{surr}}}{T} = \frac{-\Delta H_{\text{sys}}}{T}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \left( \frac{-\Delta H_{\text{sys}}}{T} \right)$$

- On rearrangement:

$$T\Delta S_{\text{total}} = T\Delta S_{\text{sys}} - \Delta H_{\text{sys}}$$

- For the spontaneous process

$$\Delta S_{\text{total}} > 0$$

$$\text{So, } T\Delta S_{\text{sys}} - \Delta H_{\text{sys}} > 0$$

$$-(\Delta H_{\text{sys}} > T\Delta S_{\text{sys}}) > 0$$

Now we can say

$$-\Delta G > 0$$

$$\Delta G = \Delta H - T\Delta S < 0$$

Here  $\Delta H$  = enthalpy change of a reaction

$T\Delta S$  = energy which is not available to do work

$\Delta G$  = the total energy available to do work or free energy.

- ❖  $\Delta G$  provide a criterion for spontaneity at constant p and T:
  1. If  $\Delta G = -ve$  means ( $< 0$ ) then process will be spontaneous.
  2. If  $\Delta G = +ve$  means ( $> 0$ ) then process will be non-spontaneous.

#### 4. Entropy and second law of thermodynamics:

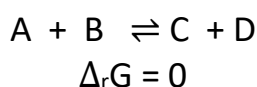
- According to II law of thermodynamics the increase in entropy in isolated systems is the natural direction of a spontaneous change.
- In exothermic reactions the heat released by the reaction increases the disorder of the surroundings and overall entropy change is +ve, it makes the reaction spontaneous.

#### 5. Absolute entropy and third law of thermodynamics:

- In case of pure crystalline substances if the temperature reaches to absolute zero then the entropy also approaches zero. It is known as third law of thermodynamics.
- At absolute zero temperature there is a perfect order in the crystal.
- This law helps to calculate the absolute values of entropy of pure substance from thermal data only.

### Gibbs energy change and equilibrium

- In case of equilibrium



Here  $\Delta_r G$  = Gibbs energy for a reaction in which all the reactants and the products are in standard state.

It is related to the equilibrium constant (K) of reaction:

$$0 = \Delta_r G^\circ + RT \ln K$$

$$\Delta_r G^\circ = - RT \ln K$$

$$\Delta_r G^\circ = - 2.303 RT \log K$$

As we know :  $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ = -RT \ln K$

- Using above equation
  - We can estimate  $\Delta G^\circ$  with the help of  $\Delta H^\circ$  and  $\Delta S^\circ$ .
  - If equilibrium constant K is measured in laboratory, then  $\Delta G^\circ$  can be calculated at any temperature.

Table: Effect of Temperature on Spontaneity of Reactions

$\Delta_r H^\circ$	$\Delta_r S^\circ$	$\Delta_r G^\circ$	Description
-	+	-	Reaction is spontaneous at all temperatures
-	-	-(at low T)	Reaction is spontaneous at low temperature
-	-	+(at high T)	Reaction is nonspontaneous at high temperature
+	+	+(at low T)	Reaction is nonspontaneous at low temperature
+	+	-(at high T)	Reaction is spontaneous at high temperature
+	-	+(at all T)	Reaction is nonspontaneous at all temperatures

