→ Thermodynamics :→

→ Introduction :→

- The word 'thermodynamics' means flow of heat. The thermodynamics deals with energy change associated with all physical and chemical change.
- Thermodynamics implies a field concerned with mechanical action produced by heat. Actually, it deals with energy in its various forms, which include thermal, Chemical, electrical and mechanical, with the restrictions on the transformation of one type of energy into the other types, and with the relation of energy changes to physical and chemical changes.
- Thermodynamic is based on laws of thermodynamics. These laws are evolved from human observation or experience made on macroscopic world. They are more empirical than theoritical. There is no formal proof for these laws.
- The predictions based on the laws of thermodynamics have been verified in most cases. However, cases are known where these laws show deviations. But the reasons for these deviations are well known.
- The science dealing with the macroscopic properties of matter is known as classical thermodynamics. Here the entire formulation has been developed without the knowledge that the matter is made up of atoms and molecules.
- Stastistical thermodynamics or stastistical mechanics provides a link between quantum mechanics (or wave mechanics) and classical mechanics. quantum mechanic deals with the study of matter at microscopic level. Each microscopic system can be described by a wave function.

- Chemical thermodynamics or thermochemistry is the branch of thermodynamics which deals with the study of processes in which only chemical energy is involved.

→ Importance of thermodynamics :→

- Thermodynamics is a fundamental subject of great importance in physical chemistry. Most of the important generalisations of physical chemistry, including van't Hoff law of dilute solutions, Raoult's law of vapour pressure lowering, distribution law, law of chemical equlibrium the phase rule and the laws of thermochemistry, can be deduced from the law of thermodynamics.
- Thermodynamics also helps to predict feasibility or spontaneity of a process, including a chemical reaction, under a given set of conditions.

→ Limitations of thermodynamics :→

- The law of thermodynamics apply to matter in bulk and not to individual atoms or molecules.
- Thermodynamics can only predict feasibility of a chemical reaction under a given set of conditions; it does not tell about rate of a chemical reaction.
- Thermodynamics does not give any sepecic, direct information about the nature or structure of matter.

→ System and surroundings:→

→ System:→

- A system may be defined as any specified portion of matter under study which is separated from the rest of the universe with a boundary surface.

OR

- A thermodynamical system is a part of the universe which is arbitrarily set off from the rest of the universe by definite boundaries for the purpose of experimental or theoritical studies.
- A system may consist of one or more substances.

→ Surroundings:→

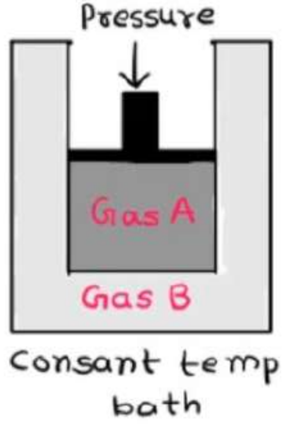
- The remainder of the universe other than system is called surroundings.

OR

- The rest of the universe which might be in a position to exchange energy and matter with the system is called the surroundings.
- The surroundings are restricted to a region in the immediate vicinity of the system under study.

→ Boundary:→

- The space separating the system from its surroundings is termed as boundary.



→ Types of boundaries or walls:→

1. A rigid wall:→ This is a wall whose position and shape are fixed.
2. An impermeable wall:→ This is the wall which does not permit the passage of matter.

3. A permeable wall :→ It is that type of wall which permits the passage of matter and consequently, also of energy.

4. An adiabatic wall :→ It is that type of wall which when held rigid will not permit the passage of matter or energy provided no external force fields are present.
example :- Thermos bottles.

5. A diathermal or diathermic wall :→ This is that type of wall which when held rigid will not permit the passage of matter but allow the passage of energy in the absence of any external force field. It mean that a diathermal wall is impermeable but not adiabatic.
example:- Aluminium can.

→ Types of system:→

1. Real system:→

- In experimental work, the system is called real.

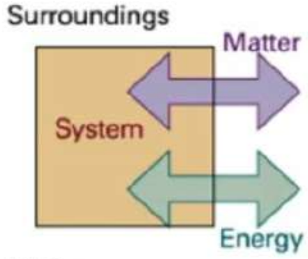
2. Ideal system:→

- In pencil and paper work, the system treated is called ideal. A ideal system is always considered to simplify the thermodynamic problems.

3. open system:→

- An open system is one which can exchange both energy and matter with surroundings.

Example:- A beaker containing water (the system) in a thermostated water bath (the surroundings) is an open system.

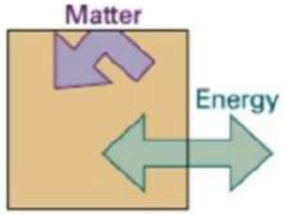


(a) Open

4. closed system:→

- A system is said to be closed when it permits the passage of energy, but not mass, across the boundary.

Example:- A liquid in equilibrium with its vapours in a sealed tube is an example of a closed system.

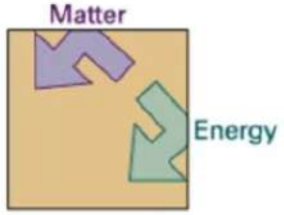


(b) Closed

5. Isolated system:→

- A system is said to be isolated when it can neither exchange energy nor matter with its surroundings.

Example:- If the sealed tube containing liquid and vapour was thermally insulated so that heat energy could not enter or leave the liquid-vapour, system would be an isolated system.



(c) Isolated

6. Homogeneous system:→

- A system is said to be homogeneous when it is completely uniform throughout or a homogeneous system consist of one phase.

  Example:- A pure solid, a liquid or a solution, or a mixture of gases.

7. Heterogeneous system:→

- A system is said to be heterogeneous when it is not uniform throughout. In other words heterogeneous system consist of two or more phases.

  Example:- system consisting of two or more immiscible liquids, or a solid in contact with a liquid in which it does not dissolve, is a heterogeneous system.
  - A liquid in contact with its vapour is also a heterogeneous system because it consists of two phases.

8. Macroscopic system:→

- A macroscopic system is one in which there are a large number of particles (may be molecules, atoms, ions, etc.)

→ Thermodynamic equilibrium:→

- A system in which the macroscopic properties* do not undergo any change with time is said to be in thermodynamic equilibrium.

  suppose a system is heterogeneous, i.e. it consists of more than one phase. Then, if it is in equilibrium, the macroscopic properties in the various phases remain unaltered with time.

- Thermodynamic equilibrium implies the existance of three kinds of equilibria in the system.

(i) Thermal equilibrium:→

- A system is said to be in thermal equilibrium if there is no flow of heat from one portion of the system to another. This is possible if the temperature remains the same throughout in all parts of the system.

(2) Mechanical equilibrium:→

- A system is said to be in mechanical equilibrium if no mechanical work is done by one part of the system on another part of the system. This is possible if the pressure remains the same throughout in all parts of the system.

(3) Chemical equilibrium:→

- A system is said to be in chemical equilibrium if the composition of the various phases in the system remain the same throughout.

* Macroscopic properties:→

- The properties associated with a macroscopic system (i.e. cosisting of large number of particles) are called macroscopic properties. Example:- pressure, volume, temperature, density, composition, viscosity, surface tension, refractive index etc.

→ State and state variables:→

1. State of a system:→

- When macroscopic properties of a system have definite values, the system is said to be in definite state.
- Whenever there is a change in any one of the macroscopic properties, the system is said to change in a different state. Thus, the state of a system is fixed by its macroscopic properties.

2. State variables:→

- Since the state of a system changes with change in any of the macroscopic properties, these properties are called state variables.
- When a system changes from one state (called initial state) to another state (called final state), there is always a change in one or more of the macroscopic properties.
- Pressure, temperature, volume, mass and composition are the most important state variables.
- In the case of single gas, composition is not one of the variable because it remain always 100 %.. Further, if the gas is ideal and one mole of the gas is under examination, it obeys the equation $PV = RT$, where R is gas constant. Evidently, if only two of the three variables (P, V and T) are known, the third can be easily be calculated. The two variables, generally specified are temperature and pressure. The are called independent variables. The third variable, generally volume, is said to be a dependent variable, as its value depends upon the values of P and T. Thus, the thermodynamic state of a system consisting of a single gaseous substance may be completely defined by specifying any two of the three variables, viz., temperature, pressure and volume.

→ Intensive and Extensive properties:→

1. Intensive properties:→

- An intensive property of a system is that which is independent of the amount of the substance present in the system.

  Example:- temperature, pressure, density, viscosity, refractive index, surface tension, specific heat, boiling point, freezing point, Free energy per mole, molar volume.

2. Extensive properties:→

- An extensive property of a system is that which depends upon the amount of the substance or substances present in the system.

  Example:- Volume, mass, free energy, number of moles, entropy, enthalpy, Heat capacity.

- From the above definitions it follows that, extensive properties of a single (pure) substance will depend upon the number of moles(n) of the substance present and also on any two of the three variables P, V and T. If n is kept constant, the extensive properties of the system will depend only on the two independent variables.
- If a system is mixture of two or more gases, the extensive properties will vary with the number of moles, n_A, n_B, n_C etc. of the constituents A, B, C etc, present in the system and also with the two independent variables. The intensive properties in such cases will depend upon the concentration of various species, besides the two independent variables.
- Any extensive property if expressed as per mole or per gram becomes an intensive property.

$$\frac{\text{mass}}{\text{Volume}} = \text{density}$$

→ Thermodynamic process:→

- Thermodynamics deals with changes that occur in the properties of system when the system goes from one equilibrium state to other. such a change in the values of the properties of the system is called a process.
- Alternatively, a thermodynamic process is the path or operation by which a system changes from one state to another.
- A system can usually change from one equilibrium state to another through a ways.

→ Types of thermodynamic processes:→

1. Adiabatic process:→

- when a process is carried out under such conditions that no exchange of heat takes place between the system and surroundings, the process is called adiabatic.
- If the process is exothermic, the heat evolved will remain in the system and, therefore, the temperature of the system rises. If on other hand, the process is endothermic, heat absorbed is supplied by the system itself and hence the temperature of the system falls.

2. Isothermal process:→

- The process which occurs at constant temperature is called a isothermal process.
- In this process, the system exchanges heat with the surroundings.

3. Isobaric process:→

- If the pressure of the system remains constant during each step of change in the state of a system, this process is said to be an isobaric process.
- The volume of system changes during an isobaric process.

4. Isochoric process:→

- A process is defined to be isochoric if the volume of the system remains constant during each step of the process. The pressure of the system changes during an isochoric process.

5. Cyclic process:→

- When a system undergoes a series of state changes in such a way that the final state becomes identical with the initial state, it is said to have passed through a cyclic process.
- If a series of changes are conducted at a constant temperature, the cycle is known as an isothermal cycle. If the changes are carried out reversibly, then the cycle is known as reversible cycle.
- As the internal energy of a system depends only upon its state, it means that in a cyclic process, the net change of internal energy is zero. i.e.

$$\Delta E = 0$$

→ Exact and Inexact differentials :→

\- Let $z = f(x, y)$ — ①

The total differential of z, is given by

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \quad — ②$$

or $dz = M\,dx + N\,dy$ — ③

where $M = \left(\frac{\partial z}{\partial x}\right)_y$ and $N = \left(\frac{\partial z}{\partial y}\right)_x$

Taking mixed second derivative of eq. ③ , we have

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right) = \frac{\partial^2 z}{\partial y \partial x} \quad — ④$$

and $$\left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right) = \frac{\partial^2 z}{\partial x \partial y} \quad — ⑤$$

From equations ④ and ⑤

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \; — ⑥ \quad \text{or} \quad \frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y} \; — ⑦$$

Eq. ⑥ is called the Euler reciprocity (reciprocal) relation. It corresponds to an exact differential.

- If any function follows Euler reciprocal relation then differential of function is an exact differential and if does not follows then differential of function is an inexact differential.
- Exact differential can be integrated between the appropriate limits. This cannot be done in the case of inexact differentials. Thus

$$\int_{z_1}^{z_2} dz = z_2 - z_1 \qquad\qquad \int_{z_1}^{z_2} dz \neq z_2 - z_1$$

Exact differential　　　　Inexact differential

→ State and path functions and their differentials:→

① State function:→

- The state function is a property of a thermodynamic system which has a definite value for a particular state of the system. It is independent of the manner which the state is reached.
- The change in the value of a state function depends only on the initial and final state and not on the path of the process carried out in going from intial state to final state.

  Example:- Pressure, temperature, volume and energy.
- change in volume is given by

$$\Delta V = V_B - V_A$$

where V_A = Volume of initial state
V_B = Volume of final state

- Differential of state function is an exact or perfect differential. Exact differentials can be integrated between the appropriate limits.
- state functions follow Euler reciprocal (reciprocity) relation.

$$\int_{V_A}^{V_B} dv = V_B - V_A = \Delta V$$

(2) Path function :→

- The path function is a property of thermodynamic system which does not depend on initial and final state of the system but depends on the path by which the change is brought about.

  Example :- heat and work.
- Differentials of path functions are inexact differentials. Inexact differential cannot be integrated between the appropriate limits.
- Path functions do not follows Euler reciprocal (reciprocity) relation.

$$\int_{q_A}^{q_B} dq \neq q_B - q_A \qquad \int_{W_A}^{W_B} dW \neq W_B - W_A$$

→ Examples:→

ⓐ For an ideal gas $PV=RT$, prove that dv is an exact differential.

We know that $v = f(T,P)$ — ①

$$dv = \left(\frac{\partial v}{\partial T}\right)_P dT + \left(\frac{\partial v}{\partial P}\right)_T dP \quad -②$$

For an ideal gas

$$PV = RT$$

or $$V = \frac{RT}{P} \quad —③$$

Hence $$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P} \text{ and } \left(\frac{\partial v}{\partial P}\right)_T = -\frac{RT}{P^2}$$

Substituting these values in equation ②

$$dv = \left(\frac{R}{P}\right)dT - \left(\frac{RT}{P^2}\right)dP \quad —④$$

Taking mixed second derivative of eq. ④

$$\left[\frac{\partial(R/P)}{\partial P}\right]_T = -\frac{R}{P^2} \quad —⑤$$

$$-\left[\frac{\partial(RT/P^2)}{\partial T}\right]_P = -\frac{R}{P^2} \quad —⑥$$

— Eq. ⑤ and ⑥ follows Euler reciprocity relation hence dv is an exact differential.

ⓑ For an ideal gas $PV=RT$, prove that dw is an inexact differential.

We know that $V = f(T,P)$ — ①

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \quad -②$$

For an ideal gas

$$PV = RT$$

or $$V = \frac{RT}{P} \quad —③$$

Hence

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \quad \text{and} \quad \left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2}$$

Substituting these values in equation ②

$$dV = \left(\frac{R}{P}\right)dT - \left(\frac{RT}{P^2}\right)dP \quad —④$$

We know that

$$dw = PdV \quad —⑤$$

from eq. ④ and ⑤

$$dw = P\left(\frac{R}{P}\right)dT - P\left(\frac{RT}{P^2}\right)dP$$

or $$dw = RdT - \left(\frac{RT}{P}\right)dP$$

or $$dw = RdT - VdP \quad —⑥ \quad \left(\because V = \frac{RT}{P}\right)$$

Taking mixed second derivative of eq. ⑥

$$\left(\frac{\partial R}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad — ⑦$$

since R is gas constant, hence

$$\left(\frac{\partial R}{\partial P}\right)_T = 0$$

Accordingly, from equation ⑦, $\left(\frac{\partial V}{\partial T}\right)_P = 0$

But this is not true because there is always change in volume with temperature at constant pressure. This leads to the conclusion that dw is an inexact differential.

→ Concept of heat and work:→

- Whenever a system changes from one state to another, there will be change in energy. The change in energy may appear in the form of heat, work etc.
- The unit of energy is joule. It is defined as the work done when a resistance of 1 newton is moved through a distance of 1 metere. Thus, J = N.m
- The british physicist P. Joule (1818-1889) showed in 1850 that there is a definite relationship between mechanical work done W and heat produced, i.e.

$$W \propto H$$

or

$$W = JH$$

where J = Joule mechanical equivalent of heat. Its numerical value is taken as 4.184 joules. Thus, the expenditure of 4.184 joules of mechanical energy, 1 calorie of heat is produced. Thus, 1 calorie = 4.184 joules. Heat is now invariably expressed in joules.

- Energy expresses itself not only in the form of mechanical work (as in Joule's experiment) but also as heat energy, electrical energy and chemical energy. Whatever be the form, energy is composed of two factors: (i) an intensity factor and (ii) a capacity factor. The product of these two factors gives the energy.
- Heat energy is product of temperature (intensity factor) and heat capacity (capacity factor).
- Electrical energy is product of potential difference (intensity factor) and quantity of electricity (capacity factor)

- When a body of mass m kg is moved through a height of h m, the work done against gravity is obtained by multiplying the intensity factor (mg newtons) with the capacity factor (h meter). The work performed is mgh joules.

→ First law of thermodynamics:→

- The is also known as law of conservation of energy.
- According to this law, " energy can neither be created nor destroyed although it can be transformed from one form to another. Whenever energy in one form disappears, an equal amount of energy in some other form must appear.

→ Various statements of first law:→

1. First statement:→

- Joule stated that, " There is an exact equivalence between the amount of work overcome and the heat generated."
- In other words of Maxwell, Joule's law may be stated that, " when work is transformed into heat or heat into work, the quantity of work is mechanically equivalent to the quantity of heat."

2. Second statement:→

- " Energy of an isolated system must remain constant, although it may be transformed from one form to another.

3. Third statement:→

- " Energy in one form, if it disappears, will make its appearance in an exactly equivalent quantity in another form."

4. Fourth statement:→

- " It is never possible to construct a perpetual motion machine that could produce work without consuming any energy."

→ Basis of first law:→

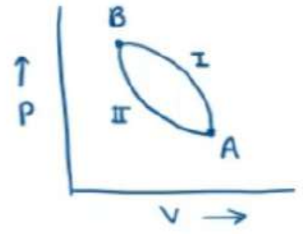
- A thermal machine which may operate without any expenditure of fuel and may thus create energy out of nowhere is generally called a perpetual motion machine. The first law rules out such machines. The fact that no exception to the first law has been found yet and no one succeeded in building such a machine forms an experimental basis for the first law.

→ Mathematical form of first law:→

Let E_A be the energy of system in its state A and E_B is the energy in its state B. suppose the system while undergoing change from state A to B absorbs heat q from the surroundings and also performs some work (mechanical or electrical), equal to w. The absorption of heat by the system tends to raise the energy of the system. The performance of work by the system, on the other hand, tends to lower the energy of the system because performance of work requires expenditure of energy. Hence, the change of internal energy ΔE, accompanying the above process will be given by -

$$\Delta E = E_B - E_A = q - w \quad ①$$

In general, in a given process, the quantity of heat transfered from the surroundings to the system is q and the work done in the process is w, then the change in internal energy is given by



$$\Delta E = q + w \quad ②$$

Eq. ② is the mathematical statement of the first law of thermodynamics.

- If work is done by the surroundings on the system (during compression of gas), w is taken positive so that $\Delta E = q + w$ (Eq. 2.). If, however, work is done by the system on the surroundings (during expansion of gas), w is taken negative so that $\Delta E = q - w$ (Eq. 1)

→ Internal energy:→

- Internal energy is represented by E or U.
- Every substance is associated with a definite amount of energy which depends upon its chemical nature as well as upon its temperature, pressure and volume. This energy is known as internal energy.
- The exact magnitude of this energy is not known because the chemical nature includes such indeterminat factor as the translational, rotational and vibrational movements of the molecules, the manner in which the molecules are put together, the nature of the individual atoms, the arrangement and number of electrons, the energy possessed by the nucleus etc. But, one thing is certain that the internal energy of a substance or system is a definite quantity and it is a function only of the state of the system at the given moment, irrespective of manner in which that state has been brought about.
- It is true that the actual value of internal energy cannot be determined. It is, therefore, essential to consider changes in internal energy.
- Suppose a system undergoes a thermodynamic change from state A to B. Then change in internal energy is given by

$$\Delta E = E_B - E_A$$

E_A = Internal energy of initial state A
E_B = Internal energy of final state B

→ Enthalpy :→

- Suppose the change of state of a system is brought about at constant pressure. In that case, there will be change of volume. Let the volume increase from V_A to V_B, at constant pressure P. Then, the work done (w) by the system will be given by

$$W = -P\Delta V$$

or $W = -P(V_B - V_A)$ — ①

From the first law of thermodynamics

$\Delta E = q + W$ — ②

Substituting value of w in eq. ②

$$\Delta E = q - P(V_B - V_A)$$

or $E_B - E_A = q - P(V_B - V_A)$

or $E_B - E_A + P(V_B - V_A) = q$

or $E_B - E_A + PV_B - PV_A = q$

or $(E_B + PV_B) - (E_A + PV_A) = q$ — ③

The quantity E + PV is known as the enthalpy of the system and is denoted by H. It represents the total energy stored in the system. Thus,

$H = E + PV$ — ④

Since E is a definite quantity and P and V are also definite quantities which define the state of a system, hence H is also a definite quantity. From eq. ③ and ④

$H_B - H_A = \Delta H = q$ — ⑤

- Since H_A and H_B are definite quantities, it is evident that ΔH, like ΔE, is a definite quantity depending only on the initial and final state of a system. Obviously, ΔH represents increase in the enthalpy of a system when it changes from state A to state B.
- Since ΔH is a definite quantity, the heat absorbed (q) under the condition of the experiment i.e. at constant pressure, is also a definite quantity.
- Further, it follows from eq. ③

$$(E_B - E_A) + P(V_B - V_A) = q \quad — ⑥$$

Substituting the above value of q in eq. ⑤. we have

$$\Delta H = (E_B - E_A) + P(V_B - V_A)$$

$$\text{or} \quad \Delta H = \Delta E + P\Delta V \quad — ⑦$$

where ΔV = the increase in volume undergone by the system.

→ Enthalpy of vaporisation:→ The change in enthalpy (ΔH) when a liquid changes into vapour or when vapours change into liquid state, is known as enthalpy of vaporisation. This has +ve sign in the formar case and -ve sign in the latter case.

→ Enthalpy of fusion:→ The change in enthalpy (ΔH) when a solid changes into liquid or liquid change into solid state, is known as enthalpy of fusion. This has +ve sign in the formar case and -ve sign in the latter case.

→ Heat capacity :→

- Heat capacity of a system, between any two temperatures, is defined as the quantity of heat (q) required to raise the temperature of the system from the lower to the higher temperature divided by the temperature difference.
- If the mass of the system is one gram, the heat capacity is called the specific heat of the system. If, however, the mass of the system is one mole, the the heat capacity is termed as molar heat capacity. It usually denoted by C. Thus, the molar heat capacity of a system between temperatures T_1 and T_2 will be expressed as

$$C = \frac{q}{(T_2 - T_1)} = \frac{q}{\Delta T} \quad — ①$$

- Since the heat capacity varies with temperature, hence the true molar heat capacity is defined by the differential equation.

$$C = \frac{dq}{dT} \quad — ②$$

→ Heat capacity at constant volume :→

- From the first law of thermodynamics

$$q = \Delta E - W \quad — ③$$

At constant volume, no external work is done by the system or on the system (i.e. $w = 0$)

$$q = \Delta E$$

$$C_V = \left(\frac{q}{\Delta T}\right)_V \quad \text{OR} \quad C_V = \left(\frac{\Delta E}{\Delta T}\right)_V \quad \text{OR} \quad C_V = \left(\frac{\Delta E}{T_2 - T_1}\right)_V$$

→ Heat capacity at constant pressure:→

- At constant pressure, however, there is change of volume and some work is done. suppose, the volume increases by ΔV and the work done is w. Then, from first law of thermodynamics.

$$q = \Delta E - W \quad \text{and} \quad C_p = \left(\frac{q}{\Delta T}\right)_p$$

- Increase in volume means that the work done by the system on the surroundings so that w, by convention, is negative. Hence

$$W = -P\Delta V$$

$$q = \Delta E - (-P\Delta V)$$

$$q = \Delta E + P\Delta V$$

$$C_p = \left(\frac{\Delta E + P\Delta V}{\Delta T}\right)_p \quad \text{or} \quad C_p = \left(\frac{\Delta H}{\Delta T}\right)_p \quad \text{or} \quad C_p = \left(\frac{\Delta H}{T_2 - T_1}\right)_p$$

- Thus, while the molar heat capacity of a gaseous system of mass one mole at constant volume is defined as the increase in internal energy of the system per degree rise of temperature, that at constant pressure is defined as the increase in enthalpy of system per degree rise of temperature.

→ Relation between C_p and C_v in gaseous systems:→

- When a gas is heated at constant volume, no external work is done by the gas. In other words, all the heat supplied to the gas is used in increasing its internal energy. Thus. temperature of the one mole of gas is raised through 1°c (say increasing from T to T+1), the increase in its internal energy itself gives the molar heat capacity at constant volume.
- When a gas is heated at constant pressure, there will be increase in its volume, that is, the gas will expand and do some external work. Therefore, some extra heat (in addition to the heat required by it to increase the internal energy of its molecules) must be supplied to the gas to enable it to perform this external work.

Hence, the molar heat capacity of a gas at constant pressure must be greater than that at constant volume, i.e. $C_p > C_v$.

Thus $C_p - C_v$ = work done by one mole of the gas in expansion when heated through 1°c at constant pressure.

- As we know, the work done by the gas in expansion at constant pressure is numerically given by $w = P\Delta V$

For one mole of gas ideal equation is

$$PV = RT \quad — ①$$

When the temperature is raised by 1°c from T to T+1 so that the volume is $V+\Delta V$, then

$$P(V+\Delta V) = R(T+1)$$

$$\text{or} \quad PV + P\Delta V = RT + R \quad —②$$

Substracting eq. ① from eq. ②, we have

$$P\Delta V = R \quad — ③$$

- Thus, the work done by one mole of an ideal gas in expansion at constant pressure when heated through 1°C is equal to R. Hence

$$C_p - C_v = R \text{ — } ④$$

- Thus, the difference between the molar heat capacity of a gas at constant pressure (C_p) and at constant volume (C_p) is equal to the gas constant R.

→ Joule's law or Joule-Thomson effect :→

- If the stream of a gas at high pressure is allowed to expand by passing through a porous plug into vacuum or a region of low pressure, under adiabatic conditions, it gets cooled appreciably.
- Hydrogen and helium are exceptions as they get warmed up under similar circumstances. But, at very low temperatures, these gases also show the usual behaviour.
- The temperature below which a gas becomes cooler on expansion is known as the inversion temperature.

Inversion temp. for hydrogen is −48°C
and Inversion temp. for Helium is −242°C

- The phenomenon of change of temperature produced when a gas is made to expand adiabatically from a region of high pressure to a region of extremely low pressure is known as the Joule-Thomson effect.
- The Joule-Thomson experiment was performed in 1850s by the two brilliant British physicists J.P. Joule (1818-1889) and William Thomson (1824-1907), later remembered as Lord Kelvin.
- The cooling effect is due to decrease in the kinetic energy of the gaseous molecules since a part of this energy is used up in overcoming the van der Waals force of attraction existing between molecules during expansion.
- The Joule-Thomson effect is very small when a gas approaches ideal behaviour. Therefore, the Joule-Thomson effect is zero for an ideal gas. because, in an ideal gas, the van der Waals forces are negligible and there is no expenditure of energy in overcoming these forces during expansion.
- When an ideal gas expands in vaccum, there is neither absorption nor evolution of heat, i.e., $q=0$.

- Further, when an ideal gas expands in vacuum, it does not work because the pressure against which it expands is zero. In other words, $w = 0$.
- It follows from the general equation of the first law that $\Delta E = 0$.

Thus, when an ideal gas undergoes expansion under adiabatic conditions in vacuum, no change takes place in its internal energy.

- In other words, the internal energy of a given quantity of an ideal gas at a constant temperature is independent of its volume, i.e.

$$\left(\frac{\partial E}{\partial V}\right)_T = 0$$

- An ideal gas may, therefore, be defined thermodynamically by the following two equations

(i) $PV =$ constant, at constant temperature.

(ii) $\left(\frac{\partial E}{\partial V}\right)_T = 0$

The quantity $\left(\frac{\partial E}{\partial V}\right)_T = 0$ is called the internal pressure. Thus, internal pressure of an ideal gas is zero.

→ Joule - Thomson coefficient (μ_{JT}):→

- The experimental technique used to explain Joule-Thomson effect is illustrated schematically in Fig. 1

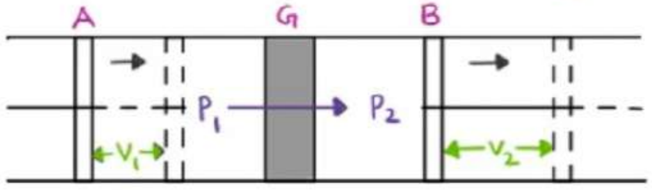


Fig. 1 - Porous plug experiment

- A tube made of a non-conducting material is fitted with a porous plug G in the middle and two pistons A and B on the sides, as shown. The tube is thoroughly insulated to ensure adiabatic conditions.
- A volume V_1 of the gas enclosed between the piston A and the porous plug G at a pressure P_1. The volume V_1 of the gas forced through the porous plug by moving the piston A inwards and is allowed to expand to a volume V_2 at a lower pressure P_2 by moving the piston B outward, as shown.

$\therefore$ Work done on the system at piston A = $+P_1V_1$

work done by the system at piston B = $-P_2V_2$

$\therefore$ Net work done by the system = $-P_2V_2 + P_1V_1$

- Since the expansion of the gas has taken adiabatically, the system neither absorbs or evolve heat to the surroundings. The system, therefore, performs work at the expense of its internal energy. Consequenty, the internal energy of the system changes, say, from E_1 to E_2.

$$\therefore \quad -P_2V_2 + P_1V_1 = E_2 - E_1$$

or $$-E_2 - P_2V_2 = -E_1 - P_1V_1$$

or $$E_2 + P_2V_2 = E_1 + P_1V_1$$

or $$H_2 = H_1 \qquad (\because \; H = E + PV)$$

or $$\Delta H = 0$$

Thus, the Joule-Thomson expainson of real gas occurs not with constant internal energy but with constant enthalpy. This is, therefore, called an isenthalpic process.

- Since H is a state function, dH is a complete differential. Taking H as a function of P and T

$$H = f(P,T)$$

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT \quad \text{—} \quad ①$$

But

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

$$\therefore \quad dH = \left(\frac{\partial H}{\partial P}\right)_T dP + C_P dT$$

Since for adiabatic expansion, dH = 0, hence

$$\left(\frac{\partial H}{\partial P}\right)_T dP + C_P dT = 0$$

or

$$C_P dT = -\left(\frac{\partial H}{\partial P}\right)_T dP$$

or

$$\frac{dT}{dP} = -\frac{(\partial H/\partial P)_T}{C_P} \quad \text{—} \quad ②$$

i.e.

$$\left(\frac{dT}{dP}\right)_H = -\frac{(\partial H/\partial P)_T}{C_P} \quad \text{—} \quad ③$$

The quantity $\left(\frac{dT}{dP}\right)_H$ is called Joule-Thomson coefficient and is denoted by μ_{JT}

$$\mu_{JT} = -\frac{(\partial H/\partial P)_T}{C_P} \quad — ④$$

- Assuming μ_{JT} to be constant over a small pressure range, Eq. ③ may be written as

$$\Delta T = -\frac{(\partial H/\partial P)_T}{C_P}\,\Delta P - ⑤$$

where ΔT is the fall of temperature produced as a result of the fall of pressure ΔP.

- Joule and Thomson verified eq. ⑤ experimentally by accurately measuring the fall of temperature (ΔT) accompanying the expansion of a number of real gases. In every case, ΔT was found to be proprotional to the difference of pressure ΔP on the two sides of the porous plug.

→ Nature of Joule-Thomson coefficient :→

(i) μ_{JT} → +ve value → Cooling on expansion

(ii) μ_{JT} → −ve value → Warming on expansion

(iii) μ_{JT} → 0 → No temperature change on expansion.

The temperature at which neither cooling nor heating effect occurs, is called the inversion temperature.

The Joule-Thomson expansion is one of the most important methods for liquefaction of gases.

→ Joule - Thomson coefficient in an ideal gas :→

— We know that Joule - Thomson coefficient is

$$\left(\frac{\partial T}{\partial P}\right)_H = \mu_{JT} = -\frac{1}{C_p}\left(\frac{\partial H}{\partial P}\right)_T \quad — ①$$

or $$= -\frac{1}{C_p}\left(\frac{\partial (E+PV)}{\partial P}\right)_T \qquad \because \; H = E + PV$$

or $$= -\frac{1}{C_p}\left[\left(\frac{\partial E}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T\right] — ②$$

Multiply and divide $\frac{\partial E}{\partial P}$ by ∂V in eq. ②

$$= -\frac{1}{C_p}\left[\left(\frac{\partial E}{\partial V} \times \frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T\right] — ③$$

When an ideal gas undergoes expansion under adiabatic condition in vacuum, no change takes place in its internal energy. In other words, the internal energy of a given quantity of an ideal gas at a constant temperature is independent of its volume, i.e.

$$\left(\frac{\partial E}{\partial V}\right)_T = 0 \qquad \text{so} \qquad \left(\frac{\partial E}{\partial V} \times \frac{\partial V}{\partial P}\right)_T = 0$$

Also, since for an ideal gas, PV is constant at constant temperature, $\left(\frac{\partial (PV)}{\partial P}\right)_T = 0$. Hence, eq. ③ reduces to $\mu_{JT} = 0$. The Joule-Thomson coefficient for an ideal gas is zero.

→ Joule - Thomson coefficient and inversion temperature :→

- Joule - Thomson coefficient can be easily calculated with the help of van der Waals equation.
- van der Waals equation for one mol of gas is

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT \quad — ①$$

$$\text{or} \quad PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT \quad — ②$$

Since both a and b are small, the term ab/V^2 in the van der Waals equation can be neglected provided the pressure is not too high.

$$PV - Pb + \frac{a}{V} = RT$$

$$\text{or} \quad PV = RT - \frac{a}{V} + Pb \quad — ③$$

For one mole of gas

$$PV = RT$$

$$\text{or} \quad V = \frac{RT}{P}$$

on substituting value of V in eq. ③ , we have

$$PV = RT - \frac{aP}{RT} + Pb \quad — ④$$

on dividing eq ④ by P

$$\frac{PV}{P} = \frac{RT}{P} - \frac{aP}{RTP} + \frac{Pb}{P}$$

$$v = \frac{RT}{P} - \frac{a}{RT} + b \quad — ⑤$$

on differentiating eq. ⑤ with respect to temp at constant pressure,

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P} + \frac{a}{RT^2} \quad — ⑥$$

Rearranging eq. ④, we have

$$RT = P(v-b) + \frac{aP}{RT} \quad — ⑦$$

Divide both sides by PT,

$$\frac{RT}{PT} = \frac{P(v-b)}{PT} + \frac{aP}{RT\,PT}$$

$$\frac{R}{P} = \frac{(v-b)}{T} + \frac{a}{RT^2} \quad — ⑧$$

substituting value of $\frac{R}{P}$ from eq. ⑧ in ⑥, we have

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{(v-b)}{T} + \frac{a}{RT^2} + \frac{a}{RT^2}$$

or $\left(\frac{\partial v}{\partial T}\right)_P = \frac{(v-b)}{T} + \frac{2a}{RT^2}$

or $\left(\frac{\partial v}{\partial T}\right)_P = \frac{1}{T}\left[(v-b) + \frac{2a}{RT}\right]$

or $$T\left(\frac{\partial V}{\partial T}\right)_P = V - b + \frac{2a}{RT}$$

or $$T\left(\frac{\partial V}{\partial T}\right)_P - V = \frac{2a}{RT} - b \quad \text{——} ⑨$$

Using the well known thermodynamic relation

$$V = T\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial H}{\partial P}\right)_T$$

or $$-\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial V}{\partial T}\right)_P - V \quad — ⑩$$

Eq. ⑨ may be written as

$$-\left(\frac{\partial H}{\partial P}\right)_T = \frac{2a}{RT} - b$$

or $$\left(\frac{\partial H}{\partial P}\right)_T = -\left(\frac{2a}{RT} - b\right) \quad — ⑪$$

we know that Joule-Thomson coefficient

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T \quad — ⑫$$

From eq. ⑪ and ⑫

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[\frac{2a}{RT} - b\right] \quad — ⑬$$

$$\mu_{JT} = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right] \quad — ⑭$$

(i) $\frac{2a}{RT} > b$ then μ_{JT} is +ve, cooling of gas.

(ii) $\frac{2a}{RT} < b$ then μ_{JT} is −ve, heating of gas.

(iii) $\frac{2a}{RT} = b$ then μ_{JT} is 0, no change in temp.

- Since a, b and R are constants, it is evident that the magnitude and sign of the Joule-Thomson coefficient depends only upon the temp at which gas is allowed to expand.
- The temperature at which the Joule-Thomson coefficient changes sign is known as the inversion temperature. At this temperature μ_{JT} is zero so that.

$$\frac{2a}{RT_i} = b$$

$$\text{or} \quad T_i = \frac{2a}{Rb} \quad — ⑮$$

- where T_i represents the inversion temperature. Thus, the inversion temperature depends upon the van der Waals constants a and b of the gas.

→ Calculation of w, q, dE and dH for the expansion of ideal gas under isothermal conditions for reversible process :→

1. Calculation of w :→

- Consider a gas enclosed in a cylinder fitted with a weightless and frictionless piston, as shown in figure.
- The external pressure p on the piston is equal to the pressure of the gas within the cylinder. If the external pressure is lowered by an infinitesimal amount dp, i.e. it falls from p to $p-dp$, the gas will expand by infinitesimal volume dv, i.e. volume changes from v to $V+dV$. As a result of expansion, the pressure of gas within the cylinder falls to $p-dp$, i.e. it becomes again equal to the external pressure. The piston then comes to rest.

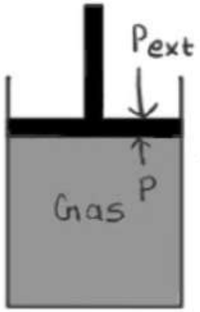


Fig. Rversible expansion of gas

- Since the system is in thermal equilibrium with the surroundings, the infinitesimally small cooling produced as a result of infintesimally small expansion of the gas is offset by the heat absorbed from the surroundings and the temperature remains constant throughout the operation.
- Since during expansion, pressure decreases and volume increases, these two parameters are assigned opposite signs. The work done by the gas is given by -

$$w = -(p-dp)dV$$

$$\text{or} \quad w = -pdV + dpdV$$

Ignoring the product $dpdV$, as both quantities are infinitesimal.

$$w = -pdV \text{ — ①}$$

- The total work for a finite volume change, say from V_1 to V_2 can be obtained by integrated eq. ①

$$W = -\int_{V_1}^{V_2} PdV \quad — ②$$

where V_1 = Volume of the gas in initial state
V_2 = Volume of the gas in final state

For one mole of an ideal gas

$$PV = RT$$

$$P = \frac{RT}{V}$$

Thus, eq. ② becomes

$$W = -RT\int_{V_1}^{V_2} \frac{dV}{V}$$

or $$W = -RT\ln\frac{V_2}{V_1} \quad — ③$$

Since in an ideal gas $P_1V_1 = P_2V_2$, at constant temperature, the above equation may also written as

$$W = -RT\ln\frac{P_1}{P_2} \quad — ④ \qquad \because \frac{P_1}{P_2} = \frac{V_2}{V_1}$$

- For n moles of gas, above expression may be written as

$$W = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2} \quad \text{—— ⑤}$$

Since during expansion V_2 is more than V_1 and P_2 is less than P_1, hence, from eq. ⑤, the w comes out to be negative in conformity with the convention used in this regard.

2 Calculation of q :→

- From the first law of thermodynamics

$$q = \Delta E - W$$

For an isothermal process

$$\Delta E = 0$$

so $q = -W$

This shows that in an isothermal expansion, the work is done at the expense of heat absorbed.

3. Calculation of dE :→

- In an Isothermal process, the temperature of the system remains constant throughout the process of expansion. Since for an ideal gas, internal energy E depends only on temperature, it follows that at constant temperature (isothermal process), the internal energy of the gas remains constant. This means that $\Delta E = 0$

4. Calculation of ΔH :→

- We know that enthalpy is

$$H = E + PV$$

or $$\Delta H = \Delta(E + PV)$$

$$\Delta H = \Delta E + \Delta PV$$

For an ideal gas

$$PV = nRT$$

$$\Delta H = \Delta E + \Delta nRT$$

Since for an isothermal process,

$$\Delta T = 0 \quad \text{and} \quad \Delta E = 0$$

hence $$\Delta H = 0$$

→ Calculation of w, q, dE and dH for the expansion of ideal gas under adiabatic conditions for reversible process :→

1. Calculation of w :→

- From the first law of thermodynamics

$$\Delta E = q + w$$

For adiabatic expansion

$$q = 0$$

so $\Delta E = w$

or $W = C_V \Delta T$ $\left(\because C_V = \frac{\Delta E}{\Delta T} \text{ or } \Delta E = C_V \Delta T\right)$

or $w = C_V(T_2 - T_1)$

2. Calculation of q :→

- In case of adiabatic expansion, no heat is allowed to enter or leave the system. Hence, $q = 0$.

3. Calculation of dE :→

- Molar heat capacity at constant volume of an ideal gas is given by

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V$$

or $dE = C_V dT$

and, for a finite change

$\Delta E = C_V \Delta T$

or $\Delta E = C_V(T_2 - T_1)$

4. Calculation of dH :→

- We know that, Enthalpy is given by

$H = E + PV$

or $\Delta H = \Delta E + \Delta(PV)$

For one mole of ideal gas

$PV = RT$

and $\Delta E = C_V \Delta T$

so $\Delta H = C_V \Delta T + R\Delta T$

$\Delta H = (C_V + R)\Delta T$

or $\Delta H = C_p \Delta T$ $(\because C_p - C_V = R$ or $C_p = C_V + R)$

or $\Delta H = C_p(T_2 - T_1)$

→ Thermochemistry:→

- All chemical reactions are accompained by energy change. These changes appear in the form of evolution or absorption of heat.
- The branch of chemistry which deals with energy change involved in chemical reaction is called thermochemistry.
- The energy given out during a chemical change appears in the form of heat, while that which is absorbed may be in the form of thermal, electrical or photo energy. The amount of energy evolved or absorbed during a chemical change always remains same for the same quantities of reacting substances.
- The subject matter of thermochemistry is based on the first law of thermodynamics. The energy change in chemical reactions are generally due to breaking up of existing bonds between atoms and the formation of new bonds. Thus Thermochemistry provides important information regarding the bond energies.

→ Exothermic and endothermic reactions:→

- Reactions that give out heat, i.e. which are accompained by evolution of heat, are called exothermic reactions. In such reactions $H_P < H_R$ so that ΔH is negative.
- On the other hand, reactions that take in heat, i.e. which are accompained by absorption of heat, are called endothermic reactions. In these reactions, $H_P > H_R$ so that ΔH is positive.

→ Thermochemical equation:→

- An equation which indicates the evolution or absorption of heat in the reaction or process is called a thermochemical equation.

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -393.5 \text{ kJ mol}^{-1}$$

$$2C(s) + H_2(g) \longrightarrow C_2H_2(g) \quad \Delta H = +226.8 \text{ kJ mol}^{-1}$$

→ Standard state :→

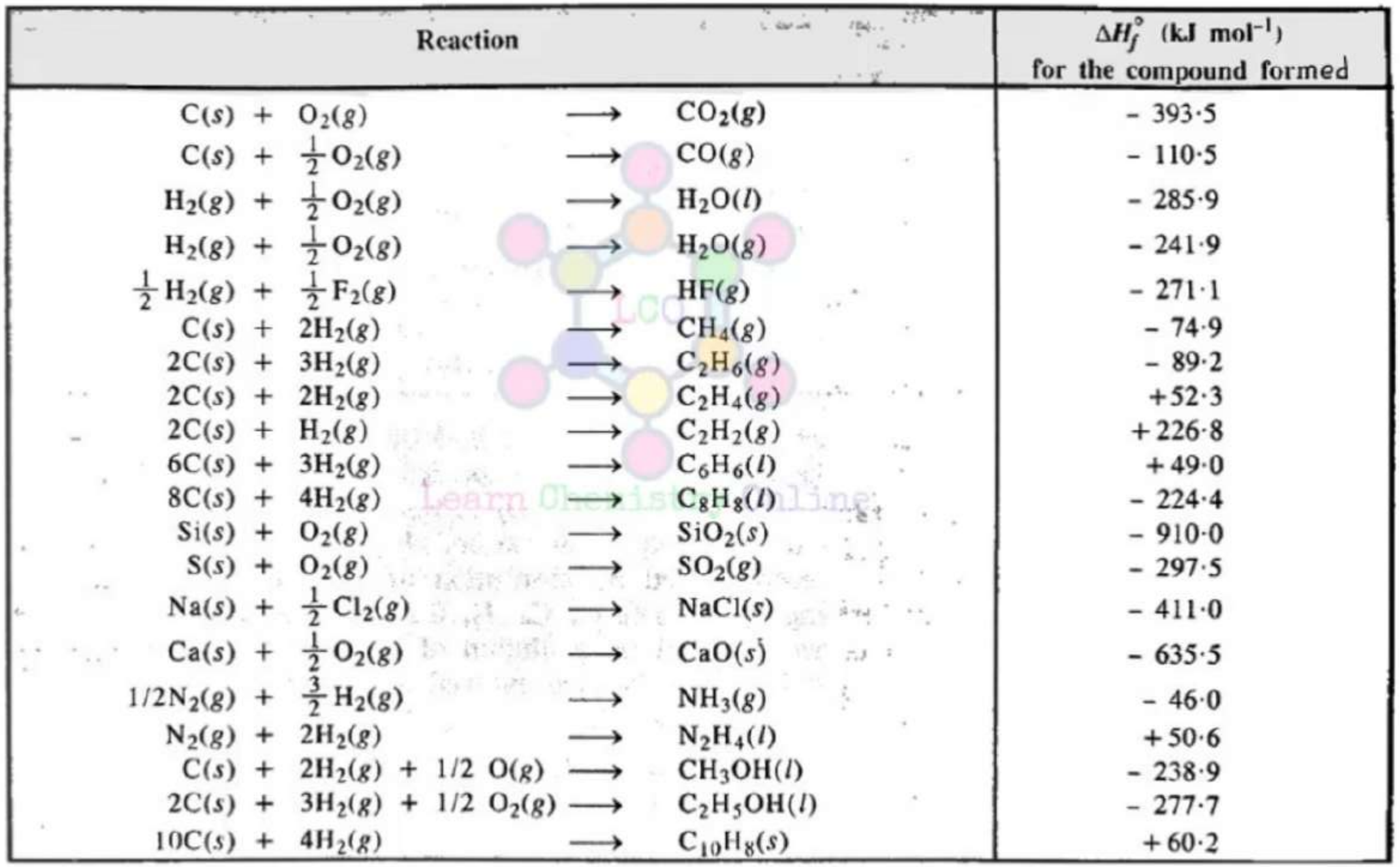
- The standard state of a substance at a specified temperature is its pure form at 1 bar.
- For a pure gaseous substance, the standard state at a given temperature is the ideal gas at one bar pressure.
- For a pure liquid substance, the standard state at a given temperature is the pure liquid at one bar pressure.
- For a pure crystalline substance, the standard state at a given temperature is the pure crystalline substance at one bar pressure.
- For a substance or ion in solution, the standard state at a given temperature is the unit molality of the species in ideal solution at a one bar pressure.

For example:→

- The standard state of liquid ethanol at 298K is pure liquid ethanol at 298K and 1 bar.
- The standard state of solid iron at 500K is pure iron at 500K and 1 bar.

→ Standard enthalpy of formation: → (ΔH_f°)

- The standard enthalpy of formation, is defined as the enthalpy change when one mole of substance is formed from its elements in their standard states.
- ΔH_f° may be negative or positive.



Reaction	ΔH_f° (kJ mol^{-1}) for the compound formed
$C(s) + O_2(g) \longrightarrow CO_2(g)$	- 393·5
$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$	- 110·5
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$	- 285·9
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$	- 241·9
$\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \longrightarrow HF(g)$	- 271·1
$C(s) + 2H_2(g) \longrightarrow CH_4(g)$	- 74·9
$2C(s) + 3H_2(g) \longrightarrow C_2H_6(g)$	- 89·2
$2C(s) + 2H_2(g) \longrightarrow C_2H_4(g)$	+52·3
$2C(s) + H_2(g) \longrightarrow C_2H_2(g)$	+226·8
$6C(s) + 3H_2(g) \longrightarrow C_6H_6(l)$	+49·0
$8C(s) + 4H_2(g) \longrightarrow C_8H_8(l)$	- 224·4
$Si(s) + O_2(g) \longrightarrow SiO_2(s)$	- 910·0
$S(s) + O_2(g) \longrightarrow SO_2(g)$	- 297·5
$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$	- 411·0
$Ca(s) + \frac{1}{2}O_2(g) \longrightarrow CaO(s)$	- 635·5
$1/2N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$	- 46·0
$N_2(g) + 2H_2(g) \longrightarrow N_2H_4(l)$	+50·6
$C(s) + 2H_2(g) + 1/2\ O(g) \longrightarrow CH_3OH(l)$	- 238·9
$2C(s) + 3H_2(g) + 1/2\ O_2(g) \longrightarrow C_2H_5OH(l)$	- 277·7
$10C(s) + 4H_2(g) \longrightarrow C_{10}H_8(s)$	+60·2

→ Determination of enthalpies of reaction:→

- Enthalpies of reactions at 25°c can be determined if ΔH_f° values of reactants and products involved in the reactions are known since

$$\boxed{\Delta H^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})}$$

- By convention, ΔH_f° values for elements in their standard states are taken as zero.

- Example:→

- Calculate the enthalpy of combustion of methane at 25°c and 1 atm pressure.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = ?$$

−74.9	0	−393.5	−285.9
KJ mol⁻¹	KJ mol⁻¹	KJ mol⁻¹	KJ mol⁻¹

$$\Delta H^\circ = \left[-393.5 + (2 \times -285.9) - (-74.9 + 0)\right]$$

$$\Delta H^\circ = \left[-965.3 + 74.9\right]$$

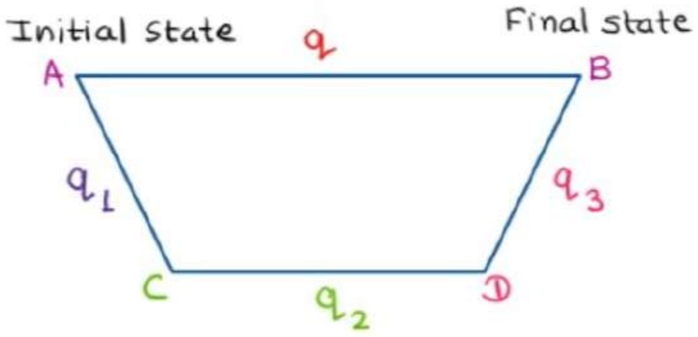
$$\Delta H^\circ = -890.5 \text{ KJ mol}^{-1}$$

→ Hess's law of heat summation:→

- This law was given by Russian chemist G.H. Hess in 1840.
- According to this law, "The enthalpy change of a given chemical reaction is the same whether the process takes place in one or several steps."

OR

"The amount of heat evolved or absorbed in a process, including a chemical change, is the same whether the process takes place in one or several steps."



- Suppose in a process, the system changes from A to B in one step and the heat exchanged in this change is q. Now suppose the system changes from state A to B in three steps involving a change from A to C, C to D and finally from D to B. If q_1, q_2 and q_3 are the heats exchanged in the first, second and third step, respectively, then, according to Hess's law,

$$q_1 + q_2 + q_3 = q \quad — ①$$

This generalisation means, in effect, that the enthalpy of reaction depends only on the initial reactants and final products and not at all on the intermediate products that may be formed.

→ Experimental illustration:→

- For example, carbon dioxide may be produced by two process

1. First procedure:→

- The burning of carbon takes place in single step to form CO_2.

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad ; \quad \Delta H = -393.5 \text{ KJ mol}^{-1} \quad — ①$$

2. Second procedure:→

- It is also possible to carry out the above reaction in two steps.

$$C(s) + \tfrac{1}{2} O_2(g) \rightarrow CO(g) \quad ; \quad \Delta H = -111.5 \text{ KJ mol}^{-1} \quad — ②$$

$$CO(g) + \tfrac{1}{2} O_2(g) \rightarrow CO_2(g) \quad ; \quad \Delta H = -282.0 \text{ KJ mol}^{-1} \quad — ③$$

on adding eq. ② and ③

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad ; \quad \Delta H = -393.5 \text{ KJ mol}^{-1} \quad — ④$$

From eq. ① and ④, it follows that the enthalpy change in both the procedures is same.

→ Applications of Hess's law:→

1. Calculation of enthalpies of reaction:→

- Hess's law can be easily used for those reactions for which enthalpy of reaction cannot be determined experimentally.
- Example:- It is extremely difficult to measure the heat evolved when carbon burn in oxygen to form carbon monoxide.

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \quad ; \quad \Delta H = ?$$

According to Hess's law, heat evolved in the combustion of 1 mole of carbon is same, viz., 393.5 KJ (i.e. $\Delta H = -393.5$ KJ), whether the reaction takes place in a single step as

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad ; \quad \Delta H = -393.5 \text{ KJ}$$

or in two steps as

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \quad ; \quad \Delta H = x \text{ KJ}$$

$$CO(s) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \quad ; \quad \Delta H = y \text{ KJ}$$

Although x, the heat change involved in the combustion of carbon to carbon monoxide cannot be determined easily but y, the heat change involved in combustion of carbon monoxide to give carbon dioxide can be measured and has been found to be -282.0 KJ. According to Hess's law.

$$x + y = -393.5$$

$$\text{or} \quad x = -393.5 - y = -393.5 - (-282.0) = -111.5 \text{ KJ}$$

Thus, ΔH for the combustion of carbon to give carbon monoxide is -111.5 KJ.

2. Determination of enthalpies of slow reactions:→

- For example, the transformation of rhombic sulphur into monoclinic sulphur is so slow that direct measurement of enthalpy is not possible. But the enthalpies of combustion of rhombic sulphur and monoclinic sulphur are known to be −297.5 and −300.0 KJ mol^{-1}, respectively, i.e.

(i) $S(\text{rhombic}) + O_2(g) \longrightarrow SO_2(g)$; $\Delta H = -297.5$ KJ

(ii) $S(\text{monoclinic}) + O_2(g) \rightarrow SO_2(g)$; $\Delta H = -300.0$ KJ

Substracting (i) from (ii) and transposing, we get

$S(\text{monoclinic}) \longrightarrow S(\text{rhombic})$; $\Delta H = -2.5$ KJ

or $S(\text{rhombic}) \longrightarrow S(\text{monoclinic})$; $\Delta H = +2.5$ KJ

3. Calculation of enthalpies of formation:→

- The enthalpies of formation of compounds can be calculated by application of Hess's law when it is not possible to determine these experimentally.
- Example:- It is impossible to determine experimentally the enthalpy of formation of benzene from its elements : carbon and oxygen.

However, it can be calculated from the enthalpy of combustion of benzene and the enthalpies of formation of water and carbon dioxide.

- The solution is carried out in two steps:

Step 1 :- The thermochemical equations for the known values are written as

(i) $C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$; $\Delta H = -3267.7$ KJ

(ii) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -393.5$ KJ

(iii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$; $\Delta H = -285.9$ KJ

Step 2 :- Equation (ii) is multiplied by 6 and equation (iii) is multiplied by 3

(iv) $6C(s) + 6O_2(g) \longrightarrow 6CO_2(g)$; $\Delta H = -2361.0$ KJ

(v) $3H_2(g) + \frac{3}{2}O_2(g) \longrightarrow 3H_2O(l)$; $\Delta H = -857.7$ KJ

Adding (iv) and (v) and substracting (i), we get

$6C(s) + 3H_2(g) \longrightarrow C_6H_6(l)$; $\Delta H = +49.0$ KJ

$= [-2361.0 + (-857.7)] - [-3267.7]$

$= -3218.7 + 3267.7$

$= +49.0$

Thus, the enthalpy of formation of benzene is +49.0 KJ.

→ Heat of reaction :→

- The amount of heat evolved or absorbed during a chemical reaction is called the heat of reaction.

→ Heat of reaction at constant pressure :→

- Let q_p be the heat exchanged in the chemical reaction taking place at constant pressure. The heat exchanged at constant pressure is termed as the enthalpy change. Thus,

$$\Delta H = q_p$$

In general if H_R = Enthalpy of the reactants and
H_p = Enthalpy of the products, then

$$\Delta H = H_p - H_R = q_p$$

This statement is schematically represented as follows :

$$\begin{tikzcd}
\text{Reactants } (H_R) \arrow[d, "\Delta H = H_p - H_R = q_p = \text{Enthalpy of reaction.}"] \\
\text{Products } (H_p)
\end{tikzcd}$$

2. Heat of reaction at constant volume :→

- Let us consider a chemical reaction taking place at constant volume.
- In such case, $w = 0$ and hence from the equation of first law ($\Delta E = q + w$),

$$\Delta E = q_v \qquad (q_v = \text{heat exchanged at constant volume})$$

- Suppose E_R is the internal energy of reactants and E_P is the internal energy of the products, then

$$\Delta E = E_P - E_R = q_v$$

This statement is schematically represented as follows :

$$\begin{tikzcd}
\text{Reactants } (E_R) \arrow[d, "\Delta E = E_P - E_R = q_v = \text{Heat of reaction at constant volume.}"] \\
\text{Products } (E_P)
\end{tikzcd}$$

→ Relation between heat of reaction at constant pressure and constant volume :→

Enthalpy is given by

$$\Delta H = \Delta E + P\Delta V \quad - ①$$

or $$q_p = q_v + P\Delta V - ② \quad (\because \Delta H = q_p \text{ and } \Delta E = q_v)$$

For n moles of ideal gas

$$PV = nRT$$

or $$P\Delta V = \Delta n_g RT \quad (\because \Delta n_g = n_2 - n_1)$$

n_1 = No. of moles of gaseous reactants.
n_2 = No. of moles of gaseous products.

Substituting in eq. ②

$$q_p = q_v + \Delta n_g RT$$

or $$\Delta H = \Delta E + \Delta n_g RT$$

→ Enthalpy of neutrilization:→

- The enthalpy change accompanying the neutrilization of 1 mole of an acid by a base in dilute solution is called enthalpy of neutrilization of the acid by the base.
- The enthalpy change accompanying the neutrilization of 1 mole of an acid by a base in dilute solution at 25°c and 1 atm pressure is called standard enthalpy of neutrilization of the acid by the base.
- The neutrilization of HCl by NaOH in dilute solutions when the acid, alkali and the salt formed are completely dissociated, may be represented as :

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O$$

or

$$H^+ + OH^- \rightarrow H_2O(l)$$

- Considering neutrilization of strong acid by strong bases, it will be seen that in every case, neutralisation reaction is the same as it simply involves the combination of H^+ ions and OH^- ions to form unionised H_2O. It is expected, therefore, that the enthalpy of neutrilisation of every strong acid by a strong base and vice versa should be identical. (The data are given in table-1).
- If however, the acid or alkali is weak, the enthalpy of neutrilization is different because the reaction now involves dissociation of weak acid or weak alkali as well.

Table-1 :- Standard enthalpy of neutrilisation of strong acid by strong base (kJ mol⁻¹)

Acid	Base	Enthalpies of neutrilization
HCl	NaOH	−57.32
HNO_3	NaOH	−57.28
HCl	KOH	−57.45
HCl	LiOH	−57.38

→ For example, the neutralisation of acitic acid by sodium hydroxide, involves the dissociation of the acid as well as the neutrilization of H^+ and OH^- ions, as represented below:

(i) $CH_3COOH (aq.) \rightleftharpoons CH_3COO^- (aq.) + H^+ (aq.)$

(ii) $H^+ (aq.) + OH^- (aq.) \longrightarrow H_2O (l)$

As H^+ ions are neutralised by OH^- ions furnished by the completely dissociated sodium hydroxide, more H^+ ions are formed by the dissociation of acetic acid to re-establish the equilibrium. Thus, both the reactions proceed side by side till acetic acid is completely neutralised.

Table - 2

Standard Enthalpy of neutrilisation of weak Ocid with NaOH

Acid	Enthalpy of neutrilisation ($kJ\ mol^{-1}$)	Value of combination of H^+ & OH^- ($kJ\ mol^{-1}$)	Enthalpy of dissociation ($kJ\ mol^{-1}$)
Acetic acid	−55.23	−57.32	+2.09
Formic acid	−56.06	−57.32	+1.26
Hydrocynamic acid	−12.13	−57.32	+45.19
Hydrogen sulphide	−15.90	−57.32	+41.42

→ Bond energy:→

- Bond energy for any particular type of bond in a compound may be defined as the average amount of energy required to dissociate (*i.e.* break) one mole of bonds of that type present in the compound. Bond energy is also called the enthalpy of formation of the bond.
- It has been found by experiment that isomeric compounds have the same value for enthalpy of formation. Also, in any homologous, the increase in enthalpy of formation for each CH_2 group is almost constant. This shows that enthalpy of formation of a bond of a particular type is largely an additive property.

→ Calculation of bond energy from thermochemical data:→

- In order to calculate bond energies of different types of bonds, it is necessary to know the enthalpies of dissociation of molecules of common elements into atoms. These have been obtained spectroscopically and are given below for hydrogen, oxygen, nitrogen and carbon.

(i) $H_2(g) \longrightarrow 2H(g)$; $\Delta H = 435.1$ KJ

(ii) $O_2(g) \longrightarrow 2O(g)$; $\Delta H = 489.5$ KJ

(iii) $N_2(g) \longrightarrow 2N(g)$; $\Delta H = 937.4$ KJ

(iv) $C(s) \longrightarrow C(g)$; $\Delta H = 719.6$ KJ

→ Example:→ Calculation of enthalpy of formation of C–H bond in methane.

– We should know the enthalpy of formation of methane. This has been calculated from the enthalpy of combustion of methane to be −74.9 KJ. Thus,

(v) $C(s) + 2H_2(g) \rightarrow CH_4(g)$; $\Delta H = -74.9$ KJ

Multiplying eq. (i) by 2, we have.

(vi) $2H_2(g) \longrightarrow 4H(g)$; $\Delta H = 870.2$ KJ

Adding equation (iv) and (vi) and substracting from eq. (v), we have

$C(g) + 4H(g) \rightarrow CH_4(g)$; $\Delta H = -1664.7$ KJ

$$\left[\begin{aligned} &= -74.9 - (719.6 + 870.2) \\ &= -74.9 - 1589.8 \\ &= -1664.7 \end{aligned}\right]$$

1664.7 KJ of energy is required to break four moles of C–H bonds in methane. Therefore, the average bond energy per mole of C–H bonds is

$\frac{1664.7}{4} = 416.2$ KJ (Enthalpy of formation of C–H bond)

→ Applications of Bond energies:→

1. Determination of enthalpies of reactions 2. Determination of enthalpies of formation of compounds.
2. Determination of resonance energy.

Enthalpies of formation of Bonds (Bond energies) at 25°c

Bond	Enthalpy of formation (kJ mol^{-1})	Bond	Enthalpy of formation (kJ mol^{-1})
H—H	435·1	C—Cl	330·5
H—F	564·8	C—Br	276·1
H—Cl	430·9	C—S	259·4
H—Br	368·2	C=S	477·0
O—O	138·1	C—N	292·9
O=O	493·7	C=N	615·0
O—H	464·4	C°N	878·6
C—H	416·2	N—N	159·0
C—O	351·4	N=N	418·4
C=O	711·3	N≡N	945·6
C—C	347·3	N—H	389·1
C=C	615·0	F—F	154·8
C°C	811·7	Cl—Cl	242·7
C—Fψ	439·3	Br—Br	192·5

→ Temperature dependence of enthalpy - Kirchhoff equation:→

- The enthalpy of any process, whether physical or chemical, varies with temperature.
- The enthalpy of the reaction

$$aA + bB \longrightarrow cC + dD$$

is given by

$$\Delta H = \Sigma H_{products} - \Sigma H_{reactants}$$

$$\Delta H = (cH_C + dH_D) - (aH_A + bH_B)$$

or $$\Delta H = cH_C + dH_D - aH_A - bH_B \quad — ①$$

differentiating eq. ① with temperature at constant pressure

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_P = c\left(\frac{\partial H_C}{\partial T}\right)_P + d\left(\frac{\partial H_D}{\partial T}\right)_P - a\left(\frac{\partial H_A}{\partial T}\right)_P - b\left(\frac{\partial H_B}{\partial T}\right)_P$$

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_P = cC_{P,C} + dC_{P,D} - aC_{P,A} - bC_{P,B} \qquad \because C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_P = \Delta C_P \quad — ②$$

Where ΔC_P = Sum of heat capacities of products - sum of heat capacities of reactants.

Eq. ② is called the Kirchhoff equation. It states that the variation of ΔH of a reaction with temperature at constant pressure is equal to ΔC_P of the system. Eq. ② can be written as

$$d(\Delta H) = \Delta C_P dT \quad — ③$$

- Analogously, the temperature-dependence of enthalpy of reaction at constant volume is given by

$$\left[\frac{\partial(\Delta E)}{\partial T}\right]_V = \Delta C_V \quad — ④$$

OR $$d(\Delta E) = \Delta C_V dT \quad — ⑤$$

- If the temperature range is small, eq. ③ and ⑤ can be easily integrated by assuming that the heat capacities are independent of temperature. Accordingly

$$\int_{T_1}^{T_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_p dT$$

$$\int_{T_1}^{T_2} d(\Delta H) = \Delta C_p \int_{T_1}^{T_2} dT$$

$$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1) \quad — ⑥$$

$$\int_{T_1}^{T_2} d(\Delta E) = \int_{T_1}^{T_2} \Delta C_V dT$$

$$\int_{T_1}^{T_2} d(\Delta E) = \Delta C_V \int_{T_1}^{T_2} dT$$

$$\Delta E_2 - \Delta E_1 = \Delta C_V (T_2 - T_1) \quad — ⑦$$

- If temperature range is not small, then heat capacities are no longer constant and are function of temperature. So, It is convenient to express the heat capacity as a power series in T, viz.

$$C_p = \alpha + \beta T + \gamma T^2 \quad \text{—— ⑧}$$

where α, β and γ are constants for given species.

$$\Delta C_p = \left[(c\alpha_C + d\alpha_D) - (a\alpha_A + b\alpha_B)\right] + \left[(c\beta_C + d\beta_D) - (a\beta_A + b\beta_B)\right]T + \text{-----}$$

or $$\Delta C_p = \Delta\alpha + \Delta\beta T + \Delta\gamma T^2 \quad \text{—— ⑨}$$

Substituting equation ⑨ in equation ③ and integrating between T_1 and T_2, we have

$$\int_{T_1}^{T_2} d(\Delta H) = \int_{T_1}^{T_2} (\Delta\alpha + \Delta\beta T + \Delta\gamma T^2)\, dT$$

or $$\Delta H_2 - \Delta H_1 = \Delta a(T_2 - T_1) + \frac{1}{2}\Delta\beta(T_2^2 - T_1^2) + \frac{1}{3}\Delta\gamma(T_2^3 - T_1^3) \quad \text{—— ⑩}$$

Eq. ⑩ is the integrated Kirchhoff equation