**First Law of Thermodynamics**

The 1st law of thermodynamics is the direct consequence of conservation of energy, *i.e*. “It is impossible to create or destroy energy, but may be converted from one form to another.” There are various ways of staying the 1st law of TD. Some of the selected statements are as follows —

**First statement of 1st law of TD**: It may be put as —

**According to Joule**, “There is an exact equivalence between the amount of work overcome and the heat generated.”

**According to Maxwell**, “When work is transformed into heat or heat into work, the quantity of work is mechanically equivalent to the quantity of heat.”

The above statements of Joule and Maxwell are regarded as the statements of the 1st law of TD. These statements find valid applications in engineering thermodynamics.

**Second statement of 1st law of TD**: It may be put as —

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

**Explanation**: In exothermic reactions, heat is given out to the surroundings, thereby the internal energy of the system decreases, while for surroundings it is increases correspondingly. Hence, the total energy of the system and the surroundings (i.e. isolated system) taken together remains constant, i.e. unchanged.

In endothermic reactions, heat is absorbed from the surroundings; thereby the internal energy of the system increases, while for surroundings it is decreases correspondingly. Hence, the total energy of the system and the surroundings taken together remains constant, *i.e*. unchanged.

**Third statement of 1st law of TD**: It is as stated below —

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

**For Example:** Coal contains a huge source of energy, during its burning this chemical energy produces heat. The heat is converted into mechanical energy of the system, which moves the engine to move a train. In this example, energy disappeared in one form and appeared in another form in an exactly equivalent quantity.

**Forth statement of 1st law of TD**: It may be put as —

“It is never possible to construct a ***perpetual*** (never ending or lasting forever or continuous) motion machine that could produce work without consuming any energy.”

**Explanation**: Since work can be produced only by the expenditure of energy in whatever form it may be, it follows directly from it that it is impossible to make a perpetual-motion-machine, i.e. a device to obtain useful work continually without drawing on any energy source, i.e. out of nothing (it is also called perpetual motion machine of 1st kind). This picture is applicable to all kinds of engines. A thermal machine which may operate without any expenditure of fuel and may thus create energy out of no-where is generally called a perpetual motion machine of 1st kind. The 1st law rules out such machines. The fact that no exception to the 1st law has been found yet, because of the conservation of energy, *i.e*. energy can’t be created or destroyed but can be transformed from one form to another.

**Mathematical formulation of 1st law of TD**:

Suppose a system absorbs a quantity of heat ‘’ and, its state changes from . This heat is used up —

1. In increasing the internal energy of the system, *i.e*.

Here, represents the internal energies associated with the system in its states respectively.

1. To do some external work ‘’ by the system on its surroundings,

The net energy of the system at ‘’, before transformation is , and

The net energy of the system after transformation is

According to conservation of energy,



Thus, heat absorbed by the system = Increases in its internal energy + Work done by the system.

**Differential form of 1st law of TD**:

Mathematically, the first law of thermodynamics is —

For an infinitesimal process, equation (1) can be written as —

**In equation (2), the differential is distinguished in notations by “” from “”. This can be explained from the following discussions** —

**() Change in internal energy is independent of the path taken:** Internal energy is an exact differential, *i.e.* it is independent of the path taken. In mathematical terminology, an exact differential is always denoted by the symbol ‘’ for example, in equation (2).

**That is an exact differential, can be proved as**— When the temperature and volume of a reacting system remains constant, then the change in internal energy of the system is equal to the heat exchanged with the surroundings. Thus, we can mathematically define internal energy “” as a function of . Thus —

Therefore, ‘’ is an exact differential //

**() Nature of :** The thermodynamic quantities  are not state functions because changes in their magnitude for a process depend upon —

1. The path by which the change is accomplished, and
2. The previous history of the system.



This fact can be explained from the following figure. The work done in passing from state ‘’ to the state ‘’ by 4 different paths are as shown in the figure. The values of will be equal to the area under the curve in the diagram, which is shown by the shaded portion. From the figure it is seen that in passing from by different paths, work done is different. It means that ‘’ is not a definite quantity. Again, from equation (), *i.e.* —

As is a definite quantity and is not a definite quantity, hence it follows that can’t be a definite quantity. **Mathematically**, infinitesimally changes in are not exact differentials but are **inexact differentials**. (***Mathematical proof for this given in next page***)

In mathematical language, we always write the inexact differential by ‘’, for example , , etc. and exact differential by ‘’, for example Hence, the 1st law of TD,

From this equation, following fact may arise —

1. For a cyclic process, the change in internal energy of the system is zero because the system is brought to the original condition. Thus —

Therefore, total work obtained is equal to the net heat supplied.

1. In an isolated system, there is no exchange of heat with the surroundings,

Indicating that in an isolated system, the work performed will be equal to the decrease in internal energy.

1. In a non-isolated system, system gains heat () and performs work (). For the system,

If one considers the surroundings, it loses amount of heat, but receive units of work. The internal energy change of the surroundings will be given by —

It means that the net change in the internal energies of the systems and surroundings taken together would be nil.

**Sign of , the change in Internal Energy**:

For a chemical reaction, if is the energy of the reactants and that for the products, then, change in internal energy for the reaction will be,

If, then,

Energy is absorbed from the surroundings and the reaction is **endothermic**

If, then,

Energy is absorbed from the surroundings and the reaction is **exothermic**

**Problem (1)**: Prove that the heat ‘’ is a path dependent function, i.e. ‘’is not a perfect differential.

**Solution**: Suppose heat ‘’ is a state function, i.e. independent of path, and ‘’ is an exact differential. From the first law of thermodynamics, we have,

Substituting equation (1) in equation (2), we get,

Differentiating the above equation again with respect to , at constant , we have, —

Differentiating the above equation again with respect to , at constant , we have, —

If ‘’ is a state function, then ‘’ is an exact differential, and for this,

But from equation (4) and (5), we have,

But, “” is a state function, and

From equation (6) & (7), we have,

Which is not possible, due to the wrong assumption about ‘’, therefore, is a path dependent function // Proved

**Problem (2)**: Prove that the heat ‘’ is a path dependent function, i.e. ‘’ is not a perfect differential.

**Solution**: Already proved in page number 12?

**Enthalpy or Heat Content ()**:

Energy is expressed as the product of pressure () and volume (); the two thermodynamic variables for a system. The sum of the two energy terms *viz*. internal energy () and - energy associated with a system is universally denoted by ‘’and called the enthalpy or heat content of the system. Thus, —

In the differential form, the above equation (1) is —

If the system undergoes a change at constant pressure, and hence,

Since, are the properties of the system, hence is a state function, and is therefore, a perfect differential. This means that like is independent of the path of transformation of the system.

Since, the mechanical work (i.e. work of expansion or contraction) is given by —

And, from the 1st law of TD, we have, —

From equation (3) and (4), we have —

For finite change, the above relation is,

Hence, the change in enthalpy () of the system may be defined as the amount of heat absorbed at constant pressure provided that the work done is of only type.

**OR This statement can also be proved as**:

We have, —

In the differential form, the above equation (1) is, —

From equation (1) & (2) it follows that the absolute value of can’t be calculated from classical TD, as is undetermined. Hence, it is required to obtain a meaningful expression for . The change in enthalpy () for a given system is given by —

Here, denotes the initial value of enthalpy and is the final value.

Since, from the 1st law of TD,

In general, if is the enthalpy of the reactant and that for products, then,

Now, if , then Reaction is exothermic

And, if , then Reaction is endothermic //

**Heat Capacity:**

The amount of heat required to raise the temperature of of a substance by is called its **specific heat**. But, the **heat capacity** ‘’ of a system is defined as the quantity of heat required to raise the temperature of of substance by .

Since, the **heat capacity** ‘’ (of a system) varies with temperature, hence it is essential to define it more accurately in different form. Suppose, on absorbing an amount of heat “”, the temperature of  mole of a substance raises through “”, then the heat capacity is,

As ‘’ is not an exact differential, hence it represents the inexactness of the heat quantity.

Depending upon the condition imposed on equation (1), *i.e*. whether the system is being heated at constant pressure or at constant volume, heat capacity may be of - types —

1. Heat capacity at constant volume, and
2. Heat capacity at constant pressure,

**Heat capacity at constant volume ()**:

From the 1st law of thermodynamics, we have, —

If the volume is kept constant, *i.e*. , then equation (1) becomes —

For finite process,

**Thus, the heat capacity at constant volume of a given system may be defined as the rate of change of internal energy with temperature**.

**Heat capacity at constant Pressure ()**:

From the 1st law of thermodynamics, we have —

Since, the enthalpy or heat content, is defined as —

This on differentiating at constant pressure, we get, —

Substituting equation (2) in equation (1), we get, —

For finite process,

**Thus, the heat capacity at constant pressure of a given system may be defined as the rate of change of enthalpy with temperature**.

**Heat capacity of Gases:**

For gases, heat capacity at constant pressure , increases slowly with temperature, and conveniently expressed as the power series,

Where are constants and is the absolute temperature

**Work done in Adiabatic Expansion of an Ideal Gas:**

**(Reversible Adiabatic Expansion)**

From the 1st law of thermodynamics, we have, —

For adiabatic system,

Equation (1) implies that all the work performed will be done at the expense of internal energy of the system.

During adiabatic expansion at constant , the temperature of the system falls from to and the volume increases from

Work done at constant

Since, the work is being done at the expense of internal energy; hence the internal energy of the system will decrease from .

Since, for an ideal gas,

Integrating above equation between the limits , we have, —

By substituting in equation (2), we can express equation (3) in the following form also —

One can write one more expression for equation (3), as follows:

From ideal gas equation,

Therefore, equation (4) becomes,

Now from —

Since, therefore,

This equation gives the work done in an adiabatic expansion of an ideal gas. When, work done is on the gas. //

**Problem (4a, 2004):** A sample of argon at expands reversibly and adiabatically to thrice its initial volume. If for argon is , find out the final pressure of the gas. 2

**Solution**: Since, for the reversible adiabatic () expansion,

Here, , the heat capacity ratio

Given, Initial Final

Pressure,

Volume,

For argon,

**Problem (3c, 2004):** In a reversible adiabatic expansion process when the external pressure is matched to the internal pressure, find the expression between the changes in temperature to the change in volume.

**Solution**: Let, for the reversible adiabatic () expansion of a perfect gas from initial volume to final volume , the pressure inside and outside be *i.e*. the external pressure is matched to the internal pressure throughout.

The work done when the gas expands by volume , is

But, for prefect gas, the change in internal energy at constant volume is —

Here, Heat capacity at constant volume

Now, from the 1st law of thermodynamics, we have, —

For adiabatic system,

Since, for perfect gas,

Integrating above equation between the limits , we have, —

This is the required relation. By substituting in equation, we can express the above equation in the following form also —

**Adiabatic Irreversible Expansion Work:**

In an irreversible expansion, at constant pressure, the work done is given by —

**Variation of Energy () with Temperature () and Volume ():**

Since, energy, E depends on , *i.e*.

Here, Heat capacity at constant volume

If we know the value of and the derivative equation (1) can be integrated and, the change in energy with can be calculated. But, can be measured calorimetrically. Therefore, only problem remains to measure and, this derivative is called the internal pressure which depends on the intermolecular forces and determined by Joule’s law i.e. **Joule’s experiment**.

**Question (3a, 2004)**: **What is internal energy? How does it very with temperature**? 1 + 2 = 3

**Answer**: The energies of the microscopic particles (molecules, atoms, etc.) constituting a system, together make the internal energy of the system. Thus, the internal energy is due to the energies of the constituting particles, and contributes a part of the total energy of the system. It is denoted by , and —

Total Energy

**Variation of ‘’ with Temperature**:

Since, energy, E depends on , *i.e*. —



Here, Heat capacity at constant volume

Therefore, at constant volume,

Thus, the internal energy of a substance increases with the raise in temperature (at constant volume). Figure drawn below shows the variation of internal energy of a system with temperature held at constant volume. The slope of the tangent to the curve at any temperature is the heat capacity at constant volume ().

**Joule’s law:**

If a fixed mass of gas is allowed to expand without doing external work under the condition that no heat can enters or leaves the gas, i.e. the gas is allowed to undergo what is called **free expansion**, then if the molecules of the gas attract one another, internal work will have to be done by the gas in pulling them apart and will happen at the expense of internal kinetic energy (heat energy) of the gas, which will, therefore, be cooled by the expansion. On the other hand, if the molecules repel one another, the expansion should be accompanied by a rise in temperature and if there are no intermolecular attractions, there should be no change in temperature.

**The Joule’s Experiment: Measurement of :**

Joule measured the internal pressure, of gases by the experimental arrangement depicted as below: —



Bulb ‘’ was filled with air while ‘’is evacuated, and are connected by a stop cock. The surrounding water bath was stirred and its temperature was recorded. After opening the stop-cock, temperature was recorded and found to be no change in value, i.e. no work is done by the gas, as it is expanding into vacuum, and it is not exchanging any heat with the surrounding water (otherwise the temperature of water would have changed). Hence, the 1st law of TD along with the result of Joule’s experiment would become as follows —

Since,

But, at

As the energy is independent of volume, it means that the energy of the gas is a function of temperature only. This is nothing but Joule’s law. However, this is only true for ideal gases in which internal pressure or force of attraction between the molecules of the gas is zero.

**Joule’s Coefficient ():**

Since, Joule’s law have concerned with the variation of temperature () with volume () at constant internal energy . This quantity is called Joule’s coefficient, denoted by . Thus, —

For ideal gas,

**Values of Joule’s Coefficient (): [Relation with TD variables]**

Since,

Applying cyclic rule, we have —

Since,

Therefore, from equation (1), we have —

**Variation of Enthalpy () with Temperature () and Pressure ():**

**[Note: Variation of with yields Joule’s law; but the variation of with yields Joule – Thomson Effect]**

Since, enthalpy, depends on , *i.e*.

Here, Heat capacity at constant pressure

If we know the value of and the derivative equation (1) can be integrated between the suitable limits to get the total change in enthalpy. The measurement of is simple, but the evaluation of the derivative is a difficult task.

1. **Determination of , for Solid substances**:

Since,

Again,

Therefore, from equation (1), we have,

At constant

On dividing throughout by , we get —

Since, for solids the derivative [**compressibility factor**] is negligibly small, therefore, the 1st term of LHS of equation (2) can be neglected in comparison to , and thus —

Again, as the molar volumes of solids are very small, it means that the variation of enthalpy with pressure with would be negligible for very small pressure change.

1. **Determination of , for Liquid substances**:

If we argue on the same line as discussed above for solids we conclude that can be ignored for liquids.

1. **Determination of , for Gaseous substances**:

For ideal gases the derivative , is zero and for real gases its value is very small.

[] **For Ideal Gases**: For ideal gases,

This can be proved as follows —

Since, enthalpy is defined as —

For an ideal gas,

Since, for ideal gas, is a function of , hence, we can write —

Thus, at constant ‘’,

**OR** We have,

Again, enthalpy is defined as —

Substituting the values of from equation (a) & (b) in equation (1), we have,

At constant

On dividing throughout by , we get —

For an ideal gas, according to **Joule’s law**,

Again, for an ideal gas,

At constant temperature,

Substituting equation (3) & (4) in equation (2), we have —

[] **For Real Gases**: For ideal gases, the derivative is very small and **Joule – Thomson experiment** has been suitably used to measure it.

**Joule-Thomson Effect:**

The Joule -Thomson effect may be stated as follows — “If a gas under higher constant pressure is allowed to pass through a porous plug (or throttle) to a region of lower pressure, its temperature gets lowered.”

**Joule-Thomson Experiment**: Joule and Thomson used a long tube being thermally insulated from outside by fitting it with a porous plug to allow the gas to be kept at different pressures on the two sides of the tube. As soon as the flow becomes steady, its temperature at the two extreme ends of the tube was recorded by very sensitive thermometers and pressure difference by a gauge.

**Experimental Results**: When various gases were subjected to the Joule-Thomson experiment, the following results were obtained —

1. All the gases show a change in temperature when they pass through the porous plug,
2. The change in temperature is proportional to the difference in pressure on the two sides of the porous plug,
3. At sufficient low temperature, all gases show a fall in temperature when they pass through the porous plug. But at ordinary temperature, most gases suffer fall in temperature, but gases like hydrogen and helium record a rise in temperature, and
4. Every gas shows an inversion temperature at a given initial pressure. Above this temperature, the gas shows heating effect. Below this temperature, the gas shows cooling effect.

**Experimental Setup and Theory of the Experiment**:

Let us consider the following simple arrangement of the porous plug experiment —

In the figure is a long tube, which is having insulation for adiabatic conditions. The tube is fitted with the two imaginary pistons on the either sides of the porous plug .



Let, of a gas occupy a volume between the piston and plug at constant pressure, as shown in the figure (1). Let the piston move forward to press the gas to flow across the plug , this coming out gas will push the piston outwards. The pressure on the **LHS** is kept constant at a constant value of , whereas that on the **RHS**, pressure is also kept at a lower value .

Since, the external work done on the gas by the piston , and

External work done by the gas on the piston

The net work done by the gas,

As the process is carried out adiabatically, hence,

From the 1st law of thermodynamics,

Hence,

Negative value of internal energy () means that there is decrease in internal energy.

This implies that the work done is at the expense of internal energy. The decrease in internal energy in this case is —

Hence, it follows that the **Joule-Thomson** process is being carried out at constant enthalpy. //

**Joule-Thomson Coefficient**:

From Joule-Thomson experiment with various gases, it could be concluded that these experiments are conducted at constant enthalpy and are concerned with the change in temperature with pressure, *i.e*. **.** This quantity is known as the Joule-Thomson coefficient, and denoted by the symbol . Thus —

**Nature of Joule-Thomson Coefficient ()**:

Notable natures of Joule-Thomson are —

1. A value of implies cooling, because is in Joule-Thomson experiment. So, to make a quantity, should be quantity, *i.e*. the temperature will fall.
2. A value of implies warming on expansion, *i.e*. heating effect. As is , and therefore should be , *i.e*. the temperature should increase.
3. A zero value of corresponds no change in temperature on expansion. The temperature, at which neither cooling nor heating effect occurs, is called the **inversion temperature** ().

Thus, at inversion temperature,

**[Joule-Thomson Expansion/ Experiment is one of the most important methods for the Liquefaction of gases]**

**Relation of Joule-Thomson Coefficient () with TD variables**:

We know that enthalpy () is a function of any two of the three variables . If are taken as independent variables, then —

On setting up the condition of Joule-Thomson effect*, i.e*. —

Thus, it is possible to calculate from or vice-versa. //

**Applications of 1st law of Thermodynamics:**

1. **Relations between** : Following are the various relations between —

**Proofs of all these relations are given below**:

[] To prove —

**Proof**: Since, internal energy () is a state function, therefore, it is regarded as a function of two independent variables . Thus, —

Dividing both sides by , at constant , we have —

Now,

Substituting equation (1) in equation (2), we have —

Since, for ideal gas, and

Therefore, from equation (3), we get,

[] To prove —

**Proof**: Since, internal energy () is a state function, therefore, it is regarded as a function of two independent variables . Thus, —

Dividing both sides by , at constant , we have —

Now,

Substituting equation (1) in equation (2), we have —

Since, enthalpy is defined by the relation —

Substituting equation (4) in equation (3), we get —

But,

From the partial differentiation (*i.e*. ***cyclic rule***), we have —

Since, for ideal gas, and

Therefore, from equation (5), we get —

[] To prove —

**Proof**: Since, enthalpy () is a state function, therefore, it is regarded as a function of two independent variables . Thus, —

At constant enthalpy,

Substituting equation (6) in equation (5) *i.e*. —

[**Note:** This equation (i.e. equation No 7) can also be deduced from the 2nd law of TD]

1. **Important Thermodynamic Relations: For example —**

**Proofs of these relations are given below:**

Already proved in as well as in shown above

To prove—

**Proof**: Since, internal energy () is a state function, therefore, it is regarded as a function of two independent variables . Thus —

Since, for ideal gas,

Again, for ideal gas,

Since, at constant Pressure,

From equation (1) and (2), we have, —

To prove—

**Proof**: We know that —

Differentiating above equation with respect to at constant , we get —

Again, is an exact differential, hence we have —

Therefore,

Since, for ideal gas,

To prove—

**Proof**: We have —

To prove—

**Proof**: We have —

Since, for ideal gas,

But, at constant temperature,

To prove—

**Proof**: We have —

To prove—

**Proof**: Since, internal energy () is a state function, therefore, it is regarded as a function of two independent variables. Thus, we have —

Since, at constant Volume,

Since, for ideal gas,

Differentiating both sides of this equation with respect to , at constant , we have —

1. **Joule – Thomson effect:** Already discussed
2. **Variation of Heat of reaction with Temperature:** Kirchhoff’s Equation

With the help of 1st law of thermodynamics, Kirchhoff deduced the variation of heat of reaction with temperature. Considering a reaction —

The change in enthalpy —

And the change in internal energy —

Differentiating equation (1) with respect to , at constant , and equation (2) with respect to , at constant , we get —

Integrating between the limits and , we have —

Similarly,

Actually, and are the integrating constants and denote the corresponding internal enthalpy and energy at. Equation (4) and (5) are called **Kirchhoff’s equation**. From these, two cases are arrived, namely —

1. are independent of temperature, and
2. are dependent upon pressure

**Case (I):**  is constant between two temperatures independent of temperature:

Hence, —

**Case (II):** When varies with temperatures —

This is the general expression of Kirchhoff’s equation of variation of heat of reaction with temperature. //

**Problem** **[4c 2004]**: How do the reactions enthalpies depend on temperature? Derive the appropriate mathematical relation for the same. 5

**Solution**: See the **Kirchhoff’s equation** as above

**Problem** **[6c 2003]**: Obtain **Kirchhoff’s law**. The enthalpy of formation () of gaseous is . Find the value of (formation) at . The molar heat capacities at constant pressure have the values: 1 + 2 = 3

**Solution**: **First part** — See the Kirchhoff’s equation as above

**Second Part**: The reaction involved is —

For this reaction, the change in reaction heat capacity is —

Now, from the Kirchhoff’s equation, we have —

1. **Calculation of** : Calculation of these quantities are explained by considering the following numerical problems.

**Problem (1)**: One mole of a gas expands isothermally and reversibly at from a volume of . Calculate .

**Solution**: For one mole of an ideal gas, we have —

Here: Initial State Final State

Now, (**a**) **Calculation of ‘’**:

(**b**) **Calculation of ‘’**:

For isothermal expansion of an ideal gas, and therefore,

(**c**) **Calculation of ‘’**: From the first law of thermodynamics, we have —

(**d**) **Calculation of ‘’**: We have —

Since, are constants, therefore, //

**Problem (2)**: Calculate the minimum work which must be done to compress half mole of oxygen at , from a pressure of to a pressure of

**Solution**: The reversible compression work,

Here:

Since, work is done on the gas to compress it, sois  //

**Problem (3)**: of an ideal gas held by a piston under pressure and at . The pressure is suddenly released to and the gas is allowed to expand isothermally. Calculate for the process.

**Solution**: Given,

Now, (**a**) **Calculation of ‘’**: Work done irreversibly,

(**b**) **Calculation of ‘’**: As the ideal gas expands isothermally, , hence and

(**c**) **Calculation of ‘’**: From the first law of thermodynamics, we have —

**Problem (4)**: Calculate the maximum work obtained by () the isothermal expansion, () the adiabatic expansion of of an ideal gas initially at from to a volume of .

[Assume: ]

**Solution**: () Maximum work is obtained in reversible expansion, hence —

(2) Firstly, we calculate the final temperature using —

Now,

**Problem (3b, 2004)**: The enthalpy change for the combustion of of propene is . Find the change in internal energy. 3

**Solution**: Given —

Since, from the 1st law of TD —

Here,

Thus, the standard internal energy change, —

**Thermochemistry:**

**Thermochemical equations**: The chemical equations showing the physical states of the reactants as well as products along with the change in enthalpy change are called thermochemical equations. For example, considering the following thermochemical equations —

**Standard state**: The and pressure, written as ; superscript ‘’ indicates that pressure is and the reaction is in standard state.

**Heat or Enthalpy of Reaction**: The amount of heat evolved or absorbed during a chemical reaction is called heat of reaction or enthalpy of reaction. For example, for the reaction —

Change in enthalpy —

And, for the reaction —

Change in enthalpy —

For the reactions occurring at constant volume —

And —

**Relation between** : We have —

For solids —

For gases —

Again, for ideal gases —

**Problem (1)**: At constant pressure and , the heat evolved for the transformation of gaseous is . Calculate the amount of heat evolved for the reaction at constant volume.

**Solution**: We have —

For the reactions occurring at constant volume,

Thus, the heat evolved will be equal to, the change in internal energy.

Now, for the reaction —

From —

Therefore, the enthalpy change of the reaction at constant volume will be

**Exothermic and Endothermic Reactions**:



**Exothermic Reactions:** Chemical reactions which proceed with the evolution of heat are referred to as the exothermic reactions. For example —

For these reactions



If an exothermic reaction is taking place at constant temperature and constant volume, the energy change is expressed in terms of change in internal energy i.e. and,

For these reactions

**Endothermic Reactions:** Chemical reactions which proceed with the absorption of heat are referred to as the endothermic reactions. For example, —

For these reactions

**Standard Enthalpy Changes**: As the enthalpy of a reaction depends on temperature, a standard state is chosen to compare the enthalpies of reactions of different substances. A convenient standard state for a substance is most stable state of aggregation under pressure and at the specified temperature, generally at .

For pure solids, liquids and ideal gases, the standard state corresponds to the state of the substance at pressure and at the specified temperature.

For dissolved substances, the standard state of the solute is that concentration which gives unit activity.

The standard enthalpy of a reaction at temperature ‘’ and at a pressure of is denoted by the symbol and

The enthalpy of every element in its standard state is **arbitrarily given zero value**. For example, the enthalpy of formation of from its elements in the standard state is , implies that, —

Since,

**Different types of Enthalpy Changes**:

1. ***Heat or Enthalpy of Formation***: The standard enthalpy of formation of a compound (i.e. at pressure and temperature) may be defined as the enthalpy change when of a compound is formed from its constituting elements (in their standard states). It is denoted by and expresses in the unit of . For example, for the reactions —

A value of implies the formation of **exothermic** compounds, whereas a value implies the formation of **endothermic** compounds.

1. ***Heat or Enthalpy of Combustion***: The enthalpy of combustion of a substance at a given temperature may be defined as the enthalpy change accompanying the complete combustion of of the substance in excess of oxygen or air at that temperature. If the temperature is and pressure is then it is called standard enthalpy of combustion, and expresses in the unit of . For example, for the reactions —

A value of implies the formation of **exothermic** compounds, whereas a value implies the formation of **endothermic** compounds.

1. ***Enthalpy of Neutralization***: The enthalpy of neutralization of an acid at a given temperature may be defined as the enthalpy change accompanying the neutralization of **one gram equivalent** of a base by an acid in dilute solution at that temperature. For example, the enthalpy of neutralization of by in dilute solution at is .
2. ***Enthalpy of Ionization***: The required to ionize one mole of a weak acid or the weak base is called enthalpy of ionization. It is possible to calculate the enthalpy of ionization of a weak acid from the enthalpies of neutralization of strong acid and weak acid by strong bases. For example, considering the following problem —

**Problem: The neutralization enthalpy for** —

Calculate the enthalpy of ionization of , i.e.

**Solution**: Subtracting 2nd equation from the 1st equation, we get —

1. ***Heat or Enthalpy of Solution*** (up to infinite dilution): When a solute is dissolved in a solvent, heat may be either liberated or absorbed. If the heat is absorbed, the solution becomes cooler and . On the other hand, if heat is evolved, the solution gets warmer and .

The enthalpy change per mole of a solute dissolved varies to a considerable extent with dilution and to some extent with initial temperature of the solvent. The enthalpy of solution may be defined as the enthalpy change when one mole of the solute is dissolved in a specified amount of solvent.

The enthalpy of solution can be explained by considering the dilution of in water at ,

From the above equations it is evident that when is dissolved in of water, of heat are evolved. But, if the solution is further diluted to such an extent that further dilution would cause no additional heat change, the equation may be written as:

Here “aqueous” represents a large volume of water. The value ofcorresponding to this reaction is called the enthalpy of solution at infinite dilution. It is the maximum quantity of heat released in the formation of a solution of (or 1 mole of any solute) in excess of water. **There are two types of heat of solution** —

1. Integral enthalpy of solution and
2. Differential enthalpy of solution.

The integral heat of solution is defined as the enthalpy change when of a solute is dissolved in of solvent. For example, if of solute is dissolved in of water, the heat change gives the value of integral heat of solution at the of .

The differential heat of solution is defined as the enthalpy change when of solute is dissolved in an infinite amount of solution such that its concentration does not change by adding of solute. Mathematically, it is defined as —

In practice, heat change is plotted as a function of number of moles of solute and the differential heat of solution can be obtained by finding the slope at any concentration. Thus, the differential heat of solution depends on the concentration of the solution.

1. ***Enthalpy of Dilution***: It is observed that the enthalpy of solution per mole of a solute gets varied with the concentration of the solution. Therefore, it follows that if a given solution is diluted on the addition of solvent, there occurs noticeable change of enthalpy. This termed as the enthalpy of dilution.

**Enthalpy of dilution may be defined as** the change of enthalpy when a solution having of solute is diluted from one concentration to another.

1. ***Bond Energy or Bond Enthalpy***: The bond energy of a particular type of bond in a molecule may be defined as the amount of energy required to break or dissociateof that type of bond in the compound and separate the resulting atoms or radicals from one another. **For example** —

The bond energy of bond in molecule is , this means that of energy is required to break or dissociate the bond in molecule. Similarly, the bond energy of bond in and bond in molecules are respectively.

In the case of diatomic molecules (for example, , etc.) the bond energy is a definite quantity as there is only one type of bend is present in these molecules. However, it is less definite in the case of polyatomic molecules. If the polyatomic molecule contains similar types of bonds, then the bond energy is equal to the average energy required to break a particular bond in one mole of that compound. For example, bond energy in , as there are bonds in molecule, and of heat is liberated in the formation of from its elements, i.e. of energy must be supplied in order to break the molecule to form atomic carbon and atomic hydrogen.

Thus, the bond energy or bond enthalpy is a definite quantity for a given bond and it is average of enthalpies or energies required to dissociate the said bond present in different gaseous compounds into free atoms or radicals in the gaseous state.

1. ***Bond Dissociation Energy or Enthalpy***: The bond dissociation enthalpy or bond dissociation energy may be defined as the energy or enthalpy required dissociating a given bond of some specific compound. The bond energy and bond dissociation energy are always different. For example, —

From the above data, it is evident that the energy for each step is different due to the fact that in each case a different dissociating fragment is involved. The bond enthalpy would be one-fourth of the enthalpy required to break a molecule is .

**Calculation of Bond Enthalpy or Energy**: Considering the following example —

**Problem (1)**: From the following heats of combustion and heats of dissociation data, calculate the bond energy of bond in :

**Solution**: Dissociation of is expressed as —

As there are bond in , therefore, bond energy of each bond is —

Now, the equation for the dissociation of molecule can also be obtained directly just by adding all the equations from (1) to (5). Hence, —

**Hess’s Law of Constant Heat Summation: [Corollary of 1st Law of TD]**

According to Hess’s law of constant heat summation, the enthalpy change of a given chemical reaction is the same whether the process is takes place in a single step or by several intermediate steps. Thus, the law is nothing but a corollary of the law of conservation of energy and implies that the heat of reaction does not depend upon the nature of intermediate products but depends only on the initial reactants and final products and also independent of the path or manner by which the change is carried out.

**Theoretical Justification of Hess’s law of constant heat summation**:

Suppose a substance ‘’ can be changed to ‘’ directly *i.e.* by a single step,

The same change can be carried out through the intermediate stages by the evolution of heats as —



Total heat evolution

According to Hess’s law of constant heat summation,

**For example: Experimental verification of Hess’s law**:

Carbon dioxide gas can be directly prepared as —

Again, Carbon dioxide gas can be prepared indirectly as follows —

This is the same i.e. whether the chemical change brings in a single step or by through intermediate steps heat change is always same.

**Application of Hess’s law**: The law provides a mathematical method for calculating —

1. Heat of reaction,
2. Heat of transition,
3. Lattice energy of crystal (Born – Haber cycle),
4. Heat of formation, etc.

**Calculation of Heats of reaction**:

By Hess’s law it is possible to calculate heats of formation of any reactions which can’t be determined experimentally. For example, it is very difficult to measure the heat evolved when carbons burns in oxygen to form carbon monoxide, i.e.

From Hess’s law it is evident that, whether is formed in a single step or multiple steps, the heat evolved is , i.e.

Let, for the reactions,

The ‘’, the heat produced in the conversion of cannot be determined but ‘’, the heat change involved in the combination of can be measured, and found to be .

Hence, the heat evolved during the combination of is . //

**Determination of Heats of Transition**: As the transition of an element from one allotropic form to another is an extremely slow process, it requires heating of one allotropic form of the element for a long period at constant temperature. Therefore, it is not possible to determine heats of transition of element experimentally. These are, however, determined indirectly by using Hess’s law. For example, —

Suppose, we desire to determine the heat of transition of , the allotropic form of rhombic form of sulphur into , the monoclinic form of sulphur. We start with the two allotropic forms separately and measure their heats of combustion as —

Subtracting, —

This equation expresses the thermochemical equation for the transition of. In this particular case //

**Calculation of Heats of Formation**: The heats of formation for those compounds which cannot be determined experimentally can be calculated by using Hess’s law. This can be explained from the following example:

The enthalpy of formation of from graphite and hydrogen cannot be found directly as no chemical reaction occurs between graphite and hydrogen.

The value of for the above reaction can be calculated by the help of the following thermochemical reactions —

Adding equation () and (), we have —

On subtracting equation () from equation (), we get —

**Lattice Energy of a Crystal () — the Born-Haber Cycle**:

Hess’s law (of constant heat summation) can be used to determine the lattice energy of a crystal, which may be defined as the amount of heat releases when the requisite amounts of ions in the gaseous state combine to yield of ionic crystal lattice. Thus, —

**For example**, we can determine the of crystal which corresponds to the reaction —

The formation of crystal can be explained as —

The cyclic process of formation of an ionic crystal is known as the Born-Haber cycle and the cycle is used to calculate the lattice energy (). According to **Hess’s law** of constant heat summation,



For the sodium chloride crystal (or any ionic compound) —

Heat of sublimation of sodium,

Dissociation energy of chlorine (),

Ionization energy of sodium,

Electron affinity of chlorine,

Enthalpy of formation of ,

Hence, from the above equation —

**Lattice Energies of some solids/ compounds**:

|  |  |  |
| --- | --- | --- |
| **Compound** | **Lattice Energy ()** | |
| **Experimental** | **Theoretical** |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |

**The Born-Haber Cycle**:

**Experimental Determination of Lattice Energy**:

**Question (4b, 2004)**: State Hess’s law and explain its application with an example. 3

**Solution**: Hess’s law of constant heat summation is a direct consequence of 1st law of TD (i.e. conservation of heat energy) and can be stated as — whether a chemical reaction completes in a single step directly or through some several intermediate steps the total enthalpy change is always same. Thus, —

For the change , if enthalpy change is , and for the indirect process and , if enthalpy changes are respectively then, according to Hess’s law, —

**2nd Part**: Application (utility) of Hess’s law —

One of the most important applications of Hess’s law is to determine enthalpy of reaction which is difficult to determine experimentally. **For example**, the value of for the combustion of **graphite** to carbon monoxide: is very difficult to determine experimentally. However, it can be estimated indirectly from the following two reactions, for which can be determined experimentally —

Subtracting the latter from the former, we get —

Consequently, //