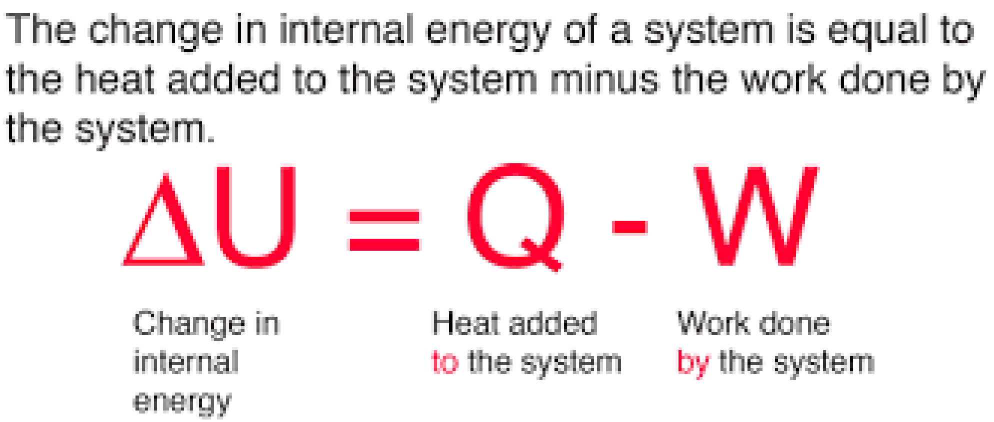


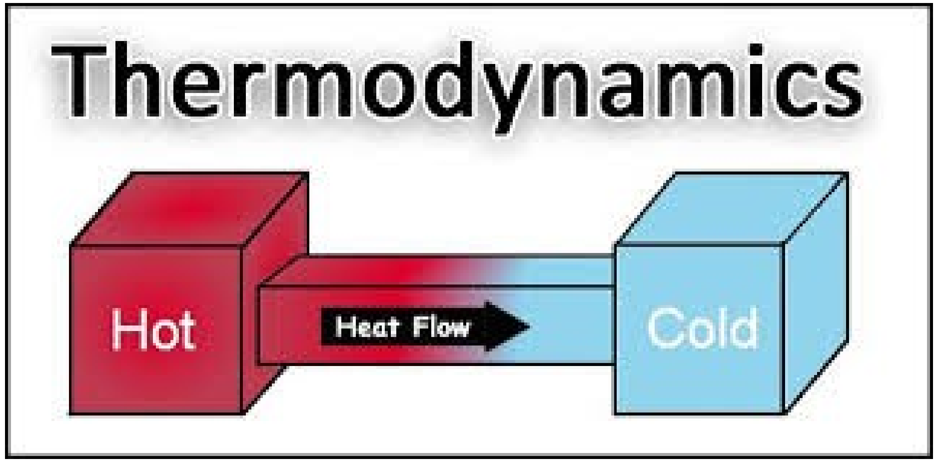
The change in internal energy of a system is equal to the heat added to the system minus the work done by the system.

$$\Delta U = Q - W$$

Change in internal energy

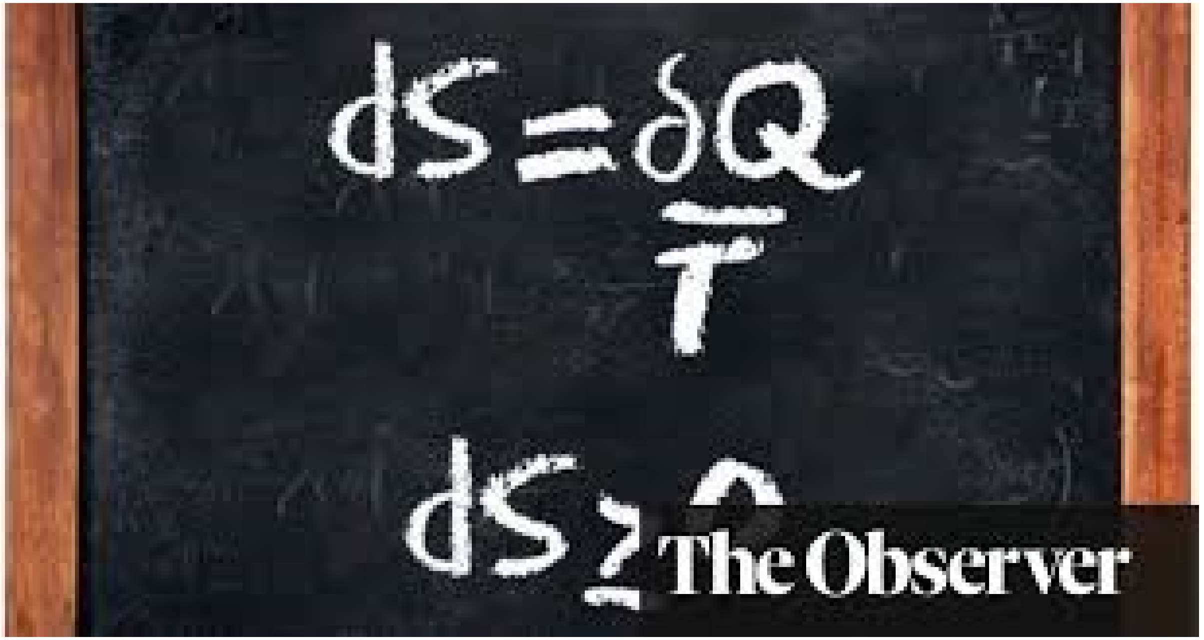
Heat added to the system

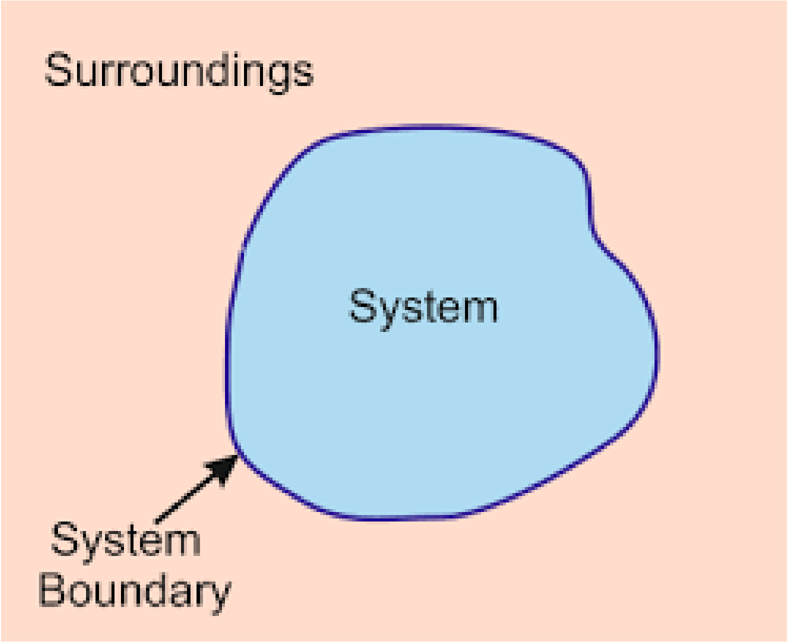
Work done by the system



THERMODYNAMICS II

Dr. Sangeeta Kumar, Dept of Chemistry





LIMITATIONS OF THE FIRST LAW

The first Law shows a definite relation between the heat absorbed and work performed by a system in a given process. But it puts no restriction on direction of flow of heat.

Can you extract heat from ice by cooling to a lower temperature and using it to heat water?

Does a metal bar having uniform temperature become hot at one end and cold at other end spontaneously?

Can water flow uphill spontaneously?

Can you stop a smell from spreading?

Can you fill toothpaste back into the toothpaste tube once it has come out?

SPONTANEOUS OR IRREVERSIBLE PROCESSES

Natural processes are *spontaneous and irreversible.*

Water flows downhill spontaneously.

If a metal bar is hot at one end and cold at the other end, ***heat flows spontaneously from hot end to cold end*** until the temperature of the rod becomes uniform throughout.

The diffusion of a solute from a more concentrated solution to a less concentrated solution when these are brought in contact proceeds *spontaneously* till the concentration becomes uniformly the same.

Heat flows spontaneously from a hot reservoir to a cold reservoir.

For the reverse to take place, as in a refrigerator, energy has to be supplied from outside the system.

SPONTANEOUS OR IRREVERSIBLE PROCESSES

Electricity flows spontaneously from a higher potential to a lower potential. The direction of flow can be reversed only by applying an external field in the opposite direction.

A piece of zinc when placed in contact with a solution of copper sulphate dissolves spontaneously, precipitating copper.

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4 + Cu(s)$$

A definite amount of heat is also evolved. The above reaction can be reversed only by passing current between copper rod and zinc sulphate solution. The electrical energy required to do so will be more than the heat energy evolved in the direct reaction.

SPONTANEOUS OR IRREVERSIBLE PROCESSES

A gas expands spontaneously from a region of high pressure to a region of low pressure.

The first law does not deny the possibility that a metal bar having uniform temperature can spontaneously become warmer at one end and cooler at the other.

All the law demands is that the heat energy lost at one end should be equal to the energy gained at the other end.

But we know from experience that such a change does not occur without expenditure of energy from another source.

SO WE CONCLUDE:

Any process which occurs without outside intervention is spontaneous.

- When two eggs are dropped they spontaneously break.
- The reverse reaction (two eggs leaping into your hand with their shells back intact) is not spontaneous.
- We can conclude that a spontaneous process has a direction.
- A process that is spontaneous in one direction is not spontaneous in the opposite direction.
- The direction of a spontaneous process can depend on temperature.
- Ice turning to water is spontaneous at $T > 0°C$.
- Water turning to ice is spontaneous at $T < 0°C$.

All natural processes proceed spontaneously and are thermodynamically Irreversible in character

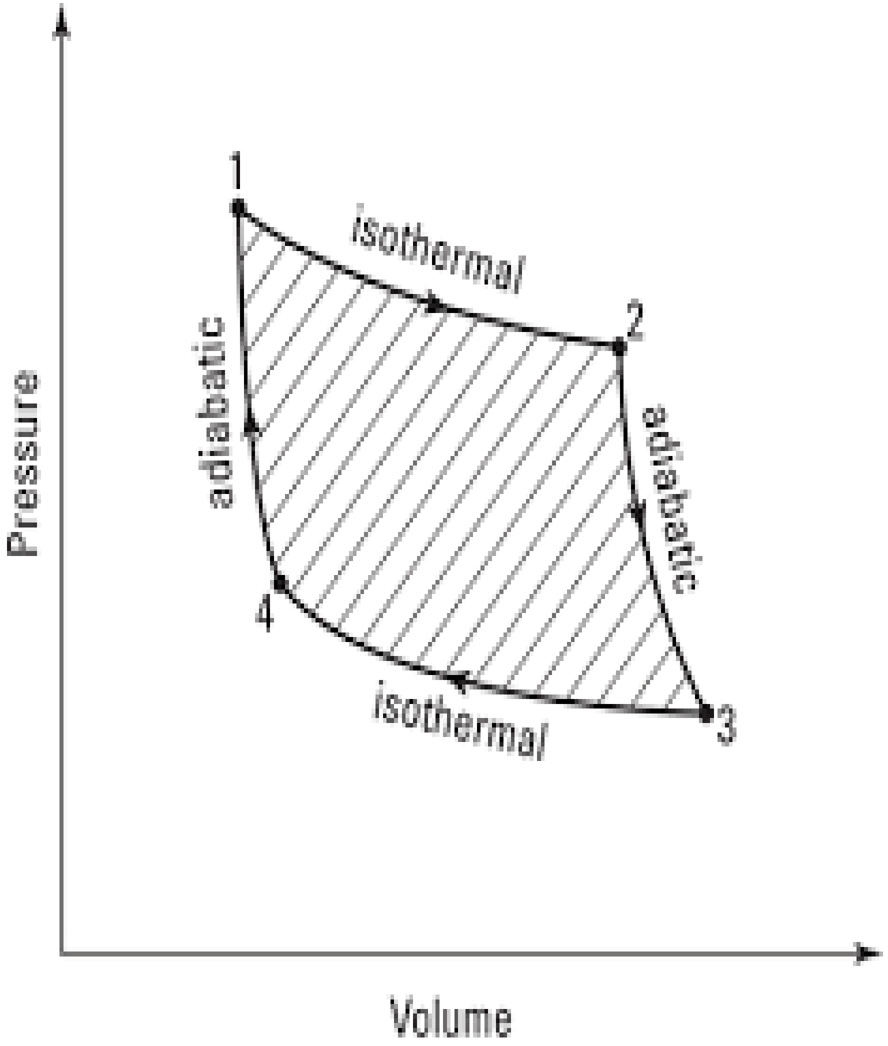
CARNOT CYCLE

Work can be obtained from spontaneous processes. But since these proceed irreversibly, The work obtained is much less than work obtained from reversible process.

Cyclic Process

When a system, after completing a series of changes, returns to its original state, it is said to have completed a cycle.

The entire process is said to be a cyclic process. Since the internal energy of a system depends only Upon the state, it means that in a cyclic process, The net change in internal energy is zero.



CARNOT CYCLE

In the early 19th century, steam engines came to play an increasingly important role in industry and transportation. However, a systematic set of theories of the conversion of thermal energy to motive power by steam engines had not yet been developed. Nicolas Léonard Sadi Carnot (1796-1832), a French military engineer, published *Reflections on the Motive Power of Fire* in 1824.

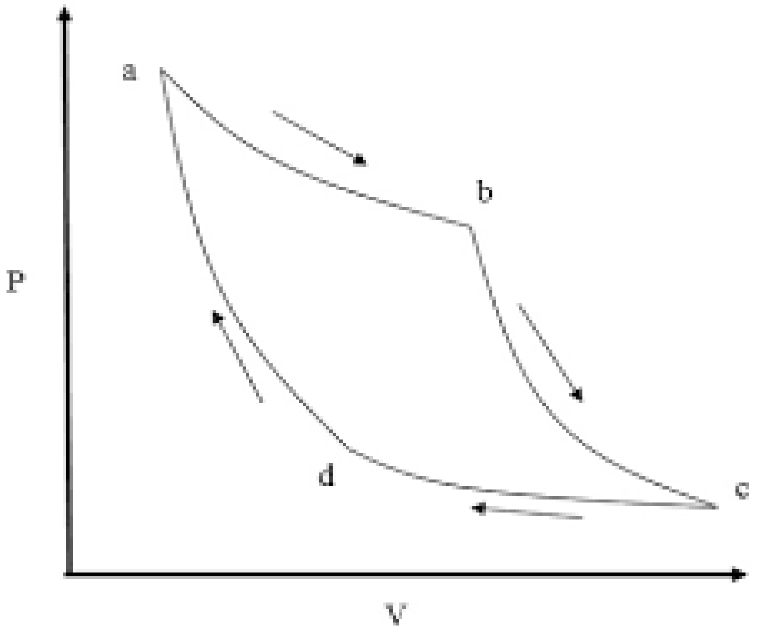
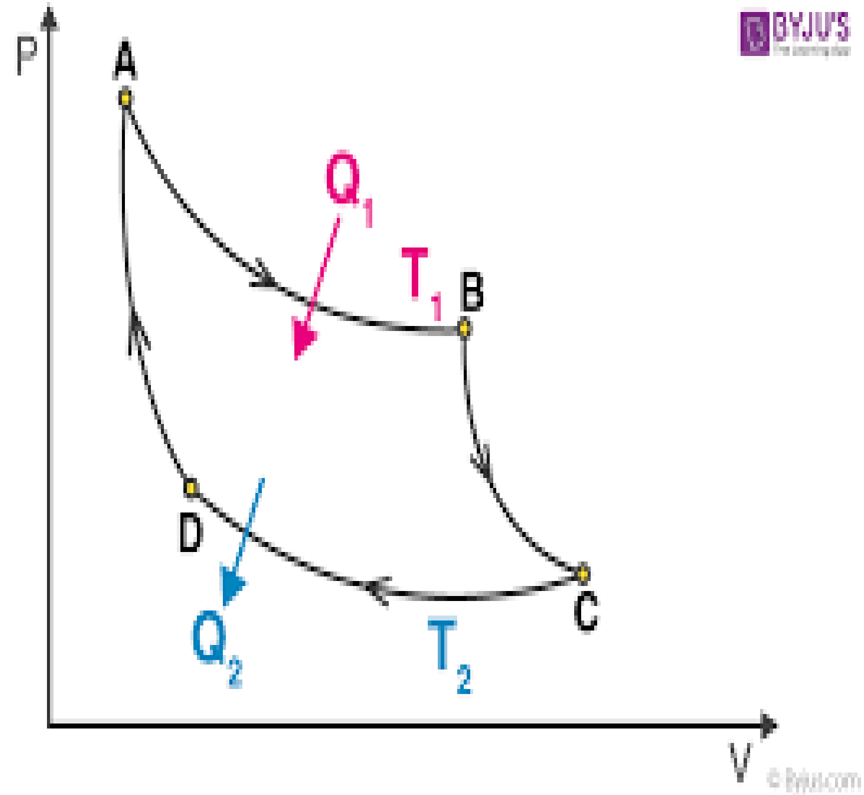


Figure 1: A schematic of P-V diagram for Carnot cycle

CARNOT CYCLE

The book proposed a generalized theory of heat engines, as well as an idealized Model of a thermodynamic system for a heat engine that is now known as the Carnot cycle.

Carnot developed the foundation of the second law of thermodynamics, and is often described as the "Father of thermodynamics."



CARNOT CYCLE

Carnot demonstrated the maximum convertibility Of heat into work. The system consists of one mole of An ideal gas which is subjected to a series of four Successive processes, commonly termed as four Strokes.

Stroke I. Isothermal expansion

The gas is allowed to expand reversibly and Isothermally at the temperature T_2 so that volume increases from V_1 to V_2. Since in isothermal expansion $\Delta E=0$, from First law equation, **$0=q-w$**

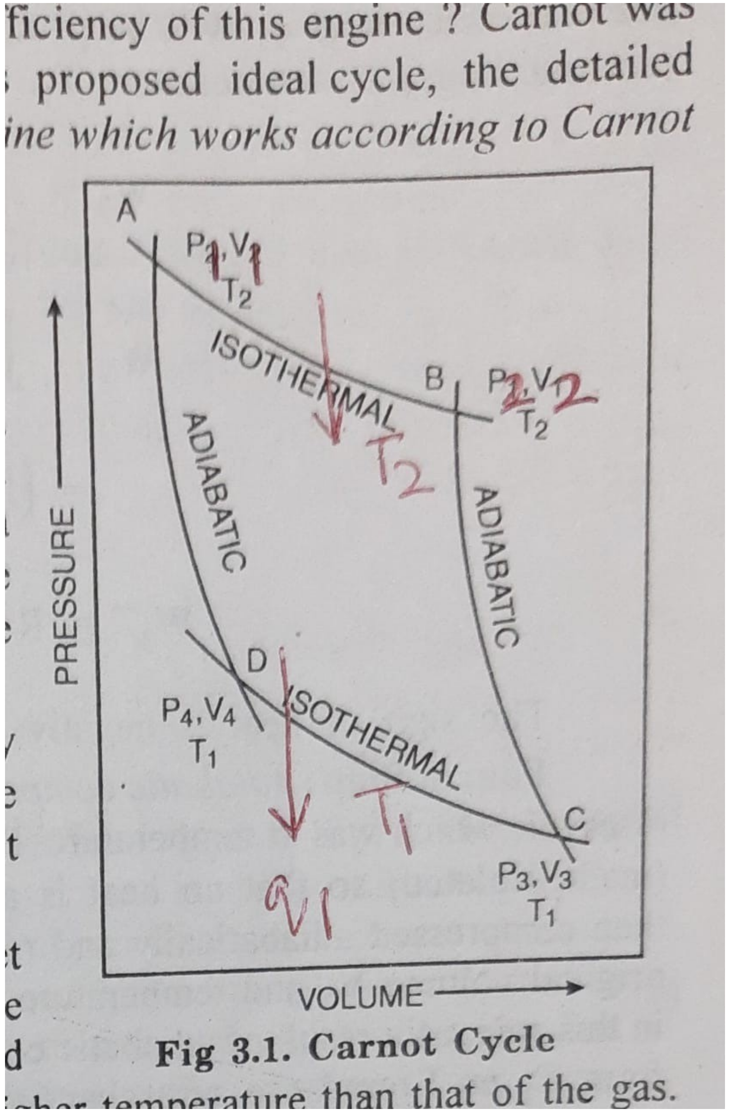

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Fig 3.1. Carnot Cycle

temperature than that of the gas.

CARNOT CYCLE

So, the heat absorbed is equal to the work done by The gas. If q_2 is the heat absorbed by the system, At temperature T_2 and w_1 be the work done by the System, then

$$q_2 = w_1 = RT_2 \ln(V_2/V_1) \qquad (1)$$

II. Stroke II. Adiabatic expansion

The gas is now allowed to expand adiabatically and Reversibly from volume V_2 to V_3.

Since the process is adiabatic, heat exchanged with Surroundings is 0. Since expansion work is taking Place, it is positive and therefore takes place at the Expense of internal energy. The temperature thus

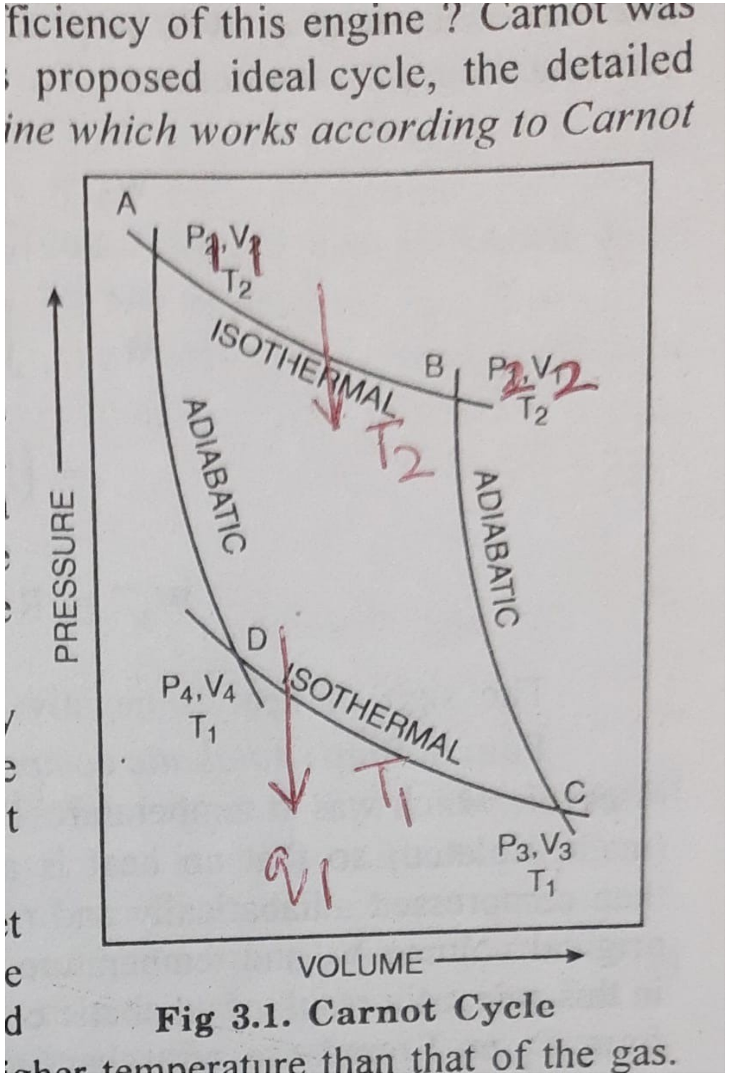

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Fig 3.1. Carnot Cycle

temperature than that of the gas.

CARNOT CYCLE

Lowered in this step to T_1. Since q=0, the first law

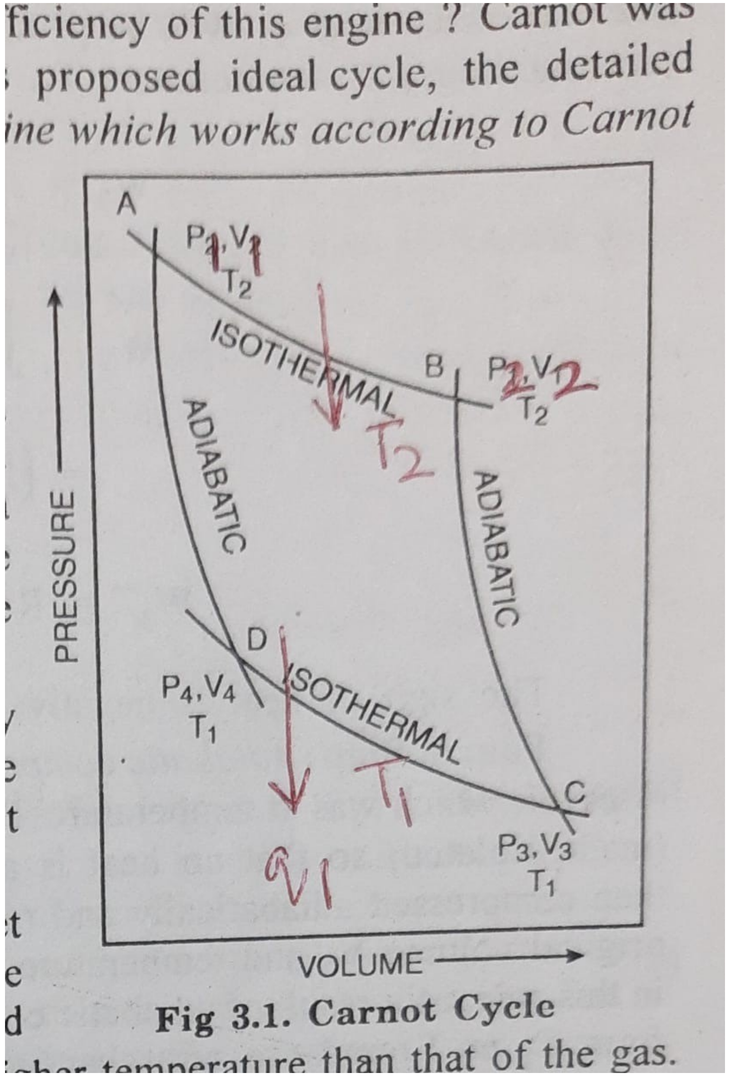
Becomes 0= ΔE + w or –ΔE=w

But – ΔE = - $C_v dT$ = -$C_v(T_1-T_2)$ = $C_v(T_2-T_1)$

Therefore, **w_2= $C_v(T_2-T_1)$** **(2)**

III. Stroke III. Isothermal Compression

The gas now undergoes isothermal reversible Compression at lower temperature T_1 and the volume decreases from V_3 to V_4. In this step work is being done on the system and heat will be produced and given out to surroundings. Call it $-q_1$



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ine which works according to Carnot

Fig 3.1. Carnot Cycle

temperature than that of the gas.

CARNOT CYCLE

Since this is an isothermal process, $\Delta E=0$.

Remembering that work done will be negative and heat Evolved will also be negative, we can write

$$-q_1 = -w_3 = RT_1 \ln (V_4/V_3) \qquad (3)$$

IV. Stroke IV. Adiabatic Compression

Finally by an adiabatic compression, the gas is restored to its initial V_1 and temperature T_2. Since work is done on the system, it is negative. Since it is an adiabatic Process, $q=0$. From the first law, $\Delta E + w=0$

$$\text{Or, } \Delta E = -w = -(-w_4)$$

$$-w_4 = -\Delta E = -C_v(T_2-T_1) \qquad (4)$$

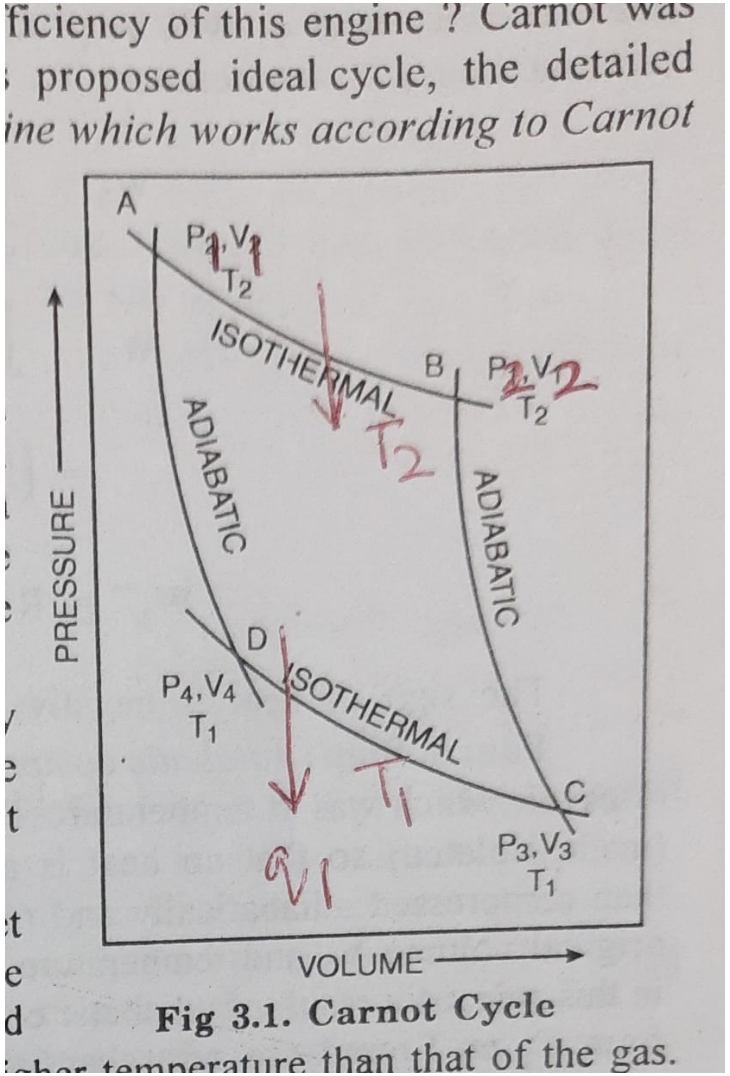

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Fig 3.1. Carnot Cycle

temperature than that of the gas.

CARNOT CYCLE

The net heat absorbed by (q) by the ideal gas in the whole cycle is given by

$$q=q_2+(-q_1) = RT_2 \ln(V_2/V_1) + RT_1 \ln (V_4/V_3) \qquad (5)$$

$$q= RT_2 \ln(V_2/V_1) - RT_1 \ln (V_3/V_4) \qquad (6)$$

We have already discussed the following expression for an adiabatic process:

$$C_v \ln (T_f /T_i)= R \ln (V_f/V_i)$$

So for step II and step IV we can write:

$$C_v \ln(T_1/T_2)=R \ln(V_3/V_2) \quad \text{for step (2)}$$

$$\text{or, } C_v \ln(T_2/T_1)=R \ln(V_2/V_3)$$

$$C_v \ln(T_2/T_1)=R \ln(V_1/V_4) \quad \text{for step (4)}$$

Equating the right hand side of both equations, we get $V_2/V_3= V_1/V_4$

$$\mathbf{V_2/V_1 = V_3/V_4}$$

CARNOT CYCLE

Hence equation (6) becomes $q = RT_2 \ln(V_2/V_1) - RT_1 \ln(V_2/V_1)$

$$\mathbf{q = R(T_2 - T_1)\ln(V_2/V_1) \qquad (7)}$$

Similarly, the net work done by the gas is given by

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

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

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

$$= RT_2 \ln(V_2/V_1) - RT_1 \ln(V_2/V_1)$$

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

$$\mathbf{w = R(T_2 - T_1)\ln(V_2/V_1) \qquad (8)}$$

It is evident from equation (7) and (8) that q=w and that is what happens in a cyclic process.

CARNOT CYCLE-EFFICIENCY

We have seen that the net work done by the system is equal to

$$w= R(T_2-T_1)\ln (V_2/V_1)$$

and the heat absorbed by the system at higher temperature T_2

$q_2=RT_2 \ln(V_2/V_1)$. From both these equations we get

$$w= q_2\frac{T_2-T_1}{T_2} \qquad (9)$$

Since $\frac{T_2-T_1}{T_2}$ <1, it follows that $w < q_2$ This means that only a part of the heat absorbed by the system at the higher temperature T_2 is transformed into work. The rest of heat (q_1) is given out by the system to the surroundings when it is at a lower temperature T_1

THE SECOND LAW OF THERMODYNAMICS

Based on the above observations, Kelvin stated the Second law in the following words:

It is impossible to use a cyclic process to transfer heat from a reservoir and to convert it into work without transferring at the same time a certain amount of heat from a hotter to a colder part of a body.

Having understood that complete conversion of heat cannot take place into work, the fraction which is converted would be important. This ratio is called the Efficiency of an engine and is defined as the following:

EFFICIENCY OF A HEAT ENGINE

The fraction of heat absorbed by an engine which it can convert into Work gives *the Efficiency(η) of the engine.*

From equation (9), it is seen that

$$\text{Efficiency, } \eta = \frac{w}{q_2} = \frac{T_2 - T_1}{T_2} \qquad (10)$$

Since $\frac{T_2 - T_1}{T_2} < 1$, ***the efficiency of a heat engine is always less than 1.***

No heat engine has been made which has an efficiency equal to 1.

It also means that efficiency depends upon difference between T_2 and T_1. Greater the value of T_2-T_1, greater the efficiency. This is why Superheated steam is used in a steam engine.

EFFICIENCY OF A HEAT ENGINE

The net heat absorbed by the system is equal to $q_2+(-q_1)$ and according to First Law of Thermodynamics, this must be equivalent to the net work done by the system. Thus,

$$q= q_2-q_1$$

Combining this with equation (10),we get

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

$$\text{Efficiency}=\eta= \frac{q_2-q_1}{q_2} =\frac{T_2-T_1}{T_2} \qquad (11)$$

This equation was derived by assuming that the series of changes were brought about in a thermodynamically reversible manner to obtain maximum work but in reality the efficiency is much less as process is not reversible.

NUMERICALS ON EFFICIENCY

Q1. Calculate the maximum efficiency of an engine operating between 110 C and 25C.

Ans. Efficiency is given by $\eta = \frac{T_2 - T_1}{T_2}$

T_2 =273+110=383K

T_1 =273+25=298K

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

NUMERICALS ON EFFICIENCY

Q2. Heat supplied to a heat engine is 453.6 kcal. How much useful work can be done by the engine which works between 0 C and 100 C?

Ans.

T_2 =273+100=373K

T_1 =273+0=273K

q_2=453.6 kcal=453.6X4.18=1897.8 kJ

$$w = q_2 \frac{T_2 - T_1}{T_2} = 1897.8X\, \frac{373 - 273}{373}\ \text{kJ}$$

=508.8 kJ

THE CONCEPT OF ENTROPY

The equation

$$\eta = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$ may be rearranged as

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

$$\text{or,} \quad \frac{q_1}{T_1} = \frac{q_2}{T_2} \qquad (12)$$

Equation (12) may be written. In the general form as:

$$\frac{q_{rev}}{T} = \text{constant} \qquad (13)$$

Where q_{rev} is the quantity of heat *exchanged* in a process carried out reversibly at a temperature T.

THE CONCEPT OF ENTROPY

This is an important generalization since the quantity $\frac{q_{rev}}{T}$ represents *a definite quantity or state function, viz, the* ***entropy change of a system.***

The concept of entropy

Equation (12) has been derived by giving a + sign to the heat absorbed and a – sign to heat evolved. If we describe q_2 and q_1 merely as heats exchanged , equation (12) may be written as

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

$$\text{or,} \quad \frac{q_1}{T_1} + \frac{q_2}{T_2} = 0 \qquad (14)$$

ENTROPY

Thus, when isothermal processes and adiabatic process are carried out in a Carnot cycle reversibly, the summation of q/T terms is equal to zero.

Any reversible cyclic process can be can be shown to be made up of a series of Carnot cycles.

Consider this figure and the cyclic process in which the process is carried out from A to B and B to A.

The path may be considered to be made up of carnot cycles. If each change is made very small by increasing the number of cycles, the paths inside the loop cancel out and the cycle corresponds to the continuous curve ABA.

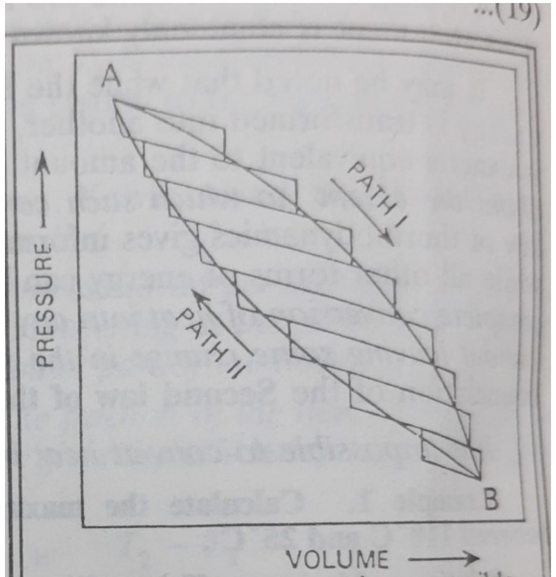


Fig. 2. Entropy change in a reversible cyclic process.

ENTROPY

Knowing that for each carnot cycle,

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

It follows that in case of reversible cycle ABA, the above expression will take the form $\sum q/T = 0$ (15)

Since the cycle is performed in two steps A→B→A, it follows that

$$\sum q/T = \int_A^B dq/T + \int_B^A dq/T = 0 \qquad (16)$$

$\int_A^B dq/T$ is the summation of all the $\frac{dq}{T}$ terms when system changes from path A→ B along path I and $\int_B^A dq/T$ is the similar integral when system returns B→ A to original state along path II

ENTROPY

It follows from equation (16) that

$$\int_A^B dq/T \text{ (path I)} = - \int_B^A dq/T \text{ (path II)}$$

or
$$\int_A^B dq/T \text{ (path I)} = \int_A^B dq/T \text{ (path II)}$$

It is thus clear that $\int_A^B dq/T$ is a *definite quantity independent of the path taken for the change and depends only upon the initial and final states of the system.*

This quantity would be a state function like ΔE and ΔH. This function is called **Entropy** and denoted by the symbol **S**. If S_A is the entropy in the initial state and S_B in the final state, the change in entropy is given by

$$\Delta S = S_B - S_A = \int_A^B dq/T$$

ENTROPY

For each small change, $dS = dq/T$

At constant temperature, for a finite change, dS becomes ΔS and dq becomes q.

$$\Delta S = q/T$$

Entropy is a function of state and therefore, ΔS for change from A to B will be the same whether reversible or not.

However, in order to know the quantity of change, it will be given by

$$\Delta S = \int_A^B dq/T$$

only when the change has been brought about **reversibly.**

ENTROPY

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

Thus the entropy change for a finite change of state of a system at constant temperature is given by

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

Thus, entropy is a state function which depends only on the initial and final state. It is independent of the manner in which the change has been brought about, reversibly or irreversibly. But for calculation of ΔS, we need to know the value of $q_{rev.}$

ENTROPY

Units of entropy

Since entropy is expressed in heat divided by temperature, entropy is expressed in terms of **calories per degree Kelvin, i.e., cal K^{-1}**

In SI unit, entropy is expressed in **Joules per degree Kelvin (J K^{-1})**

Entropy is an extensive property. Its value depends upon the quantity of the substance.

ENTROPY CHANGE IN ISOTHERMAL EXPANSION

In isothermal expansion of an ideal gas, carried out reversibly, there will be no change in internal energy, or, $\Delta E = 0$

Hence, from the first law, $q_{rev} = w$

In such a case, the work done in isothermal reversible expansion is given by

$$w = nRT \ln (V_2/V_1)$$

Therefore, , $q_{rev} = nRT \ln(V_2/V_1)$

Hence, $\Delta S = \frac{q_{rev}}{T} = \frac{1}{T} \times nRT (\ln V_2/V_1)$

or, $\boldsymbol{\Delta S = nR \ln(V_2/V_1)}$

NUMERICAL

Q1. 5 moles of an ideal gas expand reversibly from a volume of 8 litres to 80 litres at a temperature of 27 C. Calculate the change in entropy

R = 8.314 J K^{-1} mol^{-1}

Ans.

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

$= 5$ moles X 8.314 J K^{-1} mol^{-1}X2.303X log 80/8

=95.73 J K^{-1}

Given:

n=5 moles

V_1=8 lit

V_2=80 lit

T= 27 C=300K

ENTROPY CHANGE IN IRREVERSIBLE PROCESS

Consider isothermal expansion of an ideal gas at constant temperature into vacuum. This will take place irreversibly, or spontaneously.

- Since there is no opposing force, work done by system will be 0. (As P_{ext} is zero.)
- Since there is no change in temperature during the process, there will be no change in internal energy of the system, **$\Delta E=0$**
- Hence from 1st Law of thermodynamics, $q = \Delta E + w = 0$
- In other words, no heat is supplied to or removed from surroundings.
- Entropy of the surroundings, therefore, remains unchanged.

- The entropy of a system is a function of initial and final states only.
- In this case, if the volume changes from V_1 to V_2, at constant temperature T. Hence entropy increase of system , considering one mole of a gas will be given as:

$$\Delta S = R \ln(V_2/V_1)$$

- Total increase in entropy of the system and surroundings during the spontaneous process of expansion considered above is $R \ln(V_2/V_1)$
- Since $V_2 > V_1$,it is obvious that spontaneous (irreversible) isothermal expansion of a gas is accompanied by **increase in entropy of system and surroundings taken together**.

$$\mathbf{\Delta S_{sys} + \Delta s_{surr} > 0}$$

ENTROPY CHANGE IN REVERSIBLE PROCESS

Let us now consider isothermal reversible expansion of the ideal gas from volume V_1 to V_2 carried out at temperature T.

- The expansion is carried out infinitesimally slowly; the pressure on the frictionless piston is so adjusted that it remains less than that of the gas by an infinitesimally small amount.
- The gas does some work given by $w=P\Delta V$
- $\Delta E=0$ as the process is isothermal
- An amount of heat q_{rev} is absorbed by the system at temperature T reversibly from surroundings.
- Hence increase in entropy of the system is q_{rev}/T

- The heat lost reversibly at temperature T by the surroundings is also q_{rev} . Hence, decrease in entropy of the surroundings is q_{rev} /T.
- Giving proper signs , the net entropy change of system and surroundings taken together is

$$q_{rev}/T - q_{rev}/T = 0$$

or, $$\boldsymbol{\Delta S_{sys} + \Delta s_{surr} = 0}$$

- Thus in a reversible process, the total entropy change of the system and surroundings taken together is 0.

  We may conclude that **a thermodynamically *irreversible* process is always accompanied by an *increase* in the entropy of the system and its surroundings while in a thermodynamically *reversible* process, the entropy of the system and its surroundings remains unaltered.**

This generalization becomes a criterion for distinguishing between an irreversible and a reversible process.

We may put the above statement in the form of following mathematical expression:

$$\Delta S_{sys} + \Delta s_{surr} = 0 \quad (\text{ for reversible process})$$

$$\Delta S_{sys} + \Delta s_{surr} > 0 \quad (\text{ for irreversible process})$$

Combining the two, we have

$\Delta S_{sys} + \Delta s_{surr} \geq 0$ where = sign refers to a reversible process

While the **>** sign refers to an irreversible process.

This conclusion helps us to predict whether a process can take place spontaneously or not ,i.e., whether it is thermodynamically feasible or not.

SECOND LAW OF THERMODYNAMICS IN TERMS OF ENTROPY

$$\Delta S_{sys} + \Delta S_{surr} \geq 0$$

This equation represents the second law of thermodynamics in terms of entropy change. This equation may be stated in words as

“In a reversible process, the entropy of the system and the surroundings taken together remains constant while in an irreversible process, the entropy of the system and surroundings increases”.

Since all processes in nature occur spontaneously (irreversibly), it follows

that the *entropy of the universe is increasing continuously.*

Clausius summed up the first law and second law as:

The energy of the universe remains constant; the entropy of the universe tends towards a maximum.

ENTROPY CHANGE IN CHANGE OF PHASE

- Entropy change from solid phase to liquid phase (fusion)

$$\Delta S_f = \Delta H_f / T_f$$

- Entropy change from liquid phase to vapour phase (vaporization)

$$\Delta S_v = \Delta H_v / T_b$$

- Entropy change from solid phase to vapour phase (sublimation)

$$\Delta S_{sub} = \Delta H_{sub} / T_{sub}$$

- Entropy change from one crystalline form to another (transition)

$$\Delta S_t = \Delta H_t / T_t$$

In all the above processes, ΔS is positive as ΔH is positive.

ENTROPY CHANGES WITH CHANGES IN P, V AND T.

Since entropy of a system varies with the state of a system, its value for a pure substance will depend upon any of the two variables out of three, T, P and V.

Since T is generally taken as one of the variables, the other one will be V or P.

When T and V are the two variables.

The increase in entropy of the gas for an infinitesimally small change is given by the expression

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

Where dq_{rev} is the small amount of heat absorbed by the system reversibly from the surroundings at temperature T.

From the equation of first law,

$$dq_{rev}=dE + PdV \qquad (1)$$

Substituting the value of dE as C_vdT, we have

$$dq_{rev}= C_vdT +PdV \qquad (2)$$

For one mole of an ideal gas,

$$dq_{rev}= C_vdT +RTdV/V \qquad (3)$$

Dividing equation (3) by T, we have

$$dq_{rev}/T=dS= C_vdT/T +RdV/V \qquad (4)$$

Integrating equation (4) between initial state 1 and final state 2

$$\Delta S=S_2-S_1= C_v\int_{T1}^{T2}\frac{dT}{T} + \mathrm{R}\int_{V1}^{V2} dV/V \qquad (5)$$

Thus, $\Delta S = C_v \ln \frac{T2}{T1} + R \ln \frac{V2}{V1}$ (6)

Thus, entropy change for an ideal gas depends upon volumes and pressure ,both.

When T and P are the two variables.

For any two states of an ideal gas, we can write

$$P_1V_1=RT_1$$

$$P_2V_2=RT_2$$

Therefore, $\frac{V2}{V1} = \frac{P_1T_2}{P_2T_1}$ (7)

Substituting equation (7) in equation (6), we get:

Thus, $$\Delta S = C_v \ln \frac{T2}{T1} + R \ln \frac{P_1 T_2}{P_2 T_1} \qquad (6)'$$

$$\Delta S = C_v \ln \frac{T2}{T1} + R \ln \frac{P_1}{P_2} + R \ln \frac{T_2}{T_1} \qquad (8)$$

Remembering that $C_P - C_v = R$,

$$\Delta S = (Cv + R) \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} \qquad (9)$$

Which can be rewritten as

$$\Delta S = (Cv + R) \ln \frac{T_2}{T_1} - R \ln \frac{P2}{P1} \qquad (10)$$

$$\Delta S = C_P \ln \frac{T_2}{T_1} - R \ln \frac{P2}{P1} \qquad (11)$$

It is evident that the entropy change of an ideal gas depends on pressure as well as temperature.

NUMERICALS

Q1. Calculate the change in entropy accompanying the heating of one mole of Helium gas from a temperature of 298K to 1000K at constant pressure. Assume that C_v=3/2 R

$$\Delta S = n(C_v + R)\ln\frac{T_2}{T_1} - nR\ln\frac{P_2}{P_1}$$

Given:	Since P is constant the second term in this equation
n=1 mole	becomes 0.
T_1=298K	$\Delta S = 1\text{ mole X}(3/2+1)\text{X}8.314\text{ JK}^{-1}\text{mole}^{-1}\text{X}2.303\text{X }\log1000/298$
T_2=1000K	$= 2.5\text{X}8.314\text{X}2.303\text{X}\log1000/298\text{ JK}^{-1}$
C_v=3R/2	$= 25.17\text{ JK}^{-1}$

Q 2. One mole of an ideal gas is heated from 100K to 300K. Calculate ΔS if (a) Volume is kept constant (b) pressure is kept constant. C_v=1.5R

(a) $\Delta S = C_v \ln \frac{T2}{T1} + R \ln \frac{V2}{V1}$ Since V is constant, second term is 0

$\Delta S = 1 \text{mole} \times 1.5 \times 8.314\ JK^{-1}\text{mole}^{-1} \times 2.303 \times \log 300/100$

$= 13.7\ JK^{-1}$

(b) $\Delta S = (Cv + R) \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$ Since P is constant, second term is 0

Given:

n=1 mole

T_1=100K

T_2=300K

$\Delta S = 1 \text{mole} \times (1.5+1) \times 8.314 JK^{-1}\text{mole}^{-1} \times 2.303 \times \log 300/100$

$= 2.5 \times 8.314 \times 2.303 \times 0.4771$

$= 22.8\ JK^{-1}$

ENTROPY CHANGES IN DIFFERENT PROCESSES

There are three different processes that we are familiar with:

(a) Isothermal process (b) Isobaric process (c) Isochoric process

$$\Delta S = C_v \ln \frac{T2}{T1} + R \ln \frac{V2}{V1} \qquad (6)$$

$$\Delta S = C_P \ln \frac{T_2}{T_1} - R \ln \frac{P2}{P1} \qquad (11)$$

(a) Isothermal process

Since temperature is constant, from equation (6) and (11), we get

$$\Delta S_T = R \ln V_2/V_1 = -R \ln P_2/P_1$$

This means that in *isothermal expansion*, ΔS_T will be positive. Conversely, isothermal compression will be accompanied by decrease in entropy.

(b) Isobaric process

At constant pressure, equation (11) will become

$$\Delta S_P = C_P \ln \frac{T_2}{T_1}$$

It follows that in an isobaric process, if temperature increases, entropy also increases.

(c) Isochoric process

At constant volume, equation (6) will give us

$$\Delta S_V = C_v \ln \frac{T2}{T1}$$

Increase in temperature at constant volume is accompanied by increase in entropy.

ENTROPY CHANGE IN CHEMICAL REACTIONS

The entropy change of a chemical reaction is given by the *difference between the sum of the entropies of all the products and the sum of all entropies of all the reactants.*

Consider a chemical reaction of the type

$$aA + bB + cC\ldots\ldots \rightarrow lL + mM + nN\ldots.$$

The entropy change of the reaction, according to the above definition Is given by

$$\Delta S = (lS_L + mS_M + \ldots.) - (aS_A + bS_B + \ldots.)$$

$$\boldsymbol{\Delta S = \sum S_{product} - \sum S_{reactant}}$$

STANDARD ENTROPIES

Entropy of 1 mole of a substance in pure state at one atmospheric pressure and 25°C, is termed as **standard entropy** of that substance and is denoted as **S^o.**

In a reaction when every substance is in its standard state, the entropy change is said to be **standard state entropy change.** This is denoted by **ΔS^o.**

The general equation is then written as

$$\Delta S = \sum S^o_{product} - \sum S^o_{reactant}$$

PHYSICAL SIGNIFICANCE OF ENTROPY

1. **Entropy as a measure of disorder of the system.**

We have seen that all spontaneous processes are accompanied by an increase in entropy.

- Flow of heat from hot end to cold end of a conductor,
- Flow of electricity from higher potential to lower potential,
- Diffusion of a solute from a higher concentration to lower concentration,

are all *accompanied by increase of entropy.*

It can also be seen that there is *increase of disorder in the system.*

- There is a certain order when one end is hot and other is cold. As soon as heat starts flowing from hot end to cold end, there is movement of electrons. So there is an increase in disorder of the system. Finally equilibrium is restored when the temperature becomes same at both ends.
- In a similar way, when current flows from a higher to a lower potential, there is increase in disorder due to flow of electrons.
- When solutions of two concentrations are mixed, there is movement of solute molecules, leading to an increase in disorder.

Thus spontaneous processes are accompanied by an increase in entropy as well as disorder of the system.

2. Entropy as a measure of probability.

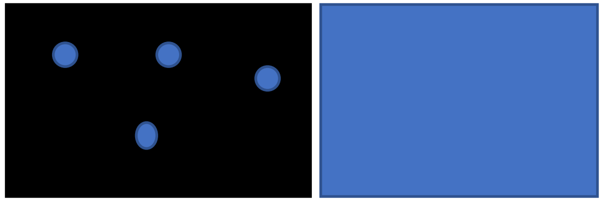
We have just seen that all spontaneous processes are accompanied by an increase in entropy and an increase in disorder of the system.

If we look carefully, we can understand that a spontaneous process goes from a less probable state to a more probable state.

In other words, a spontaneous change invariably takes place *from a less probable state to a more probable state.*

EXAMPLE OF MORE PROBABLE STATE

Let us consider an example of a gas which is in a vessel. For simplicity Let us assume that there are only 4 molecules in the first vessel. Let this vessel be connected to another vessel which is attached to the first one. The two vessels are of the same size. After opening the connecting door between the Two vessels, the molecules can be in either vessel. Let us call the Vessels L and R, denoting left and right.



Before connecting the two vessels all molecules were in left vessel.

After opening the door , the molecules can be in either vessel.

So each molecule can have two possibilities, L or R.

So the possibility of 4 molecules will be 2^4 or 16.

The probability of all molecules remaining in L will be 1/16.

The probability of molecules spreading to either vessel will be 16-1=15

So the probability of spreading will be 15/16

Since **15/16 > 1/16**, it is obvious why smells spread.

If there are a large number of molecules, let us say $6.023X10^{23}$ molecules,

The probability of not spreading would be $1/2^{6.023X10\mathbf{23}}$

Thus any system, spontaneously goes from a less probable to a more probable state.

OBSERVING THE SURROUNDINGS IS DIFFICULT!

We have seen that observing the surroundings is difficult and tedious. Another way has been devised to make things simpler. We are aware of the following relationship:

$$\Delta S_{total} = \Delta S_{surr} + \Delta s_{sys}$$

Since the surroundings give an amount of heat to the system, the Surroundings themselves lose an amount of heat given by – ΔH.

The above equation thus becomes

$$\Delta S_{total} = -\Delta H/T + \Delta S_{sys}$$

Multiplying this equation by T, we get

$$T\Delta S_{total} = -\Delta H + T\Delta S_{sys}$$

Multiplying this equation by – sign, we get

$$-T\Delta S_{total} = \Delta H - T\Delta S_{sys}$$

The quantity $-T\Delta S_{total}$ is called Gibb's Free Energy change **ΔG** .

Since ΔS_{total} is positive, it follows that $-T\Delta S_{total}$ will be negative.

That is, ΔG is negative for all spontaneous changes.

And $G=H-TS$

In a similar way , Helmholtz Energy A has been defined as A=E=TS

HELMHOLTZ AND GIBB'S FREE ENERGY

We have seen that the change in entropy of the system and surroundings taken together is a criterion of feasibility of a reaction.

However, it is not always convenient to observe the surroundings.

We may consider the change in entropy in terms of other state functions.

Two such functions are the **work function** and the **free energy function** Represented by **A** and **G** respectively.

They are defined by the equations

$$A=E-TS \tag{1}$$

$$G=H-TS \tag{2}$$

Since E,H and S depend on the state of a system, A and G will also depend On the state of the system. That is, A and G will be state functions.

Let the three functions in equation (1) be in the initial state at temperature T and given by A_1, E_1 and S_1 so that

$$A_1=E_1-TS_1 \qquad (3)$$

Let a change take place at the same temperature T so that the values of the state become A_2, E_2 and S_2 . Then,

$$A_2=E_2-TS_2 \qquad (4)$$

Subtracting (3) from (4) we get,

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

$$\Delta A=\Delta E-T\Delta S \qquad (5)$$

If the change is brought about reversibly at the temperature T and the heat absorbed is q_{rev}, then $\Delta S=q_{rev}/T$. Putting this value in (5), we get

Equation (5) then becomes

$$\Delta A=\Delta E-q_{rev} \qquad (6)$$

But from the first law of thermodynamics, $q_{rev}=\Delta E + w_{rev}$

$$\text{Therefore, } -w_{rev}= \Delta E-q_{rev} \qquad (7)$$

Comparing equations (6) and (7),

$$\Delta A=-w_{rev}$$

$$\text{or, } -\Delta A=w_{rev}$$

Since the process is carried out reversibly, w represents the maximum work.

Thus, *decrease in the function A(- ΔA) gives the maximum work that can be obtained from the system during the given change.*

The function A is therefore called the **work function** or the **Helmholtz Free energy** .

Returning to equation (2), if G_1, H_1 and S_1 are the state functions in the Initial state, then

$$G_1=H_1-TS_1 \qquad (8)$$

And temperature remaining constant all along, the system undergoes Change, at final state we can write

$$G_2=H_2-TS_2 \qquad (9)$$

Subtracting the two equations we get

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

Or,

$$\Delta G=\Delta H-T\Delta S \qquad (10)$$

We already know that $\Delta H= \Delta E+P\Delta V$, we can write equation (10) as

$$\Delta G= \Delta E+P\Delta V- T\Delta S \qquad (11)$$

Comparing with equation (5), we get

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

But since ΔA is equal to $-w_{rev}$

Therefore, $$\Delta G = -w_{rev} + P\Delta V$$

or, $$-\Delta G = w_{rev} - P\Delta V \qquad (12)$$

The quantity $P\Delta V$ is the work done by the gas on expansion against the constant external pressure P.

Therefore, $-\Delta G$ *gives the maximum work obtainable from a system other than the work due to change in volume at constant temperature and pressure. The work other than that due to change in volume is called* ***net work.*** Thus,

$$\textbf{Net work} = w_{rev} - P\Delta V = -\Delta G \qquad \textbf{(13)}$$

Thus,

$$\textbf{Net work} = w_{rev} - P\Delta V = -\Delta G$$

- Hence, - ΔG *is a measure of the maximum net work that can be obtained from a system at constant temperature and pressure.*
- The quantity G is due to Gibb’s and is called the Gibb’s free energy.
- Thus, - ΔG is a measure of *decrease in free energy.*
- The net work it measures may be electrical or chemical work.

VARIATION OF FREE ENERGY WITH TEMPERATURE AND PRESSURE

According to equation (2)

$$G=H-TS$$

Since $H=E+PV$

Therefore, $G=E+PV-TS$ (14)

Upon differentiation,

$$dG=dE+PdV+VdP-SdT-TdS \quad (15)$$

The first law equation for an infinitesimal change may be written as

$$dq=dE+dw \quad (16)$$

If work dw is only due to expansion, then

$$dq=dE+PdV \quad (17)$$

For a reversible process,

$$dS=dq/T$$

Therefore, $$TdS=dq=dE+PdV \qquad (18)$$

Combining equations (15) and (18), we have

$$dG=VdP-SdT \qquad (19)$$

This equation gives the change of free energy when a system undergoes a reversible change of pressure as well as temperature.

If pressure remains constant, then

$$dG=-SdT$$

Or, $$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad (20)$$

If temperature remains constant, then from equation (19), we have

$$dG=VdP$$

Or, $$\left(\frac{\partial G}{\partial P}\right)_T=V \qquad (21)$$

Let the free energy of a system be G_1 in the initial state and G_2 in the final state when change in pressure has taken place at *constant temperature.* Integrating equation (21), we get

$$\Delta G=G_2-G_1=\int_{P1}^{P2} VdP \qquad (22)$$

If we are considering 1 mole of an ideal gas, then PV=RT and V=RT/P

$$\Delta G=\int_{P1}^{P2} VdP=RT\int_{P1}^{P2} dP/P \qquad (23)$$

$$\boldsymbol{\Delta G = RT \ln\frac{P_2}{P_1} = RT \ln\frac{V_1}{V_2}} \qquad (24)$$

Numerical

Q1. Calculate the free energy change (ΔG) which occurs when 1 mole of an ideal gas expands reversibly and isothermally at 37^oC from an Initial volume of 55 litres to 1000 litres.

$$\Delta G = RT \ln \frac{V_1}{V_2} = 2.303RT \log \frac{V_1}{V_2}$$

Given:

N=1mole

T=37C=310K

V_1=55 lit

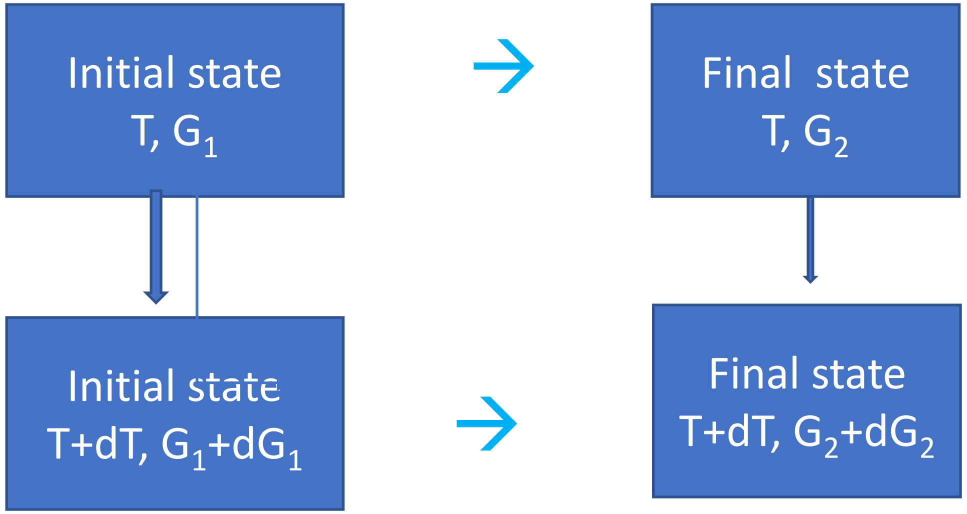
V_2=1000 lit

$$\Delta G = 2.303 X 8.314\ JK^{-1} mole^{-1} X 310 K X \log 55/1000$$

$$= -7476.8\ J\ K^{-1}$$

THE GIBB' S HELMHOLTZ EQUATION

Consider a system in the initial state at temperature T_1.If the temperature increases by an infinitesimally small amount dT and becomes T+dT.



Initial state
T, G_1

Final state
T, G_2

Initial state
T+dT, G_1+dG_1

Final state
T+dT, G_2+dG_2

If the Gibb's Free energy of the initial state be G_1 at temperature T and be G_1+dG_1 at T+ dT .Similarly, if Gibb's Free energy of the final state be G_2 at temperature T and be G_2+dG_2 at T+ dT

If the pressure remains constant all along, the equation (19), which is

$$dG=VdP-SdT \qquad (19)$$

Becomes $dG=-SdT$

So for the initial and final states we can write,

$$dG_1=-S_1dT \qquad (25)$$

$$dG_2=-S_2dT \qquad (26)$$

Subtracting (25) from (26), we get

$$d(G_2-G_1)=-(S_2-S_1)dT$$

$$d\Delta G=-\Delta SdT \qquad (27)$$

As the pressure is constant, therefore,

$$\left(\frac{\partial(\Delta G)}{\partial T}\right)_P=-\Delta S \qquad (28)$$

Also from equation $\Delta G=\Delta H-T\Delta S$ (10)

We get $-\Delta S=(\Delta G-\Delta H)/T$

Equation (28) thus becomes

$$(\Delta G-\Delta H)/T=\left(\frac{\partial(\Delta G)}{\partial T}\right)_P \tag{29}$$

$$(\Delta G-\Delta H)=T\left(\frac{\partial(\Delta G)}{\partial T}\right)_P$$

$$\boldsymbol{\Delta G=\Delta H+T\left(\frac{\partial(\Delta G)}{\partial T}\right)_P} \tag{30}$$

- This is known as the Gibb’s Helmholtz equation.
- It is applicable to all processes occurring at constant pressure.
- It has been used to calculate the heat change, ΔH, for a reaction taking place at constant pressure, provided the free energy change at two different values is known.

Numerical

Q2. The free energy change accompanying a given process is -85.77kJ At 25^{o}C and -83.68kJ at 35^{o}C. Calculate the enthalpy change, ΔH for the process at 30^{o}C.

Given:

ΔG at 25^{o}C=-85.77 kJ

ΔG at 35^{o}C=-83.68 kJ

T=30^{o}C

$\left(\frac{\partial(\Delta G)}{\partial T}\right)_P$=-83.68-(-85.77)/10=0.209 kJ K^{-1}

ΔG at 30^{o}C may be taken as the average of the values at 25^{o}C and 35^{o}C

ΔG at 30^{o}C=-(83.68+85.77)/2= -84.725 kJ

Therefore, -84.725= ΔH+303K X 0.209 kJ K^{-1}

ΔH=-148.05 kJ