PHARMACEUTICAL CHEMISTRY

Thermodynamics

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(24.07.2007)

CONTENTS

Keywords
Thermodynamics**,** systems, state variables, equilibrium, isothermal, adiabatic, reversibility, internal energy, enthalpy, entropy, molar heat capacities, thermochemistry, free energy, work function

I. Introduction

Definition: Thermodynamics is a branch of science which deals with inter conversion of different forms of energy, temperature and thermal manifestations. In other words thermodynamics is the study of the flow of energy into or out of a system as it undergoes a physical or chemical transformation. In studying and evaluating the flow of energy into or out of the system, it will be useful to consider changes in certain properties like temperature, pressure, volume and concentration of the system. The study of thermodynamics is based on fundamental laws derived from well established experimental results. These are the first, second and third law of thermodynamics. First and second laws deals with inter conversion of energy. We also have a zeroth law that forms the basis of concept of temperature.

Scope:

i) Laws of thermodynamics can be useful to derive most of the important laws of physical chemistry, including the Van't Hoff law of lowering of vapour pressure, phase rule and the distribution law.
ii) Laws of thermodynamics can be used to predict the direction in which a reaction/process would proceed.
iii) It helps in the prediction of relationship between directly observable properties.
iv) It tells whether a particular change can occur under a given set of conditions.

Limitations:

i) It does not give specific and direct information about the internal structure of atom and molecule because it is applicable to macroscopic systems consisting of matter in bulk and not to microscopic systems of individual molecules or atoms.
ii) Matter finds only consideration as carrier of energy. There is however no measurable conversion of matter into energy.
iii) It can predict only the feasibility of chemical or physical process, under a given set of conditions and does not tell anything regarding the rate of physical or chemical change.

Terms and Basic Concepts

System and its surroundings: System is a part of universe which is under observation for thermodynamic study and rest part of the universe is surroundings. The surface separating the system from the surrounding is called the boundary. The boundaries of the system may be real or imaginary.

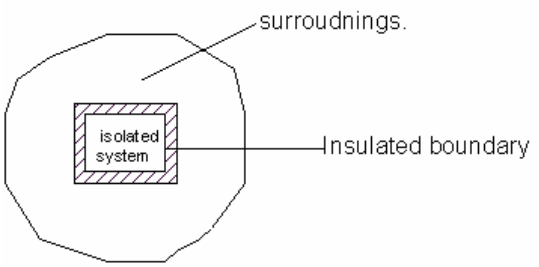
Types of boundaries:

i) **Rigid wall boundary:** Position and shape are fixed
ii) **Impermeable wall boundary:** Not permits the passage of matter
iii) **Permeable wall boundary:** Permits the passage of matter and consequently also of energy.
iv) **Adiabatic wall boundary:** When held rigid it will not permit the passage of matter or energy. e.g. thermos bottle.
v) **Diathermal wall boundary:** When held rigid it will not permit the passage of mater but allow the passage of energy.

Types of Thermodynamics systems: There are three types of thermodynamic systems depending upon the nature of boundary.

1) Isolated System: The system is said to be isolated when it can transfer neither matter nor energy with its surroundings. It is a system of constant energy within which transformation of energy may occur but total energy of the system remains constant.

Example: Water in contact with its vapour in a closed and insulated vessel.



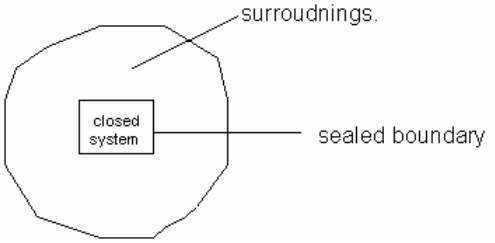
Isolated System

ii) Closed System: A system is said to be closed when it cannot transfer matter but can transfer energy across the boundary. In this system boundary is sealed but not insulated.

Examples:

i) A specific quantity of hot water in a sealed vessel constitutes a closed system

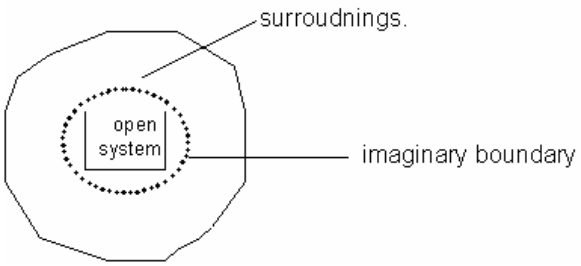
ii) A cylinder fitted with gas and fitted with piston also constitutes a closed system.



Closed System

iii) Open system: A system is said to be open when it can transfer both matter and energy with its surrounding.In this type of system matter and energy is transferred to the surroundings through the imaginary boundary.

Example: Hot water in a beaker placed on table is an open system.



Open System

Homogeneous and Heterogeneous Systems: When a system is made of one phase only, it is called Homogenous system. It is uniform throughout.

Examples:

i) Pure single solid, liquid or gas.
ii) Mixture of gases or two miscible liquids.
iii) True solution of solid in a liquid.

Heterogeneous system is one which consists of more than one phase. It is not uniform throughout.

Examples:

i) Solid in contact with liquid
ii) Solid in contact with vapour
iii) Mixture of two immiscible liquids

State of System (State Variables): The fundamental properties whose values serve to describe the system completely are called state variables or state functions or thermodynamic properties. A change in the magnitude of such properties alters the state of the system.

When the properties of the system are completely specified then it is said to be in a certain state. Temperature **(T)**, Pressure **(P),** Volume **(V),** Mass and Composition are the fundamental properties that determine the state. Change of state of system from initial to final state is always accompanied by the change in the state variables.

It is not necessary to state all the properties to define a system completely. In the case of a homogenous system, the composition is uniform. The remaining state variables are related to one another by a mathematical state equation **PV=RT**, called equation of state. If for a given amount of gas of the three state variables, Temperature **(T)** and Pressure **(P)** are specified. The value of third, Volume **(V)** is fixed automatically and can be calculated. The variables **T** and **P**, which must be specified to define the state of the system, are termed as independent variables and the third variable generally volume, which depends on temperature and pressure, is called dependent variable.

Properties of a system: Thermodynamics is applicable to macroscopic system consisting of matter in bulk. The macroscopic or bulk properties of a system can be divided into two types.

i) Extensive properties
ii) Intensive properties

i) Extensive Properties: Properties of a system which depend on the quantity of matter or amount of substance present in the system, is called extensive properties.

ii) Intensive properties: Properties of a system that do not depend on the quantity of matter present in a system are called intensive properties.

An extensive property may become intensive by specifying amount of the substance present in a system. Extensive properties are additive but intensive are not. Examples of extensive and intensive properties are given in Table-1

Table 1: Properties of a System

Extensive properties	Intensive properties
Mass	Temperature, Boiling point, Freezing point
Volume	Pressure, Vapour pressure.
Internal energy	Viscosity, Surface tension.
Enthalpy	Density (mass per unit volume)
Entropy, Free energy	Specific heat (heat capacity per unit mass)
Heat Capacity	Chemical Potential (Free energy per mole)
	Molar properties

Thermodynamic Equilibrium: A system is said to be in a sate of thermodynamic equilibrium when it has constant value of state variables and shows no further tendency to change its properties with time.

A system in which the state variables have different values in different parts of the system is said to be in non-equilibrium state.

Thermodynamics is concerned only with equilibrium states.

The criteria for equilibrium: Three types of equilibrium exist simultaneously in a system:
i) The temperature of the system must be same throughout the system that is called state of thermal equilibrium.
ii) No mechanical work is done by one part of the system on any other part of the system this is called state of mechanical equilibrium.
iii) The chemical composition of the system must be uniform and not spontaneously change with time that is called sate of chemical equilibrium.

For a heterogeneous system, the state variables of each phase remain constant in each phase.

Thermodynamic processes: A path or operation by which a thermodynamic system changes from one state to another is called a process. A process involves changes in the properties of the system. A system can change from one equilibrium to another equilibrium through a variety of ways. The various thermodynamic processes are:
i) Adiabatic process: The process in which no transfer of heat takes place between the system and its surroundings is called adiabatic process. In adiabatic process the system is completely insulated from the surrounding e.g. thermos bottle. The temperature of the system may change according to the conditions.
For adiabatic process, **dq = 0**

ii) Isothermal process: The process which occurs at constant temperature is called isothermal process. In isothermal process transfer of heat can take place into or out of the system but the temperature remains fixed.
For isothermal process, **dT = 0**

iii) Isochoric process: The process in which volume remains constant is called isochoric process.
For isochoric processes, **dV = 0**

iv) Isobaric process: The process that takes place at constant pressure is called isobaric process.
For isobaric process **dP = 0**

v) Cyclic process: When a system undergoes a series of different processes and finally returns to its initial state, the overall process is called a cyclic process.
For a cyclic process, **dE = 0, dH = O**

If a series of changes are conducted at a constant temperature the cycle is known as isothermal cycle. If the changes are carried out reversibly, then the cycle is known as reversible cycle.

Reversible and irreversible processes: A thermodynamic reverse process is one which takes place in infinite number of infinitesimally small steps and takes infinite time to occur and its direction at any point can be reversed by an infinitesimal change in the state of the system.

In a reversible process, the system is every time in internal equilibrium i.e. all the intermediate states can be defined by thermodynamic variables like temperature and pressure. At every step, the system is also in virtual equilibrium with the surroundings, because by effecting an infinitesimal amount, and finite process takes infinite time to go to completion.

Thermodynamic reversibility can be illustrated with several processes like expansion or compression of a gas.

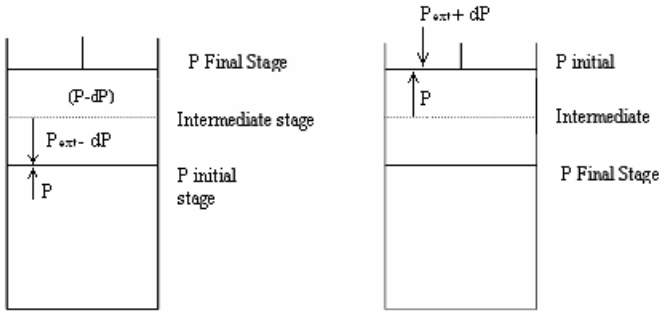


Figure 4: Reversible expansion of a gas and Reversible compression through intermediate steps which involves infinitesimal changes in pressure

The process which is carried out in a single step in finite time and cannot be reversed is called irreversible process. It is in equilibrium state only at the initial and final stages of the operation. e.g. Expansion and compression of gas rapidly in a single step.

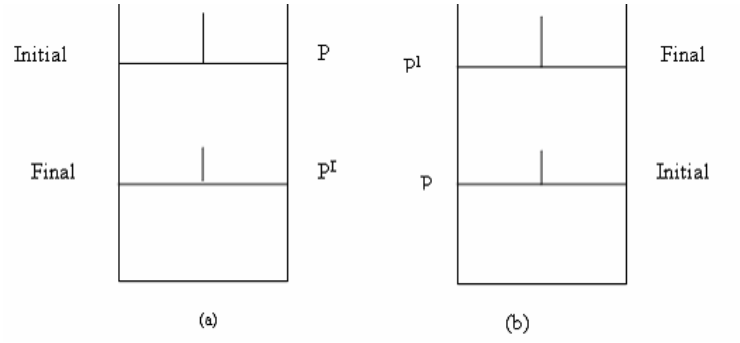


Figure-5: Irreversible compression (a) and expansion (b) of a gas in a single step.

Diagram for isobaric, isothermal and isochoric processes:

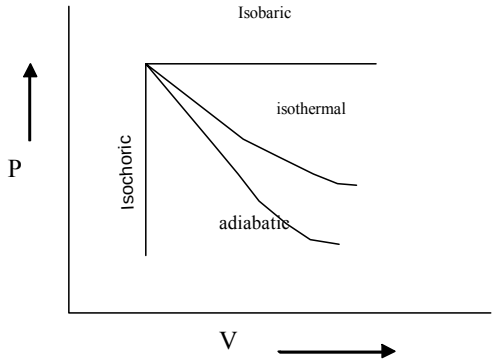


Figure-6: Diagram for isobaric, isothermal and isochoric processes

Heat, Work and Energy

A thermodynamic system is any portion of matter, solid, liquid or gas enclosed within the enveloping walls that separate it from its surroundings. These walls may be diathermic or adiabatic.

When a system undergoes a change in its state, energy is transferred to or from the surroundings. This energy may be transferred as heat or mechanical work.

Further, a portion of wall may be moved by the application of a force F it will move through a distance **l.** Then the work done by the force is **|F||l|cosθ.** The symbol of work is **w**.

If the work done on a system by its surroundings is taken to be positive, **+ w**, the energy of a system is increased. If work is done by the system on its surroundings, it is taken to be negative, **-w**, and the energy of system is decreased.
Therefore in thermodynamics, one always follows the convention of indicating the work done by a magnitude preceded by a sign e.g. **+80** Joules, **-100** Joules. The **'+'** sign shows that a work of **80** Joules has been done by the system on its surroundings and **'-'** sign implies that a work of **100** Joules has been done by the system on its surroundings.

Energy has been defined as the capacity to do work. Any system is characterized by the possession of a certain amount of energy. Energy possessed by a system is broadly of two kinds Kinetic (because of motion of its parts) and Potential (because of position of its parts). When a system does work upon its surroundings, the energy may be received from the surroundings itself, in the form of heat.

The symbol of heat is **'q'**. The sign convention used for a quantity of heat **'q'** is opposite to that used for work. If the heat is taken by the system from its surroundings to increase its energy it is taken to be positive**, +q**. If the heat is given by the system to its surroundings to decrease its energy, it is taken to be negative, **-q**.

Unit of heat and work: In CGS system unit or work is erg (erg is work done when a resistance of 1dyne is moved through a distance of 1 centimeter). Since the erg is so small, a bigger unit Joule **(J)** is used.

1 Jouls(J) = 10^7 ergs.
1 Kilo Joule(KJ) =1000J

Unit of heat is Calorie (cal).

Calorie is the quantity of heat required to raise the temperature of one gram of water by **1^oC** in the vicinity of **15^oC.**

SI unit of heat is Joule (J)

1 Joule = 0.2390 calories
1 calorie = 4.2 J
1 Kcal = 4.2 KJ

Pressure - Volume work: Mechanical work is defined as **Force x distance**. In thermodynamics work is generally considered as the work done in expansion or compression of the gas and expressed as the product of pressure and change in volume. This is known as **PV** work or pressure-volume work.

Consider a following situation, a cylinder fitted with a frictionless piston and filled with a gas. The pressure of gas, **P** exerts a force on the piston which can be balanced by an equal but opposite pressure, $\mathbf{P_{ext}}$.
If gas expands at constant pressure the expansion of the gas pushes the piston up through a small distance, **l**. The upword force, **F** exerted by the gas on the piston is:

$F = P_{ext}$ **x** A ----------(1)

Where **A** is area of underside of the piston

We know that,

Work = Force **x** distance

$$w = F \mathbf{x} l$$
$$= P_{ext} \mathbf{x} A \mathbf{x} l$$
$$w = P_{ext} \mathbf{x} \Delta V$$

When ΔV is the change in volume of gas

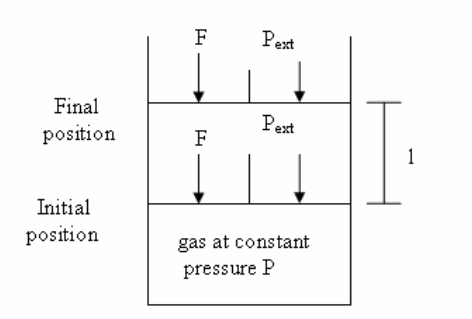


Figure 7: Illustration of Pressure-Volume work

For expansion, work is done by the system (gas) to the surroundings (piston) then;

$$w = -P_{ext} \mathbf{x} \Delta V$$

In case of compression piston will move down and work will be done by surrounding to the system, the sign of work will be +ve.

$$w = Pext \mathbf{x} \Delta V$$

PV work can be expressed in liter atmosphere. It may be noted that the work done by a system is not a state function because it is related to the process carried out rather than to the initial and final states of the system. It is a path function.

Isothermal reversible expansion work: Suppose an ideal gas confined in a cylinder with a frictionless piston, expands reversibly from volume $\mathbf{V_1}$ to $\mathbf{V_2}$ at constant temperature and pressure of gas successively reduced from $\mathbf{P_1}$ to $\mathbf{P_2}$.

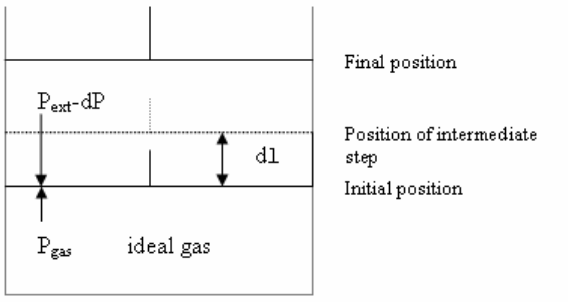


Figure 8: Isothermal reversible expansion work

In the starting piston remains stationary.

$$P_{ext} = P_{gas}.$$

Reversible expansion of gas takes place in a finite number of infinitesimally small intermediate steps.

Suppose in a single intermediate step $\mathbf{P_{ext}}$ is decreased by an infinitesimal amount **dp**, the gas expands reversibly and the piston passes through a distance **dl**.

Since **dP** is so small,

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

Work done in this single step dw is,

$$dw = P \times A \times dl$$

When, **A** is cross sectional area of piston.

$$dw = PdV$$

dV = increase in volume

For isothermal reversible expansion of a gas from $\mathbf{V_1}$ to $\mathbf{V_2}$, the total amount of work done is, therefore

$$w = -\int_{V_1}^{V_2} PdV$$

$$w = -\int_{V_1}^{V_2} nRT/V \, dV; \qquad \text{Since } PV = nRT$$

$$= -nRT \int_{V_1}^{V_2} dV/V$$

On integrating we have

$$w = -nRT \ln V_2/V_1$$

Since, $P_1V_1 = P_2V_2$

$$V_2/V_1 = P_1/P_2$$

$$w = -nRT \ln V_2/V_1 = -2.303\, nRT \log V_2/V_1$$

$$w = -nRT \ln P_1/P_2 = -2.303\, nRT \log P_1/P_2$$

Expansion into vacuum: If a gas is expanding into vaccum it can consider that it is expanding against a zero external pressure and therefore it will not be able to do any work i.e P = 0

$$w_{max} = 0$$

Isothermal irreversible expansion work: In irreversible expansion gas expands by instantaneously dropping the external pressure, $\mathbf{P_{ext}}$ to the final pressure $\mathbf{P_2}$.

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

$$w = -P_2(V_2-V_1)$$

$$= -P_2\, dV$$

Expansion against constant external pressure: If a gas is expanding against constant external pressure it has no volume dependences and hence the work in this case is

$$w_{max} = P_{ext}\,(V_2-V_1) = P_{ext}\,\Delta V$$

Reversibility and maximum work: The work done in a reversible processes is more than the same process if it is carried out irreversibly for the same increase in volume.
For a reversible expansion,

$$-w_{rev} = \int_{V_1}^{V_2} P\, dV = \text{Area ABCD.}$$

For irreversible expansion:

$$w = \int_{V_1}^{V_2} dV = P_2(V_2-V_1) = \text{Area BCDE}$$

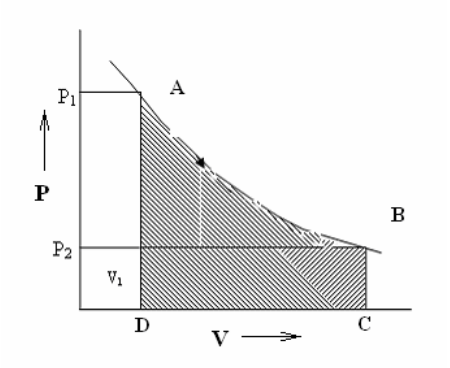


Figure-9: Reversible work of expansion

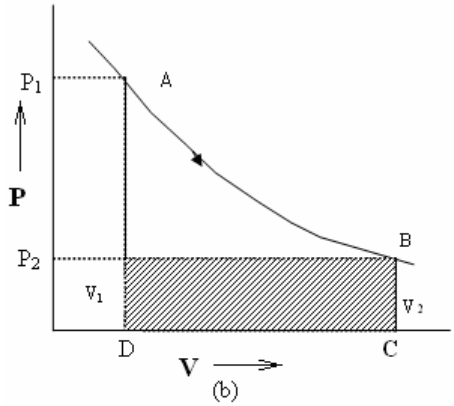


Figure-10: The irreversible work done when the external pressure is suddenly dropped to the final value $\boldsymbol{P_2}$

The work done is much more in the reversible expansion than in the irreversible expansion. Thus the mechanical work is not a state function, it is a path function.

Internal Energy

Every thermodynamic system is associated with characteristic properties like temperature, pressure and composition etc. One of its important characteristic properties is internal energy. It is the energy associated with a system by virtue of its molecular constitution and the motion of its molecules. This energy includes all type of internal potential energies and internal kinetic energies.

The total of all possible kinds of energy of a system is called its internal energy.

Internal energy is a state property of the system since the value of internal energy of a system depends on the quantity of matter contained in a system; it is also classified as an extensive property.

Symbol and Sign conventions: Symbol of internal energy is **E** (or can be represented as **U** also).

It is impossible to find out the absolute value of internal energy of a system. In thermodynamics we consider only the change in internal energy of system **(ΔE)** when a system undergoes a change from one state to another.

If, E_1 = internal energy of initial state
E_2 = internal energy of final state.
Then $\Delta E = E_2 - E_1$

If $E2 > E_1$, then **ΔE** will be **+ve** (Endothermic reaction)
When $E_2 < E_1$, then **ΔE** will be **–ve** (Exothermic reaction)

A system may transfer energy as heat or work or both
The SI unit for internal energy of a system is Joule (J)

First law of Thermodynamics: First law of thermodynamics is actually an application of law of conservation of energy to the thermodynamic systems.

"Energy can neither be created nor destroyed but may change from one form to another."
First law of thermodynamics may be stated as:

First Statement: "*Energy of an isolated system must remain constant although it may be transformed from one form to another."*

Second Statement: "*Whenever a quantity of one kind of energy is produced an exactly equivalent amount of another kind (or kinds) must be used up"*

Third Statement: Joule stated that, "*There is an exact equivalence between the amount of work overcome and the heat generated"*

In the words of Maxwell:

"*When work is transformed into heat or heat into work, the quantity of work is mechanically equivalent to the quantity of heat."*

Fourth Statement:*"It is impossible to construct a perpetual motion machine that could produce work without consuming energy."*

Mathematical Statement of First law:

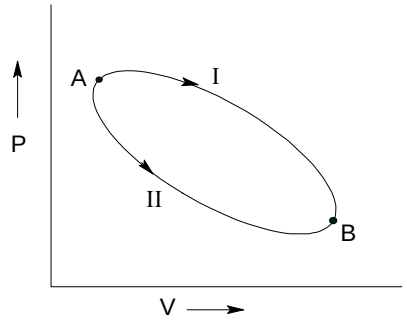


Figure 11: Illustrative diagram for first law of thermodynamics

Considering the figure, both **A** and **B** are equilibrium states of a system. The internal energy has definite values $\mathbf{E_A}$ and $\mathbf{E_B}$ at **A** and **B**. If the system is taken from the initial state **A** to the Final state, **B** along two different pathways **I** and **II**, the change in internal energy is same viz $\mathbf{E_B - E_A = \Delta E}$ for both the paths. As it is the state function of a system.

These energy changes are brought about by the evolution or absorption of heat and or by work being done by the system.

Suppose $\mathbf{q_1}$, $\mathbf{q_2}$ are the heat absorbed by the system and $\mathbf{w_1}$ and $\mathbf{w_2}$ are the work done by the system in above two pathways. In both cases internal energy change is same. Total energy of the system must remain same whatever thermal energy (heat) **q** is absorbed by the system is not destroyed but gets converted into work done in part, the remaining part augmenting the internal energy of the system.

$$q = \Delta E + w$$

For first path,

$$q_1 = \Delta E + w_1$$

For second path,

$$q_2 = \Delta E + w_2$$

$$\Delta E = q_2 - w_2 = q_1 - w_1$$

or

$$\Delta E = q - w \quad \text{--(Mathematical statement of first law.)}$$

Thus first law of thermodynamics may also be stated as:
"The total internal energy change of a closed system is equal to the heat absorbed by the system minus the work done by the system."

For a cyclic process total change in internal energy over the cyclic path is zero.

$$\Delta E = 0$$

Therefore, $q = w$

For a adiabatic process there is no heat absorbed or evolved

i.e. $q = 0$

Hence $\Delta E = -w$. The decrease in internal energy is exactly equal to the work done by the system on its surroundings.

For isochoric process no change in volume

$$\Delta V = 0$$

$$w = P\Delta V = 0$$

Hence $\Delta E = q_v$

Change in internal energy is equal to change in heat at constant volume

For isobaric process pressure remains constant

$$\Delta E = q - w$$

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

Significance of First law of thermodynamics: It tells us that a certain quantity of heat will produce a definite amount of work and vice versa. Work cannot appear without disappearing of heat. There must be an internal energy change of a system when it undergoes a change from one state to another.

State and Path Functions and Exact and Inexact Differentials: State function is a function or property which depends only on the sate of the system and change in the sate functions depends only on the initial and final states of the system and not on the path from the initial to the final sate. e.g. **E** (internal energy) is a state function while q (heat absorbed) and w (work done) are path functions. The differential of a state function is an exact or perfect differential e.g. **dE** is an exact differential, while **dq** and **dw** inexact differentials.

If dZ(x.y) is a perfect differential, then

a) Z is a single values function of **x** and **y**.
b) $\int dZ$ between two given states depends only on that states and independent of path.
c) The integral of dZ over a closed path is zero $\oint = \mathbf{0}$ ie. ΔZ in complete cyclic process is zero.
d) $\frac{\partial^2 Z}{} = \frac{\partial^2 Z}{}$ (Eulers's theorem of exactness)

$\partial x.\ \partial y \qquad \partial y.\ \partial x$

That is the order of differentiation is immaterial. All thermodynamic functions are state functions and their differentials are exact differentials. In this respect '**w**' and '**q**' are not thermodynamic functions. The difference between the two inexact differentials is an exact differential.

$$dE = \partial Q - \partial W$$

$$\oint dE = 0$$

$$\frac{\partial^2 E}{\partial V.\ \partial T} = \frac{\partial^2 E}{\partial T.\ \partial V}$$

Enthalpy

There are two different situations of interest in thermodynamics. First is the process taking place at constant volume and second is the processes taking place at constant pressure. For the processes carried at constant volume no **PV** work is done and total heat content is same as internal energy **E**. But in the processes at constant pressure the system also expends energy in doing **PV** work. Therefore the total heat content of a system at constant pressure is equivalent to the sum of internal energy **E** and the **PV** energy. This is called enthalpy of the system and represented by the symbol **H**. Thus enthalpy can be defined as total heat content of system at constant pressure.

$$H = E + PV \quad \text{----------(i)}$$

As **E**, **P** and **V** all are the state functions and value of **H**, depends on the value of state function, **H** must also be a state function of a system and its value is independent of path by which this change has been accomplished.

Change in enthalpy, $\Delta H = H_2 - H_1$----------(ii)

$\mathbf{H_1}$ and $\mathbf{H_2}$ are enthalpies of initial and final states respectively.

$$H_1 = E_1 + PV_1$$
$$H_2 = E_2 + PV_2$$

Substituting the value of $\mathbf{H_1}$ and $\mathbf{H_2}$ in equation (ii)

$$\Delta H = (E_2 + PV_2) - (E_1 + PV_1)$$

$$= E_2 + PV_2 - E_1 - PV_1$$

$$= (E_2 - E_1) - (PV_2 - PV_1)$$

$$= (E_2 - E_1) - P(V_2 - V_1)$$

$$\Delta H = \Delta E + P\Delta V \quad \text{----------} \quad \text{----------(iii)}$$

also, $\Delta H = \Delta E + w$ ---------- ----------(iv)

From the first law; $\Delta E = q-w$ ----------(v)

From equation (iv) and (v)

$\Delta H = q$ (heat transferred when change in state occurs at constant pressure).

This can be written as

$$\Delta H = H_2-H_1$$

If $\mathbf{H_2<H_1}$, **ΔH** is negative and the process will be exothermic.

For a chemical reaction at constant pressure,

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

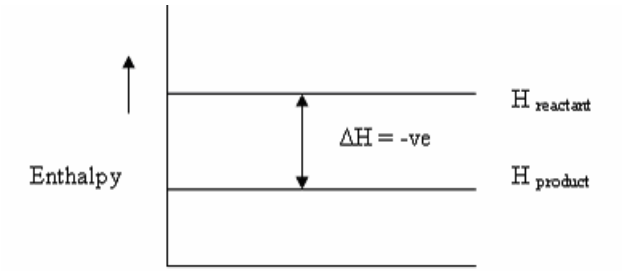


Figure12: Enthalpy change for an exothermic reaction.

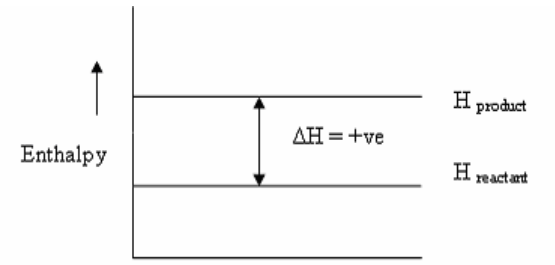


Figure-13: Enthalpy change for an endothermic reaction.

The units of **ΔH** are kilo calorie (K.Cal) or Kilo Joules (KJ).

Relationship between ΔH and ΔE [qp and qv]

From the first law , $\Delta q = \Delta E + P\Delta V$ ----------(i)

At constant volume, $\Delta V = 0$

$\Delta q = q_v = \Delta E$ ----------(ii)

At constant pressure

$q_p = \Delta E + P\Delta V$ ---------- (iii)

q_p and q_v are the heat change at constant pressure and constant volume respectively.

Enthalpy change ΔH is given by the following expression

$$\Delta H = \Delta E + P\Delta V \text{ ----------(iv)}$$

From equation (iii) & (iv)

$$\Delta H = q_p \text{ ----------(v)}$$

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

$$q_p = q_v + P\Delta V \text{ ----------(vi)}$$

If gases are involved in a reaction and we have n_1 moles of gases before reaction and n_2 moles of gases after reactions. Assuming ideal gas behaviors, we have

$$PV = nRT \text{ (ideal gas equation)}$$

$$PV_2 = n_2RT$$

$$PV_1 = n_1RT$$

$$P(V_2 - V_1) = (n_2 - n_1)RT$$

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

By putting the value in equation (iv), we get

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

$$q_p = q_v + \Delta nRT$$

Also $q_p - q_v = \Delta nRT$

Molar Heat Capacities

Enthalpy and internal energy function are used to determine heat changes accompanying a process at constant pressure and constant volume respectively. Heat capacity is a new function which relates the heat changes to the temperature changes at constant volume. Heat capacity means the capacity to absorb energy and store it. As the system absorb heat energy its kinetic energy increase which in turn rises the temperature of the system. Thus heat capacity can be defined as,

"Heat absorbed in raising temperature by one degree at a particular temperature."

Heat capacity is given by the following expression

$$C = \frac{q}{m\,(T_2 - T_1)}$$

q = heat absorbed

m = mass

T_1 & T_2 = Temperature before and after absorbing heat.

If m = 1g then it is called specific heat capacity.

If we consider mass as 1mole then the heat capacity is known as molar heat capacity, denoted by **C**.

$$C = \frac{q}{(T_2 - T_1)} \qquad (m = 1 \text{ mole})$$

Molar heat capacity of a system is defined as the quantity of thermal energy that must be absorbed by 1mole of the system to produce a change of temperature of one degree. Since the heat capacity **(C)** varies with temperature, its value will be given as:

$C = \frac{dq}{dT}$ (Ratio of amount of heat absorbed to the raise in temperature)

The units of molar heat capacity are calories per degree per mole (Cal $K^{-1}mol^{-1}$) or Joules per degree per mole (J $K^{-1}mol^{-1}$)

Heat capacity is not a state function; we must specify the process by which temperature is raised by one degree. There are two types of molar heat capacities viz at constant volume and at constant pressure.

Molar heat capacity at constant volume:

$dq = dE + PdV$ ----------(i) (From the first law)

Dividing the equation by **dT**

$$\frac{dq}{dT} = \frac{dE + PdV}{dT}$$

$$\frac{dq}{dT} = \frac{dE}{dT} + \frac{PdV}{dT} \quad \text{----------(ii)}$$

At constant volume, $dV = 0$

Equation (ii) reduces to,

$$C_v = \left[\frac{dE}{dT}\right]_V \quad \text{---------- (iii)}$$

Thus the heat capacity of constant volume, **Cv** is defined as the rate of change of internal energy with temperature at constant volume.

Molar Heat capacity at constant pressure C_P:

Consider equation (ii)

$$\frac{dq}{dT} = \frac{dE}{dT} + \frac{PdV}{dT}$$

We know that; $H = E+PV$

Differentiating this equation w.r.t temperature at constant pressure, we get

$$\left[\frac{dH}{dT}\right]_P = \left[\frac{dE}{dT}\right]_P + P\left[\frac{dV}{dT}\right]_P \quad \text{----------(iv)}$$

Comparing equation (ii) & (iv)

$$C_P = \left[\frac{dH}{dT}\right]_P \quad \text{----------(v)}$$

Thus the heat capacity at constant pressure **(C_P)** is defined as the rate of change of enthalpy with temperature at constant pressure.

Relationship between Cp and Cv:
We knows,

$$C_P = \frac{dH}{dT} \quad \text{----------(i)}$$

$$C_V = \frac{dE}{dT} \text{----------(ii)}$$

$$H = E + PV \text{ ----------(iii)}$$

For one mole of ideal gas PV = RT

$$H = E+RT \text{ ----------(iv)}$$

Differentiating w.r.t to temperature, **T**

$$\frac{dH}{dT} = \frac{dE}{dT} + R$$

Or Cp = Cv +R (From equation (i) and (ii))

Cp – Cv =R

Thus **Cp** is greater than **Cv** by a gas constant value 1.987 Cal K^{-1} mol^{-1} or 8.314 JK^{-1} $mol^{-1.}$

Calculation of ΔE and ΔH:
For 1mole of ideal gas, we know that

$$Cv = \frac{dE}{dT}$$

$$dE = Cv \mathbf{x} dT$$

For a finite change

$$\Delta E = (E_2-E_1) = Cv \mathbf{x} (T_2-T_1)$$

For **n** moles of ideal gas

$$\Delta E= n \mathbf{x} Cv (T_2-T_1)$$

We have

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

$$\Delta H = \Delta E + R\Delta T \quad [\text{ since } PV = RT(\text{for 1 mole}, P\Delta V = R\Delta T)$$

$$\Delta H = Cv (T_2-T_1) + R(T_2-T_1)$$

$$\Delta H = (Cv + R) (T_2-T_1)$$

Since $C_P - Cv = R$; $\Delta H = C_P (T_2-T_1)$

For n moles,

$$\Delta H = n \mathbf{x} C_P (T_2-T_1)$$

With the help of values of molar heat capacities at constant volume and at constant pressure we can calculate values of **ΔE** and **ΔH** accordingly.

Isothermal and Adiabatic Processes

Isothermal process takes place at constant temperature. During expansion against an external pressure, a system gets cooled, but in order to maintain the temperature of system, there must be perfect thermal communication between system and surroundings and heat must enter the system from the surrounding. Similarly during isothermal compression heat should leave the system. Finally temperature remains constant.

But in adiabatic process no heat transfer between system and surrounding takes place. Thus during expansion or compression temperature of the system must change.

PV = Constant (Boyle's law) for isothermal process is

PV^{γ} = Constant for adiabatic process.

Where, $\gamma = C_P/Cv$ (ratio of specific heats).

Slopes of adiabatic and isothermal curves

For isothermal process,

PV= Constant (Boyle's law)

Differentiation gives

$$PdV + VdP = 0$$

Or $VdP = -PdV$

Or $\frac{dP}{dV} = -\frac{P}{V}$

Slope of curve $= -\frac{P}{V}$

For adiabatic process, $PV^{\gamma} = \text{Constant}$

On differentiation gives,

$$\gamma PV^{\gamma-1} dV + V^{\gamma} dP = 0$$

Or $\gamma PV^{\gamma}.V^{-1}dV + V^{\gamma}dP = 0$

Or $[\gamma P/V\, dV + dP]V^{\gamma} = 0$

Or $\gamma PdV + VdP = 0$

Or $VdP = -\gamma PdV$

Or $\frac{dP}{dV} = -\gamma\frac{P}{V}$

Slope of adiabatic curve is , $-\gamma\frac{P}{V}$

Now , $\frac{\text{Slope of adiabatic curve}}{\text{Slpe of isothermal curve}} = \frac{-\gamma\frac{P}{V}}{-\frac{P}{V}} = \gamma$

Since $\gamma > 1$ so adiabatic curve is steeper than isothermal curve

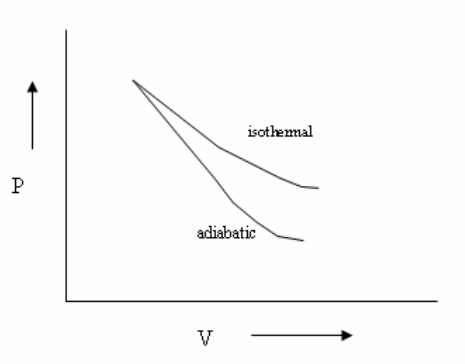


Figure 14: Slopes of adiabatic and isothermal curves

Adiabatic Expansion of an Ideal gas:

For an adiabatic process

$$dq = 0$$

$$\Delta E = q - w \text{ (first law)}$$

$$\Delta E = -w \text{ ----------(i)}$$

Consider 1 mole of ideal gas at pressure **P** and Volume **V**. In adiabatic reversible expansion, for an infinitesimal increase in volume **dV** at pressure **P**, the work done by the gas is **–PdV**. The decrease in internal energy **dE** is given by the following expression.

$$dE = -PdV \text{ ----------(ii)}$$

We know that

$$dE = C_V\, dT \text{ ----------(iii)}$$

From equation (ii) and (iii) we get,

$$-PdV = CvdT$$

From ideal gas equation,

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

$$Cv\, dT = -\frac{RT}{V} dV \text{ ----------(iv)}$$

On rearranging equation (iv) we get

$$Cv \frac{dT}{T} = -R\frac{dV}{V}$$

Integrating between $\mathbf{T_1}$ and $\mathbf{T_2}$, $\mathbf{V_1}$ and $\mathbf{V_2}$ considering **Cv** to be constant

$$Cv \int_{T_1}^{T_2} dT/T = -R \int_{V_1}^{V_2} dV/V$$

$$Cv \ln T_2/T_1 = -R \ln V_2/V_1$$

R = Cp –Cv, putting the value of R

$$Cv \ln T_2/T_1 = -(Cp - Cv) \ln V_2/V_1$$

$$\ln \frac{T_2}{T_1} = -\frac{(Cp-Cv)}{Cv} \ln \frac{V_2}{V_1}$$

$$= -(Cp/Cv - 1) \ln V_2/V_1$$

or

$$\ln T_2/T_1 = -(\gamma-1)\ln V_2/ V_1$$

Replacing (-) sign by inverting V_2/V_1 to V_1/ V_2,

$$\ln T_2/T_1 = (\gamma-1)\ln V_1/V_2$$

Now taking antilogarithm,

$$\frac{T_2}{T_1} = \left[\frac{V_1}{V_2}\right]^{\gamma-1} \text{----------(vi)}$$

$$T_2V_2^{\gamma-1} = T_1V_1^{\gamma-1}$$

Since $P_1V_1 = RT_1$, $P_2V_2 = RT_2$

$$\frac{T_2}{T_1} = \frac{P_2V_2}{P_1V_1}$$

$$\frac{P_2V_2}{P_1V_1} = \left[\frac{V_1}{V_2}\right]^{\gamma-1}$$

$$\frac{P_2}{P_1} = \left[\frac{V_1}{V_2}\right]^{\gamma-1} \cdot \frac{V_1}{V_2}$$

$$\frac{P_2}{P_1} = \left[\frac{V_1}{V_2}\right]^{\gamma}$$

$$P_2V_2^{\gamma} = P_1V_1^{\gamma}$$

$$PV^{\gamma} = \text{Constant}$$

For monatomic ideal gas, $\gamma = 1.67$.

Work done in adiabatic reversible expansion:

For an adiabatic process:

$$PV^{\gamma} = \text{Constant}$$

Differentiating this equation,

$$\gamma PV^{\gamma-1}dV + V^{\gamma}dP = 0$$

Dividing this equation by $V^{\gamma-1}$, we have

$$\gamma PdV + VdP = 0$$

$$VdP = -\gamma PdV \text{ ----------(i)}$$

For 1 mole of ideal gas

$$PV = RT$$

On complete differentiation we have

$$PdV + VdP = RdT$$

$$VdP = RdT - PdV$$

Substituting the value of VdP in equation (i)

$$RdT - PdV = -\gamma PdV$$

$$RdT = PdV - \gamma PdV$$

$$RdT = P(1-\gamma)\, dV$$

$$PdV = \frac{RdT}{1-\gamma} \text{ ----------(ii)}$$

For n moles of ideal gas

$$PdV = n\frac{RdT}{1-\gamma}$$

Integrating from $\mathbf{T_1}$ $\mathbf{V_1}$ to $\mathbf{T_2V_2}$ with γ constant,

$$P\int_{V_1}^{V_2} dV = \frac{nR}{1-\gamma}\int_{T_1}^{T_2} dT$$

$$P(V_2-V_1) = -\frac{nR(T_2-T_1)}{\gamma - 1}$$

$w_{max} = -P(V_2-V_1)$, In reversible expansion.

$$w_{max} = \frac{nR(T_2-T_1)}{\gamma - 1}$$

Since $\gamma = Cp/Cv$

γ-1 is positive because Cp> Cv .

Joule - Thomson Effect

When a gas is allowed to expand adiabatically from a region of high pressure into a region of low pressure, there is an appreciable cooling. This phenomenon of lowering of temperature in adiabatic expansion is known as Joule-Thomson effect or Joule- Kelvin effect.

In Joule-Thomson experiment an insulated tube is fitted with porous plug in middle and two frictionless pistons on both sides **A** and **B**. Gas on side **A** at volume $\mathbf{V_1}$ and Pressure $\mathbf{P_1}$ is forced through the porous plug by a slow movement of piston on this side. Gas on other side is allowed to expand to volume $\mathbf{V_2}$ and pressure $\mathbf{P_2}$ by moving the piston outward.

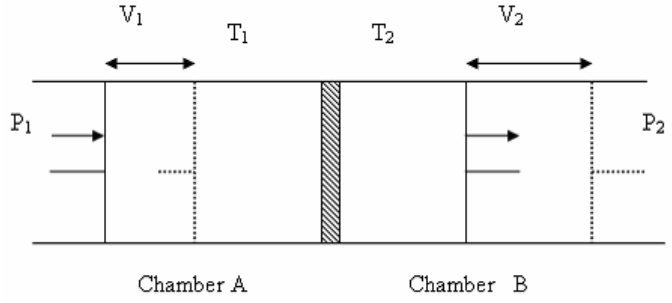


Figure 15: Joule Thomson experiment

Most of the gases found to undergo cooling on expansion through the porous plug except Hydrogen and Helium. These gases show warming up instead of cooling.

Work done on the gas at chamber **A** is $\mathbf{P_1V_1}$ and the work done by the gas at chamber **B** is $\mathbf{P_2V_2}$. Hence the net work **(w)** done by the gas is,

$$w = P_2V_2 - P_1V_1$$

$$\Delta E = q - w \quad \text{--------(First law)}$$

For adiabatic process, q =0

$$\Delta E = -w$$

$$\Delta E = E_2 - E_1 = -w = -(P_2V_2 - P_1V_1)$$

or

$$E_2 - E_1 = -(P_2V_2 - P_1V_1)$$

$$E_2 + P_2V_2 = E_1 + P_1V_1$$

$$H_2 = H_1$$

Three fore $\Delta H = 0$

It means J.T experiment takes place at constant enthalpy. At constant enthalpy, any increase in **PV** during the process should be compensated by decrease in internal energy, **E**. This leads to fall in Temperature i.e $\mathbf{T_2 < T_1}$ for hydrogen and helium decrease in **PV** with lowering of pressure, leads to increase internal energy **E** and $\mathbf{T_2 > T_1}$.The change in temperature is proportional to the difference in pressure on the two sides of the process plug. 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 a fall in temperature.

Joule-Thomson coefficient: The change in temperature with pressure under constant enthalpy conditions on passing a gas though the porous plug is called Joule-Thomson Coefficient.

$$\mu = \frac{dT}{dP}$$

A positive value of **μ** implies cooling because **ΔP** is negative in Joule-Thomson experiment so to make **μ** a **+ve** quantity, **ΔT** should be negative quantity i.e. decrease in temperature. A negative value of **μ** implies warming on expansion, as **ΔP** is negative there fore **ΔT** should be **+ve** i.e. increase in temperature .A zero value of **μ** corresponds no temperature change on expansion. The temperature at which no cooling or warming produces is called the inversion temperature.

At inversion temperature, **μ = 0**; No temperature change on expansion

Below inversion temperature, **μ = +ve**; Cooling on expansion.

Above inversion temperature, **μ = -ve**; Warming on expansion.

The inversion temperature of $\mathbf{H_2}$ is $\mathbf{-80^oC}$. At room temperature (above the inversion temperature of $\mathbf{H_2}$). Hydrogen warms on expansion.

Laws of Thermochemistry

In chemical reactions the energy in the form of heat is generally evolved or absorbed. Thermochemistry deals with the thermal or heat changes caused by chemical reactions.

Relationship between heats of reaction at constant pressure and constant volume: Consider a chemical reaction carried out at constant volume and at a definite temperature. If the total internal energies of all reactants and products, according to stoicheometric equation, are $\mathbf{E_R}$ and $\mathbf{E_P}$ respectively, then the internal energy change, **ΔE** is

$$\Delta E = E_P - E_R$$

The difference in internal energy, **ΔE** is released or absorbed as heat energy during a chemical reaction.

If $E_P > E_R$, **ΔE** is positive and reaction is endothermic

If $E_P < E_R$, **ΔE** is positive and reaction is exothermic.

If a reaction takes place at constant pressure, then there is not only change in internal energy but also work done by or on the system. In order to study heat changes for such reactions chemists have introduced a new term called enthalpy.

By definition enthalpy of a system is the sum of the internal energy and the product of its pressure and volume.

$$H = E + PV$$

At constant pressure, total enthalpy of reactant and products $\mathbf{H_R}$ and $\mathbf{H_P}$ are

$$H_R = E_R + PV_R$$

$$H_P = E_P + PV_P$$

$$H_P - H_R = (E_P - E_R) + P(V_P - V_R)$$

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

or

$$\Delta H = H_P - H_R$$

Thus;

ΔE = Heat change in a reaction at constant volume.
ΔH = Heat change in a reaction at constant pressure.

For reactions involving solids and liquids volume change, **ΔV** is very small and **P x ΔV** is negligible. For such reactions **ΔH** is equal to **ΔE**. But in case of gases one should specify that whether the reaction has taken place at constant volume or at constant pressure because of the remarkable volume change. Most of such reactions are studied at constant pressure and change in enthalpy **(ΔH)** is involved.

For exothermic reactions $\mathbf{H_P < H_R}$, **ΔH** is negative and for endothermic reaction $\mathbf{H_P > H_R}$, **ΔH** is positive.

Calculation of ΔH and ΔE :

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

$$P\Delta V = P(\Delta n \times V)$$

$$= PV \times \Delta n$$

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

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

$$\Delta n = n_P - n_R$$

When $\mathbf{n_P}$ and $\mathbf{n_R}$ are the number of moles of gaseous products and gaseous reactants.

Thermochemical equations: There are number of factors other than constant volume or pressure conditions, on which heat of reaction or enthalpy of reaction depends. These are

i) Physical state of reactants and products.
ii) Amount of the reactants and products
iii) Temperature

A thermo chemical equation is an equation which indicates the amount of heat change in the reaction or process. A thermo chemical equation necessarily be:

a) balanced .
b) mention the physical states of reactants and products.
c) give the value of **ΔE** or **ΔH** in accordance with the quantities of substances given by the equation.

Heat of Reaction or Enthalpy of Reaction

The amount of heat change during a reaction at constant temperature and pressure may also be called enthalpy of reaction. Its value depends on number of the reactants which have reacted in the given chemical reaction. Thus, heat of reaction may be defined as the amount of heat absorbed or evolved in a reaction when the number of moles of reactants in balanced chemical equation changes completely into the products. e.g.

$$CO(g) + \tfrac{1}{2} O_2(g) \longrightarrow CO_2(g);\ \Delta H = -284.5\ KJ$$

This is thermo chemical equation of formation of 1 mole of carbon dioxide from one mole of carbon monoxide and 0.5 moles of oxygen and heat of reaction is 284.5 KJ

Standard heat change or standard enthalpy change: The heat change in a reaction taking place at 298 K and one atmosphere pressure is called the standard heat change or standard enthalpy change of that reaction. It is denoted by $\mathbf{\Delta H^o}$

The enthalpy of any element in its standard state is arbitrarily given a zero value.

Different types of heat (enthalpy) of reaction:

i)Heat of formation: The enthalpy change when 1 mole of compound is formed from its element.

It is denoted by ΔH_f. For example heat of formation of sucrose may be expressed as:

$12C(\text{ graphite}) + 11\ H_2\ (g) + 1\ ½\ O_2(g) \longrightarrow C_{12}H_{12}O_{11}(S);\quad \Delta H_f = \mathbf{x}$ K.Cals.

If the compound and its elements are in the standard state, the heat of formation is referred to as standard heat or standard enthalpy of formation. It is denoted by $\mathbf{\Delta H_f^o}$.

We can calculate the heat of reaction under standard conditions $\mathbf{(\Delta H^o)}$ from the values of standards heat of formation of various reactants and products.

$\mathbf{\Delta H^o}$ = [Total standard heat of formation of products] – [Total standard heat of formation of a reactant]

$$\Delta H^o = \Delta H_F{}^o{}_{(\text{products})} - \Delta H_F{}^o{}_{(\text{reactants}).}$$

For example for following general reaction

$$xA + yB \longrightarrow pC + qD$$

$$\Delta H^o = [p\ \mathbf{x}\ \Delta H_F{}^o{}_{(C)} + q\ \mathbf{x}\ \Delta H_F{}^o{}_{(D)}] - [x\ \mathbf{x}\ \Delta H_F{}^o{}_{(A)} + y\ \mathbf{x}\ \Delta H_F{}^o{}_{(B)}]$$

Heat of combustion: Heat of combustion is the enthalpy change or heat change accompanying the complete combustion of 1 mole of the substance in excess of air or oxygen.
E.g. combustion of benzoic acid

$$C_6H_5COOH\ (s) + 15/2\ O_2\ (g) \longrightarrow 7\ CO_2\ (g) + 3\ H_2O\ (l)\ \Delta H_C{}^o = -y \text{ k.Cals.}$$

$\mathbf{\Delta H}$ for this reaction is the enthalpy of combustion of benzoic acid. It is denoted by $\mathbf{\Delta H_c}$.
As heat energy is evolved during the process of combustion, the heat of combustion of a substance $\mathbf{(\Delta H_c)}$ is always negative. We can calculate the heat of formation of the substance with the help of this heated combustion.

Calorific values of foods and fuels can also be calculated by the heat of combustion of organic fuel or food because calorific value is the value of heat produced in calories (or Joules) when one gram of a substance is completely burnt.
For example

$$CH_4(g) + 2\ O_2\ (g) \longrightarrow CO_2\ (g) + 2\ H_2O\ (l);\ \Delta H = -890.3\text{KJ}$$

Heat of combustion of methane is -890.3 KJ. The heat produced per gram of methane is

$$\frac{890.3}{16} = 55.64\ \text{KJ}^{-1}\text{g}^{-1}$$

Heat or Enthalpy of phase change: Process of change in state of matter (solid $\longrightarrow$ liquid $\longrightarrow$ vapour or gas) is called phase change or transition .e.g. Fusion, vapourisation, sublimation or transition from one allotropic state to another. Phase change is also accompanied by the change in enthalpy or heat content of the system.

i) **Heat of Fusion**: It is defined as the heat change or enthalpy change when one mole of substance is converted from solid to the liquid state at its melting point.
For example:

$$\underset{\text{Ice}}{H_2O_{(S)}} \longrightarrow \underset{\text{water}}{H_2O_{(1)}} ; \Delta H = +1.43 \text{ Kcal.}$$

ii) **Heat of Vapourisation**: It is defined as the heat or enthalpy change when one mole of liquid is converted into gaseous state at its boiling point.

$$\underset{\text{Water}}{H_2O_{(l)}} \longrightarrow \underset{\text{steam}}{H_2O_{(g)}} ; \Delta H = +9.71 \text{ Kcal.}$$

iii) **Heat of Sublimation:** It is defined as the heat or enthalpy change accompanying the conversion of 1 mole of solid directly into gaseous state at a temperature below its melting points.

For example

$$I_2\,(S) \longrightarrow I_2\,(g) \; ; \Delta H = +14.92 \text{ Kcal.}$$

iv) **Heat of Transition:** It is defined as the heat or enthalpy change when one mole of an element changes from one allotropic form to another.

For example

$$C_{\text{diamond}} \longrightarrow C_{\text{graphite}} \; ; \Delta H = +3.3 \text{ Kcal.}$$

Heat of solution: When a solute is dissolved in a solvent heat may be either liberated or absorbed.

"The enthalpy of solution is defined as the enthalpy change when one mole of solute is dissolved in a specified amount of solvent at a given temperature."

Two types of heat of solution have been recognized

i) Integral Heat or Enthalpy of solution: It is defines as the enthalpy change accompanying the dissolution of 1 mole of solute in a suitable amount of the pure solvent to give a solution at the desired concentration.

For example, if one mole of solute is dissolved in 500g of water the heat change gives the value of integral heat of solution at the concentration of 2 molal.

ii) Differential heat of enthalpy of solution: If we go on diluting the solution. A stage will come when further dilution causes no thermal effect. This is the state of infinite dilution. Thus, differential heat or enthalpy of solution is defined as "the change in enthalpy when one mole of a solute is dissolved in such a large quantity of solution so that further dilution does not give any change in enthalpy."

The heat of solution can also be expressed as:

$$KCl_{(S)} + H_2O_{(l)} \longrightarrow KCl_{(aq)}$$

Direct experimental measurement of differential heat of solution is not possible it can, however, be determined with the help of integral heat of solution.

Heat or Enthalpy of neutralization: Enthalpy of neutralization is the enthalpy change accompanying the neutralization of one g equivalent of an acid by one gram equivalent of a base or vice versa in dilute solution.

For example,

$$HCl\ (aq) + NaOH\ (aq) \longrightarrow NaCl\ (aq) + H_2O(l)\ \Delta H = -13.69\ kcal.$$

$$HNO_3\ (aq0 + NaOH\ (aq) \longrightarrow NaNO_3\ (aq) + H_2O\ (l)\ \Delta H = -13.38\ Kcal.$$

It is observed that enthalpy of neutralization of any strong base by any strong acid is constant. This constancy is due to the complete ionization of strong acid, base salt formed, and overall reaction is formation of water.

$$H^+(aq) + Cl^-(aq) + Na^+\ (aq) + {}^-OH(aq) \longrightarrow Na^+(aq) + Cl^- + H_2O\ (l)\ \Delta H = 13.69\ Kcal.$$

$$H^+(aq) + {}^-OH(aq) \longrightarrow H_2O\ (l)\ \Delta H = 13.69\ Kcal.$$

If in the neutralization either the acid or base or both are weak, enthalpy of neutralization will be less, since dissociation of weak acid or base during neutralization requires energy e.g. heat of neutralization of **NH_4OH** with **HCl** is -12.3 Kcal which is 13.7 -12.3 =1.4 K.cal less than the heat of neutralization. 1.4 Kcal heat is absorbed in the dissociation of **NH_4OH** a weak base.

Hess's law of constant heat summation: This is the direct consequence of the first law of thermodynamics. According to Hess's law the total thermal effect in a chemical reaction depends on the initial sate of reactants and the final state of products and not upon the intermediate stages involved in the conversion of reactants into products.

This law can also be stated as "The net heat change in a reaction is the same, whether the reaction takes place in one step or several steps."

Let us consider a general reaction of conversion of **A** to **Z** in one step and in several steps.

i) $A \longrightarrow Z + q$

q heat evolved in direct change

ii) $A \longrightarrow B + q_1$

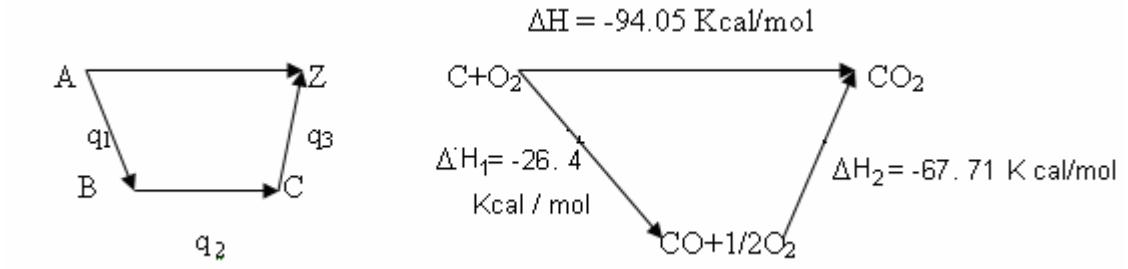
$B \longrightarrow C + q_2$

$C \longrightarrow Z + q_3$

According to Hess's law

$$q = q_1 + q_2 + q_3$$

Hess's law has been tested experimentally and shown to be true.



Thermo chemical equations may be multiplied, added or subtracted, like ordinary algebraic equations. With the help of Hess's law we can calculate the enthalpies of certain reactions in terms of enthalpies of other related reactions. Suppose the heat of formation of methane is to be calculated. The relevant equation is

$$C(s) + 2\ H_2(g) \rightarrow CH_4\ (g)\ ;\ \Delta H_F(CH_4) = \mathbf{x}\ \text{K cal / mole----------(i)}$$

The following data are available.

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}\ ;\Delta H_F(CO_2) = -96.0\ \text{K cal ----------(ii)}$$

$$H_{2\ (g)} + 1/2O_{2(g)} \rightarrow H_2O_{(l)}\ ;\Delta H_F(H2O) = -68.0\ \text{K cal ----------(iii)}$$

$$CH_{4\ (g)}+2O_{2(g)} \rightarrow CO_{2(g)}+2\ H_2O_{(l)};\ \Delta H_C(CH_4) = -212.8\ \text{K cal----(iv)}$$

We should aim at finding the value of heat of formation of methane. We have to manipulate these equations so as to get the required equation (equation (i))

Multiplying equation (iii) by **2** and adding to equation (i) we get,

$$C_{(s)}+ O_{2(g)}+2\ H_2+ O_{2(g)} \rightarrow CO_{2(g)} +2\ H_2O_{(l)};$$

$$\Delta H = [2\ X\ \Delta H_F\ (H_2O)]+ \Delta H_F(CO_2)$$

$$\Delta H = [2\ X\ -68.0\ \text{K. cal}] +(-96.0)\ \text{K.cal.}$$

$$= -232.0\ \text{K. cal.}$$

On subtracting (iii) from (v) we get

$$C_{(s)} +2\ H_{2(g)} \longrightarrow CH_{4(g)}\ ;\ \Delta H_F\ (CH_4) = -232.0\ \text{K. cal} - (-212.8\ \text{K. cal}) = -19.2\ \text{K. cal.}$$

Or

$$\Delta H_F\ (CH_4) = [2\ X\ \Delta H_F\ H_2O] + \Delta H_F\ (CO_2) - \Delta H_C\ (CH_4)$$

Similarly second application of Hess's law is calculation of heats of formation of compounds through the use of bond energy data.

Bond energy: Certain amount of energy is released during the bond formation of two atoms and same amount of energy is absorbed to break up this bond.

Bond energy is average energy required to dissociate a particular type of bond in one mole into the gaseous atoms, separated by a distance over which there is no attraction between the atoms. Thus the bond energy of **H-H** bond is the energy required to break all the bonds in one mole of hydrogen gas. Bond energy is the measure of strength of bond. It depends upon sizes of the atoms, their electro negativity and bond length.

Knowledge of bond enthalpy is useful for calculating heats of reaction for gaseous reactions for which no thermal data is available. The bond energy is one fourth of the total energy required to break all the four **C-H** bonds in 1 mole of methane.

$$CH_{4(g)} \longrightarrow C_{(g)} + 4H_{(g)}\ ;\ \Delta H = ?$$

The energy required to dissociate completely a molecule into the constituent atom is calculated from (i) enthalpy of formation of compound (ii) enthalpy of sublimation of solid element (Cs) from which compound is formed(iii) enthalpy of dissociation of gaseous molecule **($H_{2(g)}$)** into the atoms.

$$C_{(graphite)} + 2H_{2(g)} \longrightarrow CH_4 \; ; \Delta H_1 = -75.0 \text{ KJ}$$

$$C_{(graphite)} \longrightarrow C(g); \Delta H_2 = 720.0 \text{ KJ}$$

$$H_{2\,(g)} \longrightarrow 2H_{(g)} \; ; \Delta H_3 = 435.0 \text{ KJ}$$

Through the suitable rearrangement of the above thermo chemical equations and using Hess's law we can readily obtain the heat of desired reaction.

$$\Delta H = (2 \mathbf{x} \Delta H_3) + \Delta H_2 - \Delta H_1$$

$$CH_{4(g)} \longrightarrow C_{(g)} + 4H_{(g)} \; ; \Delta H = 1665 \text{ KJ}$$

Hence the C-H bond energy = ¼ **x** 1665 = 416.2 KJ.

Temperature Dependence of Heat or Enthalpy- Kirchoff's equation: The heat or enthalpy of reaction varies with temperature of gas due to variation in its specific heat. The expressions representing the variation of heat change of reaction with temperature are known as Kirchoff's equations.

Heat change of a reaction at constant volume is given by

$$\Delta E = E_2 - E_1$$

(E_1 & E_2 are internal energies of reactants and products.)

Differentiating this equation w.r.t temperature at constant volume, we have

$$\left[\frac{d(\Delta E)}{dT}\right]_v = \left[\frac{dE_2}{dT}\right]_v - \left[\frac{dE_1}{dT}\right]_v \quad \text{_____ (i)}$$

We have defined heat capacity of a substance at constant volume as

$$C_v = \left[\frac{dE}{dT}\right]_v$$

Therefore;

$$\left[\frac{d(\Delta E)}{dT}\right]_v = [C_v]_2 - (C_v)_1 = \Delta C_v \quad \text{_____ (ii)}$$

$(C_v)_1$ and **$(C_v)_2$** are the heat capacities for the reactants and products respectively. Thus change in heat of reaction with temperature at constant volume is equal to the difference in heat capacities of products and reactants, at constant volume.

$$\frac{d(\Delta E)}{dT} = \Delta Cv$$

$$d(\Delta E) = \Delta C_v dT$$

Integrating this equation between temperature $\mathbf{T_1}$ and $\mathbf{T_2}$, we get

$$\Delta E_2 - \Delta E_1 = \int_{T_1}^{T_2} \Delta C_v \, dT$$

Assuming ΔCv remain constant in the temperature range from T_1 to T_2 , then ΔCv can be taken our of integration sign.

$$\Delta E_2 - \Delta E_1 = \Delta C_v[T_2 - T_1] \text{---------- ----------(iii)}$$

Similarly at constant pressure Heat of reaction is given as

$$\Delta H = H_2 - H_1$$

Where H_2 & H_1 are the enthalpies of products and reactants respectively

Differentiating this equation with respect tot temperature, we get

$$\frac{d(\Delta H)}{dT} = \frac{dH_2}{dT} - \frac{dH_1}{dT} \text{----------(iv)}$$

We have defines heat capacities at constant pressure as

$$Cp = [dH/dT]_P$$

Therefore $$\frac{d(\Delta H)}{dT} = (C_P)_2 - (C_P)_1 = \Delta C_P \text{ ----------(v)}$$

$(Cp)_2$ and **$(Cp)_1$** are the heat capacities at constant pressure for products and reactants respectively. Thus change in heat of reactant at constant pressure (enthalpy change) with temperature is equal to the difference in heat capacities of products and reactants at constant pressure.

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

$$d(\Delta H) = \Delta C_P \, dT$$

Integrating this equation between temperature T_1 & T_2, we get

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

ΔH_2 and ΔH_1 are the enthalpy change at temperature T_2 & T_1 respectively.

Assuming ΔCp remaining constant, in the temperature range T_1 and T_2 , then ΔCp can be taken our of integration sign.

$$\Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1) \text{ ----------(vi)}$$

The relations **(ii), (iii), (v)** and **(vi)** are called Kirchoff's equations. These equations can be used to calculate the heat of reaction at given temperature if heat of reaction at some other temperature and ΔCp is known.

Limitation of First Law of Thermodynamics – Need For The Second Law of Thermodynamics:

i) First law only deals with inter conversion of one form of energy to another in specified process. This law fails to tell us under what conditions and to what extent it is possible to bring about conversion of one form of energy into other.

ii) The first law does not explain why chemical reactions do not proceed to completion.

Before giving statement of second law it is necessary to define some terms.

Spontaneous and non spontaneous processes: A Process which takes place in one direction of its own accord is a spontaneous process or natural process. The reverse process of the spontaneous process is referred as a non spontaneous process. The tendency of a process to occur naturally is called spontaneity.

Some examples of spontaneous process are,

i) Mixing of two gases to form a gaseous mixture is spontaneous process.

ii) Flow of heat from hot to cold body is spontaneous but cold to hot is not.

iii) Flow of gas from a vessel to another evacuated vessel occurs spontaneously unless the pressure is the same in both the vessels.

Criteria of spontaneity:

i) A spontaneous process may occur rapidly or very slowly.

ii) A spontaneous change is unidirectional and irreversible.

iii) A spontaneous process will continue till the system attains the state of equilibrium and after that it does not undergo further spontaneous change if left undisturbed.

iv) In most of the spontaneous change there is a decrease in internal energy or enthalpy but there are some endothermic processes which proceed spontaneously. It means there should be some other factor in addition to enthalpy which governs the spontaneity.

Second law of thermodynamics introduces this factor called entropy.

Entropy

It is observed that in all exothermic process which occurs spontaneously i.e. melting of ice and evaporation of water, there is an increase in randomness or disorderness. Increase in randomness or disorder favors a spontaneous change.

"Entropy is thermodynamic state property that is a measure of randomness or disorder of the molecular arrangement in a system" The symbol of entropy is **S**.

Characteristics of entropy:

i) It is a state properly and its differential is exact. Since entropy of the system is single valued function of its state, change in entropy, ΔS, of the system depends only on initial and final states and not on the path.

$$\Delta S = S_{final} - S_{initial}$$

ii) It is an extensive property.

iii) An increase in temperature increases the entropy of the system, and increase in volume has a similar influence.

iv) For any reversible process **ΔS** of system is equal to **ΔS** of surrounding but opposite in sign, so that

$$\Delta S_{system} + \Delta S_{surrounding} = 0$$

i.e. entropy change for an isolated system is zero.

For an irreversible process, **ΔS** of the isolated system> 0 i.e. entropy increases. A process accompanied by an increase in entropy tends to be spontaneous. It means increase in entropy is also a criterion for spontaneity other than the decrease in enthalpy.

Numerical definition of Entropy: In 1850 Clausius introduced a numerical definition. According to him entropy of a system (adiabatic) is a constant quantity. The amount of heat absorbed or liberated is not constant but depends upon the temperature. Higher the temperature more is the heat absorbed or liberated and vice versa.

If **q** represents the amount of heat liberated or absorbed at a temperature, **T** in going from one adiabatic to other. Then the entropy changes by **q/T**. Thus entropy could be precisely defined as

"The thermal property of substance which remains constant during an adiabatic change is called entropy."

Or

For a reversible change at fixed temperature **(T)**, the change in entropy **(ΔS)** is equal to heat absorbed or evolved divided by the temperature.

$$\Delta S = q/T$$

$$S_2 - S_1 = \Delta S = \frac{q_{rev}}{T}$$

Where S_1 and S_2 are the entropies of initial and final state of the system

In an infinitesimal process

$$dS = \frac{dq_{rev}}{T}$$

The quantity dq_{rev} is an inexact differential. Where as dq_{rev}/T is an exact differential represented as dS. Units of entropy are cal mol $^{-1}$ K^{-1} or entropy units (eu). In SI system the unit of entropy is $Jmol^{-1}K^{-1}$, represented by EU

$$1eu = 4.184 \text{ EU}$$

Statement of second law of thermodynamics:

First statements: Spontaneous process is always accompanied by an increase in the total entropy of the universe (system+ surrounding)

$$\Delta S_{univ} = \Delta S_{syst} + \Delta S_{sur}$$

For irreversible process:

$$\Delta S > 0 \quad \text{.....(a)}$$

For reversible process,

$$\Delta S = 0 \quad \text{.....(b)}$$

Combining (a) and (b), $\Delta S \geq 0$

Since the entire universe is undergoing spontaneous change, second law more concisely stated as: "*The entropy of the universe is constantly increasing*"

Second Statement: Given by Plank.

"Heat cannot be completely converted to an equivalent amount of work without causing other changes in the system."

Third Statement: Given by Clausius.

"It is impossible for a self acting machine to transfer heat continuously from one body at lower temperature to a body at higher temperature without aided by any external agency."

This statement explain the fact that heat flow from hot object to cold object is spontaneous and to get it follow in the opposite direction we have to expand some work.

Heat engine: The heat that flows spontaneously from hotter to colder body can be used to do work with the help of suitable device.

A machine which can do work by using heat that flows out spontaneously form a high temperature reservoir, is called a heat engine.

A heat engine running on a periodic cyclic process can yield work continuously.

Efficiency of heat Engine : The ratio of work **(w)** obtained in a cyclic process to the heat taken from the high temperature reservoir **(q_2)** is referred to as the efficiency of a heat engine. It is denoted by symbol **η**.

$$\eta = w/q_2$$

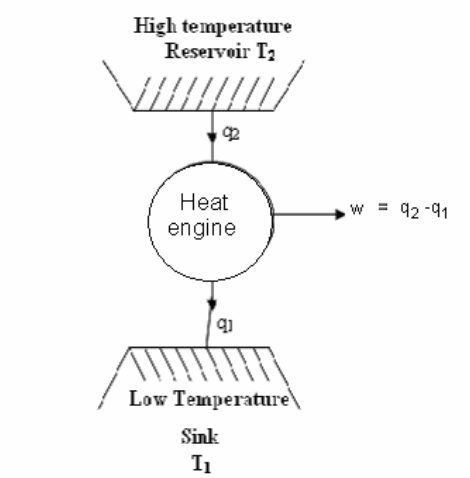


Figure-16: Illustration of principle of heat engine

Carnot's theorem: This is a direct consequence of second law of thermodynamics. It is usually stated in two parts.

i) Of all heat engines working between the same two temperature of source and sink. It is the reversible engine that has the maximum efficiency.

ii) All reversible heat engines working between same temperature limits have the same efficiency.

The Carnot Cycle: Sadi Carnot in 1824 proposed a theoretical heat engine that could perform a series of operations between temperature T_1 and T_2. So that at the end of these operations it was restored to its original state. This hypothetical four stage cycle of operations which occurred under reversible conditions is referred to as the Carnot cycle. The working substance is an ideal gas. The four operations in order are,

i) Isothermal reversible expansion

ii) Adiabatic reversible expansion

iii) Isothermal reversible compression

iv) Adiabatic reversible compression.

Above four operations are shown in the indicator diagram of Carnot cycle.

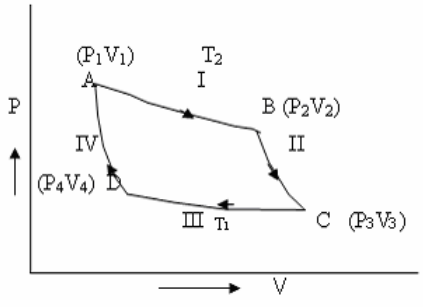


Figure-17: Indicator diagram of the Carnot's cycle.

Step I: (A→B) : The gas expands isothermally (at constant temperature T_2) and reversible from volume $\mathbf{V_1}$ to $\mathbf{V_2}$

For isothermal process $\Delta E = 0$

If q_2 = heat absorbed by the system

w_1 = work done by the system

From first law equation; $\Delta E = q-w$

$$q_2 = w_1$$

$$w_1 = \int_{V_1}^{V_2} P.dV$$

$$P = \frac{RT_2}{V}$$

$$= \int_{V_1}^{V_2} \frac{RT_2.dV}{V} = RT_2 \ln V_2/V_1 \text{ ----------(i)}$$

Step II: (B→C): The gas expands adiabatically and reversibly from volume $\mathbf{V_2}$ to $\mathbf{V_3}$ and temperature drops from $\mathbf{T_2}$ to $\mathbf{T_1}$

For adiabatic process q = 0

$$\Delta E = -w_2$$

$$w_2 = -\Delta E$$

$$= -C_V(T_1-T_2)$$

$$w_2 = C_V(T_2-T_1) \text{ ----------(ii)}$$

Step III:(C→D) The gas compressed isothermally (Temp $\mathbf{T_1}$) and reversibly from $\mathbf{V_3}$ to $\mathbf{V_4}$

$$\Delta E = 0$$

w_1 = Heat given by the system.

w_3 = Work done on the gas.

$$\Delta E = -q_1 + w_1$$

$$-q_1 = w_3$$

$$-w_3 = \int_{V_3}^{V_4} P.dV$$

$$-w_3 = \int_{V_3}^{V_4} \frac{RT_1}{V}\, dV$$

$$= RT_1 \ln V_4/V_3$$

$$w_3 = - RT_1 \ln V_4/V_3 \text{ ----------(iii)}$$

Step IV: (D→A) The gas compressed adiabatically and reversibly from volume $\mathbf{V_4}$ to $\mathbf{V_1}$ (temperature changes from $\mathbf{T_1}$ to $\mathbf{T_2}$)

$$q = 0$$

$$\Delta E = w_4 \text{ (work done on the gas)}$$

$$-w_4 = -Cv\,(T_2-T_1) \text{ ----------(iv)}$$

Net work done in a one cycle:

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

$$w = RT_2 \ln V_2/V_1 + Cv(T_2-T_1) + RT_1 \ln V_4/V_3 - Cv(T_2-T_1)$$

$$w = RT_2 \ln V_2/V_1 + RT_1 \ln V_4/V_3$$

Or

$$w = RT_2 \ln V_2/V_1 - RT_1 \ln V_3/V_4$$

Net heat absorbed in one cycle:

$$q = q_2 - q_1$$

$$= RT_2 \ln V_2/V_1 + RT_1 \ln V_4/V_3$$

Or

$$q = RT_2 \ln V_2/V_1 - RT_1 \ln V_3/V_4 \text{------ (v)}$$

For adiabatic expansion

$$\left(\frac{T_1}{T_2}\right) = \left(\frac{V_2}{V_3}\right)^{\gamma-1}$$

For adiabatic compression

$$\left(\frac{T_1}{T_2}\right) = \left(\frac{V_4}{V_1}\right)^{\gamma-1}$$

Or

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

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

By putting the value of V_3/V_4 in equation (v), we get

$$q = RT_2 \ln V_2/V_1 - RT_1 \ln V_2/V_1$$

$$q = R(T_2 - T_1) \ln V_2/V_1 \text{----------(vi)}$$

Similarly total work done in a cycle is

$$w = R (T_2 - T_1) \ln V_2/V_1 \text{ equal to net heat absorbed --------(vii)}$$

The heat absorbed q_2 form high temperature source, T_2 is

$$q_2 = RT_2 \ln V_2/V_1$$

By definition, efficiency of the engine, **η**

$$= \frac{\text{net work done by the gas in a cycle}}{\text{Heat absorbed by the gas from heat reservoir.}} = \frac{w}{q_2}$$

$$= \frac{R (T_2 - T_1) \ln V_2/V_1}{R\ T_2\ \ln V_2/V_1}$$

$$\eta = \frac{T_2-T_1}{T_2}$$

The efficiency of Carnot engine is independent on the nature of working substance and is limited by the operating temperature of the engine. The large the temperature difference **(T_2-T_1)** between the high and low temperature reservoir, the more the heat converted to work by the heat engine.

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

$$\frac{w}{q_2} = 1 - \frac{T_1}{T_2}$$

Since $w/q_2 < 1$

Therefore $q_2 > w$, it means that heat transferred by a spontaneous process is never completely converted into work.

Alternative derivation for the expression of η: Here the indicator diagram makes use of temperature **(T)** and entropy **(S)** coordinate.

Step I: (A→B): Isothermal reversible process

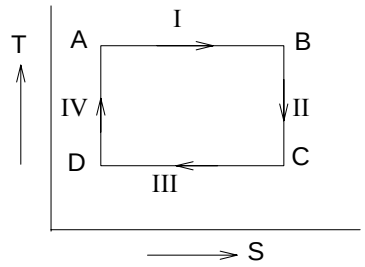


Figure 18: Indicator diagram

$$\Delta S_I = q_2/T_2$$

q_2 = heat absorbed by the gas at constant temperature $\mathbf{T_2}$.

Step II: (A→C)- Adiabatic reversible process.

$$\Delta S_{II} = 0$$

Step-III:(C→D) isothermal reversible process.

$$\Delta S_{III} = - \frac{q_1}{T_1}$$

q_1= Heat rejected to the sink at temperature T_1.

Step IV: (D→A) Adiabatic reversible process.

$$\Delta S_{IV} = 0$$

Total entropy change of the gas during the cycle;

$$= \Delta S_I + \Delta S_{II} + \Delta S_{III} + \Delta S_{IV} = 0$$

$$= \frac{q_2}{T_2} - \frac{q_1}{T_1}$$

$$q_2/T_2 = q_1/T_1$$

$$\frac{q_2}{q_1} = \frac{T_2}{T_1}$$

Subtracting 1 both sides,

$$\frac{q_2}{q_1} - 1 = \frac{T_2}{T_1} - 1$$

$$\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_1} = \eta$$

Derivation of entropy from Carnot cycle (Clausius Expression): In carnot cycle,

q_2 = (+ve), heat taken up at higher temperature T_2.
q_1= (-ve), heat given out at lower temperature, T_1

Or

$$\eta = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_1}$$

$$\frac{q_1}{q_2} = \frac{T_1}{T_2}$$

$$\frac{q_1}{T_1} = \frac{q_2}{T_2}$$

Using sign convention

$$\frac{q_2}{T_2} = -\frac{q_1}{T_1}$$

$$\frac{q_2}{T_2} + \frac{q_1}{T_1} = 0$$

Or

$$\Sigma\, q/T = 0$$

Clausius suggested that any reversible cycle may be regarded as being made up of large number of Carnot's cycles. The smooth closed curve in the figure represents cycle. Imagine a series of isothermal and adiabatic curves down across the diagram, so that a number of Carnot cycles are indicated.

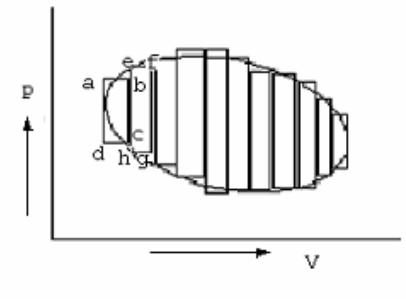


Figure-19: Reversible cycle made up of large number of Carnot's cycles.

In figure **ab** and **cd** are isothermal, while bc and da are adiabatic. So for small Carnot cycle abcd,

$$q_1/T_1 + q_2/T_2 = 0$$

Simultaneously for **efgh**, another Carnot's cycle

$$q_3/T_3 + q_4/T_4 = 0$$

Similar equations may be written for all Carnot's Cycles.
Adding all these,

$$q_1/T_1 + q_2/T_2 + q_3/T_3 + q_4/T_4 + \text{-------} = 0$$

Or, $\Sigma q/T = 0$; for the entire path which is reversible.

If number of cycle is extremely large, the zig-zag path will virtually coincide with the smooth curve. Then each cycle will be infinitesimal, so that for the entire cycle.

$$\oint \frac{\delta q_{rev}}{T} = 0$$

This suggests that $\delta q_{rev}/T$ for any path in the cycle is an exact differential, symbolized as dS, where for each infinitesimally small change,

$$dS = dq/T$$

$$\Delta S = S_{final} - S_{initial} = \int_A^B dq/T$$

ΔS is dependent only on the state of the system and can be calculated if the system, can be brought reversibly from one state to the other.

Change in entropy in an irreversible process: The efficiency of irreversible cyclic process is always less than that of a reversible one operating between the same two temperatures.

$$\frac{q_2 - q_1}{q_2} < \frac{T_2 - T_1}{T_1}$$

$$q_2/T_2 - q_1/T_1 < 0$$

It means that $\oint \delta q_{rev} = 0$ and for an irreversible cycle it is always less than zero.

Always; $S_{final} > S_{initial}$

Most of the processes occurring in nature are spontaneous and irreversible i.e. entropy of universe is constantly increasing.

Entropy change for an ideal gas: When **n** mole of an ideal gas undergoes a reversible transition from one state **(P_1,V_1,T_1)** to another **(P_2,V_2,T_2)**, if the system absorbs, **dq_{rev},** heat reversibly then increase in entropy is given by;

$$dS = dq_{rev}/T \quad \text{----------(i)}$$

$$dq_{rev} = dE + PdV \quad \text{-------- -----(First Law)}$$

Eqn (i) becomes

$$dS = \frac{dE + PdV}{T} \quad \text{----------(ii)}$$

We know that; $dE = nC_V dT$ (for n moles)

$$PV = nRT$$

Substituting this in eqn (ii)

$$dS = \frac{nCvdT}{T} + \frac{nRdV}{V}$$

Integrating between the limits S_1,S_2; T_1,T_2 and V_1,V_2, we have

$$\int_{S_1}^{S_2} dS = nCv \int_{T_1}^{T_2} dT/T + nR \int_{V_1}^{V_2} dV/V$$

$$\Delta S = S_2 - S_1 = nCv \ln T_2/T_1 + nR \ln V_2/V_1 \quad \text{----------(iii)}$$

Or

$$\Delta S = 2.303\ nCv \log T_2/T_1 + 2.303\ nR \log V_2/V_1 \quad \text{----------(iv)}$$

$$\frac{V_2}{V_1} = \frac{P_1 T_2}{P_2 T_1}$$

Substituting this in eqn (**iii**) we get;

$$\Delta S = nCv \ln T_2/T_1 + nR \ln \frac{P_1 T_2}{P_2 T_1}$$

$$= n\,Cv \ln T_2/T_1 + n\,R \ln P_1/P_2 + nR \ln T_2/T_1$$

$$= (Cv + R) \ln T_2/T_1 + n\,R \ln P_1/P_2$$

We know that

$$Cp - Cv = R$$

$$Cp = Cv + R$$

$$\Delta S = nCp \ln T_2/T_1 + n R \ln P_1/P_2 \text{ ----------(v)}$$

Or

$$\Delta S = 2.303\ nCp \log T_2/T_1 + 2.303\ n R \log P_1/P_2 \text{ --------(vi)}$$

From equation (iv) and (vi) we can calculate the entropy change of the system.

For an isothermal reversible process, $\mathbf{T_1 = T_2}$.

$$\Delta S = nR \ln V_2/V_1$$

And

$$\Delta S = 2.303\ nR \log V_2/V_1$$

$$V_2/V_1 = P_1/P_2$$

$$\Delta S = nR \ln P_1/P_2$$

And

$$\Delta S = 2.303\ nR \log P_1/P_2$$

For isochoric reversible process (constant volume)

$$\Delta S = nCv \ln T_2/T_1$$

And

$$\Delta S = 2.303\ nCv \log T_2/T_1$$

For isobaric reversible process (constant pressure)

$P_1 = P_2$ so eqn (vi) reduces to $\Delta S = nCp \ln T_2/T_1$

And

$$= 2.303\ n\ Cp \log T_2/T_1$$

Entropy change during phase change: When a system undergoes change in state from one phase to another, there is a change in entropy.

When one mole of solid melts at temperature equal to its melting point **(Tm)** and the process of melting is caused out reversibly, the change in entropy is given by

$$\Delta S_F = \frac{\Delta H_f}{T_m}$$

ΔHF = molar heat of fusion at Tm

Similarly when one mole of a liquid is boiled reversibly at its boiling point **(Tb).** It would absorb molar heat of vaporization. The entropy change in this case is given by

$$\Delta S_V = \frac{\Delta HV}{T_b}$$

ΔHV = molar heat of vaporization at T_b

Similarly for reversible phase transition form one allotropic form to another at its transition temperature Tt,

$$\Delta S_t = \frac{\Delta H_t}{T_t}$$

ΔHt = molar heat of transition at Tt.

Maxwell's Relations:A thermodynamic state of a system can be described by thermodynamic coordinates like **P,V,T, E, H,S.** Maxwell used the two law of thermodynamics and deduces following entropy relations which are perfectly general and are called Maxwell's relations.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \ldots\ldots\ldots\ldots\ldots\ldots (i)$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \ldots\ldots\ldots\ldots\ldots\ldots (ii)$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad \ldots\ldots\ldots\ldots\ldots\ldots (iii)$$

.

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad \ldots\ldots\ldots\ldots\ldots\ldots (iv)$$

First two are isothermal relations and other two are adiabatic

Thermodynamic equations of state: The relationship between E or H with P V T data is called Thermodynamic equation of state. There are two equations of state which are obtained from Maxwell's relations and are quite general, applicable to all states of matter. These are called thermodynamic equations of state.

$$P = T\left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial E}{\partial V}\right)_T$$

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

Free Energy (G) and work Functions (A) ,Gibb's Helmolt's equation: Two new functions involving energy and entropy are **A** and **G**. A portion of energy that can be converted to useful work is termed as available energy while net portion, which cannot be converted into useful work, is termed as unavailable energy. Entropy is a measure of unavailable energy and **TS** is amount of available energy.

Total energy; $X = q - TS$

$q = E$ at constant volume.

q = H, at constant pressure.

Free energy function **(G)** is defined as

$$G = H - TS$$

It is a single valued function of thermodynamic state of system and is an extensive property. When system undergoes a change of state from (1) to (2) at constant temperature

We have, $G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$

$$\Delta G = \Delta H + T\Delta S \text{ ----------(i)}$$

The work function (A) is defined as

$$A = E - TS$$

A is also a single valued function of the state of the system.

If we consider a isothermal change in state from (1) to (2)

$$(A_2 - A_1) = (E_2 - E_1) - T(S_2 - S_1)$$

$$\Delta A = \Delta E - T\Delta S \text{ -----------(ii)}$$

We know that

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

$$\Delta G = \Delta E + P\Delta V - T\Delta S$$

Or

$$\Delta G = \Delta A + P\Delta V$$

$P\Delta V$ = Expansion work.

$$-\Delta G = -\Delta A - P\Delta V$$

Net work = w – expansion work.

Therefore it is clear that decrease in free energy ($-\Delta G$) accompanying a process taking place at constant temperature and pressure is equal to the maximum work obtainable from the system other than the work of expansion.

$(-\Delta G)$ = useful work

Similarly we know that;

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

$$q_{rev} = T\Delta S$$

$$\Delta A = \Delta E - q_{rev}$$

$$\Delta E = q_{rev} - w$$

$$-w = \Delta E - q_{rev}$$

Or

$$-\Delta A = -w$$

Thus decrease in the work function **'A'** in any process at constant temperature is equal to the maximum work that can be obtained from the system during any change.
By definition:

$$G = H - TS$$

$$H = E + PV$$

$$G = E + PV - TS$$

Differentiating, we get

$$dG = dE + PdV + VdP - TdS - SdT \text{------(vi)}$$

For an infinitesimal stage of reversible process

$$dS = dq / T$$

$$TdS = dq$$

And

$$dq = dE + PdV$$

Or

$$TdS = dE + PdV \text{ ----------(vii)}$$

From **(vi)** and **(vii)**, we get

$$dG = TdS + VdP - TdS - SdT$$

$$dG = VdP - SdT \text{----------(viii)}$$

At constant pressure

$$dG = -SdT$$

$$\left[\frac{dG}{dT}\right]_P = -S$$

Similarly at constant temperature;

$$\left[\frac{dG}{dP}\right]_T = V$$

For an infinitesimal change in initial state;

$$dG_1 = -S_1 dT \text{ ----------(ix)}$$

For an infinitesimal change in final state;

$$dG_2 = -S_2 dT \text{ ----------(x)}$$

Subtracting (ix) from (x)

$$dG_2 - dG_1 = -(S_2 - S_1)\, dT$$

$$d(\Delta G) = -\Delta S dT$$

$$d\left(\frac{\Delta G}{dT}\right)_P = -\Delta S$$

Putting the value in equation **(i)** we get;

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

$$\Delta G = \Delta H + T(-\Delta S)$$

$$\Delta G = \Delta H + T\left[\frac{d(\Delta G)}{dT}\right]_P$$

This is Gibb's Helmoltz equation in terms free energy and enthalpy change at constant pressure.

By definition

$$A = E - TS$$

Differentiating we get

$$dA = dE - TdS - SdT \text{ ----------(xii)}$$

$$dq = dE + PdV$$

$$dq = TdS$$

$$dE = TdS - PdV \text{-----(xiii)}$$

From **(xii) & (xiii)**

$$dA = TdS - PdV - TdS - SdT$$

$$dA = -PdV - SdT \text{---------(xiv)}$$

At constant volume;

$$dA = -SdT$$

$$\left[\frac{dA}{dT}\right]_V = -S$$

For infinitesimal change initial and final states

$$dA_1 = -S_1dT \text{ ----------(xv)}$$

$$dA_2 = -S_2dT \text{ ----------(xvi)}$$

Subtracting (xv) from (xvi) we get

$$dA_2 - dA_1 = -(S_2 - S_1)\, dT$$

$$d(\Delta A) = -\Delta S dT$$

or $$\Delta S = d(\Delta A)/dT$$

Putting the value in eqn (ii), i.e

$$\Delta A = \Delta E - T\Delta S$$

We get,

$$\Delta A = \Delta E + T\left[\frac{d(\Delta A)}{dT}\right]_V \quad \text{----------(xvii)}$$

This equation is Gibb's Helmolt's equation in terms of internal energy and work function.

This equation can be used to calculate **ΔG** and **ΔH** when **ΔG** and **ΔA** at two temperature are given.

Free energy changes for isothermal process:

By definition;

$$G = H - TS \text{ ----------(i)}$$

$$H = E + PV$$

$$G = E + PV - TS \text{ ----------(ii)}$$

Differentiating, we get;

$$dG = dE + PdV + VdP - TdS - SdT \text{ ---------(iii)}$$

We know that.

$$dq = dE + PdV$$

$$dq = TdS$$

There fore $dG = VdP - SdT$ ----------(iv)

For isothermal change, $dT = 0$

$$dG = VdP$$

Integrating within the limits $\mathbf{G_1}$ and $\mathbf{G_2}$ and $\mathbf{P_1}$, $\mathbf{P_2}$, we get

$$\Delta G = G2\text{-}G1 = \int_{P_1}^{P_2} VdP$$

Since , $PV = RT$, for 1 mole of ideal gas.

$$V = RT/P$$

Therefore

$$\Delta G = RT \int_{P_1}^{P_2} dP/P$$

$$\Delta G = RT \ln P_2/P_1 \text{---------- (v)}$$

For n moles of ideal gas

$$\Delta G = nRT \ln P_2/P_1 \text{ ---------- (vi)}$$

Or

$$\Delta G = 2.303\ nRT \log P_2/P_1$$

We know t $P_2/P_1 = V_1/V_2$

From equation **(v)** we get

$$\Delta G = RT \ln V_1/V_2 \text{ ----------(vii)}$$

For **n** moles;

$$\Delta G = nRT \ln V_1/V_2$$

Or

$$\Delta G = 2.303\ nRT \log V_1/V_2$$

With the help of above equations we can calculate the free energy change for isothermal process having an ideal gas.

Thermo dynamical criteria for equilibrium and spontaneous change:

For a reversible process, $ds = \delta q/T$

And for irreversible process, $ds > \delta q/T$

Combining the we get, $ds \geq \frac{\delta q}{T}$

Where, = is for reversible process and > is for irreversible process.

Since $\delta q = dE + PdV$,

So, $\delta s \geq \frac{dE + PdV}{T}$

Or $TdS \geq dE + PdV$ ----------(i)

(i) in terms of entropy change of system: If the processes occurs at Constant E and V then,

$dE = dV = 0$

So $TdS \geq 0$

Or $(dS)_{E.V} \geq 0$

i.e if ds = 0 the process is reversible and if ds > O the process is irreversible or spontaneous .

(ii) in terms of internal energy : If the process occurs at constant S and V then, dS = dV= 0. So eqn (i) reduces to

$(dE)_{S.V} \leq 0$, = for reversible and < for irreversible.

i.e spontaneous or irreversible processes involves decrease in internal energy.

(iii) in terms of enthalpy change: If S and P are kept constant then eq. (i) becomes

$(dE) + PdV \leq 0$ $(\because TdS = 0)$

But $dE + PdV = dH$

So, $(dH)_{P,S} \leq 0$, = for reversible

< for irreversible.

(iv) in terms of Free energy change: Since G = H-TS

$= E + PV - TS \qquad (\because H = E + PV)$

$dG = dE + PdV + VdP - TdS - SdT$

$dE + PdV = dG - VdP + TdS + SdT$

Substituting the value of dE +PdV in eq.(i) we get,

$\cancel{TdS} \geq dG - VdP + \cancel{TdS} + SdT$

Or $dG - VdP + SdT \leq 0$

At constant P and T

$dP = dT = 0$

So $(dG)_{P,T} \leq 0$, = for reversible and < for irreversible.

(v) in terms of Work Function, We know

$A = E - TS$

And $dA = dE - TdS - SdT$

Or $TdS = dE - SdT - dA$

Substituting the value of TdS in eq.(i) we get

$\cancel{dE} - SdT - dA \geq \cancel{dE} + PdV$

$-SdT - dA - PdV \geq 0$

At constant T and V

$(-dA)_{T,V} \leq 0$, = for reversible and < for irreversible.

Significance of the entropy and the entropy factors: $\Delta G = \Delta H - T\Delta S$

At constant temperature and pressure, the deciding factor for spontaneity is **ΔG** and not **ΔH** alone or **ΔS** as shown below

ΔG = -ve ----- Spontaneous process
Δ G = 0 ----- At equilibrium
ΔG = +ve ----- Non spontaneous process.

Condition for ΔG to be negative: sign of ΔH, ΔS and ΔG, Prediction of spontaneity.

Table-2: Sign of ΔH, ΔS and ΔG, Prediction of spontaneity

Sl.No	ΔH	ΔS	ΔG	
(i)	-ve	+ve	-ve	Spontaneous at all temperature
(ii)	-ve	-ve	-ve (if $\Delta H > T\Delta S$) +ve (if $\Delta H < T\Delta S$)	Spontaneous Non spontaneous
(iii)	+ve	-ve	+ve	Non spontaneous at all temperature
(iv)	+ve	+ve	-ve ($\Delta H<T\Delta S$) +ve ($\Delta H>T\Delta S$)	Spontaneous Non spontaneous

Suggested readings

- Physical Chemistry by G.W.Castellan, 3rd edition.
- Physical Chemistry by Gordon M. Barrow, 5th edition.
- Physical Chemistry by Robert J. Silbey and Robert A. Alberty, 6th edition.