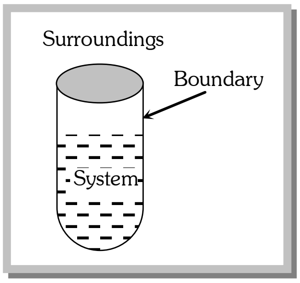
Thermodynamics

Thermodynamics (thermo means heat and dynamics means motion) is the branch of science which deals with the study of different forms of energy and the quantitative relationships between them.

The complete study of thermodynamics is based upon three generalizations celled first, second and third laws of thermodynamics. These laws have been arrived purely on the basis of human experience and there is no theoretical proof for any of these laws.

Basic Terms of Thermodynamics.

(1) **System, surroundings and Boundary :** A specified part of the universe which is under observation is called the ***system*** and the remaining portion of the universe which is not a part of the system is called the ***surroundings.***



The system and the surroundings are separated by ***real or imaginary boundaries.*** The boundary also defines the limits of the system. The system and the surroundings can interact across the boundary.

(2) **Types of systems**

(i) ***Isolated system*** : This type of system has no interaction with its surroundings. The boundary is sealed and insulated. Neither matter nor energy can be exchanged with surrounding. A substance contained in an ideal thermos flask is an example of an isolated system.

(ii) ***Closed system*** : This type of system can exchange energy in the form of heat, work or radiations but not matter with its surroundings. The boundary between system and surroundings is sealed but not insulated. For example, liquid in contact with vapour in a sealed tube forms a closed system. Another example of closed system is pressure cooker.

(iii) ***Open system*** : This type of system can exchange matter as well as energy with its surroundings. The boundary is not sealed and not insulated. Sodium reacting with water in an open beaker is an example of open system.

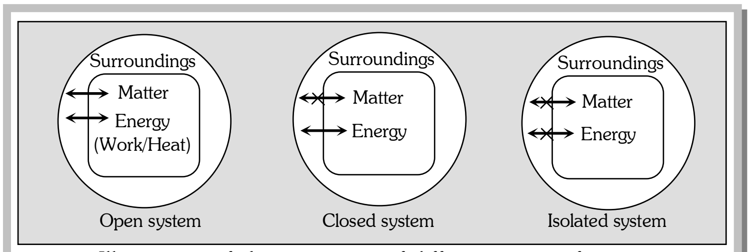


Illustration of characteristics of different types of systems

(iv) ***Homogeneous system*** : A system is said to be homogeneous when it is completely uniform throughout. A homogeneous system is made of one phase only. Examples: a pure single solid, liquid or gas, mixture of gases and a true solution.

(v) ***Heterogeneous system*** : A system is said to be heterogeneous when it is not uniform throughout, *i.e.*, it consist of two or more phases. Examples : ice in contact with water, two or more immiscible liquids, insoluble solid in contact with a liquid, a liquid in contact with vapour, etc.

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

Note :✹ *All physical and chemical processes taking place in open in our daily life are **open systems** because these are continuously exchanging matter and energy with the surroundings.*

(3) **Macroscopic Properties of the System :** Thermodynamics deals with matter in terms of bulk (large number of chemical species) behaviour. The properties of the system which arise from the bulk behaviour of matter are called ***macroscopic properties***. The common examples of macroscopic properties are pressure, volume, temperature, surface tension, viscosity, density, refractive index, etc.

The macroscopic properties can be sub – divided into two types

(i) ***Intensive properties*** : The properties which do not depend upon the quantity of matter present in the system or size of the system are called ***intensive properties***. Pressure, temperature, density, specific heat, surface tension, refractive index, viscosity, melting point, boiling point, volume per mole, concentration etc. are the examples of intensive properties of the system.

(ii) ***Extensive properties*** : The properties whose magnitude depends upon the quantity of matter present in the system are called ***extensive properties***. Total mass, volume, internal energy, enthalpy, entropy etc. are the well known examples of extensive properties. These properties are additive in nature.

Note :✹ *Any extensive property if expressed as per mole or per gram becomes an intensive property. For example, mass and volume are extensive properties, but density and specific volume, i.e. the mass per unit volume and volume per unit mass respectively are intensive properties. Similarly, heat capacity is an extensive property but specific heat is an intensive property.*

(4) **State of a system and State Variables :** The state of a system means the condition of existence of the system when its macroscopic properties have definite values. If any of the macroscopic properties of the system changes, the state of the system is also said to change. Thus, the state of the system is fixed by its macroscopic properties.

Macroscopic properties which determine the state of a system are referred to as ***state variables*** or ***state functions*** or ***thermodynamic parameters***. The change in the state properties depends only upon the ***initial and final states of the system***, but is independent of the manner in which the change has been brought about. In other words, the state properties do not depend upon a path followed.

Following are the state functions that are commonly used to describe the state of the system

(i) Pressure (P)	(ii) Temperature (T)	(iii) Volume (V)	(iv) Internal energy (E)
(v) Enthalpy (H)	(vi) Entropy (S)	(vii) Free energy (G)	(viii) Number of moles (n)

(5) **Thermodynamic equilibrium :** *"A system is said to have attained a state of thermodynamic equilibrium when it shows no further tendency to change its property with time".*

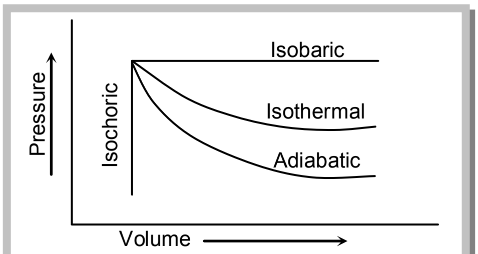
The criterion for thermodynamic equilibrium requires that the following three types of equilibrium exist simultaneously in a system.

(i) ***Chemical Equilibrium*** : A system in which the composition of the system remains fixed and definite.

(ii) ***Mechanical Equilibrium*** : No chemical work is done between different parts of the system or between the system and surrounding. It can be achieved by keeping pressure constant.

(iii) ***Thermal Equilibrium*** : Temperature remains constant *i.e.* no flow of heat between system and surrounding.

(6) **Thermodynamic process** : When the thermodynamic system changes from one state to another, the operation is called a **process**. The various types of the processes are



Graphical representation of four basic thermodynamic process

(i) ***Isothermal process*** : The process is termed ***isothermal*** if temperature remains fixed, *i.e.*, operation is done at constant temperature. This can be achieved by placing the system in a constant temperature bath, *i.e.*, thermostat. For an isothermal process $dT = 0$, *i.e.*, heat is exchanged with the surroundings and the system is not thermally isolated.

(ii) ***Adiabatic process*** : If a process is carried out under such condition that no exchange of heat takes place between the system and surroundings, the process is termed ***adiabatic.*** The system is thermally isolated, i.e., $dQ = 0$. This can be done by keeping the system in an insulated container, i.e., thermos flask. In adiabatic process, the temperature of the system varies.

(iii) ***Isobaric process*** : The process is known as ***isobaric*** in which the pressure remains constant throughout the change i.e., $dP = 0$.

(iv) ***Isochoric process*** : The process is termed as ***isochoric*** in which volume remains constant throughout the change, i.e., $dV = 0$.

(v) ***Cyclic process*** : When a system undergoes a number of different processes and finally return to its initial state, it is termed ***cyclic process***. For a cyclic process $dE = 0$ and $dH = 0$.

(vi) ***Reversible process*** : A process which occurs infinitesimally slowly, i.e. opposing force is infinitesimally smaller than driving force and when infinitesimal increase in the opposing force can reverse the process, it is said to be ***reversible process***.

(vii) ***Irreversible process*** : When the process occurs from initial to final state in single step in finite time and cannot be reversed, it is termed an ***irreversible process***. Amount of entropy increases in irreversible process.

Irreversible processes are spontaneous in nature. All natural processes are irreversible in nature

Difference between reversible and irreversible process

Reversible process	***Irreversible process***
It is an ideal process and takes infinite time.	**It is a spontaneous process and takes finite time.**
The driving force is infinitesimally greater than the opposing force.	**The driving force is much greater than the opposing force.**
It is in equilibrium at all stages.	**Equilibrium exists in the initial and final stages only.**
Obtained work is maximum.	**Obtained work is not maximum**
It is difficult to realise in practice.	**It can be performed in practice.**

Internal energy, Heat and work.

(1) **Internal energy** (E) : "*Every system having some quantity of matter is associated with a definite amount of energy. This energy is known as internal energy.*" The exact value of this energy is not known as it includes all types of energies of molecules constituting the given mass of matter such as translational vibrational, rotational, the kinetic and potential energy of the nuclei and electrons within the individual molecules and the manner in which the molecules are linked together, etc.

$$E = E_{\text{translational}} + E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{bonding}} + E_{\text{electronic}} + \ldots\ldots$$

(i) ***Characteristics of internal energy***

(a) Internal energy of a system is an extensive property.

(b) Internal energy is a state property.

(c) The change in the internal energy does not depend on the path by which the final state is reached.

(d) There is no change in internal energy in a cyclic process.

(e) The internal energy of an ideal gas is a function of temperature only.

(f) Internal energy of a system depends upon the quantity of substance, its chemical nature, temperature, pressure and volume.

(g) The units of E are ergs (in CGS) or joules (in SI)

$$1\ Joule = 10^7\ ergs.$$

(ii) ***Change in internal energy*** (ΔE) : It is neither possible nor necessary to calculate the absolute value of internal energy of a system. In thermodynamics, one is concerned only with energy change which occurs when the system moves from one state to another. Let ΔE be the difference of energy of the initial state (E_{in}) and the final state (E_f), then, $\boxed{\Delta E = E_f - E_{in}}$; ΔE is positive if $E_f > E_{in}$ and negative if $E_f < E_{in}$.

(2) **Heat** (q) **and Work** (w) **:** The energy of a system may increase or decrease in several ways but two common ways are *heat and work*.

Heat is a form of energy. It flows from one system to another because of the difference in temperature. Heat flows from higher temperature to lower temperature. Therefore, it is regarded as ***energy on the move.***

Work is said to be performed if the point of application of force is displaced in the direction of the force. It is equal to the force multiplied by the displacement (distance through which the force acts).

There are three main types of work which we generally come across. These are, Gravitational work, electrical work and mechanical work. Gravitational work is said to be done when a body is raised through a certain height (h) against the gravitational field (g).

Electrical work is important in systems where reaction takes place between ions whereas mechanical work is performed when a system changes its volume in the presence of external pressure. Mechanical work is important specially in systems that contain gases. This is also known as ***pressure - volume work.***

Note :✸ *Heat is a random form of energy while work is an organised form of energy.*

(i) ***Units of Heat and Work*** **:** The heat changes are measured in calories (cal), Kilo calories (kcal), joules (J) or kilo joules (kJ). These are related as, 1 cal = 4.184 J; 1 $kcal$ = 4.184 kJ

The *S.I.* unit of heat is joule (J) or *kilojoule*. The Joule (J) is equal to *Newton – metre* (1 J= 1 Nm).

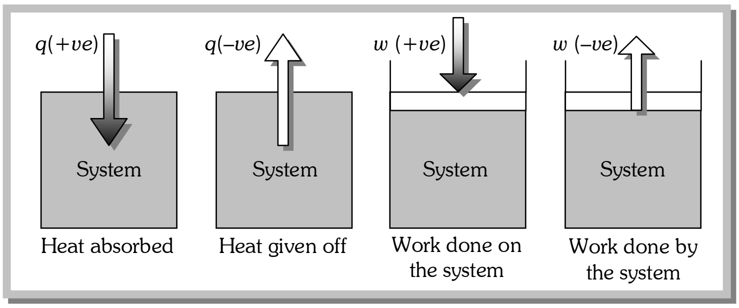
Work is measured in terms of ergs or joules. The *S.I.* unit of work is Joule.

$$1\ Joule = 10^7\ ergs = 0.2390\ cal.$$

$$1\ cal > 1\ joule > 1\ erg$$

(ii) ***Sign conventions for heat and work*** **:** It is very important to understand the sign conventions for q and w. The signs of w or q are related to the internal energy change. When w or q is positive, it means that energy has been supplied to the system as work or as heat. The internal energy of the system in such a case increases.

When w or q is negative, it means that energy has left the system as work or as heat. The internal energy of the system in such a case decreases.



Thus, to summarise,

Heat absorbed by the system = ***q* positive** ; Heat evolved by the system = ***q* negative**

Work done on the system = ***w* positive** ; Work done by the system = ***w* negative**.

Zeroth law of thermodynamics.

This law was formulated after the first and second laws of thermodynamics have been enunciated. ***This law forms the basis of concept of temperature.*** This law can be stated as follows,

"If a system A is in thermal equilibrium with a system C and if B is also in thermal equilibrium with system C, then A and B are in thermal equilibrium with each other whatever the composition of the system."

$$\boxed{A} \rightleftharpoons \boxed{C} \qquad \boxed{B} \rightleftharpoons \boxed{C}$$

First law of Thermodynamics.

First law of thermodynamics was proposed by ***Helmholtz*** and ***Robert Mayer.*** This law is also known as ***law of conservation of energy.*** It states that,

"Energy can neither be created nor destroyed although it can be converted from one form into another."

(1) Justification for the law : The first law of thermodynamics has ***no theoretical proof.*** This law is based on human experience and has not yet been violated. The following observations justify the validity of this law

(i) The total energy of an isolated system remains constant although it can undergo a change from one form to another.

(ii) It is not possible to construct a perpetual machine which can do work without the expenditure of energy, If the law were not true, it would have been possible to construct such a machine.

(iii) ***James Joule*** (1850) conducted a large number of experiments regarding the conversion of work into heat energy. He concluded that for every 4.183 joule of work done on the system, one calorie of heat is produced. He also pointed out that the same amount of work done always produces same amount of heat irrespective of how the work is done.

(iv) Energy is conserved in chemical reactions also. For example, the electrical energy equivalent to 286.4 *kJ mol*$^{-1}$ of energy is consumed when one mole of water decomposes into gaseous hydrogen and oxygen. On the other hand, the same amount of energy in the form of heat is liberated when one mole of liquid water is produced from gases hydrogen and oxygen.

$$H_2O(l) + 286.4\,kJ \longrightarrow H_2(g) + \frac{1}{2}O_2(g)\,;\, H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) + 286.4\,kJ$$

These examples justify that energy is always conserved though it may change its form.

(2) Mathematical expression for the law : The internal energy of a system can be changed in two ways

(i) By allowing heat to flow into the system or out of the system.

(ii) By doing work on the system or by the system.

Let us consider a system whose internal energy is E_1. Now, if the system absorbs q amount of heat, then the internal energy of the system increases and becomes $E_1 + q$.

If work (w) is done on the system, then its internal energy further increases and becomes E_2. Thus,

$$E_2 = E_1 + q + w \text{ or } E_2 - E_1 = q + w \text{ or } \Delta E = q + w$$

i.e. **(Change in internal energy) = (Heat added to the system) + (Work done on the system)**

If a system does work (w) on the surroundings, its internal energy decreases. In this case, work is taken as negative $(-w)$. Now, q is the amount of heat added to the system and w is the work done by the system, then change in internal energy becomes, $\Delta E = q + (-w) = q - w$

i.e. **(Change in internal energy) = (Heat added to the system) – (Work done by the system)**

The relationship between internal energy, work and heat is a mathematical ***statement of first law of thermodynamics.***

(3) Some useful conclusions drawn from the law : $\boxed{\Delta E = q + w}$

(i) When a system undergoes a change $\Delta E = 0$, *i.e.*, there is no increase or decrease in the internal energy of the system, the first law of thermodynamics reduces to

$$0 = q + w \quad \text{or} \quad q = -w$$

(heat absorbed from surroundings = work done by the system)

$$\text{or } w = -q$$

(heat given to surroundings = work done on the system)

(ii) If no work is done, $w = 0$ and the first law reduces to

$$\Delta E = q$$

i.e. increase in internal energy of the system is equal to the heat absorbed by the system or decrease in internal energy of the system is equal to heat lost by the system.

(iii) If there is no exchange of heat between the system and surroundings, $q = 0$, the first law reduces to

$$\Delta E = w$$

It shows if work is done on the system, its internal energy will increase or if work is done by the system its internal energy will decrease. This occurs in an adiabatic process.

(iv) In case of gaseous system, if a gas expands against the constant external pressure *P*, let the volume change be ΔV. The mechanical work done by the gas is equal to $-P \times \Delta V$.

Substituting this value in $\Delta E = q + w$; $\Delta E = q - P\Delta V$

When, $\Delta V = 0$, $\Delta E = q$ or q_v

The symbol q_v indicates the heat change at constant volume.

(4) Limitations of the law : The first law of thermodynamics states that when one form of energy disappears, an equivalent amount of another form of energy is produced. But ***it is silent about the extent to which such conversion can take place.*** The first law of thermodynamics has some other limitations also.

(i) It puts no restriction on the direction of flow of heat. But, heat flows spontaneously from a higher to a lower temperature.

(ii) It does not tell whether a specified change can occur spontaneously or not.

(iii) It does not tell that heat energy cannot be completely converted into an equivalent amount of work without producing some changes elsewhere.

Enthalpy and Enthalpy change.

Heat content of a system at constant pressure is called ***enthalpy*** denoted by '*H*'.

From first law of thermodynamics, $q = E + PV$ ....(i)

Heat change at constant pressure can be given as

$$\Delta q = \Delta E + P\Delta V \qquad \text{..........(ii)}$$

At constant pressure heat can be replaced at enthalpy.

$$\boxed{\Delta H = \Delta E + P\Delta V} \qquad \text{...........(iii)}$$

Constant pressures are common in chemistry as most of the reactions are carried out in open vessels.

At constant volume, $\Delta V = 0$; thus equation (ii) can be written as,

$$\Delta q_v = \Delta E$$

$\therefore \Delta H =$ Heat change or heat of reaction (in chemical process) at constant pressure

$\Delta E =$ Heat change or heat of reaction at constant volume.

(1) In case of solids and liquids participating in a reaction,

$$\Delta H = \Delta E (P\Delta V \approx 0)$$

(2) Difference between ΔH and ΔE is significant when gases are involved in chemical reaction.

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

$$\boxed{\Delta H = \Delta E + \Delta nRT}$$

$$P\Delta V = \Delta nRT$$

Here, $\Delta n =$ Number of gaseous moles of products – Number of gaseous moles of reactants.

Using the above relation we can interrelate heats of reaction at constant pressure and at constant volume.

Specific and Molar heat capacity.

(1) **Specific heat** (or specific heat capacity) of a substance is the quantity of heat (in *calories*, *joules*, *kcal*, or *kilo joules*) required to raise the temperature of 1*g* of that substance through $1^o C$. It can be measured at constant pressure (c_p) and at constant volume (c_v).

(2) **Molar heat capacity** of a substance is the quantity of heat required to raise the temperature of 1 *mole* of the substance by $1^o C$.

$\therefore$ Molar heat capacity = Specific heat capacity × Molecular weight, *i.e.*,

$$C_v = c_v \times M \text{ and } C_p = c_p \times M.$$

(3) Since gases on heating show considerable tendency towards expansion if heated under constant pressure conditions, an additional energy has to be supplied for raising its temperature by $1^o C$ relative to that required under constant volume conditions, *i.e.*,

$$C_p > C_v \text{ or } C_p = C_v + \text{Work done on expansion, } P\Delta V (= R)$$

where, C_p = molar heat capacity at constant pressure; C_v = molar heat capacity at constant volume.

Note : ✹ *C_p and C_v for solids and liquids are practically equal. However, they differ considerable in case of gas because appreciable change in volume takes place with temperature.*

(4) **Some useful relations of C_p and C_v**

(i) $C_p - C_v = R = 2\,calories = 8.314 J$

(ii) $C_v = \frac{3}{2}R$ (for monoatomic gas) and $C_v = \frac{3}{2} + x$ (for *di* and polyatomic gas), where *x* varies from gas to gas.

(iii) $\frac{C_p}{C_v} = \gamma$ (Ratio of molar capacities)

(iv) For monoatomic gas $C_v = 3\,calories$ whereas, $C_p = C_v + R = 5 calories$

(v) For monoatomic gas, $(\gamma) = \frac{C_p}{C_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = 1.66$

(vi) For diatomic gas $(\gamma) = \frac{C_p}{C_v} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = 1.40$

(vii) For triatomic gas $(\gamma) = \dfrac{C_p}{C_v} = \dfrac{8R}{6R} = 1.33$

Values of Molar heat capacities of some gases,

Gas	C_p	C_v	$C_p - C_v$	$C_p/C_v = \gamma$	Atomicity
He	**5**	**3.01**	**1.99**	**1.661**	**1**
N_2	**6.95**	**4.96**	**1.99**	**1.4**	**2**
O_2	**6.82**	**4.83**	**1.99**	**1.4**	**2**
CO_2	**8.75**	**6.71**	**2.04**	**1.30**	**3**
H_2S	**8.62**	**6.53**	**2.09**	**1.32**	**3**

Expansion of an Ideal gas.

(1) **Isothermal Expansion** : For an isothermal expansion, temperature remains fixed *i.e.* $\Delta E = 0$ (ΔE of ideal gases depends only on temperature)

According to first law of thermodynamics,

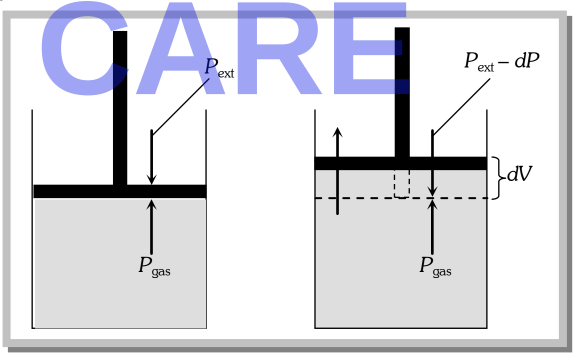
$$\Delta E = q + w$$

$$\therefore q = -w$$

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

Since for isothermal process, ΔE and ΔT are zero respectively, hence, $\Delta H = 0$

(i) ***Work done in reversible isothermal expansion*** : Consider an ideal gas enclosed in a cylinder fitted with a weightless and frictionless piston. The cylinder is not insulated. The external pressure, P_{ext} is equal to pressure of the gas, P_{gas}. Let it be P.



$$P_{ext} = P_{gas} = P$$

If the external pressure is decreased by an infinitesimal amount dP, the gas will expand by an infinitesimal volume, dV. As a result of expansion, the pressure of the gas within the cylinder falls to $P_{gas} - dP$, *i.e.*, it becomes again equal to the external pressure and, thus, the piston comes to rest. Such a process is repeated for a number of times, *i.e.*, in each step the gas expands by a volume dV.

Since the system is in thermal equilibrium with the surroundings, the infinitesimally small cooling produced due to expansion is balanced by the absorption of heat from the surroundings and the temperature remains constant throughout the expansion.

The work done by the gas in each step of expansion can be given as,

$$d_w = -(P_{ext} - dP)dV = -P_{ext}.dV = -PdV$$

$dP.dV$, the product of two infinitesimal quantities, is neglected.

The total amount of work done by the isothermal reversible expansion of the ideal gas from volume V_1 to volume V_2 is, given as,

$$w = -nRT\log_e \frac{V_2}{V_1} \quad \text{or} \quad \boxed{w = -2.303nRT\log_{10}\frac{V_2}{V_1}}$$

At constant temperature, according to Boyle's law,

$$P_1V_1 = P_2V_2 \text{ or } \frac{V_2}{V_1} = \frac{P_1}{P_2} \text{ So, } \boxed{w = -2.303nRT\log_{10}\frac{P_1}{P_2}}$$

Isothermal compression work of an ideal gas may be derived similarly and it has exactly the same value with positive sign.

$$\boxed{w_{compression} = 2.303nRT\log\frac{V_1}{V_2} = 2.303nRT\log\frac{P_2}{P_1}}$$

(ii) ***Work done in irreversible isothermal expansion :*** Two types of irreversible isothermal expansions are observed, *i.e.,* (a) Free expansion and (b) Intermediate expansion. In free expansion, the external pressure is zero, *i.e.,* work done is zero when gas expands in vacuum. In intermediate expansion, the external pressure is less than gas pressure. So, the work done when volume changes from V_1 to V_2 is given by

$$w = -\int_{V_1}^{V_2} P_{ext} \times dV = -P_{ext}(V_2 - V_1)$$

Since P_{ext} is less than the pressure of the gas, the work done during intermediate expansion is numerically less than the work done during reversible isothermal expansion in which P_{ext} is almost equal to P_{gas}.

Note : ✹ *The work done by the system always depends upon the external pressure. The higher the value of P_{ext}, the more work is done by the gas. As P_{ext} cannot be more than P_{gas}, otherwise compression will occur, thus the largest value of P_{ext} can be equal to P_{gas}. Under this condition when expansion occurs, the maximum work is done by the gas on the surroundings.*

(2) **Adiabatic Expansion :** In adiabatic expansion, no heat is allowed to enter or leave the system, hence, $q = 0$.

According to first law of thermodynamics,

$$\Delta E = q + w$$

$$\therefore \quad \Delta E = w$$

work is done by the gas during expansion at the expense of internal energy. In expansion, ΔE decreases while in compression ΔE increases.

The molar specific heat capacity at constant volume of an ideal gas is given by

$$C_v = \left(\frac{dE}{dT}\right)_v \text{ or } dE = C_v.dT$$

and for finite change $\Delta E = C_v \Delta T$ So, $\boxed{w = \Delta E = C_v \Delta T}$

The value of ΔT depends upon the process whether it is reversible or irreversible.

(i) ***Reversible adiabatic expansion :*** The following relationships are followed by an ideal gas under reversible adiabatic expansion.

$$\boxed{PV^{\gamma} = \text{constant}}$$

where, P = External pressure, V = Volume

$$\boxed{\gamma = \frac{C_p}{C_v}}$$

where, C_p = molar specific heat capacity at constant pressure, C_v = molar specific heat capacity at constant volume.

$$\boxed{\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_1}{P_2}\right)^{\gamma-1} = \left(\frac{P_2}{P_1}\right)^{1-\gamma}}$$

knowing γ, P_1, P_2 and initial temperature T_1, the final temperature T_2 can be evaluated.

(ii) **Irreversible adiabatic expansion :** In free expansion, the external pressure is zero, *i.e,* work done is zero. Accordingly, ΔE which is equal to w is also zero. If ΔE is zero, ΔT should be zero. Thus, in free expansion (adiabatically), $\Delta T = 0$, $\Delta E = 0$, $w = 0$ and $\Delta H = 0$.

In intermediate expansion, the volume changes from V_1 to V_2 against external pressure, P_{ext}.

$$w = -P_{ext}(V_2 - V_1) = -P_{ext}\left(\frac{RT_2}{P_2} - \frac{RT_1}{P_1}\right) = -P_{ext}\left(\frac{T_2P_1 - T_1P_2}{P_1P_2}\right) \times R$$

$$\text{or } w = C_v(T_2 - T_1) = -RP_{ext}\left(\frac{T_2P_1 - T_1P_2}{P_1P_2}\right)$$

Example 1. The work done in ergs for the reversible expansion of one mole of an ideal gas from a volume of 10 litres to 20 litres at 25° C is **[CMC Vellore 1991]**

(a) $2.303 \times 298 \times 0.082 \log 2$
(b) $-298 \times 10^7 \times 8.31 \times 2.303 \log 2$
(c) $2.303 \times 298 \times 0.082 \log 0.5$
(d) $2.303 \times 298 \times 2 \log 2$

Solution: (b) $w = -2.303 nRT \log \frac{V_2}{V_1} = -2.303 \times 1 \times 8.31 \times 10^7 \times 298 \log \frac{20}{10} = -298 \times 10^7 \times 8.31 \times 2.303 \log 2$

Example 2. An ideal gas expands from $10^{-3}\ m^3$ to $10^{-2}\ m^3$ at 300 *K* against a constant pressure of $10^5\ Nm^{-2}$. The work done is

(a) $-10^3\ kJ$
(b) $10^2\ kJ$
(c) $0.9\ kJ$
(d) $-900\ kJ$

Solution: (c) $w = -P(V_2 - V_1) = -10^5(10^{-2} - 10^{-3}) = -10^5 \times 10^{-2}(1 - 0.1) = -0.9 \times 10^3\ J = -0.9\ kJ$

Example 3. At 27°C one mole of an ideal gas is compressed isothermally and reversibly from a pressure of 2 atm to 10 atm. The values of ΔE and q are (R = 2) **[BHU 2001]**

(a) 0, –965.84 *cal*
(b) – 965.84 *cal*, + 965.84 *cal*
(c) + 865.58 *cal*, –865.58 *cal*
(d) –865.58 *cal*, –865.58 *cal*

Solution: (a) $w = -2.303 nRT \log \frac{P_1}{P_2} = 2.303 \times 1 \times 2 \times 300 \log \frac{2}{10} = 965.84$

At constant temperature $\Delta E = 0$

$\Delta E = q + w$; $q = -w = -965.84 cal$

Example 4. The work done by a system is 8 *joule*, when 40 *joule* heat is supplied to it, what is the increase in internal energy of system **[BHU 2001]**

(a) 25 *J*
(b) 30 *J*
(c) 32 *J*
(d) 28 *J*

Solution: (c) $q = 40J$

$w = -8J$ (work done by the system)

$\Delta E = q + w = 40 - 8 = 32J$

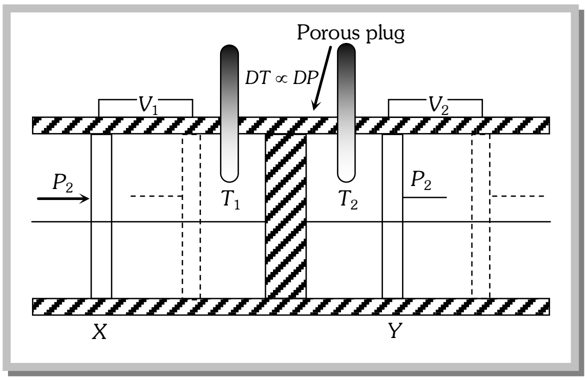
Example 5. One mole of an ideal gas is allowed to expand reversibly and adiabatically from a temperature of 27° C. If the work done during the process is 3 *kJ*, the final temperature will be equal to ($C_v = 20\ JK^{-1}$) **[KCET 2000]**

(a) 150 *K*
(b) 100 *K*
(c) 26.85 *K*
(d) 295 *K*

Solution: (a) Work done during adiabatic expansion = $C_v(T_2 - T_1)$

$-3000 = 20(T_2 - 300)$ or $T_2 = 150\,K$.

Joule – Thomson effect.



The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure, is known as Joule-Thomson effect.

During this process, enthalpy remains constant. It is, therefore, called ***isoenthalpic process.***

The actual change in temperature on expansion of the gas is expressed in terms of ***Joule–Thomson coefficient*** (μ), defined as

$$\boxed{\mu = \left(\frac{\partial T}{\partial P}\right)_H}$$

i.e. it is the temperature change in degrees produced by a drop of one atmospheric pressure when the gas expands under conditions of constant enthalpy.

(1) For cooling, $\mu = +ve$ (because dT and dP both will be $-\,ve$)

(2) For heating, $\mu = -ve$ (because $dT = +ve$, $dP = -\,ve$)

(3) $\mu = 0$ means $dT = 0$ for any value of dP, *i.e.*, there is neither cooling nor heating.

The temperature at which a real gas shows no cooling or heating effect on adiabatic expansion (i.e. $\mu = 0$), is called ***Inversion temperature***. Below this temperature it shows cooling effect while above this temperature, it shows heating effect.

Most of the gases have inversion temperature above room temperature. H_2 and He have low inversion temperatures (being – 80°C and –240°C respectively). That is why they show heating effect at room temperature.

Spontaneous and Non-spontaneous processes.

(1) Definition : A process which can take place by itself under the given set of conditions once it has been initiated if necessary, is said to be a ***spontaneous process.*** In other words, a spontaneous process is a process that can occur without work being done on it. The spontaneous processes are also called ***feasible*** or ***probable processes.***

On the other hand, the processes which are forbidden and are made to take place only by supplying energy continuously from outside the system are called ***non-spontaneous processes.*** In other words, non spontaneous processes can be brought about by doing work.

Note :✹ *A spontaneous process is unidirectional and irreversible.*

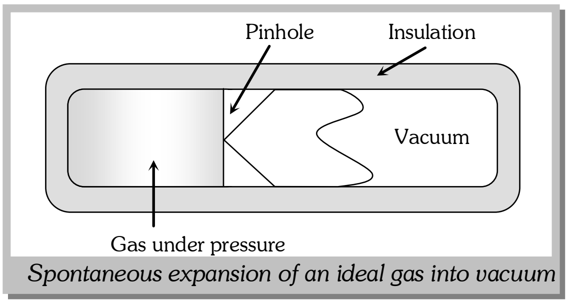
(2) Examples of Spontaneous and Non-spontaneous processes

(i) A river flows from a mountain towards the sea is spontaneous process.

(ii) Heat flows from a conductor at high temperature to another at low temperature is spontaneous process.

(iii) A ball rolls down the hill is spontaneous process.

(iv) The diffusion of the solute from a concentrated solution to a dilute solution occurs when these are brought into contact is spontaneous process.



Spontaneous expansion of an ideal gas into vacuum

(v) Mixing of different gases is spontaneous process.

(vi) Heat flows from a hot reservoir to a cold reservoir is spontaneous process.

(vii) Electricity flows from high potential to low potential is spontaneous process.

(viii) Expansion of an ideal gas into vacuum through a pinhole is spontaneous process.

All the above spontaneous processes becomes non-spontaneous when we reverse them by doing work.

(3) **Spontaneous process and Enthalpy change :** A spontaneous process is accompanied by decrease in internal energy or enthalpy, *i.e.*, work can be obtained by the spontaneous process. It indicates that only exothermic reactions are spontaneous. But the melting of ice and evaporation of water are endothermic processes which also proceeds spontaneously. It means, there is some other factor in addition to enthalpy change (ΔH) which explains the spontaneous nature of the system. This factor is entropy.

Second law of thermodynamics.

All the limitations of the first law of thermodynamics can be remove by the second law of thermodynamics. This law is generalisation of certain experiences about heat engines and refrigerators. It has been stated in a number of ways, but all the statements are logically equivalent to one another.

(1) Statements of the law

(i) ***Kelvin statement :*** *"It is impossible to derive a continuous supply of work by cooling a body to a temperature lower than that of the coldest of its surroundings."*

(ii) ***Clausius statement :*** *"It is impossible for a self acting machine, unaided by any external agency, to convert heat from one body to another at a higher temperature* ***or*** *Heat cannot itself pass from a colder body to a hotter body, but tends invariably towards a lower thermal level."*

(iii) ***Ostwald statement :*** *"It is impossible to construct a machine functioning in cycle which can convert heat completely into equivalent amount of work without producing changes elsewhere, i.e., perpetual motions are not allowed."*

(iv) ***Carnot statement:*** *"It is impossible to take heat from a hot reservoir and convert it completely into work by a cyclic process without transferring a part of it to a cold reservoir."*

(2) **Proof of the law :** No rigorous proof is available for the second law. The formulation of the second law is based upon the observations and has yet to be disproved. No deviations of this law have so far been reported. However, the law is applicable to cyclic processes only.

Conversion of heat into work: The Carnot cycle.

Carnot, a *French engineer*, in 1824 employed merely theoretical and an imaginary reversible cycle known as carnot cycle to demonstrate the maximum convertibility of heat into work.

The system consists of one mole of an ideal gas enclosed in a cylinder fitted with a piston, which is subjected to a series of four successive operations. The four operations are

(1) Isothermal reversible expansion, $q_2 = -w_1 = RT_2 \log_e \frac{V_2}{V_1}$ .....(i)

(2) Adiabatic reversible expansion, $\Delta E = -w_2 = -C_v(T_2 - T_1)$ .....(ii)

(3) Isothermal reversible compression, $-q_1 = w_3 = RT_1 \log e \frac{V_4}{V_3}$ .....(iii)

(4) Adiabatic reversible compression, $w_4 = C_v(T_2 - T_1)$ .....(iv)

The net heat absorbed, q, by the ideal gas in the cycle is given by

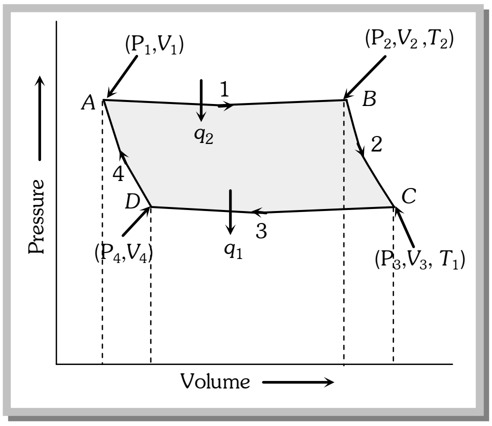
$$q = q_2 + (-q_1) = RT_2 \log_e \frac{V_2}{V_1} + RT_1 \log_e \frac{V_4}{V_3} = RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_3}{V_4} \qquad \text{......(v)}$$

According to the expression governing adiabatic changes,

$$\frac{T_2}{T_1} = \left(\frac{V_3}{V_2}\right)^{\gamma-1} \qquad \text{(For adiabatic expansion)}$$

$$\frac{T_1}{T_2} = \left(\frac{V_1}{V_4}\right)^{\gamma-1} \qquad \text{(For adiabatic compression)}$$

or $\frac{V_3}{V_2} = \frac{V_4}{V_1}$ or $\frac{V_2}{V_1} = \frac{V_3}{V_4}$



Substituting the value of $\frac{V_3}{V_4}$ in eq. (v),

$$q = q_2 - q_1 = RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_2}{V_1}$$

$$q_2 = R(T_2 - T_1)\log_e \frac{V_2}{V_1} \qquad \text{......(vi)}$$

Similarly, net work done by the gas is given by

$$w = -w_1 - w_2 + w_3 + w_4$$

So, $w = R(T_2 - T_1)\log_e \frac{V_2}{V_1}$ ......(vii)

Thus, $q = w$. For cyclic process, the essential condition is that net work done is equal to heat absorbed. This condition is satisfied in a carnot cycle. Dividing Equation (vii) by (vi) we get,

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2} = \text{Thermodynamic efficiency}$$

Thus, the larger the temperature difference between high and low temperature reservoirs, the more the heat converted into work by the heat engine.

Since $\frac{T_2 - T_1}{T_2} < 1$, it follows that $w < q_2$. This means that only a part of heat absorbed by the system at the higher temperature is transformed into work. The rest of the heat is given out to surroundings. The efficiency of the heat engine is always less then 1. This has led to the following enunciation of the second law of thermodynamics.

It is impossible to convert heat into work without compensation.

Example 6. An engine operating between 150°C and 25°C takes 500 J heat from a higher temperature reservoir if there are no frictional losses then work done by engine is **[MH CET 1999]**

(a) 147.7J (b) 157.75 J (c) 165.85J (d) 169.95J

Solution: (a) $T_2 = 150 + 273 = 423K$

$T_1 = 25 + 273 = 298K$

$q_2 = 500J$

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2}$$

$$w = 500\left[\frac{423-298}{423}\right] = 147.7J$$

Example 7. Find out the working capacity of an engine which is working between 110° to 25°C, if temperature of boyler is increased up to 140°C and sink temperature equal to its.

(a) I – 20.2%, II – 18% (b) I – 22.2%, II - 27.8% (c) I – 28%, II – 30% (d) None of these

Solution:(b) First condition

$$T_2 = 110^\circ C = 110 + 273K = 383K \qquad \eta = ?$$

$$T_1 = 25^\circ C = 25 + 273K = 298K$$

$$\eta = \frac{T_2 - T_1}{T_2} = \frac{383-298}{383} = 0.222 \text{ or } 22.2\%$$

Second condition

$$T_2 = 140^\circ C = 140 + 273K = 413K \qquad \eta = ?$$

$$T_1 = 25^\circ C = 25 + 273K = 298K$$

$$\eta = \frac{T_2 - T_1}{T_2} = \frac{413-298}{413} = 0.278 \text{ or } 27.8\%$$

Entropy and Entropy change.

(1) Definition : Entropy is a thermodynamic state quantity which is a measure of randomness or disorder of the molecules of the system.

Entropy is represented by the symbol "S". It is difficult to define the actual entropy of a system. It is more convenient to define the change of entropy during a change of state.

The entropy change of a system may be defined as the integral of all the terms involving heat exchanged (q) divided by the absolute temperature (T) during each infinitesimally small change of the process carried out reversibly at constant temperature.

$$\boxed{\Delta S = S_{final} - S_{initial} = \frac{q_{rev}}{T}}$$

If heat is absorbed, then $\Delta S = +ve$ and if heat is evolved, then $\Delta S = -ve$.

(2) Units of entropy : Since entropy change is expressed by a heat term divided by temperature, it is expressed in terms of ***calorie per degree, i.e.,*****cal deg^{-1}** . In *SI* units, the entropy is expressed in terms of joule per degree Kelvin, i.e., JK^{-1}.

(3) Characteristics of entropy : The important characteristics of entropy are summed up below

(i) Entropy is an extensive property. Its value depends upon the amount of the substance present in the system.

(ii) Entropy of a system is a state function. It depends upon the state variables (T, p, V, n).

(iii) The change in entropy in going from one state to another is independent of the path.

(iv) The change in entropy for a cyclic process is always zero.

(v) The total entropy change of an isolated system is equal to the entropy change of system and entropy change of the surroundings. The sum is called ***entropy change of universe***.

$$\Delta S_{\text{universe}} = -\Delta S_{sys} + \Delta S_{Surr}$$

(a) In a reversible process, $\Delta S_{universe} = 0$ and, therefore

$$\Delta S_{sys} = -\Delta S_{Surr}$$

(b) In an irreversible process, $\Delta S_{universe} > 0$. This means that there is increase in entropy of universe is spontaneous changes.

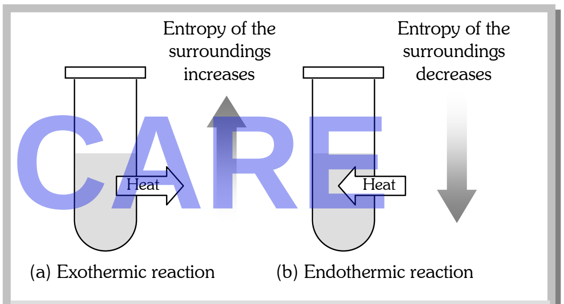
(vi) Entropy is a measure of unavailable energy for useful work.

$$\text{Unavailable energy} = \text{Entropy} \times \text{Temperature}$$

(vii) Entropy, S is related to thermodynamic probability (W) by the relation,

$$\boxed{S = k\log_e W \text{ and } \mathrm{S} = 2.303\mathrm{k}\log_{10} W}$$; where, k is Boltzmann's constant

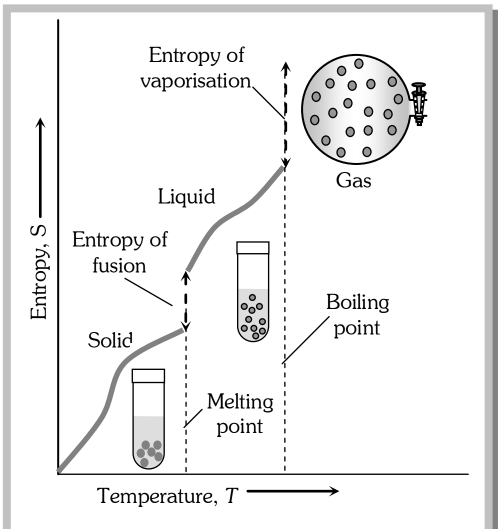
(4) Entropy changes in system & surroundings and total entropy change for Exothermic and Endothermic reactions : Heat increases the thermal motion of the atoms or molecules and increases their disorder and hence their entropy. In case of an exothermic process, the heat escapes into the surroundings and therefore, entropy of the surroundings increases on the other hand in case of endothermic process, the heat enters the system from the surroundings and therefore. The entropy of the surroundings decreases.



(a) Exothermic reaction (b) Endothermic reaction

Entropy changes in (a) exothermic and (b) endothermic processes

In general, there will be an overall increase of the total entropy (or disorder) whenever the disorder of the surroundings is greater than the decrease in disorder of the system. The process will be ***spontaneous only when the total entropy increases***.



Increase in disorder or entropy when a solid change to liquid to gas

(5) Entropy change during phase transition : The change of matter from one state (solid, liquid or gas) to another is called ***phase transition***. Such changes occur at definite temperature such as melting point (solid to liquid). boiling point (liquid to vapours) etc, and are accompanied by absorption or evolution of heat.

When a solid changes into a liquid at its fusion temperature, there is absorption of heat (latent heat). Let ΔH_f be the molar heat of fusion. The entropy change will be

$$\boxed{\Delta S_f = \frac{\Delta H_f}{T_f}}$$

Similarly, if the latent heat of vaporisation and sublimation are denoted by ΔH_{vap} and ΔH_{sub}, respectively, the entropy of vaporisation and sublimation are given by

$\boxed{\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}}$ and $\boxed{\Delta S_{sub} = \frac{\Delta H_{sub}}{T_s}}$

Since $\Delta H_f, \Delta H_{vap}$ and ΔH_{Sub} are all positive, these processes are accompanied by increase of entropy.

The reverse processes are accompanied by decrease in entropy.

Note : ✹ *Entropy increases not only in phase transition but also when the number of moles of products is greater than the number of moles of reactants.* $(n_{\text{product}} > n_{\text{reactant}}$ *i.e.*$\Delta n = +ve)$

(6) **Entropy change for an ideal gas :** In going from initial to final state, the entropy change, ΔS for an ideal gas is given by the following relations,

(i) When T and V are two variables, $\Delta S = nC_v \ \ln \frac{T_2}{T_1} + nR \ \ln \frac{V_2}{V_1}$. Assuming C_v is constant

(ii) When T and p are two variables, $\Delta S = nC_P \ \ln \frac{T_2}{T_1} - nR \ \ln \frac{p_2}{p_1}$. Assuming C_p, is constant

(a) Thus, for an *isothermal process* (T constant), $\Delta S = nR \ \ln \frac{V_2}{V_1}$ *or* $= -nR \ \ln \frac{p_2}{p_1}$

(b) For *isobaric process* (p constant), $\Delta S = nC_p \ln \frac{T_2}{T_1}$

(c) For *isochoric process* (*V* constant), $\Delta S = nC_v \ln \frac{T_2}{T_1}$

(d) *Entropy change during adiabatic expansion* : In such process *q=0* at all stages. Hence $\Delta S = 0$. Thus, reversible adiabatic processes are called *isoentropic process*.

Example 8. The enthalpy of vapourisation of a liquid is 30 *kJ mol*$^{-1}$ and entropy of vapourisation is 75*mol*$^{-1}$ *K*. The boiling point of the liquid at 1 *atm* is **[IIT JEE 2004]**

(a) 250 *K* (b) 400 *K* (c) 450 *K* (d) 600 *K*

Solution: (b) $\Delta S_v = \frac{\Delta H_v}{T_b}$ $30kJ = 30000\,J$

$\Delta H_v = 30000\,J$; $\Delta S_v = 75\,mole^{-1}K$; $T_b = \frac{30000}{75} = 400K$

Example 9. If 900 *J/g* of heat is exchanged at boiling point of water, then what is increase in entropy **[BHU 1998]**

(a) 43.4 *J/mole* (b) 87.2 *J/mole* (c) 900 *J/mole* (d) Zero

Solution: (a) Boiling point $(T_b) = 100°C = 373K$; $\Delta H_v = 900J/g$

$\Delta S_{vap} = \frac{\Delta H_v}{T}$; Molecular weight of water = 18

$\Delta S_{vap} = \frac{900 \times 18}{373} = 43.4JK^{-1}mol^{-1}$

Example 10. The standard entropies of $CO_2(g), C(s)$ and $O_2(g)$ are 213.5, 5.690 and 205 JK^{-1} respectively. The standard entropy of formation of $CO_2\,(g)$ is **[CPMT 2001]**

(a) 1.86 JK^{-1} (b) 1.96 JK^{-1} (c) 2.81 JK^{-1} (d) 2.86 JK^{-1}

Solution: (c) Formation of CO_2 is, $C(s) + O_2(g) \rightarrow CO_2(g)$

$\Delta S^0 = \Delta S^0{}_{\text{(product)}} - \Delta S^0{}_{\text{(reactants)}} = 213.5 - [5.690 + 205] = 2.81\,JK^{-1}$

Free energy and Free energy change.

Gibb's free energy (G) is a *state function* and is a measure of maximum work done or useful work done from a reversible reaction at constant temperature and pressure.

(1) Characteristics of free energy

(i) The free energy of a system is the enthalpy of the system minus the product of absolute temperature and entropy *i.e.*, $\boxed{G = H - TS}$

(ii) Like other state functions E, H and S, it is also expressed as ΔG. Also $\Delta G = \Delta H - T\Delta S_{system}$ where ΔS is entropy change for system only. This is ***Gibb's Helmholtz equation.***

(iii) At equilibrium $\Delta G = 0$

(iv) For a spontaneous process decrease in free energy is noticed *i.e.*, $\Delta G = -ve$.

(v) At absolute zero, $T\Delta S$ is zero. Therefore if ΔG is $-ve$, ΔH should be $-ve$ or only exothermic reactions proceed spontaneously at absolute zero.

(vi) $\Delta G_{system} = T\Delta S_{universe}$

(vii) The standard free energy change, $\Delta G^o = -2.303RT\log_{10}K$, where K is equilibrium constant.

(a) Thus if $K > 1$, then $\Delta G^o = -ve$ thus reactions with equilibrium constant $K>1$ are thermodynamically spontaneous.

(b) If $K<1$, then $\Delta G^o = +ve$ and thus reactions with equilibrium constant $K<1$ are thermodynamically spontaneous in reverse direction.

(2) Criteria for spontaneity of reaction : For a spontaneous change $\Delta G = -ve$ and therefore use of $\Delta G = \Delta H - T\Delta S$, provides the following conditions for a change to be spontaneous.

ΔH	ΔS	ΔG	***Reaction characteristics***	***Example***
–	+	**Always negative**	**Reaction is spontaneous at all temperatures**	$2O_{3(g)} \to 3O_{2(g)}$
+	–	**Always positive**	**Reaction is non spontaneous at all temperatures**	$3O_{2(g)} \to 2O_{3(g)}$
–	–	**Negative at low temperature but positive at high temperature**	**Reaction is spontaneous at low temperature but becomes non spontaneous at high temperature**	$CaO_{(s)} + CO_{2(g)} \to CaCO_{3(s)}$
+	+	**Positive at low temperature but negative at high temperature**	**Reaction is non spontaneous at low temperature but becomes spontaneous at high temperature**	$CaCO_{3(s)} \to CaO_{(s)} + CO_{2(g)}$

Example 11. For a reaction at 25°C enthalpy change and entropy change are $-11.7\times10^3\ J\ mol^{-1}$ and $-105 J\ mol^{-1}K^{-1}$ respectively, what is the Gibb's free energy. **[BHU 2001]**

(a) 15.05 kJ (b) 19.59 kJ (c) 2.55 kJ (d) 22.55 kJ

Solution: (b) $\Delta G = \Delta H - T\Delta S$, $T = 25 + 273 = 298K$

$$\Delta G = -11.7\times10^3 - 298\times(-105) = 19590J = 19.59\,kJ$$

Example 12. For reaction $Ag_2O(s) \to 2Ag(s) + \frac{1}{2}O_2(g)$ the value of $\Delta H = 30.56 kJ\ mol^{-1}$ and $\Delta S = 0.066 kJ\ mol^{-1}\ K^{-1}$. Temperature at which free energy change for reaction will be zero is **[MH CET 1999]**

(a) 373 K (b) 413 K (c) 463 K (d) 493 K

Solution: (c) $\Delta G = \Delta H - T\Delta S$

$\Delta H = 30.56 kJ\,mol^{-1}$; $\Delta S = 0.066\,kJmol^{-1}\,K^{-1}$; $\Delta G = 0$ at equilibrium; $T = ?$

$\therefore \Delta H = T\Delta S$ or $30.56 = T \times 0.066$

$T = 463\,K$

Example 13. The free energy change for the following reactions are given below

$C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$; $\Delta G^o = -1234 kJ$

$C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta G^o = -394 kJ$

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O\ (l)$; $\Delta G^o = -237 kJ$

What is the standard free energy change for the reaction $H_2(g) + 2C(s) \rightarrow C_2H_2(g)$ **[Kerala PMT 2002]**

(a) $-209\ kJ$ (b) $-2259\ kJ$ (c) $+2259\ kJ$ (d) $209\ kJ$

Solution : (a) $\Delta G = \Delta G^0{}_{\text{(Product)}} - \Delta G^0{}_{\text{(Reactants)}} = (-1234) - [-237 + 2(-394)] = -1234 + 1025 = -209 kJ$

Example 14. Calculate the free energy per mole when liquid water boils against 1 *atm* pressure $(\Delta H_{vap} = 2.0723\,kJ/g)$ **[DPMT 1995]**

(a) 0 (b) 0.2 (c) 0.3 (d) 0.4

Solution: (a) $\Delta H = 2.0723 \times 18 kJ/mole = 37.3 kJ/mole$; $T = 373K$; $\Delta G_{vap} = ?$

$$\Delta S = \frac{\Delta H_{vap}}{T} = \frac{37.3 kJ}{373} = 0.1 kJK^{-1}mol^{-1}$$

$$\Delta G_{vap} = \Delta H_{vap} - T\Delta S_{vap} = 37.3 - 373 \times 0.1 = 0$$

Example 15. ΔG^0 for the reaction $x + y = z$ is -4.606 *kcal*. The value of equilibrium constant of the reaction at $227^o C$ is $(R = 2.0\,kcal\,mol^{-1}K^{-1})$ **[Roorkee 1999]**

(a) 100 (b) 10 (c) 2 (d) 0.01

Solution: (a) $R = 2.0\,kcal\,mol^{-1}K^{-1}$; $T = 500\,K$; $\Delta G^0 = -4.606\,kcal$;

$\Delta G^0 = -2.303 RT \log K$

$-4.606 = -2.303 \times 0.002 \times 500 \log K$

$\log K = 2, K = 100$

Third law of thermodynamics.

This law was first formulated by German chemist ***Walther Nernst*** in 1906. According to this law,

"The entropy of all perfectly crystalline solids is zero at the absolute zero temperature. Since entropy is a measure of disorder, it can be interpreted that at absolute zero, a perfectly crystalline solid has a perfect order of its constituent particles."

The most important application of the third law of thermodynamics is that it helps in the calculation of absolute entropies of the substance at any temperature *T*.

$$\boxed{S = 2.303 C_p \log T}$$

Where Cp is the heat capacity of the substance at constant pressure and is supposed to remain constant in the range of 0 to *T*.

Limitations of the law

(1) Glassy solids even at 0K has entropy ***greater than zero***.

(2) Solids having mixtures of ***isotopes*** do not have zero entropy at 0K. For example, entropy of solid chlorine is not zero at 0K.

(3) Crystals of Co, N_2O, NO, H_2O, etc. do not have perfect order even at 0K thus their entropy is not ***equal to zero***.

Thermochemistry

"Thermochemistry is a branch of physical chemistry which is concerned with energy changes accompanying chemical transformation. It is also termed as chemical energetics. It is based on the first law of thermodynamics."

Thermochemical equations.

A balanced chemical equation which tells about the amount of heat evolved or absorbed during the reaction is called a **thermochemical equation**. A complete thermochemical equation supplies the following information's.

(1) It tells about the physical state of the reactants and products. This is done by inserting symbol (s), (l) and (g) for solid, liquid and gaseous state respectively along side the chemical formulae.

(2) It tells about the allotropic form (if any) of the reactant by inserting the respective allotropic name, for example, C (graphite) (s).

(3) The aqueous solution of the substance is indicated by the word *aq*.

(4) It tells whether a reaction proceeds with the evolution of heat or with the absorption of heat, *i.e.* heat change involved in the system.

Remember that like algebraic equations, thermochemical equations can be reversed, added, subtracted and multiplied.

Exothermic and Endothermic reactions.

(1) Exothermic reactions : The chemical reactions which proceed with the ***evolution of heat*** energy are called exothermic reactions. The heat energy produced during the reactions is indicated by writing $+q$ or more precisely by giving the actual numerical value on the products side. In general exothermic reactions may be represented as, $A + B \rightarrow C + D + q$ (heat energy)

In the exothermic reactions the *enthalpy of the products will be less than the enthalpy of the reactants*, so that the enthalpy change is negative as shown below

$$\boxed{\Delta H = H_p - H_r}\ ;\ \ H_p < H_r\ ;\ \Delta H = -ve$$

Examples : (i) $C(s) + O_2(g) \rightarrow CO_2(g) + 393.5kJ$ (at constant temperature and pressure)

or $C(s) + O_2(g) \rightarrow CO_2(g);\quad \Delta H = -393.5kJ$

(ii) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l);\quad \Delta H = -285.8kJ$

(iii) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g);\quad \Delta H = -92.3kJ$

(iv) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g);\quad \Delta H = -694.6kJ$

(v) $CH_4(g)+2O_2(g)\rightarrow CO_2(g)+2H_2O;\quad \Delta H=-890.3kJ$

(vi) Fermentation is also an example of exothermic reaction.

(2) **Endothermic reactions** : The chemical reactions which proceed with the absorption of heat energy are called endothermic reactions. Since the heat is added to the reactants in these reactions, the heat absorbed is indicated by either putting (–) or by writing the actual numerical value of heat on the reactant side

$$A+B\rightarrow C+D-q \text{ (heat energy)}$$

The heat absorbed at constant temperature and constant pressure measures enthalpy change. Because of the absorption of heat, the enthalpy of products will be more than the enthalpy of the reactants. Consequently, ΔH will be positive $(+ve)$ for the endothermic reactions.

$$\Delta H=H_p-H_r;\ H_p>H_r;\quad \Delta H=+ve$$

Example : (i) $N_2(g)+O_2(g)+180.5\,kJ\rightarrow 2NO(g)$

or $N_2(g)+O_2(g)\rightarrow 2NO(g);\Delta H=+180.5\,kJ$

(ii) $C(s)+2S(s)\rightarrow CS_2(l)\,\Delta H=+92.0kJ$

(iii) $H_2(g)+I_2(g)\rightarrow 2HI(g);\Delta H=+53.9kJ$

(iv) $2HgO(s)\rightarrow 2Hg(l)+O_2(g);\Delta H=+180.4kJ$

(v) $SnO_2(s)+2C(s)\rightarrow Sn(s)+2CO_2(g);\Delta H=+360.0kJ$

(vi) $Fe+S\rightarrow FeS$

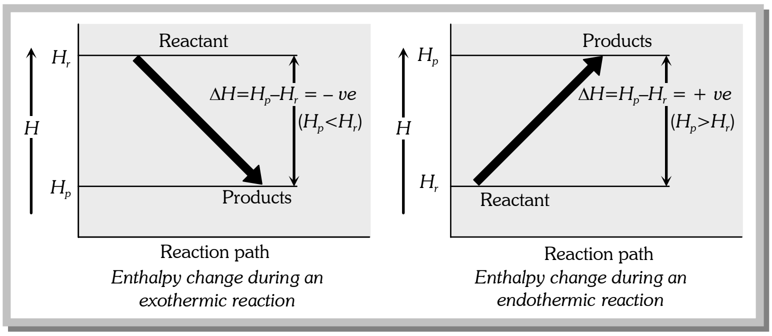
(vii) Preparation of ozone by passing silent electric discharged through oxygen is the example of endothermic reaction.

(viii) Evaporation of water is also the example of endothermic reaction.

The enthalpy changes for exothermic and endothermic reactions are shown in figure.

Similarly, if we consider heat change at constant volume and temperature, ΔE is – *ve*, now it may be concluded that

$$\boxed{\begin{array}{l}\text{For exothermic reaction}: \Delta H \text{ or } \Delta E=-ve\\ \text{For endothermic reactions}: \Delta H \text{ or } \Delta E=+ve\end{array}}$$



Enthalpy change during an exothermic reaction

Enthalpy change during an endothermic reaction

Heat of reaction or Enthalpy of reaction.

Heat of reaction is defined as the amount of heat evolved or absorbed when quantities of the substances indicated by the chemical equation have completely reacted. The heat of reaction (or enthalpy of reaction) is actually the difference between the enthalpies of the products and the reactants when the quantities of the reactants indicated by the chemical equation have completely reacted. Mathematically,

Enthalpy of reaction (heat of reaction) $=\Delta H=\Sigma H_P-\Sigma H_R$

(1) **Factors which influence the heat of reaction** : There are a number of factors which affect the magnitude of heat of reaction.

(i) ***Physical state of reactants and products*** : Heat energy is involved for changing the physical state of a chemical substance. For example in the conversion of water into steam, heat is absorbed and heat is evolved when steam is condensed. Considering the following two reactions

$$H_2(g)+\frac{1}{2}O_2(g)=H_2O(g);\quad \Delta H=-57.8\,kcal$$

$$H_2(g)+\frac{1}{2}O_2(g)=H_2O(l);\quad \Delta H=-68.32\,kcal$$

It is observed that there is difference in the value of ΔH if water is obtained in gaseous or liquid state. ΔH value in second case is higher because heat is evolved when steam condenses. Hence, physical sate always affects the heat of reaction.

(ii) ***Allotropic forms of the element*** : Heat energy is also involved when one allotropic form of an element is converted into another. Thus, the value of ΔH depends on the allotropic form used in the reaction. For example, the value of ΔH is different when carbon in the form of diamond or in amorphous form is used.

$$C\text{ (diamond) }+O_2(g)\rightarrow CO_2(g);\quad \Delta H=-94.3\,kcal$$

$$C\text{ (amorphous) }+O_2(g)\rightarrow CO_2(g);\quad \Delta H=-97.6\,kcal$$

The difference between the two values is equal to the heat absorbed when 12*g* of diamond is converted into 12*g* of amorphous carbon. This is termed as ***heat of transition***.

(iii) ***Temperature*** : Heat of reaction has been found to depend upon the temperature at which reaction is occurring. The variation of the heat of reaction with temperature can be ascertained by using ***Kirchhoff's equation***.

$$\boxed{\frac{\Delta H_{T_2}-\Delta H_{T_1}}{T_2-T_1}=\Delta C_P}$$

Kirchhoff's equation at constant volume may be given as,

$$\boxed{\frac{\Delta E_{T_2}-\Delta E_{T_1}}{T_2-T_1}=\Delta C_v}$$

(iv) ***Reaction carried out at constant pressure or constant volume*** : When a chemical reaction occurs at constant volume, the heat change is called the internal energy of reaction at constant volume. However, most of the reactions are carried out at constant pressure; the enthalpy change is then termed as the enthalpy of reaction at constant pressure. The difference in the values is negligible when solids and liquids are involved in a chemical change. But, in reactions which involve gases, the difference in two values is considerable.

$$\Delta E+\Delta nRT=\Delta H \text{ or } \boxed{q_v+\Delta nRT=q_p}$$

$\Delta E=q_v=$ heat change at constant volume; $\Delta H=q_p=$ heat change at constant pressure,

$\boxed{\Delta n = \text{total number of moles of gaseous product - total number of moles of gaseous reactants.}}$

(2) Types of heat of reaction

(i) ***Heat of formation*** : It is the quantity of heat evolved or absorbed (*i.e.* the change in enthalpy) when one mole of the substance is formed from its constituent elements under given conditions of temperature and pressure. It is represented by ΔH_f. When the temperature and pressure are as $25°C$ and 1 atmospheric pressure. The heat of formation under these conditions is *called standard heat of formation*. It is usually represented by ΔH_f^0.

The standard heat of formation of 1 mole of $NH_3(g)$ and 1 mole of $HCl(g)$.

$$\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g)\rightarrow NH_3(g);\quad \Delta H_{(g)}=-11kcal$$

$$\frac{1}{2}H_2(g)+\frac{1}{2}Cl_2(g)\rightarrow HCl;\quad \Delta H_f=-22\,kcal$$

It may be calculated by

$$\Delta H^0=\begin{bmatrix}\text{Sum of standard heats of}\\ \text{Formation of products}\end{bmatrix}-\begin{bmatrix}\text{Sum of standard heats of}\\ \text{Formation of reactants}\end{bmatrix}$$

$$\boxed{\Delta H^0=[\Sigma\Delta H^0{}_{(\text{products})}-\Sigma\Delta H^0{}_{(\text{Reactants})}]}$$

(ii) **Heat of combustion** : It is the amount of heat evolved or absorbed (*i.e.* change in enthalpy) when one mole of the substance is completely burnt in air or oxygen. For example

$$CH_4(g)+2O_2(g)\rightarrow CO_2(g)+2H_2O(l);\qquad \Delta H=-192\ kcal$$

$$C_2H_6(g)+3.5\ O_2(g)\rightarrow 2CO_2(g)+3H_2O(l);\ \ \Delta H=-372.8\ kcal$$

It may be calculated by

$$\Delta H^0=\begin{bmatrix}\text{Sum of the standard heats of}\\ \text{Combustion of products}\end{bmatrix}-\begin{bmatrix}\text{Sum of the standard heats}\\ \text{Combustion of reactants}\end{bmatrix}$$

$$\boxed{\Delta H^0=[\Sigma\Delta H^0_{f\,(\text{Products})}-\Sigma H^0_{f\,(\text{Reactants})}]}$$

Note : ✹*Heat of combustion increases with increase in number of carbon and hydrogen.*

✹*Heat of combustion of carbon is equal to the intrinsic energy of* CO_2.

The enthalpy or heat of combustion have a number of applications. Some of these are described below,

(a) *Calorific value of foods and fuels* : Energy is needed for the working of all machines. Even human body is no exception. Coal, petroleum, natural gas etc. serve as the principal sources of energy for man-made machines, the food which we eat serves as a source of energy to our body.

The energy released by the combustion of foods or fuels is usually compared in terms of their combustion energies per gram. It is known as ***calorific value***. The amount of heat produced in calories or Joules when one gram of a substance (food or fuel) is completely burnt or oxidised.

When methane burns, 890.3 $kJ\ mol^{-1}$ of energy is released.

$$\underset{1\text{ mole (16g)}}{CH_4(g)}+2O_2(g)\rightarrow CO_2(g)+2H_2O(l);\ \ \Delta H_{CH_4}=-890.3\,kJ$$

So, the calorific value of methane $=-\dfrac{890.3}{16}=-55.6kJ/g$

Calorific values of some important food stuffs and fuels

Fuel	*Calorific value (kJ/g)*	*Food*	*Calorific value (kJ/g)*
Wood	**17**	**Milk**	**3.1**
Charcoal	**33**	**Egg**	**6.7**
Kerosene	**48**	**Rice**	**16.7**
Methane	**55**	**Sugar**	**17.3**
L.P.G.	**55**	**Butter**	**30.4**
Hydrogen	**150**	**Ghee**	**37.6**

Out of the fuels listed, hydrogen has the highest calorific value. The calorific value of proteins is quite low.

(b) *Enthalpies of formation* : Enthalpies of formation of various compounds, which are not directly obtained, can be calculated from the data of enthalpies of combustions easily by the application of Hess's law.

$$\boxed{\text{Heat of reaction} = \Sigma\,\text{Heat of combustion of reactants} - \Sigma\,\text{Heat of combustion of products.}}$$

(iii) **Heat of neutralisation :** It is the amount of heat evolved (i.e., change in enthalpy) when one equivalent of an acid is neutralised by one equivalent of a base in fairly dilute solution, e.g., ***Neutralisation reactions are always exothermic reaction and the value of*** ΔH ***is*** $(-ve)$.

$$HCl(aq.) + NaOH\,(aq.) \rightarrow NaCl(aq.) + H_2O; \quad \Delta H = -\,13.7\ kcal$$

The heat of neutralisation of a strong acid against a strong base is always constant $(13.7\ kcal\ or\ 57\ kJ\ mole^{-1})$. It is because in dilute solutions all strong acids and bases ionise completely and thus the heat of neutralisation in such cases is actually the heat of formation of water from H^+ and OH^- ions, *i.e.,*

$$H^+ + OH^- \rightarrow H_2O; \Delta H = -\,13.7\ kcal$$

In case of neutralisation of a weak acid or a weak base against a strong base or acid respectively, since a part of the evolved heat is used up in ionising the weak acid or base, it is always less than $13.7\ kcal\ mole^{-1}\ (57\ kJ\ mole^{-1})$. For example, heat of neutralisation of HCN (a weak acid) and $NaOH$ (a strong alkali) is $-\,2.9\ kcal$ because $10.8\ kcal$ of heat is absorbed for the ionisation of HCN (i.e., the heat of dissociation or ionisation of HCN is $10.8\ kcal$) Similarly Heat of neutralization of NH_4OH and HCl is less then $13.7\ kcal$.

$$HCN\,(aq.) + NaOH\,(aq.) \rightarrow NaCN(aq.) + H_2O; \quad \Delta H = -\,2.9\ kcal$$

$$HCN\,(aq.) \rightleftharpoons H^+ + CN^-; \Delta H = 10.8\ Kcal$$

(iv) **Heat of solution** : *It is the amount of heat evolved or absorbed (i.e., change in enthalpy) when one mole of the solute is dissolved completely in excess of the solvent (usually water).* For example,

$$NH_4Cl(s) + H_2O(l) \rightarrow NH_4Cl(aq.); \quad \Delta H = +\,3.90\ kcal$$

$$BaCl_2(s) + H_2O(l) \rightarrow BaCl_2(aq.); \quad \Delta H = -\,2.70\ kcal$$

(v) **Heat of hydration** : *It is the amount of heat evolved or absorbed (i.e change in enthalpy) when* 1 *mole of an anhydrous or a partially hydrated salt combines with the required number of moles of water to form a* ***specific hydrate***. For example, $CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4 . 5H_2O(s); \ \Delta H = -\,18.69$

(vi) **Heat of vapourisation** : When a liquid is allowed to evaporate, it absorbs heat from the surroundings and evaporation is accompanied by increase in enthalpy. For example: $10.5\ k\ cals$ is the increase in enthalpy when one mole of water is allowed to evaporate at $25^\circ C$. When the vapours are allowed to condense to liquid state, the heat is evolved and condensation of vapour is accompanied by decrease in enthalpy. The value for the condensation of one mole of water vapour at $25^\circ C$ is also $10.5\ k\ cals$.

The evaporation and condensation can be represented as,

$$H_2O(l) \rightarrow H_2O(g); \ \ \Delta H = +\,10.5\ kcals \ \ (+43.93\ kJ)$$

$$H_2O(g) \rightarrow H_2O(l); \ \ \Delta H = -\,10.5\ kcals \ \ (-43.93\ kJ)$$

Thus the change in enthalpy when a liquid changes into vapour state or when vapour changes into liquid state is called ***heat of vapourisation.***

(vii) **Heat of fusion** : When a solid is allowed to melt, it changes into liquid state with the absorption of heat (increase in enthalpy) and when a liquid is allowed to freeze, it changes into solid with the evolution of heat (decrease in enthalpy). The change in enthalpy of such type of transformations is called ***enthalpy of fusion***. For example,

$$H_2O(ice) \rightarrow H_2O(liquid); \quad \Delta H = +1.44\ kcals\ \ (+6.02\ kJ)$$
$$H_2O\ (liquid) \rightarrow H_2O\ (ice); \quad \Delta H = -1.44\ kcals\ (-6.02\ kJ)$$

Note : ✹ *The enthalpy of fusion of ice* ***per mole*** *is 6 kJ.*

(viii) ***Heat of precipitation*** : It is defined as the amount of heat liberated in the precipitation of one mole of a sparingly soluble substance when solutions of suitable electrolytes are mixed, for example

$$Ba^{2+} + SO_4^{2-}(aq) \rightarrow BaSO_4(s) : \ \Delta H = -4.66\, kcal$$

(ix) ***Heat of sublimation*** : Sublimation is a process in which a solid on heating changes directly into gaseous state below its melting point.

Heat of sublimation of a substance is the amount of heat absorbed in the conversion of 1 mole of a solid directly into vapour phase at a given temperature below its melting point.

$$I_2(s) \rightarrow I_2(g); \quad \Delta H = +62.39\, kJ$$

Most solids that sublime are molecular in nature e.g. iodine and naphthalene etc.

$$\boxed{\Delta H_{sub.} = \Delta H_{\text{fusion}} + \Delta H_{vaporisation}}$$

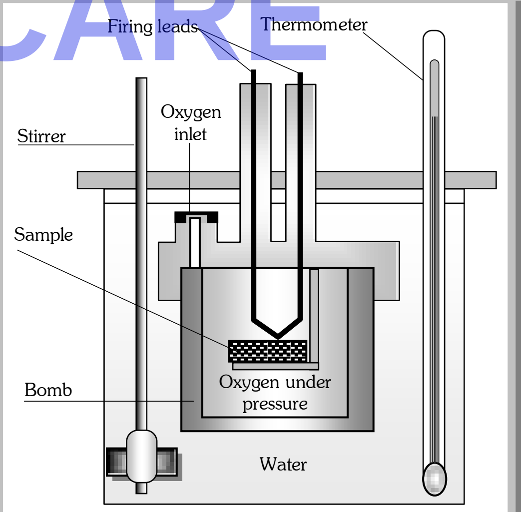
(3) **Experimental determination of the heat of reaction** : The heat evolved or absorbed in a chemical reaction is measured by carrying out the reaction in an apparatus called ***calorimeter***. The principle of measurement is that heat given out is equal to heat taken, *i.e.*, $Q = (W + m) \times s \times (T_2 - T_1)$,

Where Q is the heat of the reaction (given out), W is the water equivalent of the calorimeter and m is the mass of liquid in the calorimeter and s its specific heat, T_2 is the final temperature and T_1 the initial temperature of the system. Different types of calorimeters are used but two of the common types are,

(i) Water calorimeter and (ii) Bomb calorimeter

Bomb calorimeter : This is commonly used to find the heat of combustion of organic substances. It consists of a sealed combustion chamber called a bomb. A weigh quantity of the substance in a dish along with oxygen under about 20 atmospheric pressure is placed in the bomb which is lowered in water contained in an insulated copper vessel. The vessel is fitted with a stirrer and a sensitive thermometer. The arrangement is shown in fig.

The temperature of the water is noted and the substance is ignited by an electric current. After combustion the rise in temperature of the system is noted. The heat of combustion can be calculated from the heat gained by water and calorimeter.



Bomb calorimeter

Since the reaction in a bomb calorimeter proceeds at constant volume, the heat of combustion measured is ΔE

$$\boxed{\Delta E = \frac{(W + m)(t_2 - t_1) \times s}{w_1} \times M\, kcal}$$

Where M is the molecular mass of the substance, w_1 is the weight of substance taken, W is the water equivalent of calorimeter, m is the mass of liquid in the calorimeter and s is the specific heat of liquid.

ΔH can be calculated from the relation, $\Delta H = \Delta E + \Delta nRT$

Example 16. The heat of formations of $CO(g)$ and $CO_2(g)$ are –26.4 *kcal* and –94.0 *kcal* respectively. The heat of combustion of carbon monoxide will be **[MP PET/PMT 1988; EAMCET 1993]**

(a) + 26.4 *kcal* (b) – 67.6 *kcal* (c) –120.6 *kcal* (d) + 52.8 *kcal*

Solution:(b) $CO + \frac{1}{2}O_2 \rightarrow CO_2;\ \Delta H = ?$

$\Delta H_{CO_2} = -94.0\,kcal$, $\Delta H_{CO} = -26.4\,kcal$

$\Delta H = \Delta H_{(CO_2)} - \Delta H_{(CO)} = -94.0 - (-26.4) = -67.6\,kcal$

Example 17. Reaction $H_2(g) + I_2(g) \rightarrow 2HI(g); \Delta H = -12.40\,kcal$. According to this, the heat of formation of *HI* will be **[MP PET 1990]**

(a) 12.4 *kcal* (b) –12.4 *kcal* (c) –6.20 *kcal* (d) 6.20 *kcal*

Solution:(c) $H_2(g) + I_2(g) \rightarrow 2HI(g)$

For $2M, \Delta H = -12.40\,kcal$

$1M, \frac{-12.40}{2} = -6.20\,kcal$

Example 18. $C_{(\text{diamond})} + O_2(g) \rightarrow CO_2(g);\quad \Delta H = -\ 395\,kJ$

$C_{(\text{graphite})} + O_2(g) \rightarrow CO_2(g);\quad \Delta H = -393.5\,kJ$

From the data, the ΔH when diamond is formed from graphite is **[CBSE 1989; BHU 1987]**

(a) –1.5*kJ* (b) + 1.5*kJ* (c) +3.0*kJ* (d) –3.0*kJ*

Solution:(b) $C_{(\text{graphite})} \rightarrow C_{(\text{diamond})}$

$\Delta H_{(\text{diamond})} = -395\,kJ$; $\Delta H_{(\text{graphite})} = -393.5\,kJ$,

$\Delta H = \Delta H_{\text{graphite}} - \Delta H_{\text{diamond}} = -393.5 - (-395.0)$

$\Delta H = +1.5\,kJ$

Example 19. The enthalpy of combustion of benzene from the following data will be

(i) $6C(s) + 3H_2(g) \rightarrow C_6H_6(l);\ \Delta H = +45.9\,kJ$

(ii) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l);\quad \Delta H = -285.9\,kJ$

(iii) $C(s) + O_2(g) \rightarrow CO_2(g);\quad \Delta H = -393.5\,kJ$

(a) + 3172.8 *kJ* (b) –1549.2 *kJ* (c) –3172.8 *kJ* (d) –3264.6 *kJ*

Solution:(d) $C_6H_6 + \frac{15}{2}O_2 \rightarrow 6CO_2 + 3H_2O;\ \Delta H = ?$

$\Delta H = \Delta H_{(\text{Product})} - \Delta H_{(\text{Reactant})} = [(6 \times -393.5) + (3 \times -285.9)] - (45.9) = -3264.6\,kJ$

Example 20. The enthalpy of formation of $H_2O(l)$ is – 285.77 *kJ mol*$^{-1}$ and enthalpy of neutralisation of strong acid and strong base is –56.07 *kJ mol*$^{-1}$, what is the enthalpy of formation of OH^- ion

(a) + 229.70*kJ* (b) –229.70*kJ* (c) +226.70*kJ* (d) –22.670*kJ*

Solution:(b) $H^+(aq) + OH^-(aq) \rightarrow H_2O(l);\ \Delta H = -56.07kJ$

$\Delta H = \Delta H_f(H_2O) - [\Delta H_f(H^+) + \Delta H_f(OH)^-]$ $[\because \Delta H_f(H^+) = 0]$

$-56.07 = -285.77 - (0 + x)$

$\therefore x = -285.77 + 56.07 = -229.70\,kJ$

Example 21. The heat of combustion of glucose is given by $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$; $\Delta H = -2840\,kJ$. Which of the following energy is required for the production of .18 *gm* of glucose by the reverse reaction.

(a) 28.40 *kJ* (b) 2.84 *kJ* (c) 5.68 *kJ* (d) 56.8 *kJ*

Solution:(b) $\Delta H_{comb} = -2840\,kJ$ for $180g$ of $C_6H_{12}O_6$

$\therefore$ ΔH_{comb} for $0.18gm$ glucose $= \frac{-2840}{180} \times 0.18 = -2.84kJ$

For the reverse reaction ΔH_{comb} of glucose = 2.84 *kJ*

Example 22. One gram sample of NH_4NO_3 is decomposed in a bomb calorimeter. The temperature of the calorimeter increases by 6.12*K*. The heat capacity of the system is 1.23*kJ*/*g*/*deg*. What is the molar heat of decomposition for NH_4NO_3. **[AIIMS 2003]**

(a) – 7.53 *kJ/mole* (b) – 398.1 *kJ / mole* (c) –16.1 *kJ / mole* (d) –602 *kJ / mole*

Solution:(a) Heat evolved = 1.23× 6.12

$\therefore$ Molar heat capacity $= 1.23 \times 6.12 = 7.5276$

Molar heat of decomposition $= -7.53kJ / mole$

Example 23. If ΔH_f^0 for H_2O_2 and H_2O are – 188*kJ/mole* and $-286kJ / mole$. What will be the enthalpy change of the reaction $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$ **[MP PMT 1992]**

(a) –196 *kJ / mole* (b) 146 *kJ / mole* (c) –494 *kJ / mole* (d) –98 *kJ / mole*

Solution:(a) $H_2 + O_2 \rightarrow H_2O_2$; $\Delta H_f^0 = -188\,kJ / mole$

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ $\Delta H_f^0 = -286kJ / mole$

$\Delta H = \Delta H^0_{(product)} - \Delta H^0_{(Reactants)} = (2 \times -286) - (2 \times -188) = -572 + 376 = -196$

Example 24. The heat of combustion of carbon is –94 *kcal* at 1 *atm* pressure. The intrinsic energy of CO_2 is

(a) + 94 *kcal* (b) –94 *kcal* (c) + 47 *kcal* (d) –47 *kcal*

Solution:(b) $C_{(s)} + O_{2(g)} \rightarrow CO_2(g)$; $\Delta H = -94\,kcal$

$\Delta H = \Delta E + \Delta n_g RT$; $\Delta E = ?$

$\Delta n_g = 1 - 1 = 0$; $\Delta H = \Delta E$; $\Delta E = -94kcal$

Example 25. When 1 mole of ice melts at 0 °C and a constant pressure of 1 *atm*, 1440 cal of heat are absorbed by the system. The molar volume of ice and water are 0.0196 and 0.0180 *L*, respectively calculate ΔE

(a) 1430.03 *cal* (b) 1500.0 *cal* (c) 1450.0 *cal* (d) 1440.03 *cal*

Solution:(d) $q = 1440cal$

$\therefore \Delta H = 1440\,cal$ (absorbed)

given $H_2O(s) \rightleftharpoons H_2O(l)$

$P\Delta V = 1 \times (0.0180 - 0.0196) = -0.0016\,L\,atm$

$\because$ (1*L atm* = 24.206 *cal*)

$\therefore -0.0016L\,atm = -0.039cal$

$\Delta H = \Delta E + P\Delta V \Rightarrow \Delta E = \Delta H - P\Delta V = 1440 - (-0.039) = 1440.039\,cal$

Example 26. The difference between heats of reaction at constant pressure and constant volume for the reaction $2C_6H_6(l)+15O_2(g)\rightarrow 12CO_2(g)+6H_2O(l)$ at $25^{o}C$ in kJ is **[IIT 1991; AFMC 1994]**

(a) –7.43 (b) +3.72 (c) –3.72 (d) +7.43

Solution : (a) $\Delta n_g = 12-15 = -3$

$$q_P - q_v = \Delta n_g RT = -3\times\frac{8.314}{1000}\times 298 = -7.43 kJ.$$

Laws of thermochemistry .

(1) **Levoisier and Laplace law** : According to this law enthalpy of decomposition of a compound is numerically equal to the enthalpy of formation of that compound with opposite sign, For example,

$$C(s)+O_2\rightarrow CO_2(g);\Delta H=-94.3\,kcal\;;\;CO_2(g)\rightarrow C(s)+O_2(g);\Delta H=+94.3kcal$$

(2) **Hess's law** (the law of constant heat summation) : This law was presented by Hess in 1840. According to this law "*If a chemical reaction can be made to take place in a number of ways in one or in several steps, the total enthalpy change (total heat change) is always the same, i.e. the total enthalpy change is independent of intermediate steps involved in the change.*" The enthalpy change of a chemical reaction depends on the initial and final stages only. Let a substance A be changed in three steps to D with enthalpy change from A to B, ΔH_1 calorie, from B to $C, \Delta H_2$ calorie and from C to $D, \Delta H_3$ calorie. Total enthalpy change from A to D will be equal to the sum of enthalpies involved in various steps,

Total enthalpy change $\Delta H_{\text{steps}} = \Delta H_1 + \Delta H_2 + \Delta H_3$

Now if D is directly converted into A, let the enthalpy change be ΔH_{direct}. According to Hess's law $\Delta H_{\text{steps}} + \Delta H_{\text{direct}} = 0$, i.e. ΔH_{steps} must be equal to ΔH_{direct} numerically but with opposite sign. In case it is not so, say ΔH_{steps} (which is negative) is more that ΔH_{direct} (which is positive), then in one cycle, some energy will be created which is not possible on the basis of first law of thermodynamics. Thus, ΔH_{steps} must be equal to ΔH_{direct} numerically.

(i) ***Experimental verification of Hess's law***

(a) *Formation of carbon dioxide from carbon*

First method : carbon is directly converted into $CO_2(g)$.

$$C(s)+O_2(g)=CO_2(g);\ \Delta H=-94.0\,kcal$$

Second method : Carbon is first converted into $CO(g)$ and then $CO(g)$ into $CO_2(g)$, i.e. conversion has been carried in two steps,

$$C(s)+\frac{1}{2}O_2=CO(g)\quad;\ \Delta H=-26.0\,kcal$$

$$CO(g)+\frac{1}{2}O_2=CO_2(g);\ \Delta H=-68.0\,kcal$$

Total enthalpy change $C(s)$ to $CO_2(g)$; $\Delta H=-94.0\,kcal$

(b) *Formation of ammonium chloride from ammonia and hydrochloric acid:*

First method : $NH_3(g) + HCl = NH_4Cl(g);\ \Delta H = -42.2\,kcal$

$NH_4Cl(g) + aq = NH_4Cl(aq);\ \Delta H = +4.0\,kcal$

$NH_3(g) + HCl(g) + aq = NH_4Cl(aq);\ \ \Delta H = -38.2\,kcal$

Second method : $NH_3(g) + aq = NH_3(aq);\ \Delta H = -8.4\,kcal$

$HCl(g) + aq = HCl(aq);\ \Delta H = -17.3\,kcal$

$NH_3(aq) + HCl(aq) = NH_4Cl(aq);\ \ \Delta H = -12.3\,kcal$

$NH_3(g) + HCl(g) + aq = NH_4Cl(aq);\quad \Delta H = -38.0\,kcal$

Conclusions

- The heat of formation of compounds is independent of the manner of its formation.
- The heat of reaction is independent of the time consumed in the process.
- The heat of reaction depends on the sum of enthalpies of products minus sum of the enthalpies of reactants.
- Thermochemical equations can be added, subtracted or multiplied like algebraic equations.

(ii) *Applications of Hess's law*

(a) For the determination of enthalpies of formation of those compounds which cannot be prepared directly from the elements easily using enthalpies of combustion of compounds.

(b) For the determination of enthalpies of extremely slow reactions.

(c) For the determination of enthalpies of transformation of one allotropic form into another.

(d) For the determination of bond energies.

$$\Delta H_{\text{reaction}} = \Sigma\,\text{Bond energies of reactants} - \Sigma\,\text{Bond energies of products.}$$

(e) For the determination of resonance energy.

(f) For the determination of lattice energy.

Bond energy or Bond enthalpies.

When a bond is formed between atoms, energy is released. Obviously same amount of energy will be required to break the bond. The energy required to break the bond is termed ***bond dissociation energy***. The more precise definition is,

"The amount of energy required to break one mole of bond of a particular type between the atoms in the gaseous state, i.e., to separate the atoms in the gaseous state under 1 atmospheric pressure and the specified temperature is called bond dissociation energy."

For example, $H-H(g) \rightarrow 2H(g);\quad \Delta H = +433\,kJ\,mol^{-1}$

$Cl-Cl(g) \rightarrow 2Cl(g);\quad \Delta H = +242.5\,kJ\,mol^{-1}$

$H-Cl(g) \rightarrow H(g) + Cl(g);\ \Delta H = +431\,kJ\,mol^{-1}$

$I-I(g) \rightarrow 2I(g);\quad \Delta H = +15.1\,kJ\,mol^{-1}$

$H-I(g) \rightarrow H(g) + I(g);\quad \Delta H = +299\,kJ\,mol^{-1}$

The bond dissociation energy of a diatomic molecule is also called ***bond energy***. However, the bond dissociation energy depends upon the nature of bond and also the molecule in which the bond is present. When a molecule of a compound contains more than one bond of the same kind, the average value of the dissociation energies of a given bond is taken. ***This average bond dissociation energy required to break each bond in a compound is called bond energy***.

Bond energy is also called, the heat of formation of the bond from gaseous atoms constituting the bond with reverse sign.

$$H(g) + Cl(g) \rightarrow H-Cl\,(g);\ \Delta H = -431\,kJ\,mol^{-1}$$

Bond energy of $H-Cl = -$ (enthalpy of formation) $= -(-431) = +431\,kJ\,mol^{-1}$

Consider the dissociation of water molecule which consists of two $O-H$ bonds. The dissociation occurs in two stages.

$$H_2O(g) \rightarrow H(g) + OH(g);\ \ \Delta H = 497.89\,kJ\,mol^{-1}$$

$$OH(g) \rightarrow H(g) + O(g);\ \ \Delta H = 428.5\,kJ\,mol^{-1}$$

The average of these two bond dissociation energies gives the value of bond energy of $O-H$.

Bond energy of $O-H$ bond $= \dfrac{497.8 + 428.5}{2} = 463.15\,kJ\,mol^{-1}$

Similarly, the bond energy of $N-H$ bond in NH_3 is equal to one – third of the energy of dissociation of NH_3 and those of $C-H$ bond in CH_4 is equal to one – fourth of the energy of dissociation of CH_4.

Bond energy of $C-H = \dfrac{1664}{4} = 416\,kJ\,mol^{-1}$

$$[CH_4(g) \rightarrow C(g) + 4H(g);\ \Delta H = 1664\,kJ\,mol^{-1}]$$

Applications of bond energy

(1) Heat of a reaction $= \Sigma$ Bond energy of reactants – Σ Bond energy of products.

Note : ✹ In case of atomic species, bond energy is replaced by heat of atomization.

✹Order of bond energy in halogen $Cl > Br > F_2 > I_2$

(2) **Determination of resonance energy** : When a compound shows resonance, there is considerable difference between the heat of formation as calculated from bond energies and that determined experimentally.

Resonance energy = Experimental or actual heat of formation ~ Calculated heat of formation.

Example 27. If enthalpies of methane and ethane are respectively 320 and 360 calories then the bond energy of $C-C$ bond is **[UPSEAT 2003]**

(a) 80 calories (b) 40 calories (c) 60 calories (d) – 120 calories

Solution:(d) $CH_4 \rightarrow 4C-H;\quad \Delta H = 320$

$1E_{C-H} = \dfrac{320}{4} = 80$ calories then $6E_{C-H} = 480\ cal.$

$C_2H_6 \rightarrow E_{C-C} + 6E_{C-H}; \Delta H = 360\,cal.$

$360 = E_{C-C} + 480$

$E_{C-C} = 360 - 480 = -120 cal$

Example 28. Given that $C(g) + 4H(g) \rightarrow CH_4(g); \quad \Delta H = -166\, kJ$. The bond energy $C-H$ will be **[AMU 2002]**

(a) $208\ kJ/mol$ (b) $-41.5\ kJ/mol$ (c) $832\ kJ/mol$ (d) None of these

Solution:(b) $C_{(g)} + 4H(g) \rightarrow CH_4(g); \ \Delta H = -166 kJ$

Bond energy for $C-H = -\frac{166}{4} = -41.5\ kJ/mole$

Example 29. Calculate resonance energy of N_2O from the following data. observed $\Delta H_f^o(N_2O) = 82\, kJ\, mol^{-1}$

B.E. of $N \equiv N \Rightarrow 946\, kJ\, mol^{-1}$; B.E. of $N = N \Rightarrow 418\, kJ\, mol^{-1}$

B.E. of $O = O \Rightarrow 498\, kJ\, mol^{-1}$; B.E. of $N = 0 \Rightarrow 607\, kJ\, mol^{-1}$ **[Roorkee 1991]**

(a) $-88\ kJ\ mol^{-1}$ (b) $-44\ kJ\ mol^{-1}$ (c) $-22\ kJ\ mol^{-1}$ (d) None of these

Solution:(a) $N_2(g) + \frac{1}{2}O_2(g) \rightarrow N_2O$

$N \equiv N + \frac{1}{2} O = O \rightarrow N = N = O$

Calculated $\Delta H_f^o(N_2O) = [B.E._{(N \equiv N)} + \frac{1}{2} B.E.(O = O)] - [B.E._{(N=N)} + B.E._{N=O}]$

$= \left[946 + \frac{498}{2}\right] - [418 + 607] = +170\, kJ / mole$

Resonance energy = observed ΔH_f^0 – calculated $\Delta H_f^0 = 82 - 170 = -88 kJ\ mol^{-1}$

Example 30. If at 298K the bond energies of $C-H, C-C, C=C$ and $H-H$ bonds are respectively 414, 347, 615 and 435 $kJ\ mol^{-1}$, the value of enthalpy change for the reaction $H_2C = CH_2(g) + H_2(g) \rightarrow H_3C - CH_3(g)$ at 298 K will be **[AIEEE 2003]**

(a) $+250\ kJ$ (b) $-250\ kJ$ (c) $+125\ kJ$ (d) $-125\ kJ$

Solution: (d) $CH_2 = CH_2(g) + H_2(g) \xrightarrow{\quad} H_3C - CH_3(g)$

$4E_{C-H} \Rightarrow 414 \times 4 = 1656$ $\qquad 6E_{C-H} \Rightarrow 414 \times 6 = 2484$

$1 E_{C=C} \Rightarrow 615 \times 1 = 615$ $\qquad 1E_{C-C} \Rightarrow 347 \times 1 = 347$

$1E_{H-H} \Rightarrow 435 \times 1 = 435$

$4\Delta H_{C-H} + \Delta H_{C=C} + \Delta H_{H-H} = 2706 \xrightarrow{\quad} 6\Delta H_{C-H} + 1\Delta H_{C-C} = 2831$

$\Delta H = 2706 - 2831 = -125 kJ$

Example 31. The bond dissociation energies of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 $kcal$ respectively. The enthalpy of formation of HCl gas would be **[MP PET 1997; MP PMT 1999, 2001]**

(a) $-44\ kcal$ (b) $44\ kcal$ (c) $-22\ kcal$ (d) $22\ kcal$

Solution:(c) $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl$

$\Delta H = \Sigma B.E._{\text{(Reactants)}} - \Sigma B.E._{\text{(Products)}}$

$\Delta H = \left[\frac{1}{2} B.E.(H_2) + \frac{1}{2} BE(Cl_2)\right] - B.E.(HCl)$

$= \frac{1}{2}(104) + \frac{1}{2}(58) - 103$

$= 81 - 103 = -22\, kcal$

$\Delta H = -22\,kcal.$

Example 32. Given the bond energies $N\equiv N, H-H$ and $N–H$ bonds are 945, 436 and 391 $kJ\ mole^{-1}$ respectively the enthalpy of the following reaction $N_2(g)+3H_2(g)\rightarrow 2NH_3(g)$ is **[EAMCET 1992; JIPMER 1997]**

(a) – 93 kJ (b) 102 kJ (c) 90 kJ (d) 105 kJ

Solution:(a)

$$\underset{\underbrace{945+3\times 436}_{\text{energy absorbed}}}{N\equiv N+3H-H} \longrightarrow \underset{\underbrace{2\times(3\times 391)=2346}_{\text{energy released}}}{2\,\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}-H}$$

Net energy (enthalpy) $=$ BE$_{\text{reactants}}$ – BE$_{\text{products}}$ $= 2253-2346 =- 93$

$\Delta H = -93 kJ$

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