

Thermodynamics

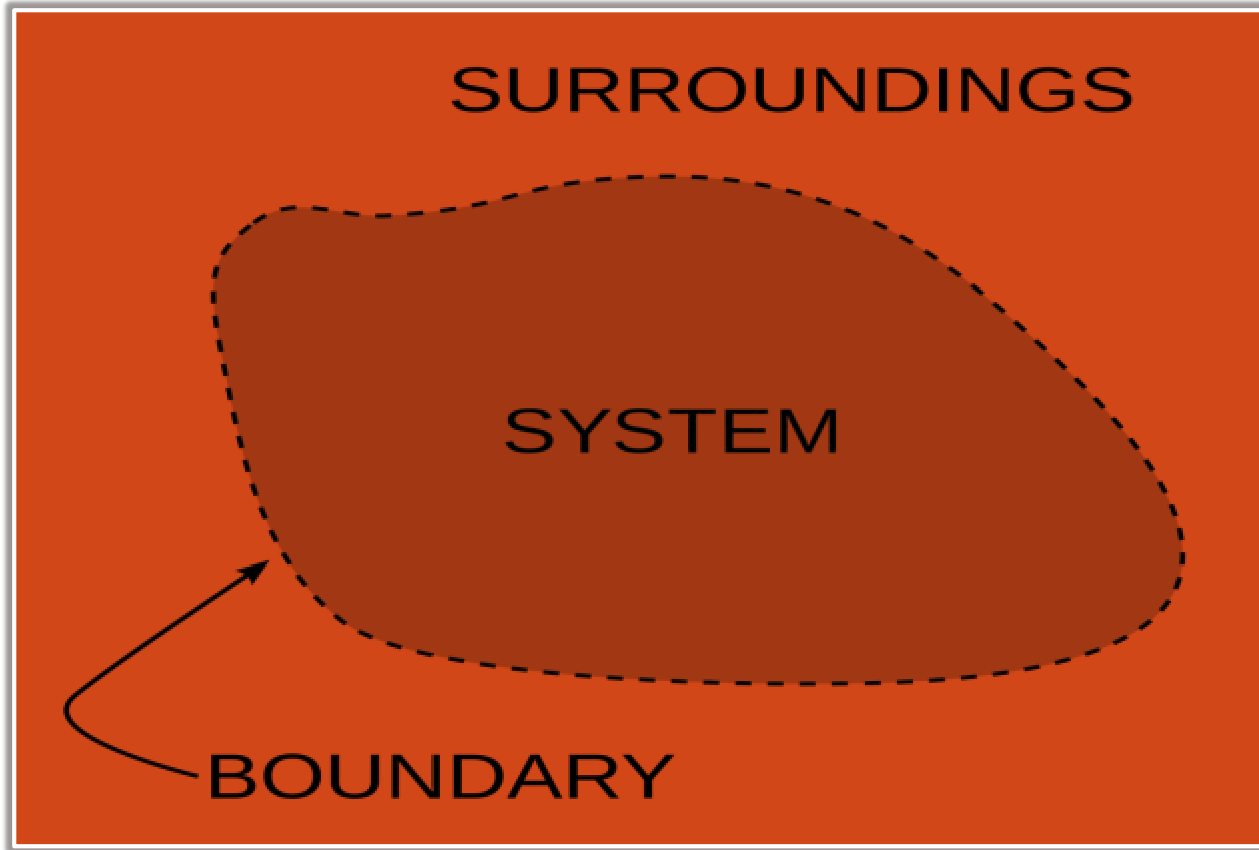
Thermodynamic terms

□ System and its 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

- For example, if we are studying the reaction between two substances A and B kept in a beaker, the beaker containing the reaction mixture is the system and the room where the beaker is kept is the surroundings.
- Note that the system may be defined by physical boundaries, like beaker or test tube, or the system may simply be defined by a set of Cartesian coordinates specifying a particular volume in space. 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. This is designed to allow us to control and keep track of all movements of matter and energy in or out of the system.



Classification of systems.

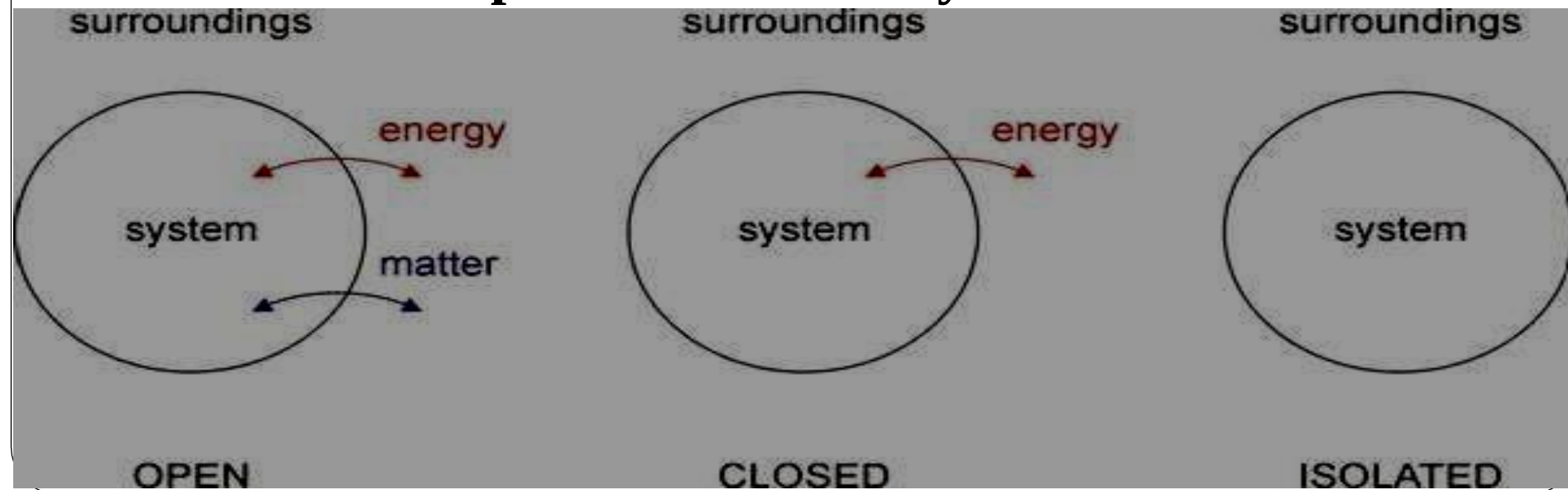
Open system: In an open system, there is exchange of energy and matter between system and surroundings. The presence of reactants in an open beaker is an example of an open system*.

Here the boundary is an imaginary surface enclosing the beaker and reactants.

Closed system: 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:-

- ❑ 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.



**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 because their values depend only on the state of the system and not on how it is reached.

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. We need to describe the system by specifying it before and after the change.
- 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 because their values depend only on the state of the system and not on how it is reached. In order to completely define the state of a system it is not necessary to define all the properties of the system; as only a certain number of properties can be varied independently.

Internal Energy.

The total of all the possible kinds of energy of a system, is called its Internal Energy.

The internal energy of a system, like temperature, pressure, volume, etc., is determined by the state of a system and is independent of the path by which it is obtained. Hence internal energy of a system is a state function.

Since the value of internal energy of a system depends on the mass of the matter contained in a system, it is classed as an extensive property.

Internal energy as state function

- **Internal energy of a system is defined as U**
- **This internal energy may be electrical chemical or mechanical. 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.**

- Let us bring the change in the internal energy of the system by doing some work on it. Let us call the initial state of the system as state A and its temperature as T_A . Let the internal energy of the system in state A be called U_A . We can change the state of the system in two different ways.
- First way: We do some mechanical work, say 1 kJ, by rotating a set of small paddles and thereby churning water. Let the new state be called B state and its temperature, as T_B . It is found that $T_B > T_A$ and the change in temperature, $\Delta T = T_B - T_A$. Let the internal energy of the system in state B be U_B and the change in internal energy, $\Delta U = U_B - U_A$.

- **Second way:** We now do an equal amount (i.e. 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, say, $T_B - T_A$.
- the internal energy U , whose value is characteristic of the state of a system, whereby the adiabatic work, was required to bring about a change of state is equal to the difference between the value of U in one state and that in another state, ΔU i.e, $\Delta U = U_2 - U_1 = W_{ad}$
- Therefore, internal energy, U , of the system is a state function.

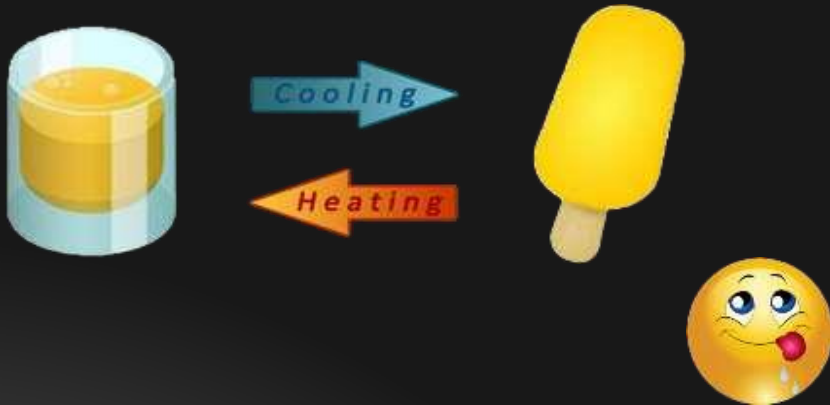
The positive sign expresses that W_{ad} is positive when work is done on the system. Similarly, if the work is done by the system, W_{ad} will be negative

□ Some of other familiar state functions are V , p , and T . For example, if we bring a change in temperature of the system from 25°C to 35°C , the change in temperature is $35^{\circ}\text{C} - 25^{\circ}\text{C} = +10^{\circ}\text{C}$, whether we go straight up to 35°C or we cool the system for a few degrees, then take the system to the final temperature. Thus, T is a state function and the change in temperature is independent of the route taken. Volume of water in a pond, for example, is a state function, because change in volume of its water is independent of the route by which water is filled in the pond, either by rain or by tubewell or by both.

work

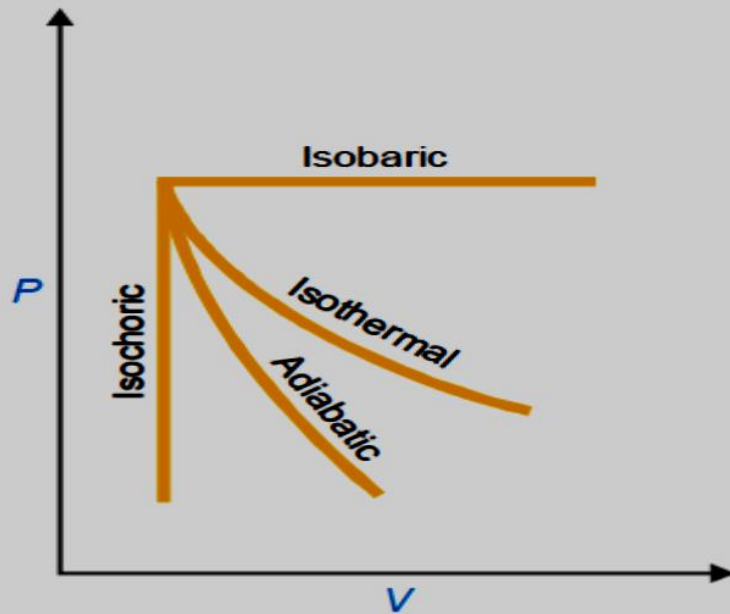
We take a system containing some quantity of water in a thermos flask or in an insulated beaker. This would not allow exchange of heat between the system and surroundings through its boundary and we call this type of system as adiabatic. The manner in which the state of such a system may be changed will be called adiabatic process. Adiabatic process is a process in which there is no transfer of heat between the system and surroundings. Here, the wall separating the system and the surroundings is called the adiabatic wall.

Reversible & Irreversible Process

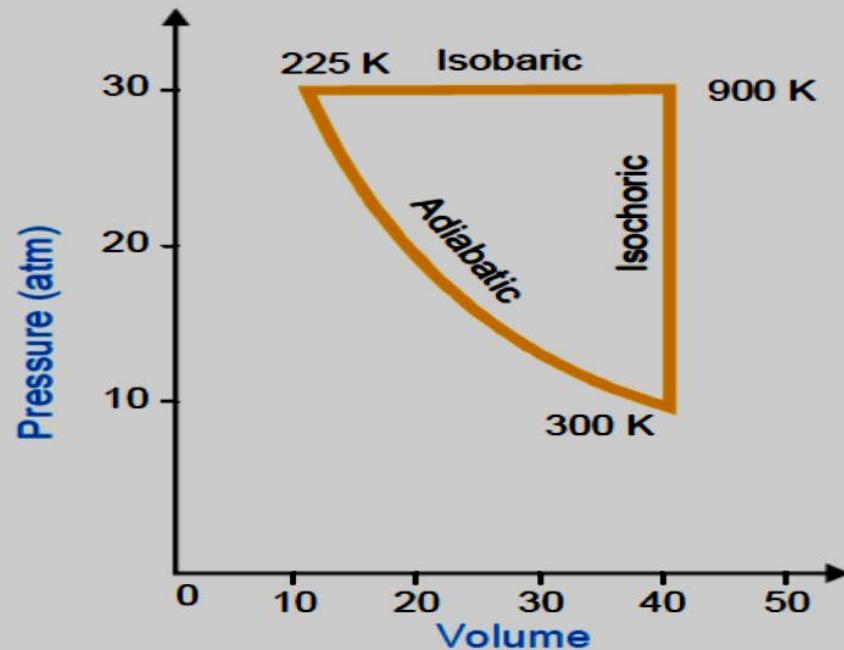


THERMODYNAMIC PROCESSES

isothermal process $dT = 0$ adiabatic process $dq = 0$
isobaric process $dp = 0$ isochoric processes $dV = 0$.
cyclic process $dE = 0, dH = 0$.



(a)



(b)

■ **Figure 7.5**

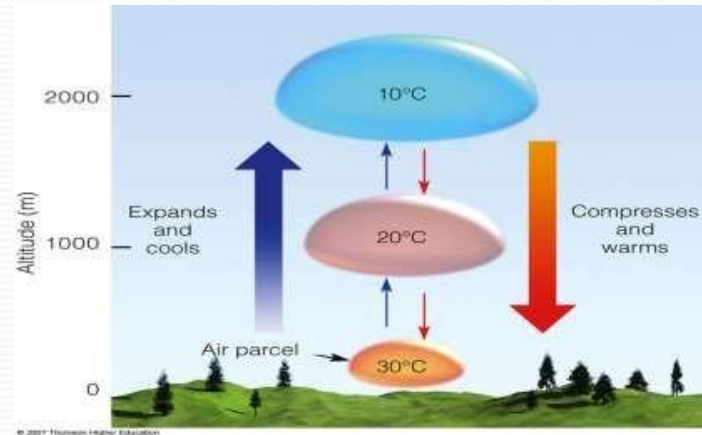
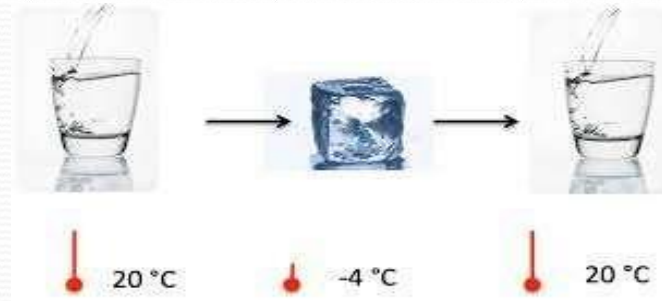
(a) Four basic thermodynamic processes; (b) A cyclic process.

Reversible Process

- A reversible process is defined as :
- *“A reversible process is a process whose direction can be "reversed" by inducing infinitesimal changes to some property of the system via its surroundings, while not increasing entropy.”*

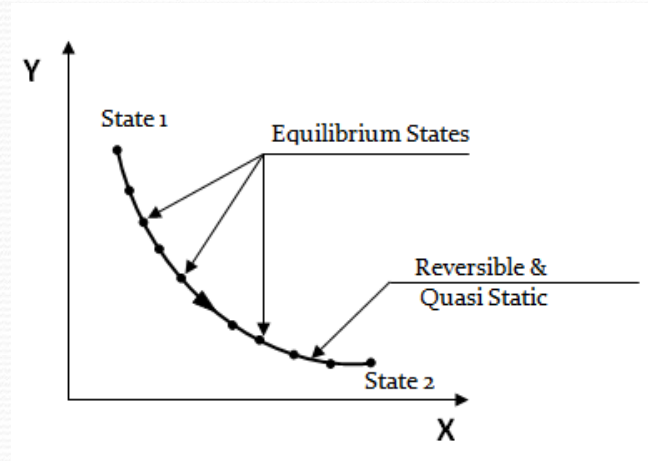
Or

- *“A process that can be reversed without leaving any change on the surroundings.”*



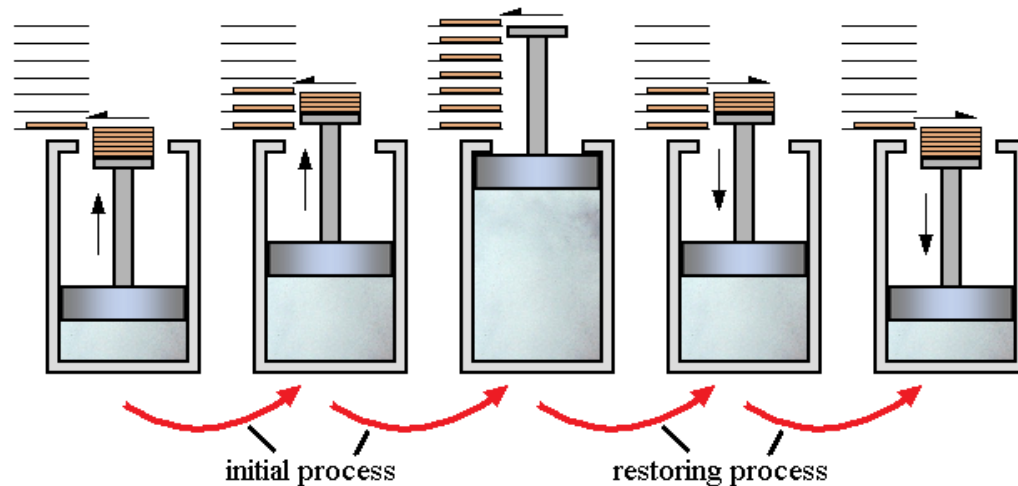
Reversible Process

- A reversible process passes through a continuous series of equilibrium states.
- It can be stopped at any stage and reversed so that the system and surroundings are exactly restored to their initial states.
- Consider the system in fig. The process take place from state 1 to state 2 by following path 1-2.
- If process is reversed, path 2-1 will be followed and system will reach its initial state. So the process 1-2 is called Reversible Process.



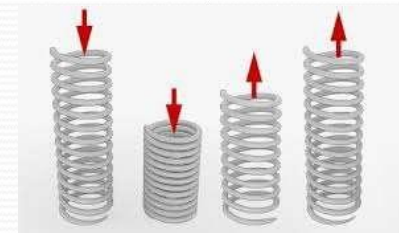
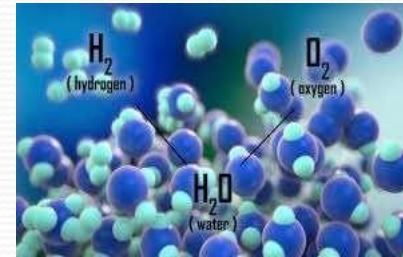
Reversible Process

- Consider expansion of a gas as shown in figure.
- The expansion of the gas takes place by removing infinitesimal weights slowly from the piston one by one, therefore process passes through equilibrium states and tending to reversible process.
- The gas can be brought back by compression after putting weights on the piston.



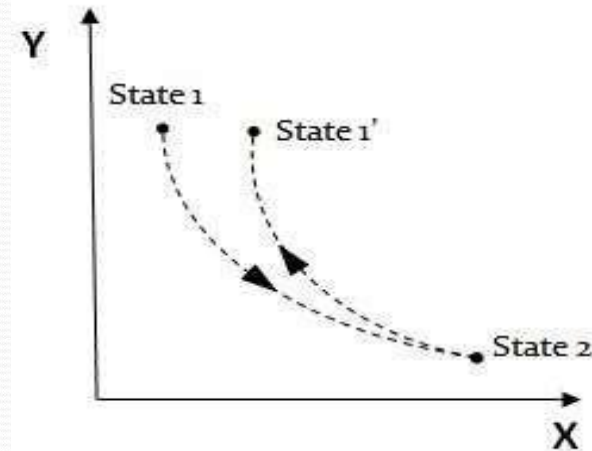
Reversible Process

- Some of the processes that can be idealized as reversible process are :
 - Frictionless relative motion
 - Expansion and compression of spring
 - Frictionless adiabatic expansion or compression of fluid
 - Isothermal Expansion or compression
 - Elastic stretching of a solid
 - Electrolysis process
- A reversible process produces the maximum work in engines and requires minimum work in devices such as heat pumps



Irreversible Process

- “A process that is not reversible is called an Irreversible Process.”
- In irreversible process, system passes through a series of non-equilibrium states.
- It is difficult to locate properties on property diagram as they don't have a unique value.
- When irreversible process is made to proceed in backward direction, it does not reach its original state.
- The system reaches a new state.
- Irreversible processes are usually represented by dotted lines.

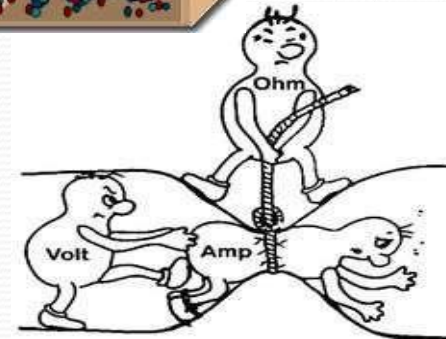
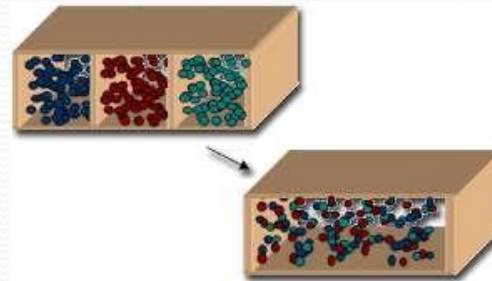


Irreversible Process

□ The factors that cause a process to be Irreversible are :

- i. Friction
- ii. Free Expansion
- iii. Mixing of two gases
- iv. Heat transfer between finite temperature difference
- v. Electric resistance
- vi. Inelastic deformation
- vii. Chemical reactions

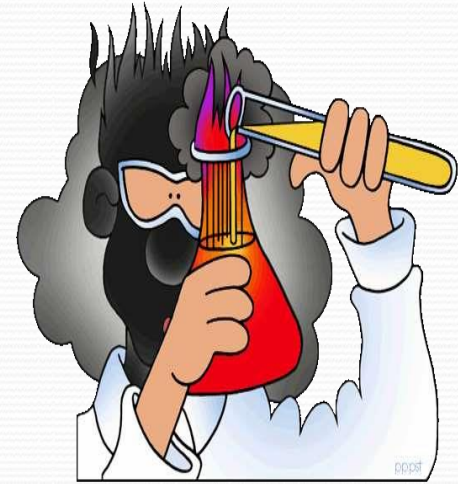
□ The presence of any of these effects makes a process irreversible.



Irreversible Process

□ Examples of irreversible processes are :

1. Relative motion with friction
2. Combustion
3. Diffusion of gases : mixing of dissimilar gases
4. Chemical reactions
5. Free expansion and throttling process
6. Plastic deformation
7. Electricity flow through a resistance.



SOME IMPORTANT FACTS ON ENTROPY

- 1. An equilibrium state has maximum disorder and hence entropy in equilibrium state is highest**
- 2. Entropy increases when temperature is increased**
- 3. Entropy can be created but can never be destroyed therefore entropy of system + surroundings can never be reduced**
- 4. Conversion of mechanical energy into heat energy increases entropy and vice – versa**
- 5. Entropy is related to absolute temperature only**

Heat

We can also change the internal energy of a system by transfer of heat from the surroundings to the system or vice-versa without expenditure of work. This exchange of energy, which is a result of temperature difference is called heat, q . Let us consider bringing about the same change in temperature by transfer of heat through thermally conducting walls instead of adiabatic walls.

We take water at temperature, T_A in a container having thermally conducting walls, say made up of copper and enclose it in a huge heat reservoir at temperature, T_B . The heat absorbed by the system (water), q can be measured in terms of temperature difference, $T_B - T_A$. In this case change in internal energy, $\Delta U = q$, when no work is done at constant volume.

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 total energy of an isolated system remains constant though it may change from one form to another.

mathematical statement of the First Law as :

$$\Delta E = q - w$$

where q = the amount of heat supplied to the system

w = work done by the system

Thus First Law may also be stated as : the net energy change of a closed system is equal to the heat transferred to the system minus the work done by the system.

Some Special Forms of First Law of Thermodynamics

Case 1 : For a cyclic process involving isothermal expansion of an ideal gas

$$\Delta E = 0$$

$$\therefore q = w$$

Case 2 : For an isochoric process (no change in volume) there is no work of expansion *i.e.* $w = 0$. Hence

$$\Delta E = q_v$$

Case 3 : For an adiabatic process there is no change in heat gained or lost *i.e.* $q = 0$. Hence $\Delta E = -w$

In other words, the decrease in internal energy is exactly equal to the work done on the system by surroundings.

Case 4 : For an isobaric process there is no change in pressure, *i.e.* P remains constant. Hence

$$\Delta E = q - w$$

$$\text{or } \Delta E = q - P\Delta V$$

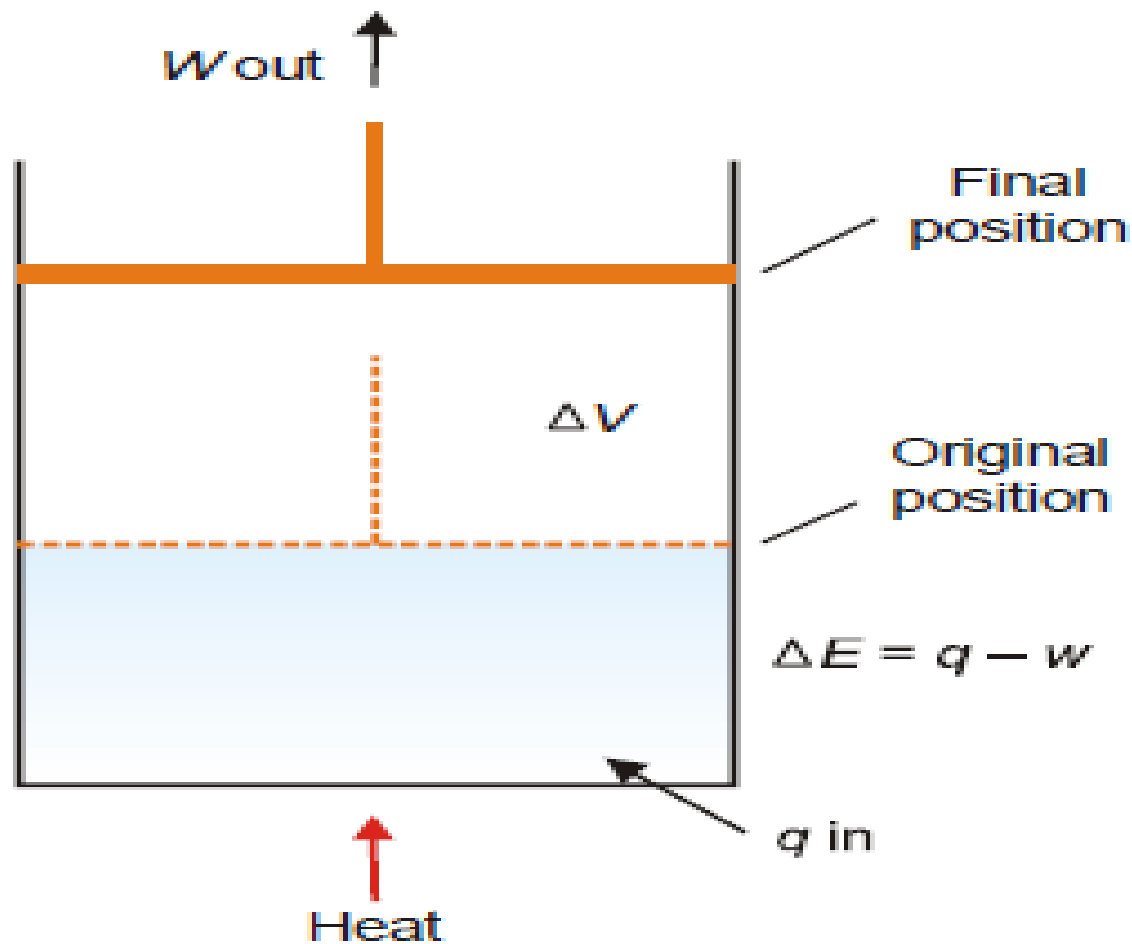


Figure 7.11

Illustration of First Law. Heat adds to internal energy, while work subtracts.

The First Law of Thermodynamics

Combining these gives the first law of thermodynamics. The change in a system's internal energy is related to the heat Q and the work W as follows:

$$\Delta U = Q - W$$

It is vital to keep track of the signs of Q and W .

TABLE 18–1 Signs of Q and W

Q positive	System <i>gains</i> heat
Q negative	System <i>loses</i> heat
W positive	Work done <i>by</i> system
W negative	Work done <i>on</i> system

Explanation First law of thermodynamics

□ Let us consider the general case in which a change of state is brought about both by doing work and by transfer of heat. We write change in internal energy for this case as:

$$\Delta U = q + w$$

For a given change in state, q and w can vary depending on how the change is carried out. However, $q + w = \Delta U$ will depend only on initial and final state. It will be independent of the way the change is carried out. If there is no transfer of energy as heat or as work (isolated system) i.e., if $w = 0$ and $q = 0$, then $\Delta U = 0$.

- 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.
- **Example:** Express the change in internal energy of a system when
- (i) No heat is absorbed by the system from the surroundings, but work (w) is done on the system. What type of wall does the system have ?
- (ii) No work is done on the system, but q amount of heat is taken out from
- the system and given to the surroundings. What type of wall does the system have?
- (iii) w amount of work is done by the system and q amount of heat is supplied to the system. What type of system would it be?

□ Answers

□ (i) $\Delta U = w_{\text{ad}}$, wall is adiabatic

□ (ii) $\Delta U = -q$, thermally conducting walls

□ (iii) $\Delta U = q - w$, closed system.

APPLICATIONS

Work-pressure volume work:

For understanding pressure-volume work, let us consider a cylinder which contains one mole of an ideal gas fitted with a frictionless piston. Total volume of the gas is V_i and pressure of the gas inside is p . If external pressure is p_{ex} which is greater than p , piston is moved inward till the pressure inside becomes equal to p_{ex} . Let this change be achieved in a single step and the final volume be V_f .

Enthalpy diagrams for exothermic reactions and endothermic reactions

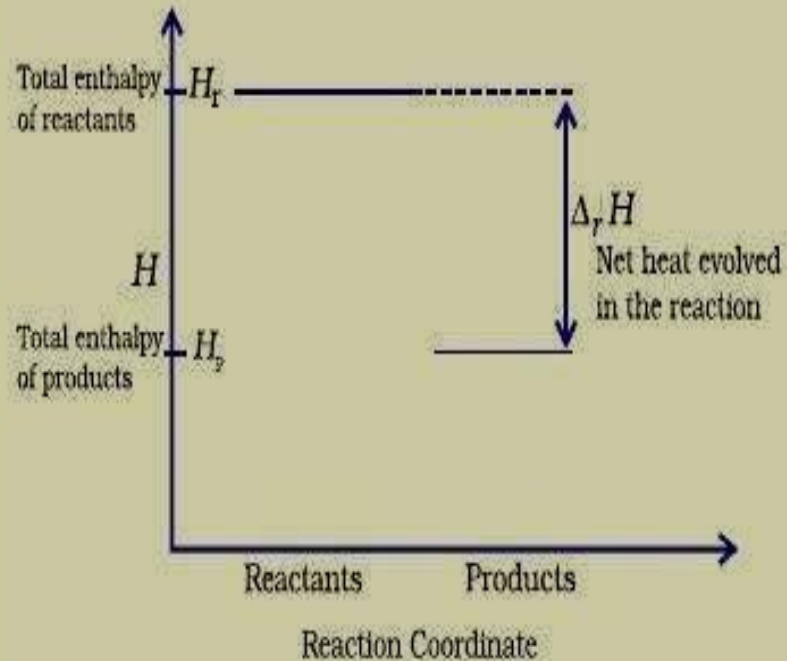


Fig. 6.10 (a) Enthalpy diagram for exothermic reactions

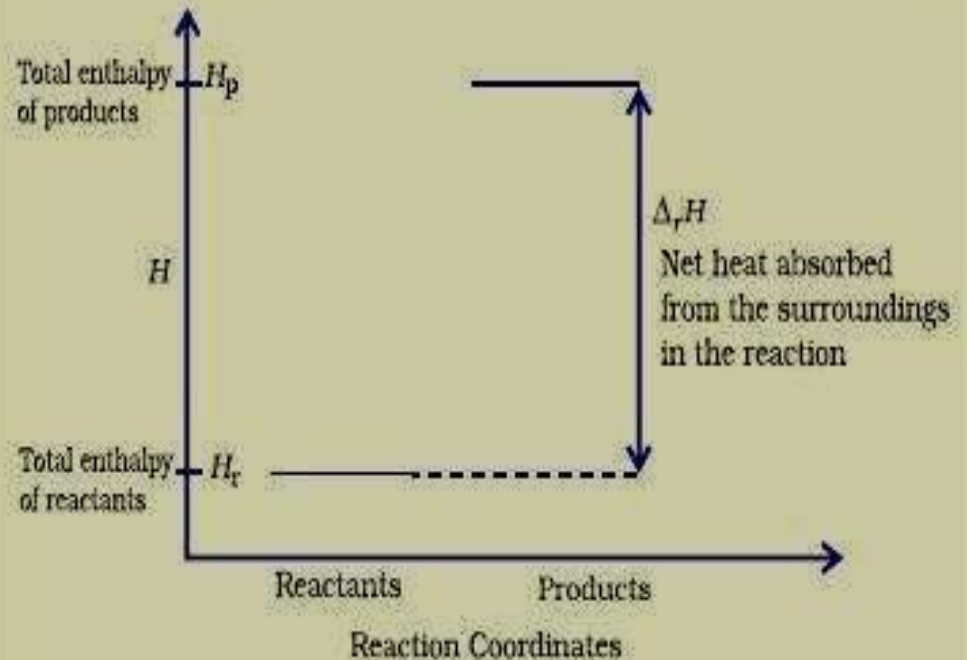
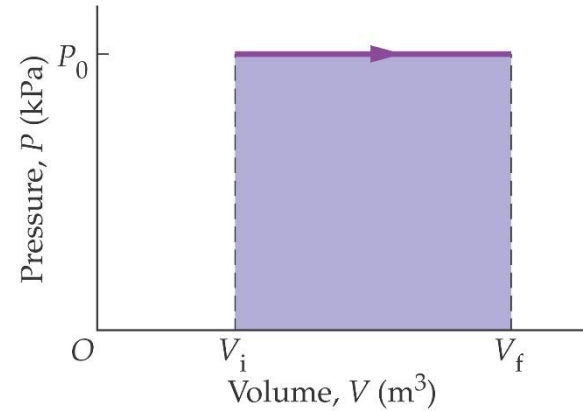
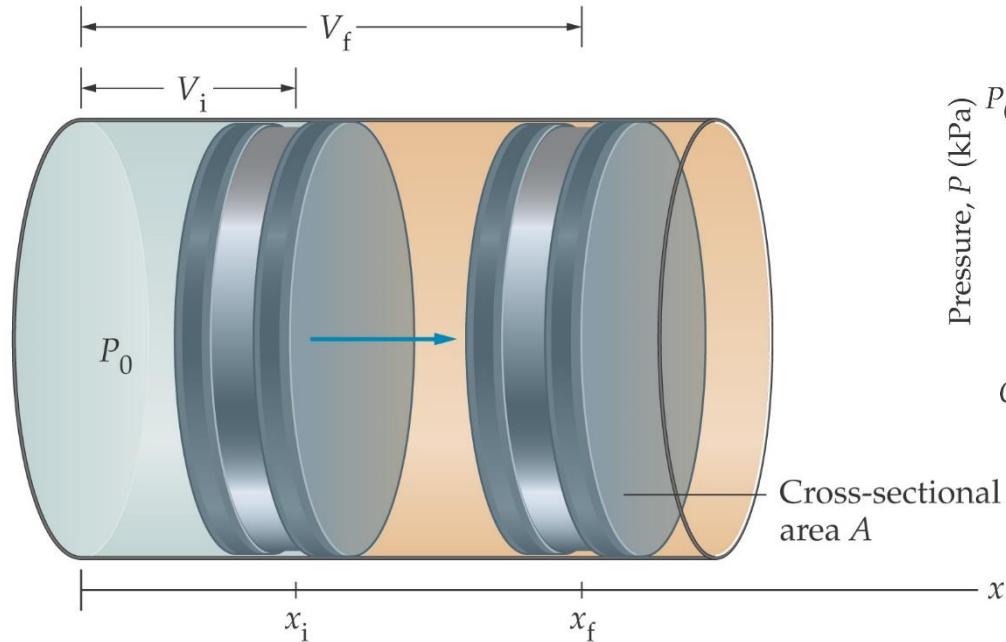


Fig. 6.10 (b) Enthalpy diagram for endothermic reactions

Thermal Processes

Work done by an expanding gas, constant pressure:

$$W = P\Delta V \quad (\text{constant pressure})$$

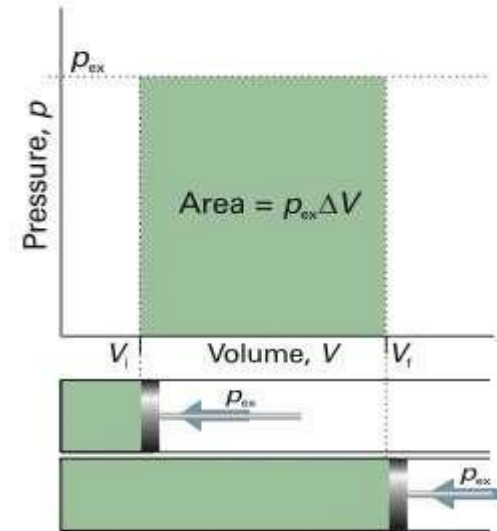


□ During this compression, suppose piston moves a distance, l and A is cross-sectional area of the piston then,
 volume change $= l \times A = \Delta V = (V_f - V_i)$

we know that pressure = $\frac{\text{force}}{\text{area}}$

Therefore, force on the piston $= p_{\text{ex}} \cdot A$. If w is the work done on the system by movement of the piston then
 $W = \text{force} \times \text{displacement} = p_{\text{ex}} \times A \cdot l$

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



- The negative sign of this expression is required to obtain conventional sign for w , which will be positive. It indicates that in case of compression work is done on the system. Here $(V_f - V_i)$ will be negative and negative multiplied by negative will be positive. Hence the sign obtained for the work will be positive. 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 summed over all the steps and will be equal to $-\sum \Delta p V$.
- If the pressure is not constant but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV . In such a case we can calculate the work done on the gas by a relation as given in the next slide.

$$w = - \int_{V_i}^{V_f} p_{\text{ex}} dV \quad (6.3)$$

Here, p_{ex} at each stage is equal to $(p_{\text{in}} + dp)$ in case of compression. In an expansion process under similar conditions, the external pressure is always less than the pressure of the system i.e., $p_{\text{ex}} = (p_{\text{in}} - dp)$. In general case we can write, $p_{\text{ex}} = (p_{\text{in}} + dp)$. 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, at any moment, be reversed by an infinitesimal change. A reversible process proceeds infinitely slowly by a series of equilibrium states such that system and the surroundings are always in near equilibrium with each other. Processes other than reversible processes are known as irreversible processes.

Relation of work to internal pressure

$$W_{ad} = - \int_{V_i}^{V_f} p_{ex} dV = - \int_{V_i}^{V_f} (p_{in} + dp) dV$$

since $dp \times dV$ is very small we can write

$$W_{ad} = - \int_{V_i}^{V_f} p_{in} dV$$

now the pressure of the gas is expressed in terms of its volume through the ideal gas equation

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

$$= W_{rev} = - \int_{V_i}^{V_f} nRT \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i} = -2.303 nRT \log \frac{V_f}{V_i}$$

Free expansion

- Expansion of a gas in vacuum ($p_{\text{ex}} = 0$) is called free expansion. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible.
- We know that $w = -p_{\text{ex}}\Delta V$ (we substituted in equation of area of piston and integration (6.3))

therefore the internal energy $\Delta U = q - p_{\text{ex}}\Delta V$

$$\text{therefore } \Delta U = q_v$$

q_v denotes that heat is supplied at constant volume.

Isothermal and free expansion of a ideal gas

- For isothermal ($T = \text{constant}$) expansion of an ideal gas into vacuum ; $w = 0$ since $p_{\text{ex}} = 0$. Also, Joule determined experimentally that $q = 0$; therefore, $\Delta U = 0$,
- $\Delta U = q + w$ can be expressed for isothermal irreversible and reversible changes as follows:
- (a) for isothermal irreversible change:

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

□(b) for a reversible process:

$$q = -w = nRT \ln \frac{v_f}{v_i}$$

$$= 2.303 \ nRT \log \frac{v_f}{v_i}$$

• (c) for adiabatic change, when $q=0$

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

Enthalpy (H).

- We know that the heat absorbed at constant volume is equal to change in the internal energy i.e., $\Delta U = q_V$. But most of chemical reactions are carried out not at constant volume, but in flasks or test tubes under constant atmospheric pressure.
- We may write equation THIS as $\Delta U = q_p - p\Delta V$ at constant pressure, where q_p is heat absorbed by the system and $-p\Delta V$ represent expansion work done by the system.

□ We can rewrite the above equation as:

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

□ On rearranging we get:

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

Now we can define another thermodynamic function the enthalpy H [Greek word enthalpien, to warm or heat content] as:

$$H = u + pV$$

So the equation becomes:

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

Although q is a path dependent function, H is a state function because it depends on U, p and V, all of which are state functions. Therefore, ΔH is independent of path. Hence, q_p is also independent of path.

For finite changes at constant pressure,

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

Since p is constant, we can write

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

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.

□ At constant volume, $\Delta H = \Delta U = q_v$

Now we know that $pV = nRT$

Therefore let n_A be total number of moles of reactants and let n_B be total number of moles of products then:

$$pV_A = n_A RT$$

Similarly then: $pV_B = n_B RT$

Thus combining both these equations we get:

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

$$\text{Therefore, } p(V_B - V_A) = (n_B - n_A)RT$$

$$\text{Or, } p\Delta V = \Delta n_g RT$$

Extensive and Intensive properties

- An extensive property is a property whose value depends on the quantity or size of matter present in the system. example: mass, volume, internal energy etc :-
- An intensive property is a property whose value does not depend upon temperature, density, pressure etc :-
- A molar property (m) is the value of an extensive property of the system 1 mol of the substance. If n is the amount of matter then $m = \frac{x}{n}$ is independent of the amount of matter.

Heat capacity

- We measure heat capacity by the measure of transfer of heat
- The increase of temperature is proportional to the heat transferred therefore :-
$$q = \text{coeff} \times \Delta T$$

The magnitude of the coefficient depends on the size, composition and nature of the system. We can also write this equation as $q = C\Delta T$

Where coeff, (C) means heat capacity.

When C is large, the amount of heat given out results in a very small rise in temperature, .

- C is directly proportional to the amount of substance. The molar heat capacity of a substance,

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

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

Thus specific heat capacity of a substance = $q = c \times m \times \Delta T = C \Delta T$, Where mass remains constant

The relationship between C_p and C_v for an ideal gas

- At constant volume, the heat capacity C at constant volume is denoted by C_v and at constant pressure it is denoted by C_p .
- The relationship between them is as follows:
At constant volume $q_v = C_v \Delta T = \Delta U$.
and , At constant pressure $q_p = C_p \Delta T = \Delta H$.
Now the difference between C_v and C_p can be derived for an ideal gas for one mole as given in the next slide.

□ For one mole of an ideal gas : $\Delta H = \Delta U + \Delta(pV)$
 $= \Delta U + \Delta(RT)$
 $= \Delta U + R\Delta T$

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

Now on substituting the values we get : $C_p\Delta T = C_v\Delta T + R\Delta T$

Therefore: $C_p = C_v + R$

So, $C_p - C_v = R$

Measurement of ΔU and ΔH : calorimetry

- Energy changes can be measured with chemical or physical processes by an experimental technique called calorimetry.
- In this process a vessel called calorimeter is immersed in a known volume of a liquid. Knowing the heat capacity of the liquid in which the calorimeter is immersed and the heat capacity of the calorimeter it is possible to determine the heat evolved by measuring the temperature changes under two conditions:
 - (1) At constant volume q_v
 - (2) At constant pressure q_p

ΔU measurements

- For ΔU measurements heat is absorbed at constant volume and hence these measurements.
- here a steel vessel is immersed in a water bath. The whole device is called a calorimeter. The steel vessel is immersed in the water bath to ensure that no heat is lost in its surroundings. A combustible substance is burnt in pure dioxygen supplied in the steel bomb. Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored. Since the bomb calorimeter is sealed, its volume does not change. The energy changes associated with the reactions are measured at constant volume. Under these conditions, no work is done as the reaction is carried out at constant volume in the bomb calorimeter. Even for reactions involving gases, there is no work done as $\Delta V=0$, Temperature change of the reaction is then converted to q_v by using the known heat capacity of the calorimeter.

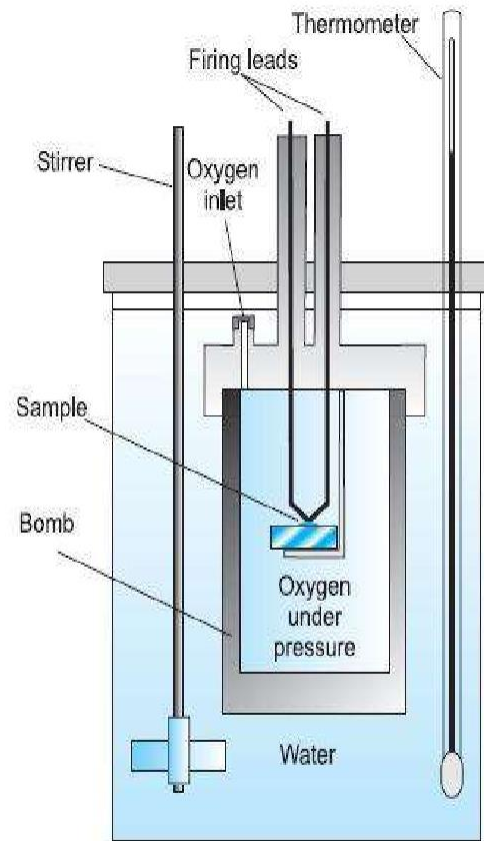


Fig. 6.7 Bomb calorimeter

ΔH measurements

□ We can measure heat change at constant pressure in a calorimeter by the following technique:-

We know that $\Delta H = q_p$ and therefore heat absorbed or evolved q_p .

At constant pressure is also called heat of reaction or enthalpy of reaction ($\Delta_r H$). In an exothermic reaction, heat is evolved and system loses heat to the surroundings. Therefore q_p will be negative. Similarly in an endothermic reaction, heat is absorbed and q_p and $\Delta_r H$ will be positive.

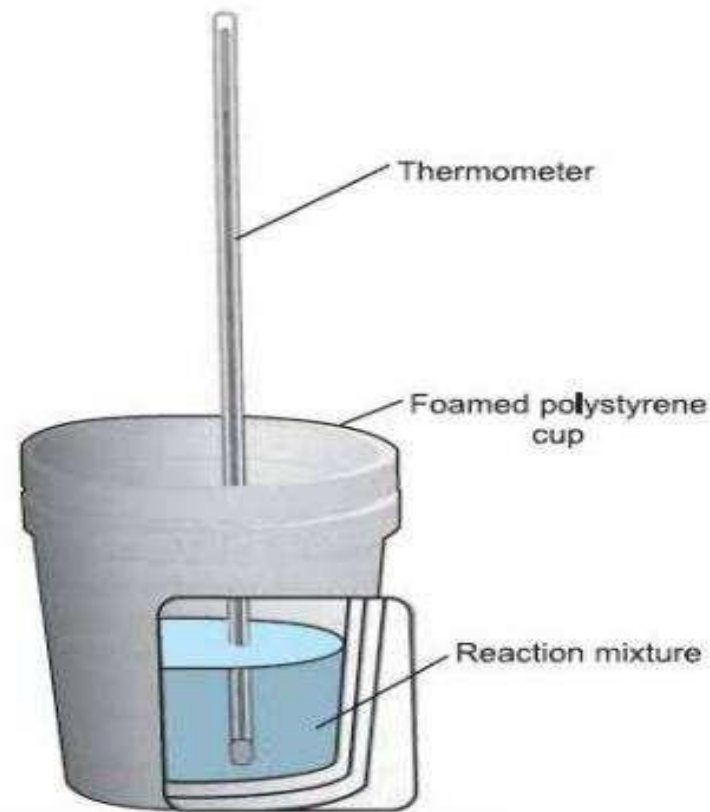


Fig. 6.8 Calorimeter for measuring heat changes at constant pressure (atmospheric pressure).

Enthalpy change ($\Delta_r H$) of a reaction- reaction enthalpy

□ In a chemical reaction, reactants are converted into products and they are represented by :



The enthalpy change accompanying a reaction is called the reaction enthalpy of that particular reaction. The enthalpy change of a chemical reaction is denoted by $\Delta_r H$.

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

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

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 of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.
- 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 298K is pure liquid ethanol at 1 bar : standard state of solid iron at 500K is pure iron at 1 bar .we denote standard enthalpy of reactions as $\Delta H^\ominus$

Enthalpy changes during phase transformations

- Phase transformations also involve energy changes in short it requires heat for doing a action, for example ice for melting into water.
- For example : $\text{H}_2\text{O}(\text{s}) \longrightarrow \text{H}_2\text{O}(\text{L})$ $\Delta_{\text{fus}}H^\ominus = 6 \text{ kJ/mol}$

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. It is denoted by $\Delta_{\text{fus}}H^\ominus$

□ The amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1 bar) is called standard enthalpy of vaporization or molar enthalpy of vaporization

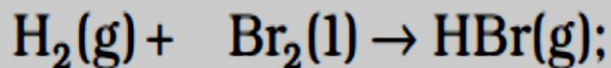
□ It is denoted by: $\Delta_{vap}H^\ominus$

standard enthalpy of sublimation is the change in enthalpy when one mole of a solid substance sublimates at a constant temperature and under standard pressure (1 bar).

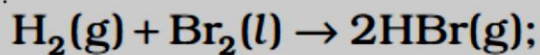
It is denoted by : $\Delta_{sub}H^\ominus$

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.
- It is denoted by $\Delta_f H^\ominus$



$$\Delta_f H^\ominus = -36.4 \text{ kJ mol}^{-1}$$

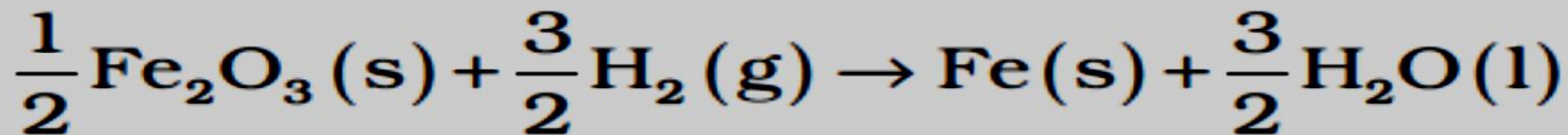


$$\Delta_r H^\ominus = -72.8 \text{ kJ mol}^{-1}$$

Here two moles, instead of one mole of the product is formed from the elements, i.e.,

$$\Delta_r H^\ominus = 2\Delta_f H^\ominus .$$

AN IMPORTANT CONCLUSION



$$\Delta_r H_2^\ominus = \frac{3}{2}(-285.83 \text{ kJ mol}^{-1}) - \frac{1}{2}(-824.2 \text{ kJ mol}^{-1})$$

By convention, standard enthalpy for formation, $\Delta_f H^\ominus$, of an element in reference state, i.e., its most stable state of aggregation is taken as zero.

Standard enthalpy of combustion

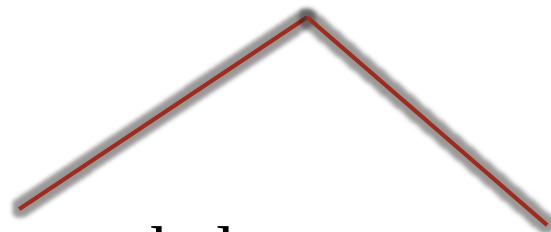
- These are exothermic in nature. Standard enthalpy of combustion is defined as the enthalpy change per mole of a substance when it undergoes combustion and all the reactants and products being in their standard states.
- It is represented as $\Delta_c H^\ominus$

Standard enthalpy of atomization

- The enthalpy change in the process of breaking of bonds is called standard enthalpy of atomization.
- It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase
- It is represented as $\Delta_a H^\ominus$

Bond enthalpy $\Delta_{\text{bond}} H^\ominus$

- Bond enthalpy in thermodynamics is divided into two parts:



bond dissociation enthalpy

mean bond enthalpy

For diatomic molecules:

For diatomic molecules, the enthalpy change involved in this process is the bond dissociation enthalpy of H-H bond. The bond dissociation enthalpy is the change in the enthalpy when one mole of covalent bonds of gaseous covalent compounds is broken to form products in the gas phase.

□ **For polyatomic molecules:** In this case we use the mean bond enthalpy of C-H bond. The reaction enthalpies are very important quantities as these arise from the changes that accompany the breaking of old bonds and formation of new bonds.

$\Delta_r H^\ominus$ is related to the bond enthalpies of the reactants and products in the gas phase reaction as:

$$\Sigma \text{ bond enthalpies (reactants)} - \Sigma \text{ bond enthalpies (products)}$$

□ This relationship is particularly more useful when the required values $\Delta_r H^\ominus$ are not available. The net enthalpy of a reaction is the amount of energy required to break all the bonds in the reactant molecules minus the amount of energy required to break all the bonds in the product molecules. This is only possible in the gaseous state.

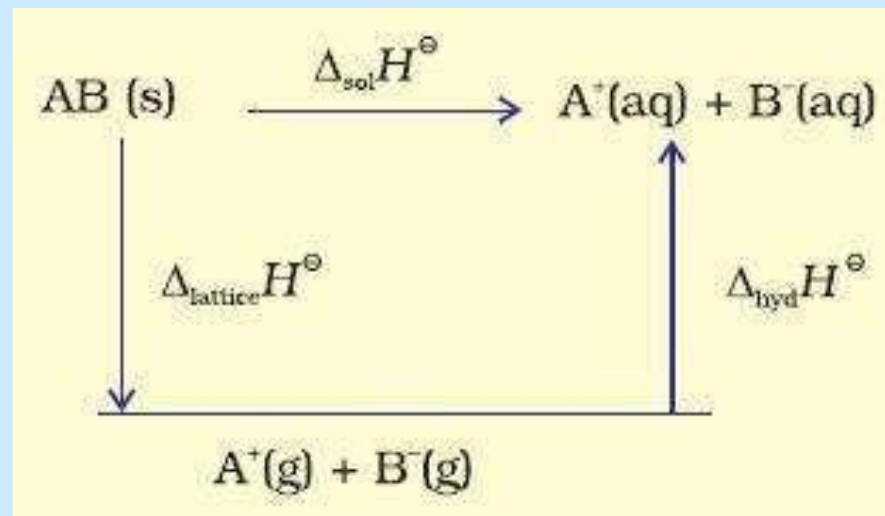
Enthalpy of a solution($\Delta_{sol}H^{\ominus}$)

- Enthalpy of a solution of a substance is the enthalpy change when one mole of it dissolves in the specified amount of solvent.
- The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving the substance in an infinite amount of solvent when the interactions between the ions are negligible.
- When an ionic compound dissolves in a solvent, the ions leave their ordered position on their crystal lattice. These ions now become more free to move in the solution.
- But solvation of these ions also occurs at the same time.

Hydration of water (compound AB)

□ This picture shows the hydration of water. Then enthalpy of a solution $\Delta_{sol}H^\ominus$ in water is therefore determined by selective values of lattice enthalpy, $\Delta_{lattice}H^\ominus$ and the enthalpy of hydration of ions $\Delta_{hyd}H^\ominus$ as:

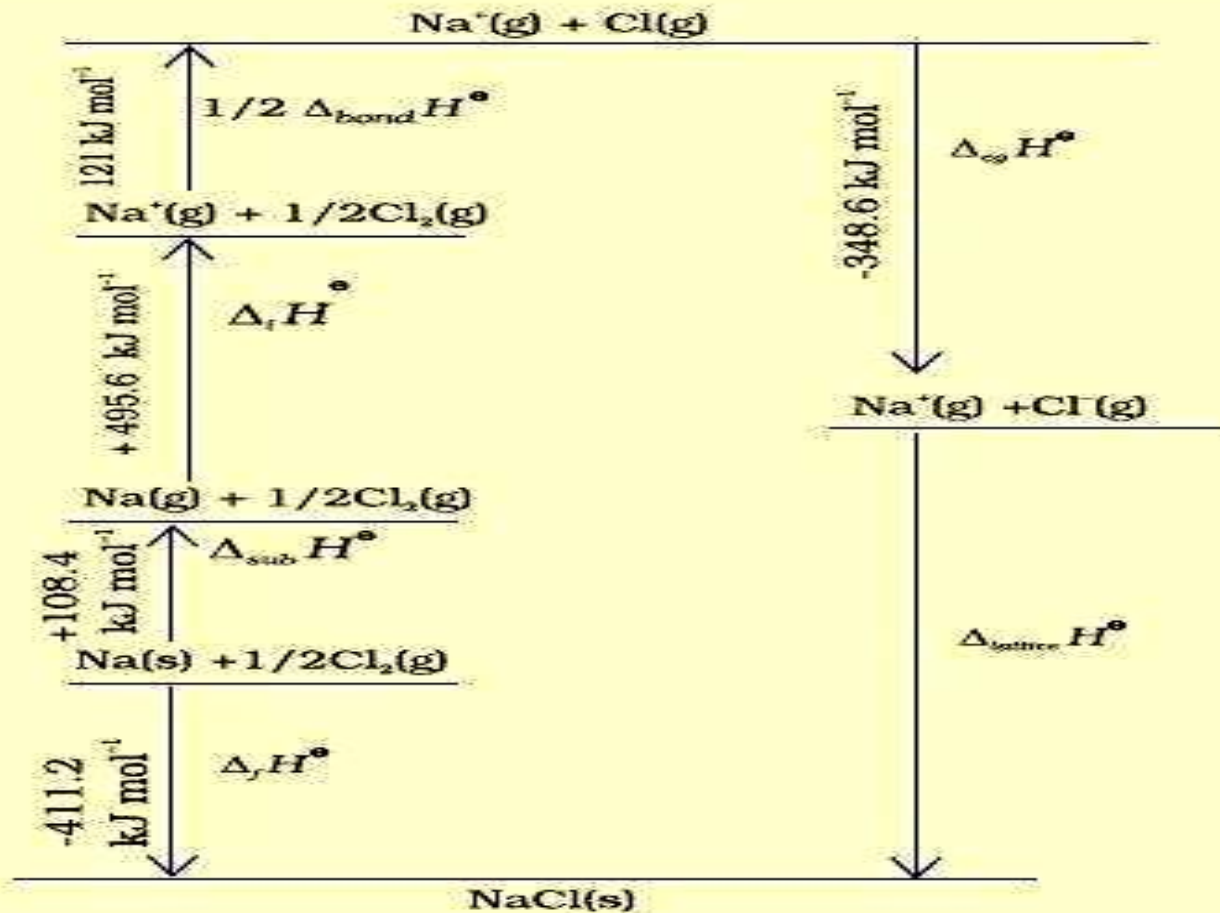
$$\Delta_{sol}H^\ominus = \Delta_{lattice}H^\ominus + \Delta_{hyd}H^\ominus$$



Lattice enthalpy

- The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in its gaseous state.
- Since it is impossible to determine lattice enthalpies directly by an experiment, we can use it by an indirect method by constructing an enthalpy diagram called the **BORN HABER CYCLE**
- **The example of chlorine is a very good example given in the textbook**

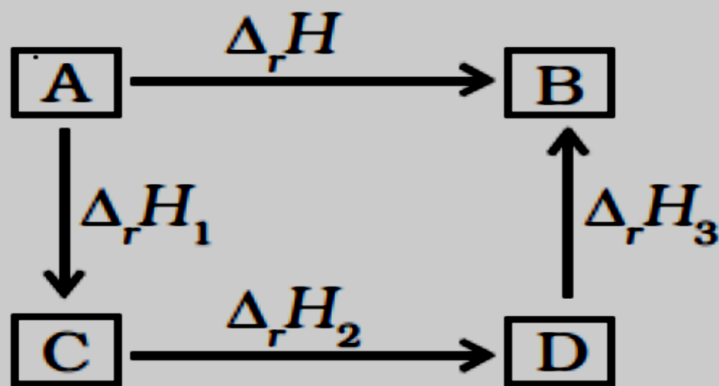
Enthalpy diagram for lattice enthalpy of NaCl



Hess's 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.

It can be represented as:



Thermochemical equations

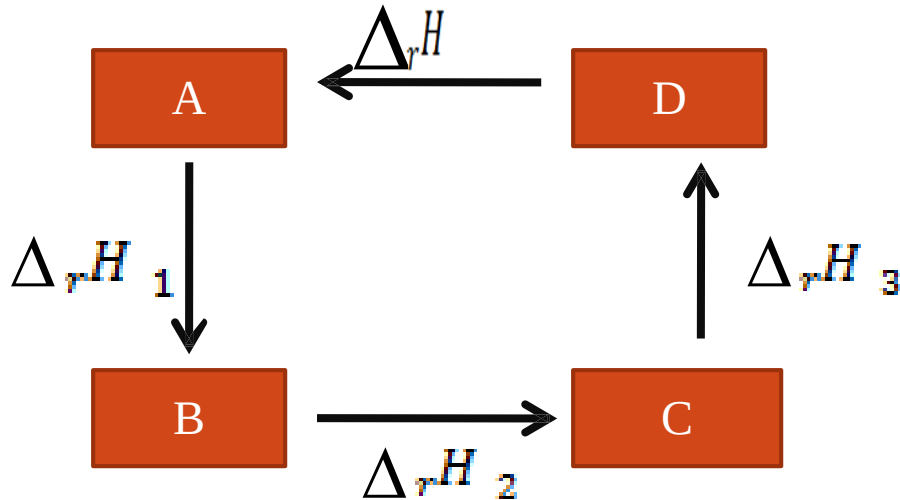
- A balanced chemical equation together with the value of its $\Delta_r H$ is called a Thermochemical equation.
- Point to remember in a Thermochemical reaction:-
 - (1) The coefficients in a balanced Thermochemical equation refer to the number of moles of substances of reactants and products involved in the reaction
 - (2) The value of $\Delta_r H$ refers to the number of moles of substances specified by an equation. Standard enthalpy change $\Delta_r H^\ominus$ will have the units as kJ/mol.

Hess's law of constant heat summation

- The enthalpy is a state function and therefore the change in enthalpy is independent of the path between the initial state and the final state. In other words, enthalpy change for a reaction is the same whether it occurs in one step or a series or a sequence of steps.
- 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.

□ In general, if enthalpy of an overall reaction $A \rightarrow B$ along one route is, $\Delta_r H$, Δ representing the enthalpies of reactions leading to the same product, B along another route, then we have.

$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \dots$$



SPONTANEOUS PROCESSES

A process which proceeds of its own accord, without any outside assistance, is termed a spontaneous or natural process.

CRITERIA OF SPONTANEITY

- 1. A spontaneous change is one-way or unidirectional.**
- 2. For a spontaneous change to occur, time is no factor**
- 3. If the system is not in equilibrium state (unstable), a spontaneous change is inevitable.**
- 4. Once a system is in equilibrium state, it does not undergo any further spontaneous change in state if left undisturbed.**
- 5. A spontaneous change is accompanied by decrease of internal energy or enthalpy (ΔH).**

Spontaneity

- A spontaneous process is an irreversible process and may only be reversed by an external agency.
- **Decrease in the enthalpy a criterion for spontaneity ? :**
Decrease in the enthalpy may be a contributory factor for spontaneity but it is not true for all the cases.
- A spontaneous reaction may be a fast one but not may be the function of the first one....
- Any two gases can combine to form a product but the rate of spontaneity differs from equation to equation.

ENTROPY AND SPONTANEITY

- We introduce another thermodynamic function here called, entropy (S). higher the isolation, higher the entropy.
- The change in entropy accompanying a chemical reaction, may be estimated qualitatively taking some structures in mind.
- A crystalline solid will have the lowest entropy, whereas the gaseous state will have the highest entropy.
- Entropy, like any other thermodynamic function includes internal energy (U), enthalpy (H) is a state function and ΔS independent of its path.
- Whenever heat is added to a system its molecular motions increase causing randomness in the system. Thus this heat (q) has a **randomising effect**.
- Thus, the temperature is the measure of the average chaotic motion of particles in a system.

Mathematical representation

- Heat added to a system at lower temperature causes greater randomness than when the same quantity of heat is added to it at higher temperature, therefore entropy change is inversely proportional to temperature and therefore:-

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

The total entropy change (ΔS_{total}) for the system and surroundings of a spontaneous process is given by:-

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

when a system is in equilibrium, the entropy is maximum, and the change in entropy $\Delta S = 0$

□ We can say that entropy for a spontaneous process increases till it reaches its maximum and at equilibrium the change in entropy is 0. since entropy is a state property, we can calculate the entropy as a reversible process by the following formula:-

$$\frac{Q_{sys,rev}}{T}$$

We will find that both for reversible and irreversible expansion for an ideal gas , under isothermal conditions $\Delta U=0$, but $\Delta S_{sys} + \Delta S_{surroundings}$ is not equal to zero .therefore ΔU does not discriminate between reversible and irreversible process whereas ΔS does.

Gibbs energy and spontaneity

- We know that neither an increase nor a decrease in the entropy of a substance can determine the spontaneity of the process, for this we determine a new thermodynamic function called Gibbs (G).

$$G = H - TS$$

Gibbs is an extensive property and a state function, therefore the change in the Gibbs energy for a system is defined as follows :-

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

Therefore, simply we can write this equation as :-

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

- Thus, gibbs energy change = enthalpy change-temperature x entropy change and is therefore referred to gibbs equation.
- Gibbs energy's SI unit is joules (J)
- If the system is in thermal equilibrium with the surroundings , then the temperature of the surroundings is the same as that of the system. Also increase in enthalpy of the surroundings is equal to decrease in the enthalpy of the system.
- Therefore entropy change (in surrounding)is equal to :-

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

Therefore:

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

□ Rearranging the above equation we get :-

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

□ For a spontaneous process , $\Delta S_{total} > 0$

Therefore $T\Delta S_{sys} - \Delta H_{sys} > 0$

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

Therefore we can also write : $-\Delta G > 0$

or,

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

ΔG is the net energy available to do useful work and thus is a measure to do useful work and thus a measure of '**free energy**'.

□ ΔG gives a criteria for spontaneity at constant pressure and temperature.

(a) if ΔG is negative (<0) the process is spontaneous.

(b) if ΔG is positive (>0) the process is non spontaneous.

If a reaction has positive enthalpy change and positive entropy change, it can be spontaneous when $T\Delta S$ is large enough to outweigh ΔH . This can happen in 2 ways:-

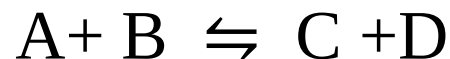
(a) The positive entropy change of the system can be small in which T can be large.

(b) The positive entropy change of the system can be large in which case, T can be small.

(T refers to temperature)

Gibbs energy change and equilibrium

□ The criteria for an equilibrium reaction is :-



Hence, $\Delta_r G = 0$

Gibbs energy for a reaction in which all reactant and products are in standard state, $\Delta_r G^\ominus = 0$ is related to the equilibrium constant of the reaction as follows :

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

$$\text{or } \Delta_r G^\ominus = -RT \ln K$$

$$\text{Therefore } \Delta_r G^\ominus = -2.303 RT \log K$$

- In case of endothermic reactions heat evolved will be large and positive whereas in case of exothermic reactions the heat evolved will be small and negative.
- Therefore depending upon the temperature and other factors like internal energy entropy change, and rate of kinetic diffusion the entropy change is determined.
- It is possible to estimate the value of $\Delta G^\ominus$ from the measurement of $\Delta H^\ominus$ and $\Delta S^\ominus$ and then calculate the value of K at any temperature for economic yields of the products.
- If K is measured directly in the laboratory and value of $\Delta G^\ominus$ at any other temperature can be calculated