

Unit - V

Thermodynamics and Thermochemistry

Thermodynamic

Intensive and Extensive variables or properties

A *property* of a system is anything that is directly felt or measured by experiments: Properties that could be measured are divided into two classes. Properties whose values depend on the amount of the material present in the system are called *extensive properties*. Properties whose values do not depend on the amount of the material present in the system are called *intensive properties*.

Some extensive and intensive properties or variables are given below:

Examples of extensive variables :

Volume, Number of moles, Mass, Free energy, Entropy, Heat capacity.

Examples of intensive variables:

Molar volume, Refractive index, Density, Surface tension, Viscosity, Free energy/mole, Specific heat, Specific gravity, Latent heat, Pressure. Temperature : Boiling point, Freezing point.

Types of Systems :

A *system* is defined as any particular part of the universe about which we are interested. The rest of the universe is called *surroundings*. There are three different systems. They are isolated closed and open systems.

1. Isolated system :

A system which can exchange neither energy nor matter with its surroundings is called an isolated system.

To take an example consider a closed vessel containing water which is in contact with its vapour. Since the vessel is closed, no matter (liquid or vapour) can leave or enter the vessel. Further if the vessel is also insulated it can neither lose heat nor gain heat from the surroundings. In short the system cannot exchange energy with the surroundings. Thus this is an isolated system.

2. Closed system

A system which can exchange energy but not matter with its surroundings is called a closed system. In the above example, if the vessel is closed but not insulated, then it will be able to exchange energy but not matter with the surroundings. Thus this is a closed system.

3. Open system

A system which can exchange both matter and energy with its surroundings is called an open system. Consider evaporation of water taken in an open beaker. The water vapours (matter) will escape into the surroundings. Further heat (energy) required for the vapourisation will be taken from the surroundings. Thus this is an open system.

Thermodynamic Process

The operation by which a system changes from one state to another is called a process.

1. Cyclic processes

When a system, after completing a series of changes returns to its original state, it is said to have completed a cycle. Such a process is known as a cyclic process.

2. Reversible processes

A thermodynamically reversible process is a process which is carried out infinitesimally slowly so that the driving force is only infinitesimally greater than the opposing force.

Criteria for thermodynamically reversible process:

- i. There should be equilibrium at every intermediate stage of the process.
- ii. The process should be capable of proceeding in both directions.
- iii. The process should take place infinitesimally slowly.
- iv. The initial state of process should be attainable back without producing any permanent effect in the surroundings.

3. Irreversible process

An irreversible process is a process which does not take place infinitesimally slowly.

Distinctions between reversible and irreversible processes

Reversible process	Irreversible process
1. A slow process with a series of intermediate equilibrium states	A process with measurable speed
2. Driving force of the reaction is only infinitesimally greater than the opposing force.	Driving force is usually considerably larger than the opposing force.
3. Proceeds in both direction,	Proceeds only in one direction
4. Work done is greater	Work done is less
5. Can be brought back to the initial state without producing any permanent effect in the surroundings	Cannot be brought back to the initial state without producing any permanent effect on the surroundings.

All natural processes are irreversible :

Reason :

A reversible process, in a true thermodynamic sense cannot be realised because it would require infinite time for its conditions of thermodynamic reversibility are unattainable. So all natural processes are considered to be irreversible.

1. Isothermal process

A process is said to be isothermal if the temperature of the system remains constant during each step of the process. Suppose a process say a chemical reaction is carried out in a vessel which is not insulated. The system is thus in thermal equilibrium with the surroundings. If the process is exothermic, heat is evolved in the process. The heat is given out to the surroundings instantaneously. Therefore the temperature of the system remains unchanged. On the other hand if the reaction is endothermic, then the heat required is absorbed instantaneously from the surroundings. Then again the temperature of the system remains unchanged. Such a system is called isothermal system and the process is called **isothermal process**.

2. Adiabatic process

A process is said to be adiabatic if no heat enters or leaves the system during any step of the process. Suppose a process, say a chemical reaction is carried out in an insulated vessel. In, this case no heat can leave or enter the vessel from the surroundings. If the process is exothermic, the heat evolved remains with in the system and therefore the temperature of the system rises. If on the otherhand, the process is endothermic, the heat required is absorbed from the system itself. Therefore the temperature of the system falls. Such a system is called adiabatic system and the process is called **adiabatic process**.

Thermodynamic Functions :

State and path functions

State functions are variables which are determined only by the initial and final states of the system and not by the path followed during the change from initial to the final state.

Examples :

Internal energy (U), enthalpy (H), entropy (S) free energy (G), work function (Δ) etc.

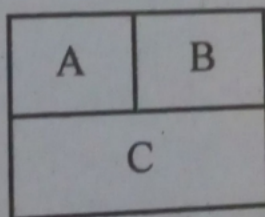
Path functions are quantities that depend on the path followed during a change. Example : Heat absorbed (Q), work done (W).

Zeroth Law of Thermodynamics :

This law was formulated after the declaration of the first law of thermodynamics. But, since this law was considered to be of primary importance. It was called zeroth law. The law states as follows :

Statement :

If the temperature of the body A is in equilibrium with body C and body B is also in equilibrium with body C, Then the temperature of bodies A and B are in equilibrium with each other.



Explanation :

Consider the bodies A and B. Let the body A is at a high temperature at T_2 and B is at a lower temperature at T_1 when A and B are allowed to come in to contact, the heat is conducted from the hotter body A to B till it attain temperature equilibrium.

Then the bodies A and B are allowed to come into contact with C. The body A is then separated from B after some time A and C will attain temperature equilibrium B and C also attain temperature equilibrium. Even though there is no direct contact between A and B they attain temperature equilibrium.

Uses :

Based on the principle of Zeroth law the thermometers are constructed and used.

Concept of Heat

Definition :

Heat is defined as a quantity that flows across the boundary of a system during a change in its state by virtue of a difference in temperature between the system and its surroundings and flows from a point of higher temperature to a point of lower temperature.

Again several things must be understood.

1. Heat appears only at the boundary of the system and during change in state.
2. Heat is manifested by an effect in the surroundings.
3. The quantity of heat is measured by its absorption or release from water in the surroundings.
4. Heat is an algebraic quantity. It is positive if the surroundings are cooled. It is negative if the surroundings are warmed : Heat and work are different forms of energy. They are expressed as number of joules.

Concept of Work :

Definition :

Work is defined as any quantity that flows across the boundary of a system during a change in its state and completely convertible into the lifting of a weight in the surroundings.

The following points should be noted in this definition of work.
 1. Work appears only at the boundary of a system and during a change in state.

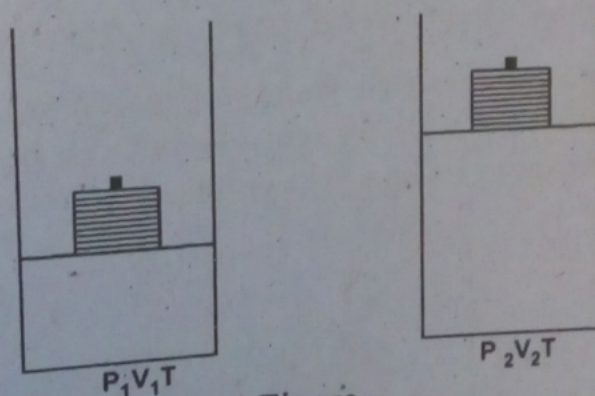
2. Work is understood by an effect in the surroundings.

3. The amount of work is equal to mgh , where m is the mass lifted, g is acceleration due to gravity, h is the height through which the weight is lifted.

4. Work is an algebraic quantity. It is positive if the weight has been lifted. Here we say work is done by the system. It is negative when the weight is lowered. In this case we say the work is done on the system.

Work of expansion :

Work done during the expansion of a gas is called work of expansion. Consider a gas enclosed in a cylinder with the help of a weightless and frictionless piston. When this gas expands, it lifts the body placed on the piston. The initial state of the gas is described by T, P_1 and V_1 . After the expansion the final state is described by T, P_2, V_2 .



Figure

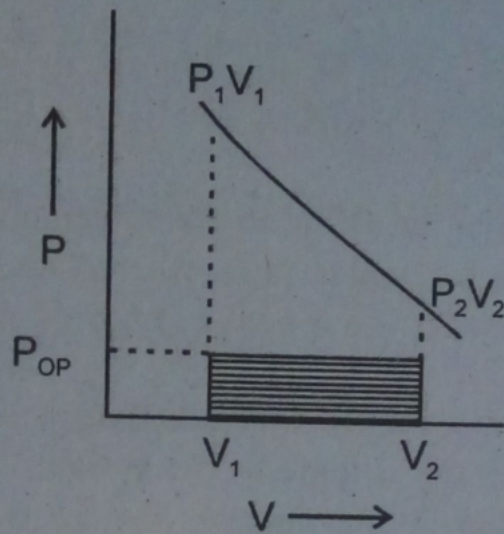
During the expansion, the gas opposes the pressure on the piston. If A is the cross sectional area of the piston, the pressure on the piston is $P_{OP} = mg / A$. m is the mass of the body on the piston. If the piston moves through a height h , the amount of work done is given as,

$$W = mgh$$

$$W = P_{OP} Ah$$

$$W = P_{OP} \Delta V = P_{OP} (V_2 - V_1)$$

ΔV is the increase in volume of the gas. In this particular expansion the opposing pressure is constant. The work of expansion can also be known from the following graph.



Figure

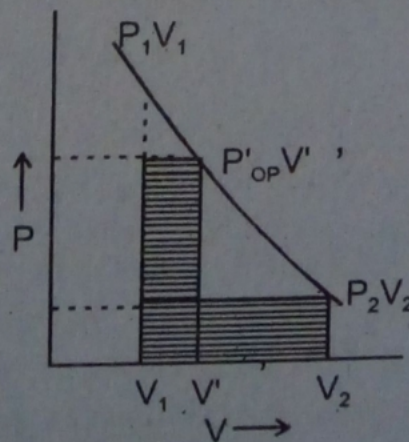
Area of the shaded portion is equal to the work done.

The above expansion can be carried out in two stages. If the gas expands opposing the pressure P_{OP} in the first stage and P_2 in the second stage, the work done is given as

$$W = P'_{OP}(V' - V_1) + P_2(V_2 - V')$$

Again the work of expansion can be known from the graph.

The work done in this two stage-expansion is larger than the singlestage expansion. So more amount of work can be derived from a several stage expansion to a same final volume.



Figure

Different Forms of Energy :

The different forms of energy are as follows :

1. **Kinetic Energy** : A body possesses potential energy by virtue of its motion.
2. **Potential Energy** : A body possesses kinetic energy by virtue of its position in a field. e.g., a cricket ball above the ground, an electrically charged particle in an electric field.
3. **Chemical Energy** : A compound has chemical energy due to electronic interactions (chemical bonds).
4. **Nuclear Energy** : This is the energy due to the structure of the nucleus of an atom.
5. **Electrical Energy**
6. **Mechanical Energy**

First Law of Thermodynamics

Statement

1. The energy of a system in a definite state is fixed and is independent of the method of formation of the system or the method of attaining the state.
or
2. Energy may change from one to another, the total amount, of it in an isolated system always remains unchanged.
or
3. Although energy may be converted from one form to another, it cannot be created or destroyed.
or
4. Whenever a quantity of one kind of energy is produced, an exactly equivalent amount of another kind (or kinds) must be used up.
or
5. Mathematical statement :

i.e., $dE = q - w$ or $dE = q - PdV$ or

$$\Delta E = Q - W$$
$$\Delta E = Q - P\Delta V$$

Internal Energy (E)

Every substance is associated with a certain amount of energy known as **internal energy**. It is denoted by E. Internal energy of a substance is due to its molecular constitution and the motion of the molecules. The contributions of these factors are called internal potential energy and internal kinetic energy. So,
 Internal Energy = Internal potential energy + Internal kinetic energy

Internal energy of a system varies with temperature, volume, pressure and chemical composition. The absolute value of the internal energy of a system cannot be determined. But the change in the internal energy of the system, ΔE , accompanying changes in temperature, volume, pressure and composition can be measured experimentally. i.e.,

$$\Delta E = E_2 - E_1$$

Where E_1 and E_2 are the internal energies of a system in the initial and final states respectively. The internal energy change of a system depends upon the initial and the final state of the system and it is independent of path or method by which this change is caused i.e., it is a state function.

According to the first law of thermodynamics

$$\Delta E = Q - W$$

Where ΔE change in the internal energy of a system, Q the amount of heat absorbed by the system and W is the amount of work done by the system.

If W is the pressure-volume work done by a gas, then

$$\Delta E = Q - P\Delta V$$

Work done during isothermal changes for ideal gases

According to first law of thermodynamics,

$$\Delta E = Q - W$$

For an isothermal process $\Delta E = 0$

$$\therefore Q = w$$

i.e., For an isothermal process.

Heat absorbed = Work done

The magnitude of W or Q depends on the manner in which the process is carried out. i.e., whether it is carried out reversibly or irreversibly.

Work done during isothermal reversible expansion of an ideal gas.

$$\text{Expressions : } W = 2.303 n RT \log \frac{V_2}{V_1}$$

$$\text{or } W = 2.303 n RT \log \frac{P_1}{P_2}$$

For one mole of an ideal gas

$$W = 2.303 RT \log \frac{V_2}{V_1}$$

$$\text{or } W = 2.303 RT \log \frac{P_1}{P_2}$$

Derivation :

When the isothermal expansion is carried out reversibly the work done can be obtained as follows.

$$W = P_{OP} dV$$

For reversible expansion

$$P_{OP} = P$$

$$\therefore W = PdV$$

If n moles of ideal gas is taken P is $\frac{nRT}{V}$ Substituting the value of P ,

$$W = \frac{nRT}{V} dV$$

Integration of the equation gives the definite quantity of work done in a reversible isothermal expansion of an ideal gas.

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

$$W = 2.303 nRT \log \frac{V_2}{V_1}$$

Replacing V with $\frac{RT}{P}$ we get the following expression for the work done in a reversible isothermal expansion of an ideal gas

$$W = 2.303 n RT \log \frac{P_1}{P_2}$$

Work done during adiabatic changes for ideal gases.

Since in an adiabatic process no heat is absorbed or evolved $Q = 0$.

From First Law of thermodynamics

$$\begin{aligned} \Delta E &= Q - W \\ \text{as } Q &= 0 \\ \Delta E &= -W \\ \text{or } W &= -\Delta E \end{aligned} \quad (15)$$

$$\begin{aligned} \text{We know } \Delta E &= C_v \Delta T \\ \therefore W &= -\Delta E = -C_v \Delta T \end{aligned} \quad (16)$$

From equations (15), (16) it is clear that in an adiabatic change, ΔE , ΔH and W depend on the magnitude of ΔT . ΔT depends on the final temperature of the process. Final temperature depends on the manner in which the process is carried out, i.e., whether it is carried out reversibly or irreversibly. Thus the magnitudes of ΔE , ΔH and W vary with the nature of the process.

Work done during adiabatic reversible expansion of an ideal gas

$$\text{Expression } W = C_v(T_1 - T_2) \quad (17)$$

Derivation : From the first law

$$\begin{aligned} dE &= q - W \\ \therefore q &= dE + W \\ \text{We know } E &= f(T, V) \end{aligned} \quad (18)$$

$$\therefore dE = \left[\frac{\partial E}{\partial T} \right]_V dT + \left[\frac{\partial E}{\partial V} \right]_T dV \quad (19)$$

$$\text{and } W = PdV$$

substituting (18) and (19) in (17)

$$q = \left[\frac{\partial E}{\partial T} \right]_V dT + \left[\frac{\partial E}{\partial V} \right]_T dV + PdV \quad (20)$$

For an adiabatic change $q = 0$

and for an ideal gas $\left[\frac{\partial E}{\partial V} \right]_T = 0$

By definition

$$\left[\frac{\partial E}{\partial T} \right]_V = C_V$$

\therefore Substituting these values in (20) we get

$$0 = C_V dT + 0 + PdV$$

i.e., $PdV = -C_V dT$

Work done in an adiabatic expansion PdV

$$\begin{aligned} \text{i.e., } W &= \int PdV = - \int_{T_1}^{T_2} C_V dT \\ &= -C_V (T_2 - T_1) \\ &= C_V (T_1 - T_2) \end{aligned}$$

Differences between isothermal and adiabatic processes

Property	Isothermal process	Adiabatic process
Temperature	Constant	Changes
Heat change	$Q = W$, Varies with nature of process.	$Q = 0$, Varies with nature of process.
ΔE	$\Delta E = 0$. Does not vary with nature of process	$\Delta E = -W$ $= C_v \Delta T$ Varies with nature of process.
ΔH	$\Delta H = 0$. Does not vary with nature of process.	$\Delta H = C_p \Delta T$ Varies with nature of process.
Final Pressure	More	Less
Final Volume	More	Less
W	More	Less

$$E_2 - E_1 = \Delta E = nC_v (T_2 - T_1) - an^2 \left[\frac{1}{V_1} - \frac{1}{V_2} \right]$$

$$W = -\Delta E = -nC_v (T_2 - T_1) + an^2 \left[\frac{1}{V_1} - \frac{1}{V_2} \right]$$

The above expression gives the work done in adiabatic change for real gases.

Joule's Law :

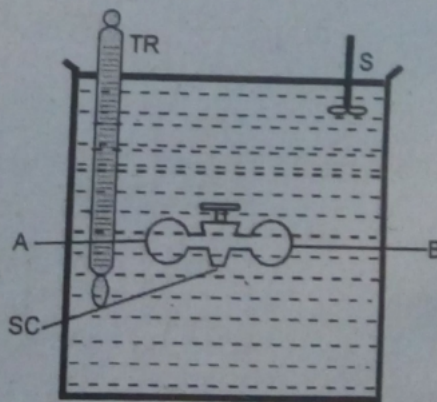
Law : *The energy of the gas is a function of temperature only. It is independent of volume.* The law may be represented mathematically as follows:

$$\left[\frac{\partial E}{\partial V} \right]_T = 0$$

Measurement of $(\partial E / \partial V)_T$: Joule's Experiment :

Determination of $(\partial E / \partial V)_T$ with readily measurable quantities is not easy. For gases it can be measured, in principle atleast, by an experiment devised by Joule. The apparatus used for the purpose is shown in figure.

Two containers A and B are connected through a stop cock, SC. Initially, A is filled with a gas at a pressure P while B is evacuated. The apparatus is immersed in a large water tub and is allowed to equilibrate with water at the temperature T, which is read on the thermometer TR. The water is stirred vigorously to hasten the attainment of thermal equilibrium. After the required equilibrium is attained, the stop cock is opened and the gas expands to fill the containers A and B uniformly. The system



is allowed to come to thermal equilibrium with the water in the tube. The temperature of the water is read again. Joule observed no temperature difference in water before and after opening the stop cock.

Interpretation of the experiment : The gas in A expands against zero opposing pressure. So no work is produced. i.e., $W = 0$. This is called free expansion of the gas. We know according to first law.

$$dE = q - W$$

$$W = 0$$

$$dE = q$$

Since the temperature of the surrounding (the water) is unchanged. $q = 0$. Hence $dE = 0$.

We know

$$dE = \left[\frac{\partial E}{\partial T} \right]_V dT + \left[\frac{\partial E}{\partial V} \right]_T dV \quad (34)$$

Since the system and water are in thermal equilibrium, the temperature of the system is also unchanged. So (34) becomes.

$$dE = \left[\frac{\partial E}{\partial V} \right]_T dV = 0$$

since $dV \neq 0$, it follows that

$$\left[\frac{\partial E}{\partial V} \right]_T = 0$$

This means that the energy is independent of the volume. This means that the energy of the gas is a function of temperature only. This is called the Joule's law.

Limitation : Joule - Thomson experiment showed that Joule's law is not precisely correct for real gases. In Joules apparatus the large heat capacity of the tub and the small heat capacity of the gas reduced the magnitude of the effect below the limits of observation. For real gases, $(\partial E / \partial V)_T$ is a very small quantity usually positive. The ideal gas obeys Joule's law exactly.

Joule Thomson Effect

Definition :

When a gas is made to expand adiabatically from a region of high pressure to a region of low pressure, the temperature of gas changes.

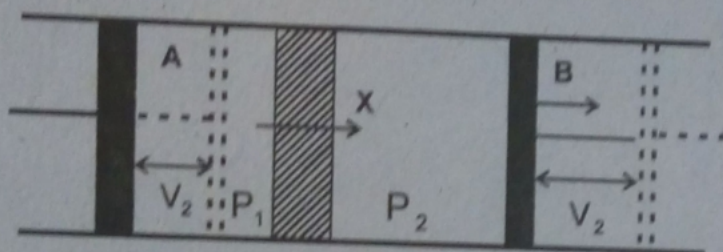
This phenomenon is called Joule Thomson effect.

Explanation :

If a stream of gas at high pressure is allowed to expand by passing it through a porous plug into vacuum or a region of low pressure, under adiabatic conditions, the temperature of the gas changes appreciably. All the gases except hydrogen and helium were cooled when they were subjected to Joule-Thomson effect. Helium and hydrogen were heated under similar circumstances.

Joule-Thomson's experiment :

The experiment devised by Joule and Thomson to derive a relation between the lowering of temperature and the fall of pressure of a gas due to expansion is given systematically above.



A non-conducting tube is fitted with a porous plug X in the middle. Two pistons A and B are fitted on either side of X. The tube is insulated to ensure adiabatic conditions. The experimental gas is enclosed between A and X. Let its pressure be P_1 . Now the gas is forced slowly to the other side. Let the volume decrease be V_1 . The gas passes through the plug and expands by pushing the piston B to the right. Let the volume of expansion be V_2 . Let the pressure against it expanded be P_2 . Let P_2 be less than P_1 .

$$\text{Now work done on the gas at A} = -P_1 V_1$$

$$\text{Work done by the gas at B} = P_2 V_2$$

$$\text{X Net work done by the gas} = P_2 V_2 - P_1 V_1$$

This expansion of the gas has taken place adiabatically. i.e., no heat has entered the system, nor has left the system. Therefore the gas has performed work at the expense of its internal energy. i.e., there will be a fall in E from E_1 to E_2 .

$$P_2 V_2 - P_1 V_1 = E_1 - E_2$$

or $E_2 + P_2 V_2 = E_1 + P_1 V_1$

we know $E + PV = H$

i.e., $H_2 = H_1$

or $\Delta H = 0$

Thus Joule-Thomson expansion is an isenthalpic process i.e., adiabatic expansion of a real gas occurs at constant enthalpy.

Application :

Joule Thomson effect is useful in the *liquefaction of gases*. A gas gets liquefied when it is cooled below its boiling point or it gets liquefied when it is cooled below its critical temperature and then compressed.

In either case, the gas has to be cooled. For this purpose Joule-Thomson effect is used. The gas which is to be liquefied, is allowed to expand through a nozzle from a high pressure region to a low pressure region. It gets cooled. This principle is used in Linde's process and Claude's process of liquefaction of air.

Limitation :

Joule-Thomson effect can be applied only if the initial temperature of the gas is below its inversion temperature.

Inversion Temperature

Definition :

The temperature below which Joule - Thomson effect is a cooling effect is called *inversion temperature*.

The temperature below which a gas gets cooled during an adiabatic expansion is known as its inversion temperature.

Explanation with example :

When a gas is subjected to Joule-Thomson effect it gets cooled appreciably. But when hydrogen and helium were subjected to Joule-Thomson effect they were heated up instead of getting cooled. But at very low temperature these gases also get cooled. For example hydrogen below -80°C and helium below -240°C behaved like this. Thus we find that for each gas, there is a particular temperature below which, the Joule-Thomson effect is always a cooling effect. This temperature is called the inversion temperature of that gas.

Significance of inversion temperature :

1. It gives information about the temperature below which a gas can be liquefied by applying pressure.
2. The gases like He and H_2 warm up when subjected to Joule Thomson effect. This anomalous behaviour was explained by the inversion temperature. This is because the inversion temperature of He is 33K and that of H_2 is 193K and hence they can show positive Joule Thomson effect only when they are cooled below these corresponding temperatures.
3. The inversion temperature $T_i = 2a/Rb$

By knowing the value of T_i , the value of Vander Waals constants a and b of a gas can be calculated using the above relation.

Relationship Between ΔH and ΔE
 (Relation between heat of reaction at constant pressure and that at constant volume)

Relationship :

$$\Delta H = \Delta E + \Delta n RT$$

$$\text{or } Q_p = Q_v + \Delta n RT$$

Derivation : We know $\Delta H = \Delta E + P\Delta V$ (6)

For n moles of an ideal gas $PV = nRT$ or $\frac{PV}{n} = RT$ (7)

Let n_1 and n_2 represent the number of moles of the gaseous reactants and gaseous products respectively. Then the change in the number of mole = $n_2 - n_1 = \Delta n$.

The corresponding change in volume $\Delta V = \left[\frac{V}{n} \right] \Delta n$

Multiplying both sides by P ; $P\Delta V = \left[\frac{PV}{n} \right] \Delta n$ (8)

Substituting (7) in (8) we have $P\Delta V = RT\Delta n$ (9)

Substituting (9) in (4) we have $\Delta H = \Delta E + RT\Delta n$ (10)

We have already seen that $Q_v = \Delta E$ (1)

$$Q_p = \Delta H \quad (5)$$

Applying (1) and (5) in (10) we have $Q_p = Q_v + RT\Delta n$ (11)

Equations (10) and (11) give the relation between heat of reaction at constant pressure and that at constant volume.

These are for finite changes. For small changes

$$dH = dE + RTdn \quad (12)$$

and $q_p = q_v + RTdn$ (13)

Temperature dependence of ΔH : Kirchoff's Equation

Thermodynamic derivation : Heat of reaction at constant pressure can be expressed in terms of molar enthalpies of reactants and products.

$$\Delta H_p = H_p - H_R$$

Differentiating this equation with respect to temperature

$$\frac{d\Delta H_p}{dT} = \frac{dH_p}{dT} - \frac{dH_R}{dT} \quad (1)$$

We know that $\frac{dH_P}{dT} = (C_P)_P$

$$\frac{dH_R}{dT} = (C_P)_R$$

Substituting these values in (16)

$$\frac{d\Delta H}{dT} = (C_P)_P - (C_P)_R$$

$$\frac{d\Delta H}{dT} = \Delta C_P \quad (2)$$

(2) is the mathematical expression of Kirchoff's equation. Rearranging Kirchoff's equation

$$d\Delta H = \Delta C_P dT$$

Integrating between two temperatures,

$$\int_{H_1}^{H_2} d\Delta H = \int_{T_1}^{T_2} \Delta C_P dT$$

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_P dT$$

For a small temperature difference, ΔC_P may be taken as a constant.

$$\therefore \Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1)$$

$$\Delta H_2 = \Delta H_1 + \Delta C_P (T_2 - T_1) \quad (3)$$

(3) is the intergrated form of Kirchoff's equation. This is another mathematical expression of Kirchoff's equation.

Statement : The rate of change of heat of reaction with temperature at constant pressure is equal to the difference between the molar heat capacities of reactants and products.

Significance : Heat of reaction changes with the temperature at which the reaction is carried out. Kirchoff's equation gives the variation of heat of reaction with temperature. Equation (3) is used to calculate heat of reaction at a certain temperature from its value at another temperature. For this calculation ΔC_P should be known. It is the difference between the total molar heat capacity of products and that of reactants. As stated earlier, if temperature difference is very small this procedure is adopted. Otherwise C_P values are expressed as a function of T and then only the Kirchoff's equation is integrated.