THERMODYNAMICS

What is Thermodynamics and why is it useful ?

Thermodynamics is the branch of science that describes the behaviour of matter and the transformation between different forms of energy on a macroscopic scale. Thermodynamics describes a system in terms of its bulk properties. Only a few such variable are needed to describe the system, and the variables are generally directly accessible through measurements. A thermodynamic description of matter does not make reference to its structure and behaviour at the microscopic level.

The laws of Thermodynamics :

The law's of thermodynamics is the law of observation. No one has ever observed that any thing goes in contrary to thermodynamics law. So we elevate this observation to the status of thermodynamic law. The real justification of this comes when things we derive using this law turn's out to be true that is verified by experiments :

Application of Thermodynamics :

(i) It provides relationship between heat, work and measurable properties of matter.

(ii) It predicts direction of natural change - like what circumstances are best for rusting of iron.

(iii) It predicts up to what extent a chemical reaction can proceed in forward direction.

Example : How much ammonia (NH_3) can be formed from N_2 and H_2 in a closed container.

(iv) It help in understanding why different phases of matter exist - and provide simple relationship between various measurable properties of system (thermodynamical variables) :

Salient featurs of Thermodynamics :

During study of this chapter you will observe that mostly you will be dealing with macroscopic properties (bulk properties) like pressure, volume, temperature density of system. This is because thermodynamics is macroscopic science and it do not concern's with detailed microscopic make up of the system.

Limitations :

(1) It tells us whether a given chemical reaction will take place or not under the given set of conditions but doesn't tell us anything about the rate of reaction.

(2) It tells us about the initial and final properties of the system but doesn't tell us anything about the path or mechanism followed by the system.

Basic definitions :

(i) System : Part of universe under investigation is called system.

(ii) Surrounding : Anything out side the system is called surrounding.

- **Types of system :**

(i) Closed system : A system which can exchange only energy with surrounding.

(ii) Open system : A system which can exchange both energy and matter with surrounding.

(iii) Isolated system : A system which cannot exchange matter or energy with surrounding.

(iv) Homogeneous system : System consist of single phase. eg. Pure solid, a pure liquid a solution, or a mixture of gases.

(v) Heterogenous system : A system consisting of many **phases**. eg. System of two immiscible liquids, two or more solids, a liquid in contact with its vapour etc. are example of heterogenous system.

(vi) Boundary : The interface between system and surrounding is called boundary. Across boundary energy and mass are transferred between system and surrounding. Boundary can be real or hypothetical.

(vii) Wall : A real boundary is called wall can be rigid,

◆ Types of wall :

Rigid wall : The wall is immovable $\Rightarrow w_{PV} = 0$.

Non Rigid wall : The wall is movable $\Rightarrow w_{PV} \neq 0$.

Adiabatic wall : The heat exchange across the wall is $q = 0$.

Dithermic wall : The heat can be exchanged across the wall $\Rightarrow q \neq 0$.

❑ **Phase :** By the term phase we mean a homogeneous physically distinct part of a system which is bounded by a surface and can be separated out mathematically from the other parts of the system.

❑ **The state of a system :**

We specify the state of a system - say, a sample of material - by specifying the values of all the variables describing the system. If the system is a sample of a pure substance this would mean specifying the values of the temperature, T, the pressure, p, the volume, V, and the number of moles of the substance, n.

❑ **State variables :** To define a thermodynamics states of a system, we have to specify the values of certain mesurable quantities. These are called thermodynamic variable or state variable.

A system can be completely defined by four variables namely pressure, temperature, volume and composition. A system is said to be in a certain definite state when all of its properties have definite value.. **Between two fixed state the change in the value of state function is same irrespective of the path connection two states.**

Differential of a state function integerated over a cyclic path returns zero. In other words summation of change in state function in a cyclic process is equal to zero.

if $\oint dX = 0$ =>X is a state function (property of state function)

note that if X is a state function, **dX** is called **definite quantity**

Example : T, V, P and U (internal energy), H (enthalpy) are state variables.

❑ EXAMPLE BASED ON BASIC DEFINITION :

1. Which one is not a state function :-

(A) internal energy (B) volume (C) heat (D) enthalpy

Ans. (C)

2. When no heat energy is allowed to enter or leave the system, it is called :-

(A) isothermal process (B) reversible process (C) adiabatic process (D) irreversible process

Ans. (C)

3. Which is the intensive property :-

(A) temperature (B) viscosity (C) density (D) all

Ans. (D)

4. A thermodynamic state function is :-

(A) one which obeys all the law of thermodynamics

(B) a quantity which is used in measuring thermal changes

(C) one which is used in thermo chemistry

(D) a quantity whose value depends only on the state of system

Ans. (D)

5. A system is changed from state3 A to state B by one path and from B to A by another path. If ΔE_1 and ΔE_2 are the corresponding changes in internal energy, then :-

(A) $\Delta E_2 + E_2 = +ve$ (B) $\Delta E_1 + \Delta E_2 = -ve$ (C) $\Delta E_1 + \Delta E_2 = 0$ (D) none of the above

Ans. (C)

6. A well stoppered thermos flask contains some ice cubes. This is an example of a :-

(A) closed system (B) open system

(C) isolated system (D) non-thermodynamics system

Ans. (C)

- **Path function or path dependent quantities :**

The value of path function depends upon path connection two states . There can be infinite vaules of path function between two states depending upon path or process.

Path functions are also called **indefinite quantities** since between two fixed state the value of path function is not fixed. **Heat** and **Work** are two important path dependent quantities with which we deal in this chapter.

- **Extensive and Intensive variables :**

Propterties which depend on the amount of the substance (or substances) present in the system are called extensive propterties. e.g. Mass, volume, heat capacity, internal energy, entropy, Gibb's free energy (G), surface area etc. These properties will change with change in the amount of matter present in the system. It is important to note that the total value of an extensive property of a system is equal to the sum of the values of different parts into which the system is divided.

Intensive properties : Properties which are independent of the amount of substance (or substances) present in the system are called intensive properties, e.g. pressure, density, temperature, viscosity, surface tension, refractive index, emf, chemical potential, sp. heat etc, These are intensive properties.

An extensive property can be converted into intensive property by defining it per unit of another extensive property.

Ex. Concentration = mole / volume

Density = mass / volume

heat capacity = heat absorbed / rise in temperature

While mole, mass, heat are extensive properties, concentration, density and heat capacity are intensive properties.

- **Thermodynamic equilibrium :**

Thermodynamic generally deals the equilibrium state of the system in which the state variable are uniform and constant throughout the whole system.

The term thermodynamic equilibrium implies the existence of three different types of equilibria in the system. These are :

(i) Mechanical equilibrium :

When there is no macroscopic movement within the system itself or of the system with respect to surroundings, the system is said to be in a state of mechanical equilibrium.

(ii) Chemical equilibrium :

When the system consists of more than one substance and the composition of the system does not vary with time, the system is said to be in chemical equilibrium. The chemical composition of a system at equilibrium must be uniform and there should be no **net** chemical reaction taking place.

(iii) Thermal equilibrium :

When the temperature throughout the entire system is the same as that of the surroundings then the system is said to be in thermal equilibrium.

- **Equation of state :**

  An equation that relates the variables T, p, V, and n to each other is called the "equation of state." The most general form for an equation of state is.

  $$f\,(p, V, T, n) = 0.$$

- **The ideal gas equation of state :**

  The best known equation of state for a gas is the "ideal gas equation of state". It is usually written in the form,

  $$pV = nRT$$

  This equation contains a constant, R, called the gas constant.

- **The vander Walls equation of state for real gases :**

  The vander Walls equation of state is,

  $$\left(p + a\frac{n^2}{V^2}\right)(V - nb) = nRT$$

  Notice that the vander Walls equation of state differs from the ideal gas by the addition of two adjustable parameters, a, and b (among other things).

Note : Equation of state for liquid and solids are also defined empirically.

- **Process :** Anything which changes state of system is called process. Usually as a result of heat and work interactions change of state take place. e.g. isothermal process

- **Path of a process :** The exact sequence of steps through which system changes state is called path of a process.e.g. reversible or irrervisible path

- **Some thermodynamic processes :**

  (1) **Isothermal process :** A process in which temperature of the system remains constant is called isothermal process.

  (2) **Isobaric process :** A process in which pressure of the system remains constant is called isobaric process. Temperature and volume of the system may change.

  Ex. All the reactions or processes taking place in open vessel like boiling of water in open vessel, burning of charcoal, melting of wax take place at contant pressure (1 atm.)

  (3) **Adiabatic process :** A process in which no heat exchange takes place is called adiabatic process. Adiatatic process occurs in isolated systems.

  (4) **Isochoric process :** The process for which volume of the system remains constant is called isochoric process i.e., Heating of gas in closed vessel.

  (5) **Cyclic process :** If a system after completing a series of different process returns to its initial state then overall process is called cyclic process.

  In cyclic process all the state variables remains constant because initial state becomes final state in cyclic process.

  Ex. $\Delta H = 0$, $\Delta E = 0$, $\Delta P.E. = 0$

- **Polytropic processes :** It is defined as a process in which PV^n=constant =k

  All of the above mentioned processes can be performed in two ways , **reversibly and irreversibly**

- **Reversible process :** When the difference between driving force and opposing force is very small and the process is carried out infinitesimally slowly, then the process is called reversible process. The reversible process is carried out in such a manner that at any moment of the change the directon of process can be reversed by making a small change in driving force.A reversible process is also called quasi static process. During a reversilbe process, the system and surrounding remain in equilibrium throught the process.

The reversible proceses are idealized processes which cannot be actually carried out, but neverthless they are very important because they help in calculation of change in state function in the process.In other words the reversible processes are **hypothetical processes.**

A quasi static process is the one in which system remain infinitesimally closer to the state of equilibrim through out the process.

- **Irreversible process** : Any process which does not take place in the above manner and difference between driving force and the opposing force is quite large is called irreversible process.All natural processes are example of irreversible process.

	Reversible process		Irreversible process
(1)	Driving force is infinitesimally small.	(1)	Driving force is large and finite.
(2)	PV work is done across pressure difference **dP**	(2)	PV work is done across pressure difference **ΔP**
(3)	A reversible heat transfer take place across temperature difference **dT**	(3)	Irrerversible heat transfer take place across temperatur difference **ΔT**
(4)	It is an **ideal process**.	(4)	It is a **real process.**
(5)	It takes infinite time for completion of process.	(5)	It takes finite time for completion of process..
(6)	It is an imaginary process and can not be realised in actual practice.	(6)	It is a natural process and occurs in particular direction under given set of conditions.
(7)	Throughout the process , the system remain infinetesimelly closer to state of equilibrium and exact path of process can be drawn	(7)	The system is far removed from state of equilibrium and exact path of process is indeterminate.

- **Heat and Work** :

Heat and work both are mode of energy transfer between system and surrounding.

Heat flows due to **temperature gradient** while work is done due to imbalance of **generalized force.** Due to imbalance of generalized force(intersive property) generalized displacement (extensive property) is produced. The product of generalized force and generalized displacement is work.

Work done on the system can reversible and irrervisible depending on magnitude of imbalance of generalized force.

Heat is also transfered between system and surrounding in two ways – reversible and irreversible.

Reverssible heating means heating an object from T_i to T_f using infinite heat reservoirs.

Irreverssible heat transfer means heat transfer across temp difference ΔT.

Heating an object from 100 K to 1000 K by using heat reservoir of temperature 1000 K is an example of irreverssible heating.

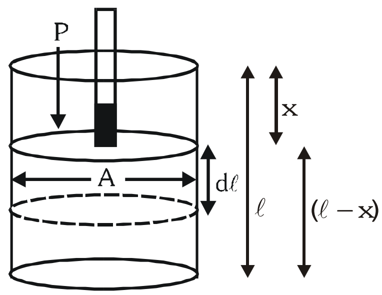
While heating an object from 100 to 1000 K using reservoir of temp 100 + dT, 100 + 2dT, ……… 1000 – dT, 1000 K is an example of reversible heating. You can clearly see reversible heating is hypothetical concept.

Work can be of many types :

The following table show different kinds of work.

Type of Work	Variables	Equation for Work	Conventional Units
Volume expansion	Pressure (P), volume (V)	$w = -\int P_{external} dV$	Pa m^3 = J
Stretching	Tension (γ), length (l)	$w = -\int \gamma dl$	N m = J
Surface expansion	Surface tension (γ), area (σ)	$w = -\iint \gamma d\sigma$	$(N\ m^{-1})\ (m^2)$ = J
Electrical	Electrical potential (ϕ),	$w = -\int \phi dq$	V C = J

❑ **PV-WORK** Consider a clylinder fitted with a frictionless piston, which enclosed n mole of an ideal gas. Let an external force F pushes the piston inside producing displacement in piston.Let distance of piston from a fixed point is x and distance of bottom of piston at the same fixed point is ℓ. This means the volume of cylinder = $(\ell - x)A$ where A is area of cross section of piston.



◆ For a small displacement dx due to force F , **work done on the system**.

$$dw = F.dx$$

Also $$P = \frac{F}{A}$$

$$F = PA$$

$$dW = PA.dx$$

$$V = (\ell - x)\ A$$

$$\Rightarrow \quad dV = -\ A\ .\ dx$$

$$\Rightarrow \quad dW = -\ P_{ext.}\ dV$$

Note: During expansion dV is +ive and hence sign of w is -ive since work is done by the system and -ive sign representing decrese in energy content of system. During compression, the sign of dV is -ive which gives +ive value of w representing the increase in energy content of system during compression.

❑ **SIGN CONVENSIONS :**

◆ According to latest sign conventions

(a) Work done is taken negative if it is done by the system since energy of system is decreased.
Ex. Expansion of gas.

(b) Work done is taken positive if it is done on the system, since energy of system is increased.
$\therefore \quad W = -\ P_{ex}.\Delta V$

Q. Find the work done in each case :

(a) When one mole of ideal gas in 10 litre container at 1 atm. is allowed to enter a vaccuated bulb of capacity 100 litre.

(b) When 1 mole of gas expands from 1 litre to 5 litre against constant atmospheric pressure.

A. (a) $W = -\ P\Delta V$

But since gas enters the vaccum bulb and pressure in vaccum is zero. This type of expansion is called **free expansion** and work done is zero.

Note : Work done in free expansion is always zero.

(b) $W = -P\Delta V = -1(5 - 1) = -4$ litre-atm.

Q. Find the work done when 18 ml of water is getting vapourised at 373 K in open vessel (Assume the ideal behaviour of water vapour).

A. $PV = nRT$ [V in litre and T in Kelvin]

$PV = 1 \quad 0.0821 \quad 373$

$PV = 30$ litre [P = 1atm.]

$V = 30$ litre

$W = -P\Delta V$

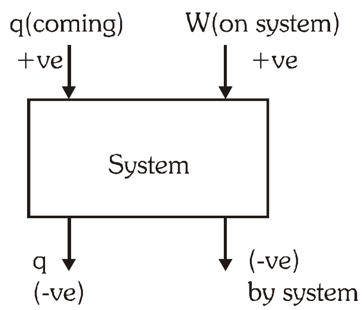
$= -1(30 - V_{gas})$ [18 ml is negligible as compared to 30 litre]

$= -1 \quad 30 = -30$ litre atm.

- **Heat** : Heat is defined as the amount of energy which flows between system and surrounding because of temperature difference.

Note : Heat always flows from high temperature to low temperature .

- **Sing convention :**
  - Heat is taken negative when it goes out of the system.
  - Heat is taken positive when it comes inside the system.



Difference between heat and work :

When a gas is supplied some heat, its molecules move faster and with greater randomness in different directions. But when work is done on the same system gas molecules are compressed and move initially in direction of force as they get condensed.

So heat is random form of energy while work is organised from of energy.

The internal energy and the first law of thermodynamics :

The first law of thermodynamics is based on experience that energy can be neither created nor destroyed, if both the system and the surroundings are taken into account.Suppose a blocks of mass 'M' is moving in gravitational field with velocity v. The total energy of blocks (in earth frame of reference) is given as :

$E = K + V + U$: (K = kinetic energy, V = potential energy, U = internal energy)

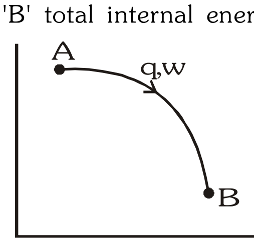
A thermodynamic system is studies generally at rest so K = 0. If effect of gravitation field (or other fields are ignored) is also ignored then we left with E = U. Thus U (internal energy) is energy of system.

If a system is present in particular thermodynamic state say 'A' it has fixed amount of internal energy U_A. Suppose by a process the system is taken from state A to state B. In the process 'q' heat is absorbed by system and w work is done on the system. Thus in the state 'B' total internal energy of system become

$U_B = U_A + q + w.$

$U_B - U_A = q + w$

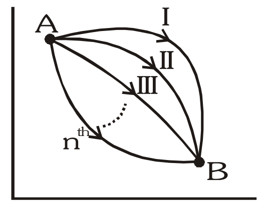
$\Rightarrow \boxed{\Delta U = q + w}$



This is mathematical statement of first law.

First law of thermodynamics states that energy is conserved. Direct consequence of this statement is U is state function. This implies between any two fixed state, there can be infinite process or path, but ΔU in all process will remain the same.(Property of a function of state)

Consider a system taken from state A to B by n^{th} different paths.



$\Rightarrow$ from first law

$U_B - U_A = q_1 + w_1 = q_2 + w_2 = \ldots\; q_i + w_i$

Here q_i, w_i are heat and work involve in respective processes.

- Note that heat and work involve in all the process are different but ΔU is same. This mean heat and work are indefinite quantities while ΔU is a definite quantity.

$\Rightarrow$ Some other statement of first law :

$\sum\limits_{\substack{\text{cyclic} \\ \text{process}}} \Delta U = 0$ = or $\oint dU = 0$ {Integral of dU over cyclic path is zero.}

First law of thermodynamics applied to close system involving only PV work.

For system involving only PV work first law mathematical statement can be written in differential from as :

$$\boxed{dU = dq - PdV}$$

The microscopic nature of First law of thermodynamics:

The internal energy of the gas confined in a container is defined relative to a coordinate system fixed on the container. Viewed at a microscopic level, the internal energy can take on a number of forms such as.

- The kinetic energy of the molecules ;
- The potential energy of the constituents of the system ; for example, a crystal consisting of dipolar molecules will experience a change in its potential energy as an electric field is applied to the system ;
- The internal energy stored in the form of molecular vibrations and rotations;
- The internal energy stored in the form of chemical bonds that can be released through a chemical reaction.

The total of all these forms of energy for the system of interest is given the symbol U and is called the internal energy.

Hence total internal energy of a system can be written as

$U = U_{translational} + U_{rotational} + U_{vibrational} + U_{intermolecular} + U_{electronic} + U_{relativistic}$

of these $U_{relativistic}$ and $U_{eletronic}$ is unaffected by ordinary heating. So basically the kinetic energy terms and $U_{intermolecur}$ accommodate heat provided to the system . Hence heat capacity of a sample depends upon these four terms.

For an ideal gas, $U_{intermolecular}$ is equal to zero, because of absence of intermolecular force of attraction in ideal gas. $U_{intermolecular}$ have large and negative value in solids and liquids.

For an ideal gas U is only function of temperature e.g. U=F(T) +Constant

Due to absence of pressure or volume terms in ideal gas internal energy, U is independent of pressure and volume of theoretical ideal gas.

Enthalpy :

Chemical reactions are generally carried out at constant pressure (atmospheric pressure) so it has been found useful to define a new state function **Enthalpy** (H) as :

$H = U + PV$ (By definition)

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

or $\Delta H = \Delta U + P\Delta V$ (at constant pressure) combining with first law. Equation (1) becomes

$\Delta H = q_p$

Heat exchange at constant volume and constant pressure (q_p and q_v) :

For an isochoric process in a system involving only PV work,

$\Delta U = q_V$

This result is valid for all the substance under isochoric conditions (when only PV work is involved) Also from the previous article it is clear that

$\Delta H = q_p$

This result is valid for all the substance involving isobaric process(when only PV work is involved)

Hence heat exchanged at constant pressure and volume are important **Definite quantities**

Heat capacity :

The heat capacity of a system may be defined as the amount of heat required to raise the temperature of the system by one degree.

If δq is the small quantity of heat added to the system, let the temperature of the system rises by dT, then heat capacity C of the system is given by

$$C = \frac{dq}{dT} \qquad \text{.....(i)}$$

In case of gases we have two types of heat capacity i.e. heat capacity at constant volume and heat capacity at constant pressure.

Heat capacity at constant volume(C_v) :

Molar heat capacity at constant volume is defined by the relation

$$C_V = \frac{dq_v}{dT} \qquad \text{....(ii)}$$

For first law of thermodynamics

$$dU = dq - dw$$

But $$dw = P\,dV$$

$\therefore$ $$dU = dq - P\,dV \qquad \text{....(iii)}$$

At constant volume

$$dU = dq_v$$

$\therefore$ Heat capacity at constant volume C_v is given by

$$C_v = \frac{dq_v}{dT} = \left(\frac{\partial U}{\partial T}\right)_v$$

or $$C_v = \left(\frac{\partial U}{\partial T}\right)_v \qquad \text{.....(iv)}$$

It may be defined as the rate of change of internal energy with temperature at constant volume.

❑ **Heat capacity at constant pressure(C_p) :**

When pressure is maintained constant, equation (i) takes the form

$$C_p = \frac{\delta q_v}{dT} \quad .....(v)$$

From first law of thermodynamics

At constant pressure

$$\delta q_p = (dU + PdV) = dH$$

$[\because\ H = U + PV \text{ At constant P, } dH = dU + PdV]$

$\therefore \quad \delta q_p = dH \quad ....(vi)$

Heat capacity at constant pressure C_p is given by

$$C_p = \frac{\delta d_p}{dT} = \left(\frac{\partial H}{\partial T}\right)_P$$

or $$C_p = \left(\frac{\partial H}{\partial T}\right)_P \quad ....(vii)$$

It is the rate of change of enthalpy with temperature at constant pressure.

Hence heat capacity of a system at constant volume C_v is equal to the increase in internal energy of the system per degree rise of temperature at constant volume. Similarly heat capacity at constant pressure C_p is numerically equally to the increase in enthalpy of the system per degree rise of temperature.

For 1 mole of an ideal gas, heat capacity at constant pressure i.e. C_p is greater than the heat capacity at constant volume i.e., C_v

$$C_p > C_v$$

These are called molar heat capacities

i.e, $$C_p = \left(\frac{\partial H}{\partial T}\right)_P$$

and $$C_v = \left(\frac{\partial U}{\partial T}\right)_V$$

Note: For ideal gases, since U and H are only function of temperature, hence subscript P and V from C_p and C_v equation can be droped , which means $C_p = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)$ which means $C_p = \left(\frac{\partial H}{\partial T}\right)$

hence for any process involving ideal gas $dH = C_p dT$

similarly for change in internal energy involving ideal gas, the subscript V from the expression of C_v can be dropped. Hence, $dU =w\ C_v dT$ for all process involving ideal gases.

Hence ΔH and ΔU is equal to zero for isothermal process involving ideal gases.

Note : The relation $dH = C_p dT$ valid for any substance other than ideal gas only in isobaric process.

The relation $dU= C_v dT$ valid for any substance other than ideal gas only in isochoric process.

Ex. 10 dm^3 of O_2 at 101.325 kP_a and 298 K is heated to 348 K. Calculate the heat absorbed, ΔH and ΔU of this process at

(a) at constant volume

(b) at constant volume

Given : $C_p/JK^{-1}\ mol^{-1} = 25.72 + 0.013\ (T/K) - 3.86 \quad 10^{-6}\ (T/K)^2$

Assume ideal behaviour.

Sol. Amount of the gas, $n = \dfrac{PV}{RT}$

or $\quad n = \dfrac{(101.325)(10)}{(8.314)(298)} = 0.409$ mol.

(a) constant pressure

$$q_P = \Delta H = n\int_{T_1}^{T_2} C_P dT$$

Here $\quad T_2 = 348$ K, $T_1 = 298$ K

or $$q_P = 0.409\left[(25.72)(T_2 - T_1) + 0.013\left(\frac{T_2^2}{2} - \frac{T_1^2}{2}\right) - (3.86\times10^{-6})\left(\frac{T_2^3}{3} - \frac{T_1^3}{3}\right)\right]$$

or $\quad q_P = 0.409 \quad 1475.775 = 603.59$ J $\quad$ **Ans.**

$\Delta U = \Delta H - \Delta(PV)$

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

at constant pressure

$\Delta U = \Delta H - P\Delta V = \Delta H - nR\Delta T$

$= 603.59 - 0.409 \quad 8.314 \quad 50$

$= 433.57$ J **Ans.**

(b) At constant volume

$$q_P = \Delta H = \int_{T_1}^{T_2} nC_V dT = \int_{T_1}^{T_2} nC_P dT - \int_{T_1}^{T_2} nR\,dT$$

$= 603.59 - 170.02 = 433.57$ J $\quad$ **Ans.**

$\Delta H = \Delta U + \Delta\ (PV) = \Delta U + nR\Delta T = 603.59$ J $\quad$ **Ans.**

Ex. Calculate the work done when 1 mol of zinc dissolves in hydrochloric acid at 273 K in :

(a) an open beaker

(b) a closed beaker at 300 K.

Sol. (a) From one mole of zinc, the no. of moles of H_2 gas evolved = 1

Hence volume of hydrogen gas evolved = 22.4 litre (when P = 1 atm and T = 273 K)

$\therefore\ w = -P\Delta V = -1 \quad 22.4$ litre atm

$= -22.4 \quad \dfrac{8.314}{0.082} J = -2271.14$ J $\quad$ **Ans.**

(b) For a closed system P_{ext} = 0., therefore, w = 0.

Degree of freedom and equipartition principle :

According to Law of equipartition of energy (i) each translation and rotational degree of freedom in a molecule contributes $\frac{1}{2}RT$ to the thermal energy of one mole of a gas, and (ii) each vibrational degree of freedom in a molecule contributes RT to the thermal energy of one mole of a gas.

The degrees of freedom in a molecule are given by the **number of coordinates** required to locate all the mass points (atoms) in a molecule. If a molecule contains only one atom (as in a monatomic gas), it has three degrees of freedom corresponding to translational motion in the three independent spatial directions X, Y and Z. If a molecule contains N atoms, each atom contributes these three degrees of freedom, so the molecule has a total of 3N degrees of freedom. Since three coordinates (degree of freedom) are required to represent the translational motion of the molecule, the remaining (3N − 3) coordinates represent what are called the **internal degrees of freedom**. If the molecule is linear, it has two rotational degrees of freedom ; for a non-linear molecule, there are three rotational degrees of freedom. The remaining degrees of free-dom, that is 3N − 5 for linear and 3N − 6 non - linear molecules are the vibrational degrees of freedom. Table list the degrees of freedom for several molecule.

In a monatomic molecule $\bar{E} = 3RT/2$ in agreement with the simple model. For a diatomic molecule, there are three translational, two rotational (because the molecule is linear) and

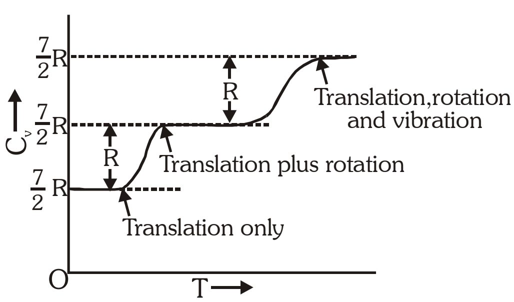
Type	Molecule	trans	rot	vib	Total
Monoatomic	He	3	0	0	3
Diatomic	N_2	3	2	1	6
Triatomic linear	CO_2	3	2	4	9
non-linear	H_2O	3	3	3	9

one vibrational degrees of freedom making a total of six. the thermal energy per mole would, therefore, be,

$$\bar{E} = (\frac{1}{2}RT)_{trans} + (\frac{1}{2}RT)_{rot} + (1RT)_{vib}$$

and $\bar{C}_V$ = 3R/2 + R + R = 7R/2 = 7 cal deg^{-1} mol^{-1}

Table shows that the observed values of $\bar{C}_V$ for diatomic molecules deviate greatly from the predicted values, The fact that the value of 5 cal deg^{-1} mol^{-1}(which is close to 5R/2) is most common for simple diatomic molecules shows that vibration degrees of freedom are active only at very high temperature.The following graph shows



Variation of heat capacity at constant volume of a di atomic gas due to excitaton of rotational and vibrational levels.

variation of C_v with temperature highlighting the fact that with increase in temperature the vibriation modes of motion also contribute to the heat capacity

- **Relationship between C_p and C_v for ideal gas :**

Hence transfer of heat at constant volume brings about a change in the internal energy of the system whereas that at constant pressure brings about a change in the enthalpy of the system.

from the first law $dH = dU + d(PV)$ for a differential change in state

if only ideal gas is involved $PV=nRT$ $dU= nC_v dT$ and $dH=nC_p dT$

substituting these results we get

$nC_p dT= nC_v dT + nRdT$

$C_p=C_v+ R$ valid only for ideal gas

relationship between C_p and C_v for real gases, liquid and solids is beyond the scope of JEE syllabus.

- **Internal energy and enthalpy change in process involving ideal gases :**

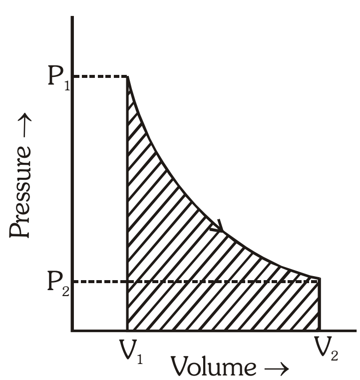
(i) Reversible isothermal process :

Take an ideal gas in a cylinder fitted with a frictionless piston. The cylinder is put in a large constant temperature bath and pressure over the piston is changed infinitesimally slowly.

If external pressure is decreased by infinitesimal small value, piston will go up by infinitesimal distance 'dx' and temperature of gas inside piston decreases by dT (due to kinetic energy transfer of molecule to piston). To maintain thermal equilibrium infinitesimally small least dq will enter into the system. If the process is continued

for infinite steps, the path of process is an isotherm on P.V. graph.

If the gas is expanded from initial volume V_1 to final volume V_2 by gradually changing external pressure infinite steps, process is called reversible isothermal process.



During reversible process :

$P_{ext} = P_{int} \pm dP$

$\Rightarrow P_{ext} = P_{int} = \dfrac{nRT}{V}$ for an ideal gas

because $P_{int} = P_{ideal} = \dfrac{nRT}{V}$

$dw_{rev,\ isothermal} = -\ PdV$

$\int dw = -\int \dfrac{nRT}{V} dV$

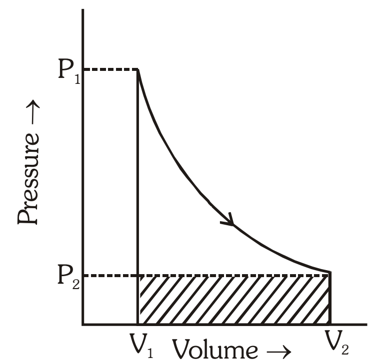
Work done in reversible isothermal expansion $\boxed{w = -nRT\ln\left(\dfrac{V_2}{V_1}\right)}$

- **Important points :**

If the reversible isothermal expansion is reversed by gradually increasing the pressure the system will return to initial state retracing it's path. This mean path of reverssible process can be exactly reversed if conditions are reversed.

- Work done by the system during reversible isothermal expansion is maximum possible work obtainable from system under similar condition.

❑ **Irreversible isothermal expansion** : If external pressure over the piston is abruptly changed from the equilibrium value, the mechanical equilibrium of system is distured and piston rushes out :

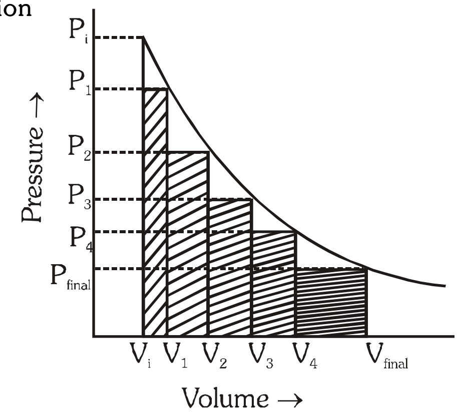


This type of P.V. work is irreversible P.V. work. To calculate irreversible P.V. work law of conservation of energy is used. Suppose as a result of difference in pressure a piston moves out and aquire kinetic energy ΔK and in the process volume increase by ΔV then $w_{irr} = -P_{ext}\ \Delta V - \Delta K$.

If after sufficient times piston come back to equilibrium final state (off course in the process it moves up and down from equilibrium position many times), $\Delta K = 0$: If all the aquired kinetic energy is transferred back to ideal gas,

$$w_{irr} = -\ P_{ext.}\ \Delta V$$

❑ **Many steps Irreversible isothermal expansion and compression** (Comparison) consider an irrerversible expansion of an ideal gas from initial pressure of P_i to final pressure of P_f in four steps. The gas is allowed to expand against constant external pressure of P_1, P_2, P_3 and P_4 and finally P_f . Hence the system passes on to final state through four equilibrium states. The work done in the process is shown graphically . The area under the isotherm is the magnitude of reversible work. Clearly the magnitude of reversible work of expansion is greater than irreversible work. As the number of intermediate steps in irrervisible expansion is incresesed, the magnitude of work increases, and as number of steps tend to infinity, w_{irr} tends to $w_{rev.}$ The graphical comparison of irreversible and reversible work is shown in fig. Here , system is taken from initial state to the final state in four steps and isotherm represent magnitude of reversible work. Clearly, $w_{reversible}$is less than $w_{irreversible}$. Once again as the number of steps in irreversible compression increases, work required to compress the ideal gas decreases, and as number of steps tends to infinity, the $\mathbf{w_{rev}} = \mathbf{w_{irr}}$.



❑ **Free expansion of ideal gas**: When ideal gas is allowed to expand against zero external pressure, the process is called free expansion. W=0 for free expansion. During the free expansion, the ideal gas do not lose any energy , and hence temperature of ideal gas remain constant. Hence, free expansion of ideal gas is an example of isothermal, adiabatic irreversible process.

However if a real gas is allowed to expand in vaccum, the gas may be cooled or heated up depending upon temperature of the real gas. The temperature above which a gas hots up upon expansion is called inversion temperature. The inversion temperature is strictly not in JEE sllaybus

❑ **Stoppered expansion(kind of an irreversible expansion)**: In this expansion , the gas is allowed to expand against constant external pressure but the piston is stopped at certain volume when system gradually attains equilibrium. In this type of expansion , the $P_{external}$ and P_{final} are different. The stoppered expansion will help you realize that there can be infinite irreversible path's connection for any two given state at same temperature.(the same can be said about reversible paths)

the work done during stoppered expansion can be given by

$$w = -\ P_{ext}\left(\frac{nRT_f}{P_f} - \frac{nRT_i}{P_i}\right) \qquad \text{where } P_{ext} \text{ and } P_f \text{ are different}$$

❑ **Reversible adiabatic process** : In an adiabatic process, no loss or gain of heat takes place i.e., dq = 0.

From first law, we have,

$dq = dU + dw$

Since $dq = 0$

∴ $dU = -dw$

For an ideal gas,

$dU = C_v\, dT$

∴ $C_v\, dT = -\, dw = -\, pdV$

or, $C_v dT = -\,(nRT/V)dV$

or, $C_v dT/T + nR\, dV/V = 0$

Intergrating the above equation between T_1 and T_2 and V_1 and V_2, the initial and final temperature and volumes, we have,

$$\int_{T_1}^{T_2} C_v \frac{\partial T}{T} + nR\int_{v_1}^{v_2}\frac{\partial V}{V} = 0$$

or $$C_v \ln \frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1} = 0$$

Here C_v is assumed to be independent of temperature.

But, $C_p - C_v = nR$

Hence, from we get

$$C_v \ln \frac{T_2}{T_1} + (C_p - C_v)\ln\frac{V_2}{V_1} = 0$$

or, $$\ln \frac{T_2}{T_1} = \frac{C_p - C_v}{C_v}\ln\frac{V_1}{V_2}$$

we put,

$C_p/C_v = \gamma$

Equation may therefore be written as,

$$(\gamma - 1)\ln\frac{V_2}{V_1} + \ln\frac{T_2}{T_1} = 0$$

or $$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

or $(T_1V_1)^{\gamma-1} = (T_2V_2)^{\gamma-1}$ = constant

For an ideal gas,

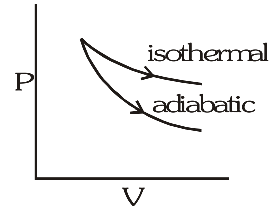
$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

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

∴ from equation we have

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

In general, for a reversible adiabatic expansion



$P.\ V^{\gamma} =$ constant

$TV^{\gamma-1} =$ constant

$TP^{1-\gamma/\gamma} =$ constant

work done is given by either $w = nC_v(T_2 - T_1)$ or rearranging it gives $w = (P_2V_2 - P_1V_1) / \gamma - 1$

For an isothermal expansion, PV = constant.but for an reversible adiabatic expansion PV^{γ} = constant differentiating both PV and $PV^{\gamma-1}$ with respect to V we get for isothermal process $dP/dV = -P/V$ while for adiabatic process $dP/dV = -\gamma\ (P/V)$ since γ is always >1 slope of P V curve is more negative in case of adiabatic process.

In figure, pressure and volume are plotted for isothermal and adiabatic cases. It is evident that a given pressure fall produces a lesser volume increase in the adiabatic case, because the temperature also falls during the adiabatic expansion.

- **The irreversible adiabatic process** : Suppose an ideal gas is confined in a adiabatic container fitted with friction less piston. If the thermodynamic equilibrium of system is disturbed by changing external pressure suddenly by finite value and let the system come to equilibrium the process is irreversible adiabatic process. The work done (w) is given by

$$\Delta U = w = -P_{ext}(V_f - V_i)$$

$$\Delta U = nC_V(T_f - T_i)$$

$$\Rightarrow \quad nC_V(T_f - T_i) = -P_{ext}(V_f - V_i)$$

$$nC_V(T_f - T_i) = -P_{ext}\left(\frac{nRT_f}{P_f} - \frac{nRT_i}{P_i}\right)$$

solving this equation for T_f

now $w = \Delta U = nC_V(T_2 - T_1)$

$$w = \left[\frac{P_fV_f - P_iV_i}{\gamma - 1}\right]$$

- **Comparison of isothermal and adiabatic process :**

Starting from same state, if system is allowed to expand to same final pressure,

$|w_{rev,\ isothermal}| > |w_{rev,adiabatic}|$.

In reversible isothermal process, heat is entering from surrounding, while in adiabatic process, work is done on the expansion of internal energy of system.

Starting from same initial state, if system is compressed to same final pressure, $w_{rev,adia} > w_{rev,iso}$. During adiabatic compression, the work done is getting stored in the system, and temperature of system increses, the gas become less and less compressible, and greater work is required to compress the system.

- **Polytropic process** : A process discribed by $PV^n = C$ is called polytropic process. where n is a real number. Work done for polytropic process :

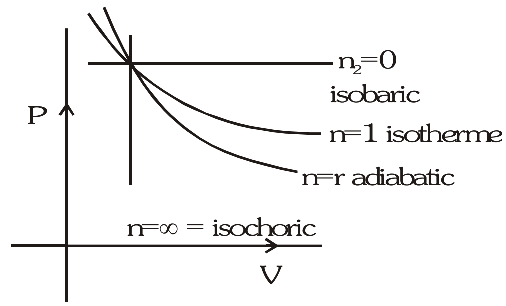
$$dw = -PdV$$

Let us suppose an ideal gas is undergoing polytropic process

$$dw = -PdV$$

$$\int dw = \int_{V_1}^{V_2} \frac{C}{V^n} dV$$

$$\Rightarrow \quad w = \frac{-C}{(-n+1)} \cdot \frac{1}{V^{n-1}}\Bigg]_{V_1}^{V_2}$$



$$= \quad \frac{C}{(n-1)} \cdot \left(\frac{1}{V_2^{n-1}} - \frac{1}{V_1^{n-1}}\right)$$

$$w = \frac{C}{(n-1)} \left(\frac{P_2V_2 - P_1V_1}{C}\right)$$

$$\boxed{w = \left(\frac{P_2V_2 - P_1V_1}{n-1}\right)}$$

- **Heat capacity for polytropic process :**

$$C = \frac{dq}{dT}$$

from first law

$$dq = dU + PdV \qquad \text{..........(i)}$$

$$\frac{dq}{dT} = \frac{nC_V dT}{dT} + \frac{nRT}{V} \cdot \frac{dV}{dT} \Rightarrow C = \frac{nC_V dT}{dT}$$

$$C = nC_V + \frac{nRT}{V} \cdot \left(\frac{dV}{dT}\right) \qquad \text{..........(ii)}$$

$$PV^n = k$$

$$V^n = \frac{k}{P} = \frac{kV}{n_g RT} \Rightarrow V^{(n-1)} = \frac{k}{n_g RT}$$

$$(n-1)\, V^{(n-2)}\, dV = \frac{-R\, dT}{n_g R\, T^2}$$

$$\Rightarrow \quad \frac{dV}{dT} = \frac{k}{(n-1)\left(\frac{k}{PV^2}\right)(PV)T}$$

$$\frac{dV}{dT} = -\left(\frac{V}{T}\right)\left(\frac{1}{n-1}\right) \qquad \text{..........(iii)}$$

substituting (iii) in equation (ii)

$$C = n_g C_V + \frac{n_g R}{1-n}$$

from 1 mole gas

$$\boxed{C = C_V + \frac{R}{1-n}}$$

❑ **Change in internal energy and enthalpy in chemical reactions** : Enthalpy and internal energy change in chemical reaction involve change in potential energy due to chemical change. During chemical change transformation of bonds take place. If the bonds in product are more stable, leading to decrease in potential energy of atom and molecules, the enthalpy and internal energies decreases . In the process surplus energy is librated and process is called exothermic process.

During endothermic chemical process which take place absorbing energy from surrounding, the potential energy of system of chemical substance increases.

Consider a chemical reaction

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

The internal energy change can be given as (Theoratically)

$\Delta U = cU_c + dU_d - aU_a - bU_b$

where U_a , U_b , U_c , U_d etc. are molar internal enegy of respective species.

since absolute internal energies cannot be determine, U_i are determined with respect to internal energy of elements in their most stable state. The internal energies of elements in their most stable allotropic modification is arbitary taken as zero at 298K and 1 atm pressure.

also, $\mathbf{\Delta_r U = q_v}$ for reaction taking place under constant volume and temperature condition. For the similar reaction occuring at constant pressure and temperature, enthalpy change, ΔH is given by

$\Delta H = cH_c + dH_d - aH_a - bH_b$

where H are enthalpies of respective species

however ΔH is equal to heat exchange during chemical process at constant pressure and temperature.

$\mathbf{\Delta_r H = q_p}$ for reaction taking place under constant pressure and temperature conditions

❑ **Relationship between $\Delta_r H$ and $\Delta_r U$ in chemical reactions** : For a general chemical reaction given by

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

$$\Delta_r H = cH_c + dH_d - aH_a - bH_b \quad \ldots\ldots\ldots. (1)$$

$$\text{but } H_i = U_i + PV_i$$

substituting the value of molar enthalpies of substance in equation (1) we get

$$\Delta_r H = cU_c + dU_d - aU_a - bU_b + P(cV_c + dV_d - aV_a - bV_b)$$

$$\Delta_r H = \Delta_r U + P(V_f - V_i) \quad \ldots\ldots\ldots\ldots\ldots. (2)$$

(a) If all the reactant and products are ideal gases V_c ,V_d ,V_a andV_b all are equal to molar volume of ideal gas e.g. $V = RT/P$ which on substitution in previous equation gives

$$\Delta_r H = \Delta_r U + (d + c - a - b)RT$$

$$\mathbf{\Delta_r H = \Delta_r U + \Delta n_g RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Where $\mathbf{\Delta n_g}$ is difference of stoichiometric cofficient of gaseous products and gaseous reactants.

(b) In case of liquid and solids present in chemical equations , their molar volumes can be ignored in comparison to molar volume of ideal gases and hence do not count stoichiometric cofficient of solid and liquids in Δn_g.

(c) In case of non ideal behaviour of gases, equation (2) should be used.

❑ **Change in internal energy and enthalpy in phase transition** : At certain temperature under one atmospheric pressure, one phase changes into other phase by taking certain amount of Heat. The temperatrue at which this happens is called **transition temperature** and heat absorbed druing the process is called Enthalpy of phase transition. Heat absorbed during transition is exchanged at constant pressure and temperatrue and it is significant to know that the process is reversible.

Fusion : Solid ice at 273K and 1 atm pressure reversibly changes into liquid water. Reversibly, isothermally and isobarically, absorbing heat know as latent heat of fusion.or enthalpy of fusion.

Vaporisation : Water at 373K and 1 atm pressure changes into its vapors absorbing heat known as latent heat of vaporisation.The latent heat of vaporisation is heat exchanged isothermally , isobarically and reversibly to convert water into its vapour at boiling point.

Internal energy change of phase transitions involving gas phase has no practical significance because it is not possible to carry out ΔU of phase transition directly through an experiment. However ΔU of phase transition can be determined theoretically from experimentally obtained value of ΔH of phase transition.

$$H_2O(\ell) \longrightarrow H_2O(g)$$

$$\Delta H_{vaporisation} = \Delta U_{vaporisation} + P(V_f - V_i)$$

$$\Delta H_{vaporisation} = \Delta U_{vaporisation} + \{RT/V\}\{Vg\}$$

ignoring volume of liquid as compared to molar volume of gas

$\Rightarrow$ $$\Delta H_{vap.} = \Delta U_{vap.} + RT$$

where R is gas constant and T absolute temperature for condensed phase transitions like solid liquid transitions

$$\Delta H_{vap.} \simeq \Delta U_{vap.}$$

- **Variation of enthalpy with temperature (KIRCHHOFF'S EQUATION):** The enthalpy of chemical reactions and phase transition do vary with temperature. Although the variation in ΔH with temprature is usually small compared to the value of ΔH itself,

  consider a reaction $A \longrightarrow B$ at temperature T_1 and pressure P

$$\begin{tikzcd}
A(T_y,P) \arrow[r, "\Delta H_1"] & B(T_1,P) \arrow[d, "\Delta H_3 = \int_{T_1}^{T_2} C_{p,B}dT"] \\
A(T_2,P) \arrow[u, "\Delta H_4 = \int_{T_2}^{T_1} C_{p,A}dT"] \arrow[r, "\Delta H_2"] & B(T_2,P)
\end{tikzcd}$$

- **Since H is state function :** Change in enthalpy in cyclic process is equal to zero. To calculate enthalpy change (ΔH_2) at temperataure T_2 at constant pressure consider cyclic process shown in figure. It is clear

ΔH_3 = change in enthalpy of A when temperature is raised from T_1 to T_2 at constant pressure. $\Delta H_3 = \int_{T_1}^{T_2} C_{p,B}dT$

ΔH_4 = Change in enthalpy taking 1 mole of B at constant pressure from T_1 to T_2 $= \Delta H_4 = \int_{T_2}^{T_1} C_{p,A}dT$

now : $\Delta H_3 + \Delta H_1 + \Delta H_4 = \Delta H_2$

$\Rightarrow \Delta H_2 - \Delta H_1 = \Delta H_3 + \Delta H_4$

$$\Rightarrow \Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} (C_{p,B} - C_{p,A})dT$$

$\Rightarrow \boxed{\Delta H_2 - \Delta H_1 = \Delta_r C_p(T_2 - T_1)}$ If $\Delta_r C_p$ is independent of 'temperature'

- **Second law :** There are two types of processes reversible process or quasi static process in which system remains in equilibrium with surrounding through out the process.

  However reversible processes can not take place on it's own - and are not natural process. Reversible process do not lead to production of disorder.

  On the other hand most of the processes taking place around us is example of irreversible process. Irreversible process also natural processes or spontaneous processes.

  Example of natural processes :

  (i) Water flowing down hill

  (ii) Heat flowing from hot body towards cold body on it's own

  (iii) mixing of two gases.

  (iv) Rusting of iron

  (v) Evaporation of water at room temperature.

(vi) Formation of $NH_3(g)$ from $N_2(g)$ and $H_2(g)$ gas in a closed container.

(vii) Expansion of ideal gas in vacuum

(viii) Burning of coal in O_2

Every natural process leads to production of disorder. (During irreversible process system moves from ordered state to disordered state).

- **The second law of thermodynamics :**

The second law of thermodynamics predict's direction of natural change. It do so with the help of state function 'S' - called entropy of system. But for predicting direction of natural change another quantity $S_{surrounding}$ is also needed. $S_{surrounding}$ which is called entropy of surrounding is a path dependent quantity.

$$\boxed{\begin{aligned} dS_{system} &= \frac{dq_{rev}}{T} \\ dS_{surr} &= -\frac{dq}{T} \end{aligned}}$$

Since S_{system} is state function - If a system make transition from state A to state B - by infinite paths in few of them may be reversible and other may be irreversible. ΔS_{AB} will be same irrespective of path (A direct consequence of S_{system} being a state function).

However, If same transition from A to B is done by different irreversible path's, $\Delta S_{surrounding}$ will be different in all processes. However if transition from A $\rightarrow$ B take place by many reversible path's, ΔS_{surr} along each path will be same because

$$-\sum_{A\to B}^{\text{path 1}} \frac{dq_{rev}}{T} = -\Delta S_{system} = -\sum_{A\to B}^{\text{path 2}} \frac{dq_{rev}}{T}$$

$$\Rightarrow \quad \underset{A\to B}{\Delta S_{surr}}(\text{path } 1) = -\underset{A\to B}{\Delta S_{system}} = -\underset{A\to B}{\Delta S_{surr}}(\text{path } 2)$$

Entropy change of system and surrounding in reversible and irrversible process

	ΔS_{system}	$\Delta S_{surrounding}$
reversible process	$\int_A^B \frac{dq_{rev}}{T}$	$-\int_A^B \frac{dq_{rev}}{T}$
Irreversible process	$\int_A^B \frac{dq_{rev}}{T}$	$\int_A^B \frac{dq_{irrev}}{T} = -\left(\frac{q_{irrev}}{T}\right)_{A\to B}$

Note that $\boxed{\Delta S_{surr} = -\frac{q_{actual}}{T}}$

The central concept of entropy is given briefly, because JEE syllabus deals with consequence of second law rather than it's derivation.

- **Prediction of spontaneity of process :** If total entropy change in a process is positive the process must be spontaneous.

$\Delta S_{system} + \Delta S_{surrounding} > 0$ for spontaneous change.

The second law of thermodynamics was developed during course of development of cyclic engines. Second law was discovered while studying efficiency of steam engines. In 1824 a french engineer Sodi carnot pointed out that for a cyclic heat engine to produce continuous mechanical works, it must exchange heat with two bodies at different temperature without a cold body to discard heat, the engine can-not function continuously.

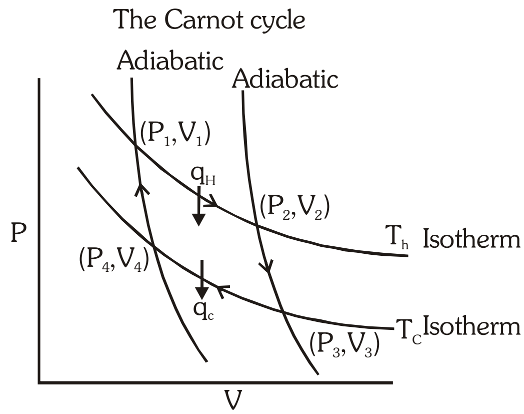
- **2^{nd} law statement :**

It is impossible for a system to undergo cyclic process whose sole effects are the flow of heat from a heat reservoir and the performance of an equivalent amount of work by the system on surrounding. The key term in above statement is cyclic engine. If the first part of it's operation when engine do work heat is absorbed and expansion on take place in second part, it must return to it's original state and to contract, it must loose heat to a cold object (sink).

In other words energy taken from source in one cycle can not be completely converted into work.

Efficiency of carnot engine.

Carnot has devised an engine based on reverssible steps. The efficiency of carnot engine is maximum, because it is based on reversible cycle. A Carnot engine completes a cycle in four steps.



Reversible isothermal expansion from P_1, V_1 to P_2, V_2 at temp T_H

Reversible adiabatic expansion from P_2, V_2 at temp T_H to P_3, V_3 at temp T_c

Reversible isothermal compression from P_3, V_3 to P_4, V_4 at temp T_H

Reversible isothermal compression from P_4, V_4 to P_1, V_1 at temp T_c

A carnot engine rejects minimum heat to the surrounding in its operation and maximum part of heat taken form source is converted into work. Hence efficiency of carnot engine is given by

$$\eta = \frac{(\text{Net work done by engine in one cycle})}{\text{Net heat absorbed from source}}$$

$$\eta = \frac{-w_{net}}{q_H}$$ where w_{net} is net work done on the engine(system) in one cycle.

It can be easily shown that $-w_{net} = q_H + q_C = w_{net}$

$$q_H + q_C = nRT_H \ln\frac{V_2}{V_1} + nRT_C \ln\frac{V_4}{V_3}$$

also $$\begin{Bmatrix} T_C V_4^{\gamma-1} = T_h V_1^{\gamma-1} \\ T_C V_3^{\gamma-1} = T_h V_2^{\gamma-1} \end{Bmatrix} \Rightarrow \left\{\frac{V_4}{V_3} = \frac{V_1}{V_2}\right\}$$

because of reversible adiabatic process

substituting these result's

$$\boxed{\eta = \frac{T_H - T_C}{T_H} = \frac{q_H + q_C}{q_H}}$$

- Efficiency of Carnot engine only depends upon temperature of source and sink and independent of choice of working substance.

- Sum of the $\frac{q_{rev}}{T}$ in a cyclic process is zero.

For the Carnot cycle $\frac{q_H}{T_H} + \frac{q_C}{T_C} = 0$ $\Rightarrow$ for carnot cycle $\Sigma\frac{q_{rev}}{T} = 0$

- The result in previous article is valid for any reversible cyclic process. It can be very easily varified.

Hence $\oint \frac{dq_{rev}}{T} = 0 \Rightarrow$ Sum of the $\frac{dq_{rev}}{T}$ over a cyclic path is zero.

now If $\oint dx = 0 \Rightarrow$ dx is differential of a state function and X is state function.

$\Rightarrow$ $dS = \frac{dq_{rev}}{T}$ = definite quantity

$\Rightarrow$ **S_{system} is a state function.**

CLASIUS INEQUALITY :

From our experience we known if any one step in carnot engine is consciously made irreversible the efficiency of carnot engine will decrease from theoretical value

$$\eta = \frac{q_H + q_C}{q_H} = \frac{T_H - T_C}{T_H}$$

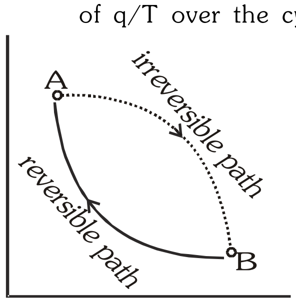
$$\Rightarrow \quad \frac{q_H}{T_H} + \frac{q_C}{T_C} < 0$$

$$\Rightarrow \quad \Sigma \frac{q_{irr}}{T} < 0$$

this mathematical statement is called **Clasius inequality.**

- **Entropy change in isolated system (isolated system = sys + surr)**

Consider a system taken from state A to state B by an irreversible path and returned to state A by a reversible path. Since one of the step is irreversible, according to Clasius inequality, sum of q/T over the cycle must be less than zero. Hence



$$\sum_{A\to B} \frac{q_{irr}}{T} + \sum_{B\to A} \frac{q_{rev}}{T} \le 0 \Rightarrow \sum_{A\to B} \frac{q_{irr}}{T} = -\sum_{B\to A} \frac{q_{rev}}{T}$$

But $-\sum_{B\to A} \frac{q_{rev}}{T} = \sum_{A\to B} \frac{q_{rev}}{T}$ since the process is reversible

for infinitesimally small change

$$\boxed{\left(\frac{dq}{T}\right)_{A\to B} = dS_{system\ A\to B}}$$

$$\Rightarrow \quad dS_{system} - \left(\frac{dq}{T}\right)_{A\to B} > 0$$

$$\Rightarrow \quad \boxed{dS_{system\ A\to B} + dS_{sur\ A\to B} > 0}$$

$$\Rightarrow \quad \boxed{\Delta S_{Total\,isolated\,sys} > 0}$$

- **Entropy calculation in process involving ideal gases.**

From First law

$$dq = dU + PdV$$

$$\Rightarrow \qquad \frac{dq_{rev}}{T} = \frac{dU}{T} + \frac{PdV}{T}$$

But for ideal gas

$$\frac{dU}{T} = \frac{nC_V dT}{T} \qquad \{\because\ dU = nC_V dT\}$$

$$\Rightarrow \qquad dS_{sys} = \frac{nC_V dT}{T} + \frac{nR}{V} dV$$

Integration gives

$$\Delta S = nC_V \ln\frac{T_2}{T_1} + nR\ln\left(\frac{V_2}{V_1}\right)$$

For isothermal process

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

For isochoric process

$$\Delta S = nC_V \ln \frac{T_2}{T_1}$$

For isobaric process

$$\Delta S = nC_p \ln \frac{T_2}{T_1}$$

◆ **Entropy change in chemical Reaction :**

From application of third law absolute entropy of every compound or element can be deduced for a general chemical reaction taking place at given condition

$$aA + bB \dashrightarrow cC + dD$$

$$\Delta S = \Delta S_{system} = \text{entropy change of reaction}$$

$$\Rightarrow \qquad = (aS_C + dS_D - aS_A - bS_B)$$

where S_C, S_D, S_A and S_B are molar entropy of substance A,B, C and D under given circumtance.

◆ **Entropy change in phase transition :**

◆ **Fusion :**

When solid ice is heated below 273 K at external pressure of 1 atm it's temperature slowly rises. At 273 K however. its start melting into liquid without increase in temperature. The process is reversible phase transition from solid to liquid represented as :

$$H_2O\ (s) \rightleftharpoons H_2O(\ell)$$

Since process is reversible (you can safely assume that phase transition at constant temperature and pressure are reversible phase transitions).

Now $\Delta S_{Total} = 0$ (since process is reversible)

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

also $\Delta S_{surrounding} = \dfrac{-\Delta H_{fusion}}{T_f}$ (here T_f = freezing point)

$\Rightarrow \quad \Delta S_{Total} = \frac{\Delta H_{fusion}}{T_f} = 0$

$\Rightarrow \quad \Delta S_{fustion} = \frac{\Delta H_{fusion}}{T_f}$ entropy of fusion at Melting point.

◆ **Vapourisation :** From you day to day experience you know that under atmospheric pressure temperature of H_2O (ℓ) can not exceed 373 K. Since at 373 K liquid H_2O undergo phase transition.

$$H_2O(\ell) \rightleftharpoons H_2O(g)$$

since $\Delta S_{Total} = 0$ (Process is reversible)

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

$$\Delta S_{system} = \Delta S_{fusion} = S_{H_2O(g)} - S_{H_2O(\ell)}$$

$$\Delta S_{surrounding} = -\frac{\Delta H_{vap}}{T_b}$$ (here T_b = melting point)

Note : Boiling point at 1 atm pressure is called normal boiling point. There can be infinite boiling points of liquid depending upon external pressure we applying on boiling vessel.

❑ **Entropy and criteria of spontanity of chemical process :**

The entropy change of chemical reaction together with entropy change of surrounding determine spontanity of a chemical process under given set of condition.

$$\Delta S_{Total} = \Delta_r S - \frac{\Delta_r H}{T}$$

If $\Delta_r S$ = positive and very large while $\Delta_r H$ is negative and large this means $\Delta S_{Total} > 0$.

If $\Delta_r S$ = positive but small and $\Delta_r H$ is negative but having large value.

$\Rightarrow$ If ΔS_{Total} is +ive due to large +ive value of $\Delta_r S$, we can say reaction is entropy driven that is increased in disorder in forward direction is the driving force of reaction which takes it in forward direction. (H_2O (ℓ) $\longrightarrow$ $H_2O(g)$ above 373 K at 1 atm)

$\Rightarrow$ Sometimes reaction go completely in forward direction inspite of negative entropy change in reaction due to large –ive value of $\Delta_r H$. These reaction are enthalpy driven.

Example : $C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(\ell)$

Spontaneous and non Spontaneous

Sign of ΔH	Sign of ΔS	Comment	Example	ΔH_{298}	ΔS_{298}
–	+	spontaneous at all temperature	$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$ $C(s) + O_2(g) \longrightarrow CO_2(g)$	–185 –394	14.1 3
–	–	spontaneous at low temperature	$H_2(g) + 1/2\ O_2 \longrightarrow H_2O(\ell)$ $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$	–44 –198	–119 –187
+	+	spontaneous at high temperature	$NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$ $N_2(g) + O_2(g) \longrightarrow 2NO(g)$	176 180	284 25
+	–	non spontaneous at all temperature	$3O_2 \longrightarrow 2O_3$ $2H_2O(\ell) + O_2(g) \longrightarrow 2H_2O_2(\ell)$	286 196	–137 –126

Ex. Will ΔS be positive or negative in the following processes ? Discuss qualitatively

(a) $H_2O(s) \longrightarrow H_2O(\ell)$

(b) $H_2O(\ell) \longrightarrow H_2O(g)$

(c) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

(d) $\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \longrightarrow NH_3(g)$

(e) $2H_2(g) + N_2(g) \longrightarrow N_2H_4(\ell)$

(f) $Cl_2(g) \longrightarrow 2Cl(g)$

Sol. As we have discussed that the entropy of reaction is more if there is a change in value of $\Delta \nu_g$ (the change in the stoichiometric number of gaseous species), since the entropy of gases is much larger than the entropy of the condensed phases.

$\therefore$ for process (a) ΔS is +ve

for process (b) ΔS is +ve

for process (c) ΔS is zero

for process (d) ΔS is negative

for process (e) ΔS is negative

for process (f) ΔS is positive

Ex. Sulphur exists in more than one solid form. The stable form. The stable form at room temperatrure is rhombic sulphur. But above room temperature the following reaction occurs :

s (rhombic) $\longrightarrow$ s (mono clinic)

Thermodynamic measurements reveal that at 101.325 kP_a and 298 K,

$\Delta_r H$ = 276.144 J mol^{-1} and $\Delta_r G$ = 75.312 J mol^{-1}

(a) Compute $\Delta_r s$ at 298 K

(b) Assume that $\Delta_r H$ and $\Delta_r s$ do not vary significantly with temperature, compute T_{eq}, the temperature at which rhombic and monoclinic sulphur exist in equilibrium with each other.

Sol. (a) Since

$$\Delta_r G = \Delta_r H - T\Delta_r S,$$

Therefore

$$\Delta_r S = \frac{\Delta_r H - \Delta_r G}{T} = \frac{276.144\,J\,mol^{-1} - 75.312\,J\,mol^{-1}}{298\,K}$$

$$= 0.674 \text{ J K}^{-1} \text{ mol}^{-1}$$

(b) When the rhombic sulphur is in equilibrium with monoclinic sulphur, we would have

$$\Delta_r G = 0 = \Delta_r H - T_{eq}\,\Delta_r S$$

Thus $$T_{eq} = \frac{\Delta_r H}{\Delta_r S} = \frac{276.144\,J\,mol^{-1}}{0.674\,J\,mol^{-1}}$$

$$= 409.7 \text{ K}$$

Ex. At 1 atm and 27 C, will the vaporisation of liquid water be spontaneous ? Given ΔH = 9710 cal and Δs = 26 eu.

Sol. $H_2O(\ell) = H_2O(g)$ (P = 1 atm)

$$\Delta G = \Delta H - T\Delta S = 9710 - 26 \quad 300 = +1910 \text{ cal}$$

since ΔG is positive, at 1 atm, vaporisation is not possible. Rather the reverse process of condensation will occur.

The temperature at which the liquid and vapour will be equiv. can be obtained, by putting $\Delta G = 0$, i.e

$$\Delta G = 9710 - 26T = 0$$

$$T = 373.4 \quad C$$

This indeed is the boiling point of water at 1 atm.

Ex.

Gases	ΔG_f (Cal/mole)
CO	–32.80
H_2O	–54.69
CO_2	–94.26
H_2	0

Estimate the standard free energy change in the chemical reaction

$$CO + H_2O = CO_2 + H_2$$

Sol. Using the necessary data from the table

	CO	H_2O	CO_2	H_2
ΔG	– 32.8	–54.69	–94.26	0 kcal

$$\therefore \; \Delta G = -94.26 + 0 - (-32.8) - (-54.69)$$

$$= -6.8 \text{ kcal/mol}$$

❑ **Third law of thermodynamics :**

Third law of thermodynamics helps in determining absolute entropy of substances. It is based on an assumption that entropy of every perfectly crystalline substance is zero at zero

Kelvin. This is justified because , at absolute zero every substance is in state of lowest energy and position of every atom or molecule is defined in solid. Hence at T=0 S(T=0)=0 Third law

If we have sufficient heat capacity data (and the data on phase changes) we could write

$$S\ (T) = S(T = 0) + \int_0^r \frac{C_p}{T} dT \text{ ....(i)}$$

(If there is a phase change between 0 K and T, we would have to add the entropy of the phase change.)

If C_p were constant near T = 0, we would have,

$$S(T) = S(T = 0) + C_p \ln \frac{T}{0},$$

Which is undefined. Fortunately, experimentally $C_p \to 0$ as $T \to 0$. For nonmetals C_p is proportional to T^3 at low temperature. For metals C_p is proportional to T^3 at low temperatures but shifts over to being proportional to T at extermely low temperatures. (The latter happens when the atomic motion "freezes out" and the heat capacity is due to the motion of the conduction electrons in the metal.)

equation (i) could be used to calculate absolute entropies for substances if we know what the entropy is at absolute zero. Experimentally it appears that the entropy at absolute zero is the same for all substances. The third law of thermodynamics modifies this observation and sets

$$S\ (T = 0) = 0$$

for all elements and compounds in their most stable and perfect crystalline state at absolute zero and one atmosphere pressure. (All except for helium, which is a liquid at the lowest observable temperatures at one atmosphere.)

The advantage of this law is that it allows us to use experimental data to compute the absolute entropy of a substance. For example, suppose we want to calculate the absolute entropy of liquid water at 25 C. We would need to known the C_p of ice from 0 K to 273.15 K. We also need the heat of fusion of water at its normal melting point. With all of this data, which can be obtained partly from theory and partly from experiment, we find

$$S_{H_2O}(25\ C) = 0 + \int_0^{273.15} \frac{C_p(s)}{T} dT + \frac{\Delta H_{fus}}{273.15} + \int_{273.15}^{298.15} \frac{C_p(l)}{T} dT.$$

Some substances may undergo several phase changes.

- **Gibb's function :**

Entropy is a universal criteria of spontaneity. This means for any process if $\Delta S_{Total} > 0$ the process is spontaneous. Most of the chemical process take place at constant temperature and pressure. A very useful criteria of spontaneity of process at constant temperature and pressure is Gibb's function :

Gibb's function (G) is defined as

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

Gibb's function and spontaneous process :

from 2^{nd} law we known :

$$\frac{dq}{T} \le dS_{system} \quad : \quad \text{Less than sign for if } q = q_{irr}$$

$\Rightarrow$ $dq \le TdS$ ....(ii)

$dq = dV + PdV$ ....(iii)

subsitituting value of dq from equation (iii) to equation (ii)

$dV + PdV - TdS \le 0$

$\Rightarrow$ $d(H - TS)_{P,T} \le 0$

$\because$ $d(H - TS)_{P,T}^{-} = (dH - TdS - SdT)_{P,T}$

$=$ $(dU + PdV + VdP - TdS - SdT)_{P,T} \le 0$

$\Rightarrow$ $d(H - TS)_{P,T} \le 0$

$\Rightarrow$ $d(dG)_{P,T} \le 0$

- **Statement :**

During course of every spontaneous process, Gibb's function decreases. If a process is allowed to run spontaneously, eventually it attain equilibrium. At equilibrium, the Gibb's function attains minimum value. No further decrease to the value of Gibb's function is possible at equilibrium.

Hence at equilibrium. $(dG)_{T,P} = 0$.

$\Rightarrow$ Entropy change in spontaneous process :

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

The sign > is for spontaneous process. A state of equilibrium in a close system is attained spontaneously. As system approaches equilibrium from non-equilibrium state – S_{Total} keeps on increasing and at equilibrium S_{Total} attains its maximum value.

$\Rightarrow$ $\Delta S_{Total} = 0$ at equilibrium

at this point **S_{Total} = maximum value at equilibrium in a close system**

SIGNIFICANCE OF GIBB'S FUNCTION :

(a) Decrease in Gibb's function at constant temperature and pressure is related to ΔS_{total} (total entropy change of system and surrounding).

We known :

$\Delta G = \Delta H - T\Delta S$ ....(i) ; at constant T and pressure

also $\Delta H = q_p$ at constant pressure

q_P = heat absorbed by system at constant pressure.

$\Rightarrow$ $\Delta G = q_p - T\Delta S$ ....(ii)

this gives $-\dfrac{\Delta G}{T} = -\dfrac{q_P}{T} + \Delta S$

$-\dfrac{q_P}{T} + \Delta S_{surrounding}$

$\Rightarrow$ $-\dfrac{\Delta G}{T} = (\Delta S_{surrounding} + \Delta S_{system})$

Student might get confused in

ex : $-\dfrac{q}{T} = \Delta S_{surr.}$

ex : q = Heat absorbed by system

$-q$ = Heat absorbed by surrounding

$\Rightarrow$ $\boxed{-\Delta G = T(\Delta S_{Total})}$

Note equation (ii) can be written as $\Delta G = q - q_{rev.}$

for spontaneous process $(\Delta G)_{T,P} < 0$

$\Rightarrow$ $q - q_{rev} < 0 \Rightarrow q_{rev} > q$

Gibbs function and non PV work :

Decrease in Gibb's function at constant temperature and pressure in a process gives an estimate or measure of maximum non-PV work which can be obtained from system in reversible, manner.

The example of non-PV work is electrical work done by chemical battery.

Expansion of soap bubble at for a closed system capable of doing non-PV work apart from PV work first law can be written as

$dU = dq - PdV = dw_{non-PV}$

$- dw_{non-PV}$ = non-PV work done by the system.

$dG = d(H - TS)$

$= dH - TdS - SdT$

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

$dG = dq - PdV - w_{non,PV} + PdV + VdP - TdS - SdT$

for a reversible change at cont. T and P

$dG = dq_{rev.} - dw_{non} + VdP - TdS - SdT$

since $dq_{rev} = TdS$

$\Rightarrow$ $-(dG)_{T,P} = dw_{non-PV}$

- Non-pV work is work done due to chemical energy transformation or due to composition change and decrease in Gibb's function in a isothermal and isobaric process provide a measure of chemical energy stored in bonds and intermolecular interaction energy of molecules.

- **Gibbs free energy change at constant temperature :**

In order to derive an equation which will enable us to calculate the Gibbs free energy change of an isothermal process but with varying pressure, we may conveniently start with the equation,

$$G = E + PV - TS$$

Differentiating the above equation, we get

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

According to first law of thermodynamics,

$$dQ = dE + PdV$$

$\therefore \quad dG = dQ + VdP - TdS - SdT$

Further since $\frac{dQ}{T} = dS$, we can replace dQ by TdS.

$\therefore \quad dG = VdP - SdT$

At constant temperature, $dT = 0$

$\therefore \quad dG = VdP$

or $\left(\frac{dG}{dP}\right)_r = V$

Thus Gibb's function of every substance increases on increasing pressure , but this increase is maximum for gases , compared to solids or liquids since gases have maximum molar volume. On intergrating equation $dG = VdP$ for very minute changes from state 1 to 2, we have

$$\Delta G = G_2 - G_1 = \int_1^2 VdP$$

In case of one mole of a perfect gas,

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

$\therefore \quad \Delta G = RT\int_1^2 \frac{dP}{P} = RT \ \ln\frac{P_2}{P_1}$

For n moles of a perfect gas, the free energy change is

$$\Delta G = nRT \ \ln\frac{P_2}{P_1}$$

- **Gibbs free energy change at constant pressure**

From equation which is

$dG = VdP - SdT$ (Only for pure substances)

when pressure is constant, $dP = 0$

$\therefore \quad dG = -SdT$

or $\left(\frac{dG}{dT}\right)_p = -S$

thus Gibb's function of every substance decreases with temperature, but this decrease is maximum for gases since they have maximum state of disorder. Hence on increasing temperature, gas phase gain maximum stability compared to solid or liquid phase.

- **For chemical reaction :**

$$\boxed{d(\Delta_r G) = \Delta_r V(dp) - \Delta_r S(dT)}$$

at constant temperature, If $\Delta_r V \simeq$ constant

$$\Rightarrow \int_1^2 d(\Delta_r C_p) = \Delta_r V \int_1^2 dp$$

$\Rightarrow$ $\boxed{\Delta_r C_{p_2} - \Delta_r C_{p_1} = \Delta_r V(P_2 - P_1)}$

only for condensed phase : equilibrium like

$H_2O(s) \rightleftharpoons H_2O(\ell)$

$S(\text{Rhombic}) \rightleftharpoons S(\text{monoclinic})$

❑ GIBBS FREE ENERGY CHANGE IN CHEMICAL REACTIONS :

Gibbs free energy changes have a direct relationship with the tendency of the system to proceed to a state of equilibrium. In view of this fact, it is desirable to have a knowledge of the free energy of chemical compounds so that the Gibbs free energy change of a possible reaction could be easily calculated. Standard free energies have been used for this case. A zero value of the Gibbs free energy is assigned to the free energies of the stable form of the elements at 25 C and 1 atm. pressure.

With this as reference point, free energies of compounds have been calculated which are called standard Gibbs free energies of formation. The difference in the Gibbs free energy of products and reactants in their standard states (at 25 C and 1 bar pressure) is denoted as ΔG .

In standard enthalpy and entropy values are available, ΔG can be written from equation as,

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

❑ GIBB'S FREE ENERGY IN CHEMICAL REACTIONS FROM GIBB'S FREE ENERGY OF FORMATION OF COMPOUNDS :

Consider a chemical reaction,

$aA + bB \rightarrow cC + dD$

The standard Gibb's free energy change ΔG can be computed on the basis discussed above (i.e., by assigning zero value to the Gibbs free energy of the stable form of elements at 25 C and 1 bar pressure). With this as reference, the standard Gibbs free energy of the products and reactants can be determined. The standard Gibbs free energy change for the overall reaction can be evaluted as :

$$\Delta G = \sum G^{\circ}_{f(\text{products})} - \sum G^{\circ}_{f(\text{reactants})}$$

$$= \left(c\,G^{\circ}_{c} + d\,G^{\circ}_{D}\right) - \left(a\,G^{\circ}_{A} + b\,G^{\circ}_{B}\right)$$

A negative sign of ΔG will show that the reaction will proceed spontaneously.

note that ΔG° can be defined at any temperature, at standard pressure of 1 bar

◆ Reversible phase transitions and Gibb's free energy change :

During reversible phase transition which occurs at transition temperatures, Gibb's function change become zero, impling the fact that these processes are reversible processes.

at 373K and 1 atm pressure $\Delta G = 0$ for $H_2O(l) \rightarrow H_2O(g)$

at 273K and 1atm pressure $\Delta G = 0$ for $H_2O(s) \rightarrow H_2O(l)$

Gibb's energy and equilibrium constant, an important topic taken up in chemical equilibrium.

Application of Gibb's function in decribing variation of vapour pressure, boiling and melting point with temperature is taken up in chemical equilibrium and liquid solutions variation of G/T with temperature , has important implication in pridicting feasibitily of process at different temperatures.This gives Famous Gibb's Helmholtz equation taken up in electrochemistry.

❑ Topics of thermodynamics taken up in later chapters :

Application of :

- Gibb's function and non-PV work is taken in electrochemistry.
- Gibb's free energy and phase equilibrium taken in liquid solution.
- Gibb's function and position of equilibrium and relationship between ΔG and K_{eq} taken up in chemical equilibrium.
- Variation of $\frac{G}{T}$ with temperature also called Gibb's helmholtz equation taken in electrochemistry.

MEMORY TIPS

- **First law of thermodynamics**

For a finite change : $q = \Delta E - w = \Delta E - P\Delta V$

where q is heat given to system, ΔE is change in internal energy and $-w$ is work done by the system.

$$dq = dE - dw = dE - PdV$$

- **Work done in an irreversible process**

$$w = -P_{ext} \quad \Delta V = -P_{ext} \quad (V_2 - V_1) = -P_{ext} \quad R\left[\frac{P_1T_2 - P_2T_1}{P_1P_2}\right]$$

P_{ext} is the pressure against which volume changes from V_1 to V_2

- **Work done in reversible process, i.e., Maximum work**

Isothermal conditions

$$w_{rev} = -2.303\ nRT\ \log_{10}(V_2/V_1)$$

$$w_{rev} = -2.303\ nRT\ \log_{10}(P_1/P_2)$$

w_{rev} is maximum work done.

- **Adiabatic conditions**

$$w_{rev} = [nR/(\gamma - 1)]\ [T_2 - T_1]$$

γ is poisson's ratio.

Also for adiabatic process, following conditions hold good :

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

$$T^{\gamma} P^{l-\gamma} = \text{constant}$$

$$V^{\gamma - l} = \text{constant}$$

- **Heat capacities :**

At constant pressure $\quad C_p = (\delta H/\delta H)_p$

C_p is molar heat capacity at constant pressure.

At constant volume $\quad C_v = (\delta E/\delta T)_v$

C_v is molar heat capacity at constant volume.

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

and $\quad C_p - C_v = R/M$

$$C_p/C_v = c_p/c_v = \gamma \qquad \text{(The poisson's ratio)}$$

c_p and c_v are specific heats at constant pressure and volume respectively.

- **Entropy**

$$\Delta S = \sum S_{products} - \sum S_{reactants}$$

$$\Delta S = q_{rev}/T = 2.303\ nR\ \log_{10}(V_2/V_1) = 2.303\ nR\ \log_{10}(P_1/P_2)$$

$$\Delta S_{fusion} = \Delta H_{fusion}/T$$

$$\Delta S_{vap} = \Delta H_{vap}/T$$

ΔS is entropy change.

- **Free energy**

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S \text{ and } \Delta G = \Delta H - T\Delta S \qquad \text{(In standard state)}$$

At equilibrium, $\Delta G = 0$

$$-\Delta G = RT \ln K_p \text{ (or } K_C)$$

$$= 2.303\ RT \log_{10} K_P \text{ (or } K_C)$$

ΔG is free energy change and ΔG is standard free energy change. K_C and K_p are equilibrium constants in terms of concentration and pressure respectively.

- **Unit conversion**

$$1 \text{ cal} = 4.1868 \text{ J} = 4.1868 \quad 10^7 \text{ erg.}$$

$$1\text{J} = 10^7 \text{ ergs}$$

$$1 \text{ eV} = 1.602 \quad 10^{-19} = 1.602 \quad 10^{-12} \text{ ergs.}$$

$$1 \text{ MeV} = 10^6 \text{ eV}$$

order : 1 cal > 1 J > 1 erg > 1 eV.

SOLVED EXAMPLES

Ex.1 During 200J work done on the system, 140 J of heat is given out. Calculate the change in internal energy.

Sol. w = 200 J; q = –140 J;

$\because$ q = ΔE + (–w); where –w is work done by the system

$\Delta E = q + w$

$\Delta E = -140 + 200 = +60J$

Ex.2 A gas absorbs 200 J of heat and expands against the external pressure of 1.5 atm from a volume of 0.5 litre. Calculate the change in internal energy.

Sol. $w = -P\Delta V = -1.5 \quad (1.0 - 0.5) = -0.75$ litre atm

$= -0.75 \quad 101.3$ J $= -75.975$ J

$\because$ 1 litre atm = 101.3 J

Now, $\Delta E = 200 - 75.975 = +124.025$ J

Ex.3 Two litre of N_2 at 0°C and 5 atm pressure are expanded isothermally against a constant external pressure of 1 atm until the pressure of gas reaches 1 atm. Assuming gas to be ideal, calculate work of expansion.

Sol. Since the external pressure is greatly different from the pressure of N_2 and thus, process is irreversible.

$w = -P_{ext}(V_2 - V_1)$

$w = -1 \quad (V_2 - V_1)$

Given V_1 = 2 litre $\qquad V_2$ = ?T = 273 K

P_1 = 5 atm $\qquad P_2$ = 1 atm

$\therefore \quad P_1V_1 = P_2V_2$

$\therefore \quad V_2 = \dfrac{2\times5}{1} = 10$ litre

$\therefore \quad w = -1 \quad (10 - 2) = -8$ litre atm

$\therefore \quad = -\dfrac{8\times1.987}{0.0821}$ calorie $= -\dfrac{8\times1.987\times4.184}{0.0821}$ J = –810.10 joule

Ex.4 The enthalpy of vaporisation of liquid diethyl ether –$(C_2H_5)_2O$, is 26.0 kJ mol^{-1} at its boiling point (35.0ºC). Calculate ΔS for conversion of : (a) liquid to vapour, and (b) vapour to liquid at 35ºC.

Sol. (a) $\Delta S_{vap.} = \dfrac{\Delta H_{vap.}}{T} = \dfrac{26\times10^3}{308} = +84.41\ JK^{-1}mol^{-1}$

(b) $\Delta S_{cond.} = \dfrac{\Delta H_{cond.}}{T} = -\dfrac{26\times10^3}{308}$ $\qquad (\because \ H_{cond} = -26\ kJ)$

$= -84.41\ JK^{-1}\ mol^{-1}$

Ex.5 Calculate the free energy change when 1 mole of NaCl is dissolved in water at 25ºC. Lattice energy of NaCl = 777.8 kJ mol^{-1} ; ΔS for dissolution = 0.043 kJ mol^{-1} and hydration energy of NaCl = –774.1 kJ mol^{-1}.

Sol. $\Delta H_{dissolution}$ = Lattice energy + Hydration energy

$= 777.8 - 774.1 = 3.7$ kJ mol^{-1}

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

$= 3.7 - 298 \quad 0.043 = 3.7 - 12.814$

$\Delta G = -9.114$ kJ mol^{-1}

Ex.6 The equilibrium constant for the reaction given below is $2.0 \quad 10^{-7}$ at 300 K. Calculate the standard free energy change for the reaction;

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

Also, calculate the standard entropy change if ΔH^o = 28.40 kJ mol^{-1}.

Sol. $\Delta G^o = -2.303 \quad 8.314 \quad 300 \log [2.0 \quad 10^{-7}]$

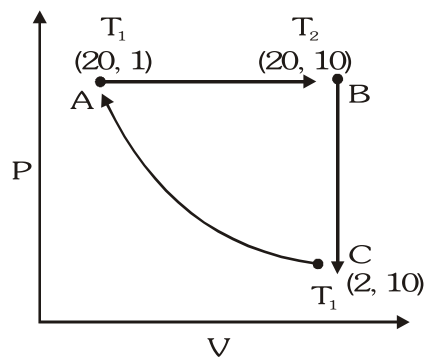
$= +38479.8 \text{ J mol}^{-1} = +38.48 \text{ kJ mol}^{-1}$

Also, $\Delta G^o = \Delta H^o - T\Delta S^o$

$$\therefore \quad \Delta S^o = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{28.40 - 38.48}{300}$$

$= -0.0336 \text{ kJ} = -33.6 \text{ JK}^{-1}$

Ex.7 One mole of a perfect monoatomic gas is put through a cycle consisting of the following three reversible steps :



(CA) Isothermal compression from 2 atm and 10 litres to 20 atm and 1 litre.

(AB) Isobaric expansion to return the gas to the original volume of 10 litres with T going from T_1 to T_2.

(BC) Cooling at constant volume to bring the gas to the original pressure and temperature.

The steps are shown schematically in the figure shown.

(a) Calculate T_1 and T_2.

(b) Calculate ΔE, q and w in calories, for each step and for the cycle.

Sol. We know,

Path CA – Isothermal compression

Path AB – Isobaric expansion

Path BC – Isochoric change

Let V_i and V_f are initial volume and final volume at respective points,

For temperature T_1 (For C) : $\quad PV = nRT_1$

$$2 \quad 10 = 1 \quad 0.0821 \quad T_1$$

$$\therefore \quad T_1 = 243.60K$$

For temperature T_2 (For C and B) : $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$

$$\frac{2 \times 10}{T_1} = \frac{20 \times 10}{T_2}$$

$$\therefore \quad \frac{T_2}{T_1} = 10$$

$$\therefore \quad T_2 = 243.60 \quad 10 = 2436.0 \text{ K}$$

Path CA : $w = +2.303\ nRT_1 \log \frac{V_i}{V_f}$

$$= 2.303 \quad 1 \quad 2 \quad 243.6 \log \frac{10}{1}$$

$$= +1122.02 \text{ cal}$$

$\Delta E = 0$ for isothermal compression ; Also q = w

Path AB : $w = -P(V_f - V_i)$

$$= -20 \quad (10 - 1) = -180 \text{ litre atm}$$

$$= \frac{-180 \times 2}{0.0821} = -4384.9 \text{ cal}$$

Path BC : $w = -P(V_f - V_i) = 0$ $\quad (\because\ V_f - V_i = 0)$

since volume is constant for monoatomic gas heat change at constant volume = $q_v = \Delta E$.

Thus for path BC $\quad q_v = C_v \quad n \quad \Delta T = \Delta E$

$$\therefore \qquad q_v = \frac{3}{2} \ R \quad 1 \quad (2436 - 243.6)$$

$$q_v = \frac{3}{2} \quad 2 \quad 1 \quad 2192.4 = 6577.2 \text{ cal}$$

Since process involves cooling $\quad \therefore \quad q_v = \Delta E = -6577.2$ cal

Also in path AB, the intenal energy in state A and state C is same. Thus during path AB, an increase in internal energy equivalent of change in internal energy during path BC should take place. Thus ΔE for path AB = +6577.2 cal

Now q for path AB = $\Delta E - w_{AB}$ = 6577.2 + 4384.9 = 10962.1 cal

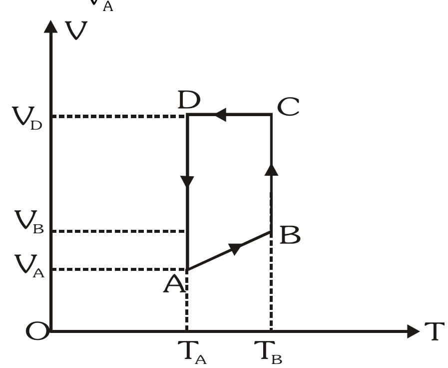
Cycle :$\Delta E = 0$; $\quad q = -w \quad = -\ [w_{\text{Path CA}} + w_{\text{Path AB}} + w_{\text{Path BC}}]$

$$= -\ [+1122.02 + -4384.9 + 0]$$

$$\therefore \qquad q = -w$$

$$= +3262.88 \text{ cal}$$

Ex.8 A monoatomic ideal gas of two moles is taken through a cyclic process starting from A as shown in figure. The volume ratios are $\frac{V_B}{V_A} = 2$ and $\frac{V_D}{V_A} = 4$. If the temperature T_A at A is 27°C, calculate :



(a) The temperature of the gas at point B.

(b) Heat absorbed or released by the gas in each process.

(c) The total work done by the gas during complete cycle.

Sol. For the given cyclic process,

$$\frac{V_B}{V_A} = 2, \quad \frac{V_D}{V_A} = 4, \quad T_A = 300\ K$$

(a) For isobaric process AB

$$\frac{V_A}{T_A} = \frac{V_B}{T_B}$$

$\therefore$ $$T_B = T_A \quad \frac{V_B}{V_A} = 300 \quad 2 = 600\ K$$

(b) The following process are there in complete cycle

(i) $A \rightarrow B$ Isobaric expansion (ii) $B \rightarrow C$ Isothermal expansion

(iii) $C \rightarrow D$ Isochoric compression (iv) $D \rightarrow A$ Isothermal compression

For (i) $q_{A \rightarrow B} = +n \quad C_P \quad \Delta T = +2 \quad \frac{5}{2} \quad R \quad 300 = +1500 \quad 2 = +3000$ cal (R = 2 cal)

(ii) $q_{B\rightarrow C} = \Delta E - w$ $(\Delta E = 0)$

$\therefore$ $q_{B\rightarrow C} = \Delta E - w = + \int PdV = +nRT \ln\frac{V_D}{V_B} = +2\times2\times600\ln\frac{4}{2} = +1.663 + 10^3$ cal

(iii) $q_{C\rightarrow D} = n \quad C_v \quad \Delta T = 2 \quad \frac{3}{2} \quad 2 \quad - 300 = -1800$ cal

(iv) $q_{D\rightarrow A} = +nRT_A \ \ln \frac{V_A}{V_D} = +2 \quad 2 \quad 300 \ \ln \frac{1}{4} = -2 \quad 2 \quad 300 \quad 1.386 = -1.663 \quad 10^3$ cal

$\therefore$ $Q = q_{A\rightarrow B} + q_{B\rightarrow C} + q_{C\rightarrow D} + q_{D\rightarrow A} = 3000 + 1663 - 1800 - 1663 = 1200$ cal

(c) Since the process ABCDA is a cyclic process

$\therefore$ $\Delta E = 0$ or $Q = \Delta E - Q = -w$ or $Q = -1200$ cal

i.e., work done on the system = 1200 cal

Ex.9 Calculate the work done when 50 g of iron reacts with hydrochloric acid in :

(i) a closed vessel of fixed volume, (ii) an open beaker at 25 C.

Sol. We know,

(i) Vessel is of fixed volume, hence $\Delta V = 0$. No work is done, $w = 0$

(ii) The H_2 gas formed drives back the atmosphere hence.

$$w = -P_{ext} \ . \ \Delta V$$

Also $$\Delta V = V_{final} - V_{initial} \simeq V_{final} \quad (\because V_{initial} = 0)$$

$\therefore$ $$\Delta V = \frac{nRT}{P_{ext}}$$

or $$w = -P_{ext} \cdot \frac{nRT}{P_{ext}} = -nRT$$

where n is the number of mole of H_2 gas obtained from n mole of $Fe_{(s)}$.

$$Fe_{(s)} = 2HCl_{(aq)} \rightarrow FeCl_{2(aq.)} + H_{2(g)}$$

1 mole 1 mole

$\therefore$ $$n = \frac{50}{56} = 0.8929 \text{ mole}$$

$\therefore$ $$w = -0.8929 \quad 8.314 \quad 298$$

$$= -2212.22\ J$$

The reaction mixture in the given system does 2.212 kJ of work driving back to atmosphere.

Ex.10 The internal energy change in the conversion of 1.0 mole of the calcite form of $CaCO_3$ to the aragonite form is +0.21 kJ. Calculate the enthalpy change when the pressure is 1.0 bar; given that the densities of the solids are 2.71 g cm^{-3} and 2.93 g cm^{-3} respectively.

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

Given $\Delta E = +0.21 \text{ kJ mol}^{-1} = 0.21 \quad 10^3 \text{ J mol}^{-1}$

$P = \bar{1} = 1.0 \quad 10^5 \text{ Pa}$

$\Delta V = V_{(aragonite)} - V_{(Calcite)}$

$= \left(\frac{100}{2.93} - \frac{100}{2.71}\right) \text{ cm}^3 \text{ mol}^{-1} \text{ of } CaCO_3$

$= -2.77 \text{ cm}^3 = -2.77 \quad 10^{-6} \text{ m}^3$

$\therefore$ $\Delta H = 0.21 \quad 10^3 - 1 \quad 10^5 \quad 2.77 \quad 10^{-6} = 209.72 \text{ J} = 0.20972 \text{ kJ mol}^{-1}$

Ex.11 For a reaction $M_2O(s) \rightarrow 2M(s) + \frac{1}{2}O_2(g)$; $\Delta H = 30 \text{kJ mol}^{-1}$ and $\Delta S = 0.07 \text{ kJ K}^{-1} \text{ mol}^{-1}$ at 1 atm. Calculate upto which temperature, the reaction would not be spontaneous.

Sol. Given, for the change, $\Delta H = 30 \quad 10^3 \text{ J mol}^{-1}$, $\Delta S = 70 \text{ JK}^{-1} \text{ mol}^{-1}$

For a non-spontaneous reaction

$\Delta G = +ve$

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

$\therefore$ $\Delta H - T\Delta S$ should be +ve

or $\Delta H > T\Delta S$

or $T < \frac{\Delta H}{\Delta S} \Rightarrow T < \frac{30 \times 10^3}{70} \Rightarrow T < 428.57 \text{ K}$

Ex.12 Predict whether the entropy change of the system in each of the following process is positive or negative.

(a) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ (b) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

(c) $N_2(g) + O_2(g) \rightarrow 2NO(g)$ (d) $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$

(e) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ (f) Cooling of $N_2(g)$ from 20 C to –50 C

Sol. Gaseous substances generally possess more entropy than solids. So whenever the products contain more moles of a gas than the reactants, the entropy change is probably positive. And hence, ΔS is

(a) positive (b) negative

(c) small, the sign of ΔS is impossible to predict (d) negative

(e) negative (f) negative

[**Note** : For a given substance at a given temperature, $S_{gas} > S_{liquid} > S_{solid}$]

Ex.13 Calculate the boiling point of bromine from the following data :

ΔH^o and ΔS^o values of $Br_2(l) \rightarrow Br_2(g)$ are 30.91 kJ/mole and 93.2 J/mol. K respectively. Assume that ΔH and ΔS do not vary with temperature.

Sol. Consider the process : $Br_2(l) \rightarrow Br_2(g)$

The b.p. of a liquid is the temperature at which the liquid and the pure gas coexist at equilibrium at 1 atm.

$\therefore$ $\Delta G = 0$

As it is given that ΔH and ΔS do not change with temperature

$\Delta H = \Delta H = 30.91 \text{ kJ}$

$\Delta S = \Delta S = 93.2 \text{ J/K} = 0.0932 \text{ kJ/K}$

We have, $\Delta G = \Delta H - T\Delta S = 0$

$\therefore$ $T = \frac{\Delta H}{\Delta S} = \frac{30.91}{0.0932} = 331.6 \text{ K.}$

This is the temperature at which the system is in equilibrium, that is, the b.p of bromine.

Ex.14 The efficiency of the Carnot engine is 1/6. On decreasing the temperature of the sink by 65K, the efficiency increases to 1/3. Find the temperature of the source and the sink.

Sol. We have,

$$\eta = \frac{T_2 - T_1}{T_2}$$, where T_1 and T_2 are the temperatures of sink and source respectively.

$$\therefore \quad \eta = \frac{T_2 - T_1}{T_2} = \frac{1}{6} \qquad \text{...........(i)}$$

Now the temperature of the sink is reduced by 65 K.

$\therefore$ temp. of the sink = (T_1 – 65)

$$\therefore \quad \eta = \frac{T_2 - (T_1 - 65)}{T_2} = \frac{1}{3} \qquad \text{...........(ii)}$$

On solving eqns. (i) and (ii), we get,

T_1 = 325 K

T_2 = 390 K

Ex.15 (a) One mole of an ideal gas expands isothermally and reversible at 25°C from a volume of 10 litres to a volume of 20 litres.

(i) What is the change in entropy of the gas ?

(ii) How much work is done by the gas ?

(iii) What is q(surroundings) ?

(iv) What is the change in the entropy of the surroundings ?

(v) What is the change in the entropy of the system plus the surroundings ?

(b) Also answer the questions (i) to (v) if the expansion of the gas occurs irreversibly by simply opening a stopcock and allowing the gas to rush into an evacuated bulb of 10-L volume.

Sol. (i) $\Delta S = 2.303nR \log \frac{V_2}{V_1} = 2.303 \quad 1 \quad 8.314 \quad \log \frac{20}{10}$ = 5.76 J/K.

(a) (ii) $w_{rev} = 2.303 \text{ nRT} \log \frac{V_2}{V_1}$

$= -2.303 \quad 1 \quad 8.314 \quad 298 \quad \log \frac{20}{10} = -1718$ J.

(iii) For isothermal process, ΔE = 0 and heat is absorbed by the gas,

$q_{rev} = \Delta E - W = 0 - (-1718) = 1718$J

$\therefore$ q_{surr} = 1718 J. ($\because$ process is reversible)

(iv) $\Delta S_{surr} = -\frac{1718}{298} = -5.76$ J/K.

As entropy of the system increases by 5.76 J, the entropy of the surroundinig decreases by 5.76 J, since the process is carried out reversible.

(v) $\Delta S_{sys} + \Delta S_{surr} = 0$ .... for reversible process.

(b) (i) ΔS = 5.76 J/K, which is the same as above because S is a state function.

(ii) w = 0. ($\because$ p_{ext} = 0)

(iii) No heat is exchanged with the surroundings.

(iv) ΔS_{surr} = 0

(v) The entropy of the system plus surroundings increases by 5.76 J/K, as we expect entropy to increases in an irreversible process.