Chapter 26

Nasir Perveiz Butt
M. Sc. (Physics) M. Phil
Assistant Professor
Govt. College, Sargodha.

ENTROPY AND 2nd LAW OF THERMODYNAMICS

Reversible & Irreversible Processes

Reversible Process:

The process performed in such a way that at the end of process both system and surroundings go back to their initial state without producing any change in the rest of the universe is called a reversible process

Irreversible Process:

A process that does not satisfy the conditions of reversible process is called an irreversible process.
All natural process are irreversible process. Reversible process is an ideal case.

Cyclic Process:

A process in which the system returns to its initial state after undergoing a series of changes is called a cyclic process

Quasi-Static Process:

The process performed so slowly that the system passes through a continuous sequence of equilibrium states is called a quasi-static process. It may and may not be reversible.

Heat Energy and 2nd Law (Kelvin Statement)

"It is a device which converts heat energy into mechanical energy."

Principle:

Every heat engine takes heat from a hot body (source) and converts a part of it into work and rejects the remaining part to a cold body (sink).

Efficiency of Heat Engine:

Suppose a heat engine takes heat Q_H from hot body at Temp T_H, converts a part of it into work and rejects the remaining heat Q_L to cold body at temp. T_L.

After completing one cycle, the system returns to the initial state. So its internal energy remains constt. in a cycle. So work done by the engine in one cycle is

$W = Q_H - Q_L$. and change in internal energy is zero.

The efficiency of heat engine is defined as,

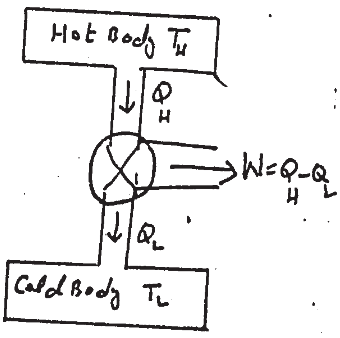
"Ratio of work done by the engine in one cycle to the heat absorbed in one cycle."

$$\therefore \quad e = \frac{\text{Work done}}{\text{Heat absorbed}}$$

$$e = \frac{W}{Q_H}$$

$$e = \frac{Q_H - Q_L}{Q_H} = \frac{Q_H}{Q_H} - \frac{Q_L}{Q_H}$$

$$\boxed{e = 1 - \frac{Q_L}{Q_H}} \quad (1)$$



From the eq. (1) it is clear that efficiency of heat engine is not 100% or 1. The efficiency can be 100% if $Q_L = 0$ i.e no heat is Transferred to the cold body and heat Q_H taken from hot body is completely converted into work. This engine which will do so is called perfectly efficient heat engine. But experiments shows that no such heat engine can be made which can convert whole heat drawn from a single body into work.

So Lord Kelvin gave the following statement based on this fact. According to him

> "It is impossible to make a heat engine which operating in a cycle can go on doing work by taking heat from a single body" without other body at lower temp."

It is called Kelvin's statement of the 2nd law of thermodynamics.

This law tells that two bodies at different temperatures are must for the working of a heat engine. The hot body is called Source or boiler while the cold body is called Sink or condenser.

Sample Problem 1

Sample Problem 1 An automobile engine, whose thermal efficiency e is 22%, operates at 95 cycles per second and does work at the rate of 120 hp. (a) How much work per cycle is done on the system by the environment? (b) How much heat enters and leaves the engine in each cycle?

Sol:- Efficiency $= e = 22\% = 0.22$

Number of cycles in one sec $= 95$

Rate of doing work $= 120HP$.

(a) Work done per cycle on the system $= ?$

(b) Heat enters or leaves per cycle $= ?$

(i) (a) Now $P = \frac{\text{Work}}{\text{Time}}$

$$\therefore \text{Work} = \text{Power} \times \text{Time}$$

$$= 120\,H.P \times 1\,\text{Sec.}$$

$$= 120 \times 746\ \text{Watt} \times 1\,\text{Sec.}$$

$$= 89520\ \frac{J}{\text{Sec}} \times \text{Sec.}$$

$$\text{Work} = 89520\,J$$

This work is done in 95 cycles.

$$\therefore \text{Work done per cycle} = \frac{89520}{95} = 942\,\text{Joule}$$

$\boxed{\therefore \text{Work done per cycle} = 942J.}$ Ans.

(ii)(b) Heat absorbed from the hot body Q_H is given by

$$e = \frac{W}{Q_H}$$

$$\therefore Q_H = \frac{W}{e} = \frac{942}{0.22} = 4281.8 = 4.28 \times 10^3 J$$

$$\boxed{Q_H = 4.3 \times 10^3 J} \text{ Ans.}$$

(iii) Now heat rejected to cold body is

$$Q_L = Q_H - W$$
$$= 4.3 \times 10^3 - 942$$
$$= 3358 \approx 3.358 \times 10^3$$

$$\boxed{Q_L = 3.4 \times 10^3 \text{ Joule}} \quad \text{Ans.}$$

Refrigerator and 2nd Law (Clausius Statement)

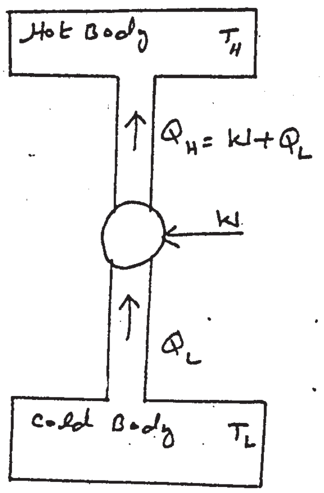
"A heat engine run in reverse is called as a refrigerator."
A refrigerator needs work to transfer heat from cold body to hot body.
If Q_L is the amount of heat removed from the cold body at temp T_L and Q_H is the amount of heat given to the hot body at temp T_H, then the difference $Q_H - Q_L$ is the external work required to drive the refrigerator.
In a refrigerator instead of efficiency we use the term co-efficient of performance K defined as

$$K = \frac{\text{Desired output}}{\text{Required Input}}$$

i.e. coefficient of performance is the ratio of heat removed from the cold body to the mechanical work required to operate the refrigerator."

$$\therefore K = \frac{Q_L}{W}$$

$$\boxed{K = \frac{Q_L}{Q_H - Q_L}}$$



In a perfect refrigerator $W=0$ and so $Q_L = Q_H$. So the coefficient of performance of perfect refrigerator is infinity.

So we have another statement of 2nd law of thermodynamics known as Clausius statement according to which

"It is impossible to cause heat to flow from cold body to hot body without expenditure of energy."

So from this we find that heat can't flow by itself from cold to hot body. So we have to do work to make this flow.

So this statement can also be stated as,

"Perfect refrigerator is impossible."

In an ordinary house hold refrigerator the working substance is the liquid (Freon) that circulates within the system. The cold body is the interior of the refrigerator and hot body is the room in which refrigerator is kept.

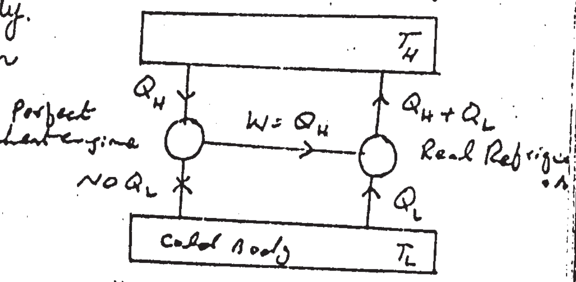
Typical refrigerator have the coefficient of performance around 5.

Equivalance of Clausius and Kelvin Statement:

The two statements of the 2nd law of thermodynamic can be shown to be identical by supposing that if one statement is false, the other is also false.

We suppose that Kelvin statement is false i.e we can construct a heat engine which can convert the heat of a single body into work without a cold body.

Suppose this engine is used to run a refrigerator as shown in fig.



In the refrigerator the heat flows from cold body to hot body.

So the work done by the engine is used to operate the refrigerator which transfers heat from cold body to hot body.

So the single refrigerator is not violating any law i.e it is working perfectly.

But the heat engine and the refrigerator both form a system which transfers heat from cold body to hot body without external work. But it is against the Clausius statement. So the Clausius statement is also false if Kelvin's statement is false. So a violation of Kelvin statement gives violation of Clausius statement. Similarly a violation of Clausius gives violation of Kelvin's statement. So we see that a violation of either statement gives a violation of other. Hence from the above discussion we find that the two statements are logically identical.

Sample Problem-2

Sample Problem 2 · A household refrigerator, whose coefficient of performance K is 4.7, extracts heat from the cooling chamber at the rate of 250 J per cycle. (a) How much work per cycle is required to operate the refrigerator? (b) How much heat per cycle is discharged to the room, which forms the high-temperature reservoir of the refrigerator?

Sol:- Coefficient of performance $= K = 4.7$

$Q_L = 250$ Joule per cycle.

(a) Work per cycle $= W = ?$

(b) Heat transferred to room per cycle $= Q_H = ?$

(i) As $K = \dfrac{Q_L}{W}$

$$\therefore W = \frac{Q_L}{K} = \frac{250}{4.7}$$

$\boxed{W = 53 \text{ Joule}}$ Ans

(ii) As $Q_H = W + Q_L$

$= 53 + 250$

$\boxed{Q_H = 303 \text{ Joule}}$ Ans.

Carnot Engine and Carnot Cycle

Carnot Engine

"It is an ideal heat engine free from all heat loses and all the processes are reversible."

Construction:

It consists of the following parts.

(i) A cylinder containing perfect gas having non-conducting walls and piston and only base conducting.
(ii) A source of heat and temp. T_H
(iii) A sink at lower temp T_L.
(iv) A non-conducting stand.

Carnot Cycle:

The operating cycle of carnot engine is called carnot cycle.

Working:

The carnot cycle consists of the following four processes

Step 1. (ab) Isothermal Expansion

The cylinder is placed on the source of heat at temp. T_H. and the gas is allowed to expand very slowly by removing weights on the piston. The gas expands and tends to cool down but it absorbs heat $Q_1 = Q_H$ from the source of heat so that its temp. remains constt $= T_H$. The process is isothermal and $\Delta E_{int} = 0$ and all the +ve added heat appears as -ve workdone on the gas.

→ This process is shown on PV diagram by the curve ab.

Step 2. (bc) Adiabatic Expansion

The cylinder is now placed on the non-conducting stand so that heat does not enter or leave the gas. The gas is allowed to to expand slowly by removing more weights from the piston. The process is adiabatic and $Q = 0$. The piston does -ve work on the gas and work is done at the cost of internal energy of the gas. So temp. of gas decreases to T_L. the process is shown on the PV diagram by curve bc.

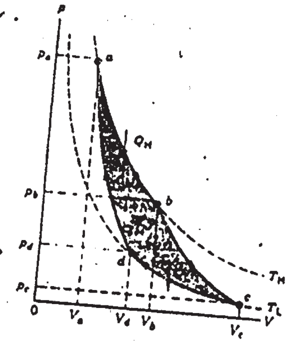
Step 3. (cd) Isothermal Compression

The cylinder is now placed on the sink and the gas is compressed by adding weights on the piston. During this process the gas rejects heat $Q_2 = Q_L$ to the sink at temp T_L. The process is isothermal compression and +ve work is done on gas during compression. The process is shown in the PV diagram by curve cd.

Step 4 (da) Adiabatic Compression:

The cylinder is finally placed on the non-conducting stand. The gas is compressed by adding more weights on the piston. As heat can't leave the gas so the process is adiabatic The process is s.t. temp.

of the gas rises to T_H and the gas goes back to its initial state. The process is shown on the PV diagram by curve da. So the gas undergoes a cycle abcda. It is a reversible cycle and is called carnot cycle.



Efficiency of Carnot Engine:

Now we calculate the efficiency of carnot cycle, (or carnot engine).

Along the isothermal path 'ab' temp. remains constt so $\Delta E_{int} = 0$. So by first law heat transferred Q_H from source is equal to magnitude of work.

$$\therefore |Q_H| = |W_1| = nRT_H \ln \frac{V_b}{V_a} \qquad (1)$$

Similarly for isothermal compression 'cd' the heat energy rejected Q_L to sink is

$$|Q_L| = |W_3| = nRT_L \ln \frac{V_c}{V_d} \qquad (2)$$

Dividing (2) by (1) we get

$$\frac{|Q_L|}{|Q_H|} = \frac{nRT_L \ln V_c/V_d}{nRT_H \ln V_b/V_a}$$

$$\frac{|Q_L|}{|Q_H|} = \frac{T_L}{T_H} \frac{\ln V_c/V_d}{\ln V_b/V_a} \qquad (A)$$

Note

[illegible] mod لیں [illegible] +ve [illegible]

Now for adiabatic path 'bc' we have

$$TV^{\gamma-1} = \text{constt}$$

$\therefore$ For path 'bc'

$$T_H V_b^{\gamma-1} = T_L V_c^{\gamma-1}$$

$$\frac{T_H}{T_L} = \frac{V_c^{\gamma-1}}{V_b^{\gamma-1}} \qquad (a)$$

Similarly for adiabatic path 'da'

$$T_L V_d^{\gamma-1} = T_H V_a^{\gamma-1}$$

$$\therefore \frac{T_H}{T_L} = \frac{V_d^{\gamma-1}}{V_a^{\gamma-1}} \qquad (b)$$

Comparing (a) and (b) we get

$$\frac{V_c^{\gamma-1}}{V_b^{\gamma-1}} = \frac{V_d^{\gamma-1}}{V_a^{\gamma-1}}$$

$$\left(\frac{V_c}{V_b}\right)^{\gamma-1} = \left(\frac{V_d}{V_a}\right)^{\gamma-1}$$

$$\frac{V_c}{V_b} = \frac{V_d}{V_a}.$$

$$\Rightarrow \frac{V_b}{V_a} = \frac{V_c}{V_d}..$$

Putting this result in (A) we get.

$$\frac{|Q_L|}{|Q_H|} = \frac{T_L}{T_H} \frac{\ln V_b/V_a}{\ln V_b/V_a}$$

$$\frac{|Q_L|}{|Q_H|} = \frac{T_L}{T_H}.$$

Now efficiency of carnot engine is

$$e = 1 - \frac{|Q_L|}{|Q_H|}$$

$$\therefore e = 1 - \frac{T_L}{T_H}.$$

From this expression we find that efficiency of carnot engine only depends upon temps. of source and sink b/w which it operates.

The efficiency is increased by decreasing T_L.

The efficiency will be 100% if $T_L = 0K$ which is not possible.

so efficiency of carnot engine can't be 100%.

Sample Problem-3

Sample Problem 3 The turbine in a steam power plant takes steam from a boiler at 520°C and exhausts it into a condenser at 100°C. What is its maximum possible efficiency?

Sol. $T_H = 520°C = 520 + 273 = 793\,K$

$T_L = 100°C = 100 + 273 = 373K.$, $e = ?$

As $e = 1 - \frac{T_L}{T_H}$

$$= \frac{T_H - T_L}{T_H} = \frac{793 - 373}{793}$$

$$= 0.529 = 0.53.$$

$$\boxed{e = 53\%}$$

Sample Problem-4

Sample Problem 4 A heat pump (see Fig. 9) is a device that—acting as a refrigerator—can heat a house by drawing heat from the outside, doing some work, and discharging heat inside the house. The outside temperature is $-10°C$, and the interior is to be kept at 22°C. It is necessary to deliver heat to the interior at the rate of 16 KW to make up for the norm heat loses. At what min rate, what energy must be supplied to heat pump?

Sol: $T_L = -10\,°C = -10 + 273 = 263\,K$,
$T_H = 22\,°C = 22 + 273 = 295\,K$, $\frac{Q_H}{t} = 16\,KW$, $\frac{W}{t} = ?$

As coefficient of perfomance of heat pump is given by,

$$K = \frac{T_H}{T_H - T_L} = \frac{263}{295 - 263} = \frac{263}{32}$$

$$K = 8.218$$

$$K = 8.22.$$

As $K = \frac{Q_L}{W}$ But $Q_L = Q_H - W$

$$\therefore \quad K = \frac{Q_H - W}{W}$$

$$KW = Q_H - W$$

$$KW + W = Q_H$$

$$W(K+1) = Q_H$$

$$W = \frac{Q_H}{K+1}$$

$$\therefore \quad \frac{W}{t} = \frac{Q_H/t}{K+1}$$

$$\frac{W}{t} = \frac{0.16}{8.22+1} = \frac{16}{9.22}$$

$$\therefore \quad \boxed{\frac{W}{t} = 1.7.\ K\,Watt.} \quad \text{Ans.}$$

Imp.

Thermodynamic Temperature Scale:

"The scale of temp. which is independent of the nature of working substance is called Thermodynamic temp scale or Kelvin Temp. Scale."

Thermodynamic temp. scale has been derived by Kelvin from the laws of Thermodynamics.

The efficiency of carnot reversible heat engine does not depend on the working substance and depend on the working temps. θ_1 and θ_2 of the source and sink where θ_1 and θ_2 are measured on the perfect gas scale.
So the efficiency e_c of carnot engine is a function of θ_1 and θ_2.

$$\therefore e_c = 1 - \frac{Q_1}{Q_2} = \phi(\theta_1, \theta_2)$$

$$1 - \frac{Q_1}{Q_2} = \varphi(\theta_1, \theta_2)$$

or $$\frac{Q_2}{Q_1} = 1 - \varphi(\theta_1, \theta_2)$$

or $$\frac{Q_1}{Q_2} = \frac{1}{1 - \varphi(\theta_1, \theta_2)}$$

$$\frac{Q_1}{Q_2} = f(\theta_1, \theta_2) \quad (\text{say})$$

Now consider three carnot engines working b/w the temps (θ_1, θ_2), (θ_2, θ_3) and (θ_1, θ_3). where $\theta_1 > \theta_2$ and $\theta_2 > \theta_3$. Then.

$$\frac{Q_1}{Q_2} = f(\theta_1, \theta_2)$$

$$\frac{Q_2}{Q_3} = f(\theta_2, \theta_3)$$

$$\frac{Q_1}{Q_3} = f(\theta_1, \theta_3)$$

Now $$\frac{Q_1}{Q_2} = \frac{Q_1}{Q_3} \times \frac{Q_3}{Q_2}$$

$$\therefore \frac{Q_1}{Q_2} = \frac{f(\theta_1, \theta_3)}{f(\theta_2, \theta_3)}$$

As $\frac{Q_1}{Q_2}$ is a function of (θ_1, θ_2) only so θ_3 can be omitted.

$$\therefore \frac{Q_1}{Q_2} = \frac{\psi(\theta_1)}{\psi(\theta_2)}$$

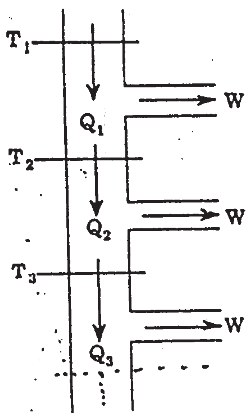
Let $$\frac{\psi(\theta_1)}{\psi(\theta_2)} = \frac{T_1}{T_2}$$

$$\therefore \frac{Q_1}{Q_2} = \frac{T_1}{T_2}.$$

$$\text{or} \quad \frac{Q_1}{T_1} = \frac{Q_2}{T_2} \qquad (1)$$

Where T_1 and T_2 are called Kelvin temps. or absolute temps.

Now consider a series of carnot engines coupled together s.t each engine does the same amount of work and also sink of preceeding engine becomes the source of next engine and so on i.e the first engine recieves heat Q_1 from the source at temp T_1, performs work W and reject heat Q_2 to the 2nd engine.



The 2nd engine recieves heat Q_2 at temp. T_2 and rejects heat Q_3 to the third engine and so on.

Then by 1st law of thermodynamics,

$$W = Q_1 - Q_2 = Q_2 - Q_3 = Q_3 - Q_4 = \ldots\ldots$$

$$\text{or} \quad Q_1\left(1 - \frac{Q_2}{Q_1}\right) = Q_2\left(1 - \frac{Q_3}{Q_2}\right) = Q_3\left(1 - \frac{Q_4}{Q_3}\right) = \ldots\ldots$$

$$\text{or} \quad Q_1\left(1 - \frac{T_2}{T_1}\right) = Q_2\left(1 - \frac{T_3}{T_2}\right) = Q_3\left(1 - \frac{T_4}{T_3}\right) = \ldots\ldots$$

$$\text{or} \quad \frac{Q_1}{T_1}(T_1 - T_2) = \frac{Q_2}{T_2}(T_2 - T_3) = \frac{Q_3}{T_3}(T_3 - T_4) = \ldots\ldots$$

$$\text{As} \quad \frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_3}{T_3} = \frac{Q_4}{T_4} = \ldots\ldots$$

$$\therefore \quad T_1 - T_2 = T_2 - T_3 = T_3 - T_4 = \ldots\ldots$$

It shows that temp difference for each carnot engine is the same. If there are 100 carnot engines working between boiling point of water and melting point of ice, then

$$T_b - T_i = 100 \text{ degrees.}$$

where T_b = Boiling pt. of water

& T_i = Melting pt. of ice.

Kelvin scale was derived on the basis of laws of thermodynamics. So it is also called thermodynamic scale of temperature.

It can be shown that thermodynamic scale of temp. and perfect gas scale are identical as described below.

Consider a carnot engine working b/w the temps T_1 and T_2 on Kelvin scale. Let these temps. be θ_1 and θ_2 on perfect gas scale.

Then by Kelvin scale

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

Also by perfect gas scale

$$\frac{Q_1}{Q_2} = \frac{\theta_1}{\theta_2}$$

$$\therefore \quad \frac{T_1}{T_2} = \frac{Q_1}{Q_2}$$

$$\therefore \quad \frac{T_b}{T_i} = \frac{\theta_b}{\theta_i}.$$

$$\because \quad T_b - T_i = 100$$

$$\therefore \quad T_b = T_i + 100$$

Similarly $\theta_b = \theta_i + 100$

So the above relation becomes

$$\frac{T_i + 100}{T_i} = \frac{\theta_i + 100}{\theta_i}$$

$$\frac{T_i\left(1 + \frac{100}{T_i}\right)}{T_i} = \frac{\theta_i\left(1 + \frac{100}{\theta_i}\right)}{\theta_i}$$

$$1 + \frac{100}{T_i} = 1 + \frac{100}{\theta_i}$$

$$\frac{100}{T_i} = \frac{100}{\theta_i}$$

$$\frac{1}{T_i} = \frac{1}{\theta_i}$$

$$\text{or } T_i = \theta_i$$

Similarly $T_b = \theta_b$

or $\boxed{T = Q}$

It shows that temps of ice and steam are same on both the scales.

Hence the Kelvin scale and perfect gas scale are identical.

Absolute Zero and -ve Temperature:

We can't have a gas below 1K and so we can't measure below 1K using constt volume gas thermometer. But by thermodynamic scale we can measure temp below 1 K.

Consider a system at temp T_2 we want to measure. We take the system around a carnot cycle. First we do work on the gas adiabatically and temp. of gas increases to T_1 which is supposed to be known. Then heat $|Q_1|$ is transferred isothermally. Then doing work adiabatically to decrease the temp back to T_2. Then in the last $|Q_2|$ is rejected isothermally to bring the system to its initial state.

So by the relation $\dfrac{T_2}{T_1} = \dfrac{|Q_2|}{|Q_1|}$

$$T_2 = T_1 \frac{|Q_2|}{|Q_1|}$$

So knowing T_1 and measuring Q_1 & Q_2, we can measure T_2. Similarly we can take the system around another carnot cycle to a still lower temp. T_3. We can continue this process to the absolute zero of temp.

But the smaller the temp, small is heat transferred $|Q|$ in the isothermal process b/w two adiabatic processes.

Near absolute zero the system will undergo an isothermal process without transfer of heat.

It is found experimentally that lower the temp. the more difficult it is to go still lower. So we can state 3rd law of thermodynamics as follows;

> "It is impossible by any procedure, no matter how idealized, to reduce any system to the absolute zero of temp. in a finite number of operations."

Hence we can't have a sink at absolute zero or a heat engine with 100% efficiency is impossible.

Entropy in Reversible Process

As we know that for a carnot cycle

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

As Q_1 and Q_2 always have opposite signs so the above expression can be written as,

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \qquad (1)$$

This eq. (1) shows that the sum of algebraic quantity $\frac{Q}{T}$ is zero for a carnot cycle.

For a finite number of cycles eq. (1) becomes

$$\sum \frac{Q}{T} = 0 \qquad (2)$$

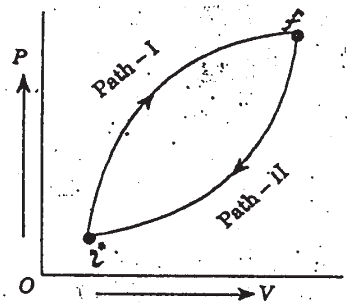
For infinite number of cycles the eq. (2) can be written as

$$\oint \frac{dQ}{T} = 0 \qquad (3)$$

The $\oint$ indicates that integral is calculated over a close path. The quantity dQ means a small quantity of heat which enters or leaves the system.

Equation (3) is called CLAUSIUS THEOREM

The Clausius theorem gives the definition of entropy function. Consider a reversible cycle represented by the closed curve shown in fig.



- Let i and f denote the initial and final states of a system.

Let the system from state i to f along path–I and back to i along path–II.

These two paths form a reversible cycle

By Clausius Theorem

$$\oint \frac{dQ}{T} = 0.$$

This integral can be written as the sum of two integrals as

$$\oint \frac{dQ}{T} = \int_i^f \frac{dQ}{T} + \int_f^i \frac{dQ}{T} = 0.$$

$$\text{or} \quad \int_i^f \frac{dQ}{T} = -\int_f^i \frac{dQ}{T}$$

$$\text{or} \quad \mathrm{I}\int^f dQ = \mathrm{II}\int^f dQ.$$

This shows that the integrals along two reversible paths are equal. It means that the integral $\int \frac{dQ}{T}$ is the same along the reversible paths from i to f.

In the language of mathematics, the integral $\frac{dQ}{T}$ is an exact differential of some function S.

$$\therefore \frac{dQ}{T} = dS$$

$$\therefore \int_i^f \frac{dQ}{T} = \int dS = S_f - S_i$$

The quantity 'S' is called entropy of the system. It should be noted that dQ is an inexact differential but $\frac{dQ}{T} = dS$ is exact differential. It means that behaviour of $\frac{1}{T}$ is to change inexact differential into an exact differential in mathematics.

Entropy change dS is independent of path and only depends on initial and final states.

Hence the change in entropy of a system is given by

$$\boxed{dS = \frac{dQ}{T}}$$

This is taken as the mathematical form of IInd law of thermodynamics. The S.I unit of entropy is J/K.

Sample Problem-5

Sample Problem 5 A lump of ice whose mass m is 235 g melts (reversibly) to water, the temperature remaining at 0°C throughout the process. What is the entropy change for the ice? The heat of fusion of ice is 333 kJ/kg.

Sol: mass of ice $= m = 235g = 0.235kg$

$T = 0°C = 273K$, $L_f = 333 \text{ KJ/kg} = 333000 \text{ J/kg}$.

The amount of heat absorbed by ice to change into water is

$dQ = mL_f$. $(dS)_{ice} = ?$

$$\text{As } dS = \frac{dQ}{T}$$

$$= \frac{mL_f}{T} = \frac{0.235 \times 333000}{273}$$

$$\boxed{dS = 2875 \text{ J/K}}$$

Entropy Function:

Entropy is a Greek term means change. It is a thermal property of a system which remains constt as long as no heat enters or leaves the system. It is a real physical quantity. The entropy of a system increases if heat flows into the system at constt temp. and decreases if leaves the system at constt temp. It is a function of state and so depends on the state of system. The absolute value of internal energy can't be determined however its change can be determined by the relation

$dS = \frac{dQ}{T}$ where dQ is the quantity of heat flowing into or out of the system at constt temp. It is a measure of disorder or randomness of molecular motion of the system. Addition of heat increases the entropy and rejection of heat decreases the entropy of the system. It is a function of thermodynamic co-ordinates. Its S.I unit is J/K.

Entropy in Irreversible Process

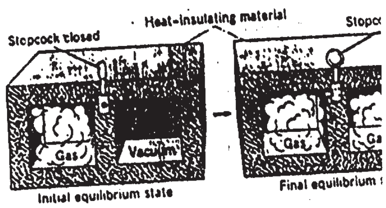
The equation $\oint \frac{dQ}{T} = dS$ gives the change in entropy in a reversible process. But in nature there is no reversible process due to friction and heat transfer. So every thermodynamic process is irreversible.

To find the entropy change for an irreversible path b/w two equilibrium states, find a reversible process connecting the same states and calculate the entropy change by the equation $dS = \int_i^f \frac{dQ}{T}$

Examples of Irreversible Process

1. Free Expansion:

Consider an ideal gas enclosed in an insulated container. When the ideal gas rushes into evacuated chamber, its temp and internal energy remains constt and heat enters or leaves the gas. no work is done against the vacuum.



$\therefore W = Q = 0$ and $\Delta E_{int} = 0$

The free expansion is an irreversible process. There is an entropy difference b/w initial and final states.
To find the entropy change we choose a reversible path from i to f.
Let us consider an isothermal expansion that takes the gas from initial state (P_i, V_i, T_i) to (P_f, V_f, T_f)

$$\therefore dS = \int_i^f \frac{dQ}{T} = \frac{1}{T}\int_i^f dQ = \frac{Q}{T}$$

$$\therefore dS = \frac{Q}{T} \qquad (1)$$

By first law $\Delta E = Q + W$

$$\because \Delta E = 0$$

$$\therefore Q = -W$$

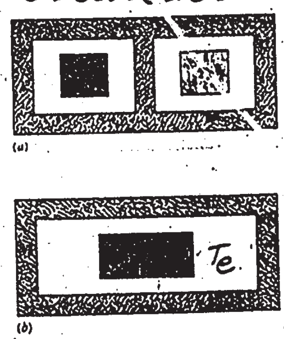
$\therefore$ Eq. (1) becomes $dS = \frac{-W}{T}$

$\because$ In isothermal expansion $W = -nRT \ln \frac{V_f}{V_i}$

$$\therefore \boxed{dS = nRT \ln \frac{V_f}{V_i}}$$

This is equal to the entropy change for irreversible free expansion.
It should be noted that dS is +ve for the system.
As there is no transfer of heat to the environment in the free expansion. So entropy change for environment is zero.
Thus the total entropy of system + environment increases during a free expansion.

2. Irreversible Heat Transfer



Consider two blocks at temps T_1 and T_2.
Both the blocks have same mass and specific heat.
We remove the insulating wall and bring the blocks into thermal contact. After some time they reach the common temp. T_e
Like free expansion, this is also irreversible process.
To find the entropy change in this irreversible process we choose a reversible path.

For this purpose consider block 1 at lower temp T_1 and imagine a series of thermal reservoirs at temps

$$T_1,\ T_1 + dT,\ T_1 + 2dT, \ldots\ldots, T_e - dT,\ T_e.$$

We first start with block 1 in contact with the 1st reservior and move it one step at a time along a sequence.
As each step a small amount of heat dQ enters the block. The process is clearly reversible because at any point we can move the block to the previous step and the same amount of heat will flow from the block to the reservior.

$$\text{Now } dQ = CmdT.$$

$\therefore$ Entropy change for block 1 is given by

$$\Delta S_1 = \int_i^f \frac{dQ}{T} = Cm \int_i^f \frac{dT}{T} = Cm \ln T \Big|_{T_i}^{T_e}$$

$$\Delta S_1 = Cm(\ln T_e - \ln T_1)$$

$$= Cm\left(\ln \frac{T_e}{T_1}\right)$$

$$\Delta S_1 = mc \ln \frac{T_e}{T_1} \qquad (1)$$

Similarly for block 2 b/w temp T_2 and T_e the entropy change is given by

$$\Delta S_2 = Cm \int_{T_2}^{T_e} \frac{dT}{T} = Cm \ln \frac{T_e}{T_2}$$

$$\Delta S_2 = mc \ln \frac{T_e}{T_2} \qquad (2)$$

$\therefore$ The total entropy change is

$$\Delta S = \Delta S_1 + \Delta S_2$$

$$= mc \ln \frac{T_e}{T_1} + mc \ln \frac{T_e}{T_2}$$

$$= mc \ln\left(\frac{T_e}{T_1} + \ln \frac{T_e}{T_2}\right)$$

$$= mc\left[\ln\left(\frac{T_e}{T_1} \times \frac{T_e}{T_2}\right)\right]$$

$$\Delta S = mc \ln \frac{T_e^2}{T_1 T_2} \qquad (3)$$

We can now show that the total entropy change ΔS is +ve.
For this purpose we have to prove that $\frac{T_e^2}{T_1 T_2} > 1$
We first find T_e by considering the total heat flow equal to zero.

$$\therefore Q_1 + Q_2 = 0.$$

$$\therefore Cm(T_e - T_1) + Cm(T_e - T_2) = 0 \qquad \because Q_1 = Cm(T_e - T_1), \; Q_2 = Cm(T_e - T_2)$$

$$2CmT_e - Cm(T_1 + T_2) = 0$$

$$2CmT_e = Cm(T_1 + T_2)$$

Hence $\dfrac{T_e^2}{T_1T_2} = \dfrac{\left(\frac{T_1+T_2}{2}\right)^2}{T_1T_2} = \dfrac{(T_1+T_2)^2}{4\,T_1T_2}$

$$\frac{T_e^2}{T_1T_2} = \frac{T_1^2+T_2^2+2T_1T_2}{4T_1T_2}$$

$$= \frac{T_1^2+T_2^2+4T_1T_2-2T_1T_2}{4T_1T_2}$$

$$= \frac{(T_1+T_2-2T_1T_2)+4T_1T_2}{4T_1T_2}$$

$$= \frac{(T_1-T_2)^2+4T_1T_2}{4T_1T_2}$$

$$= \frac{4T_1T_2}{4T_1T_2} + \frac{(T_1-T_2)^2}{4T_1T_2}$$

$$\boxed{\frac{T_e^2}{T_1T_2} = 1 + \frac{(T_1-T_2)^2}{4T_1T_2}}$$

Which shows that $\dfrac{T_e^2}{T_1T_2}$ is >1. So log of eq.(3) is greater than zero and so the entropy change is +ve placing the two blocks in thermal contact produces no change at all in the environment & so $\Delta S = 0$ for the environment.
So the total entropy of system + environment increases in this irreversible heat transfer.

Entropy and 2nd Law:

The 2nd law of thermodynamics can be stated in terms of entropy as follows

> "In any Thermodynamic process that proceeds from one equilibrium state to another, the entropy of the System + environment either remains unchanged or increases."

For reversible process the entropy does not change. For irreversible processes i.e for all natural processes the total entropy of system + environment must increase. It is possible that the entropy of system might decrease, but entropy of environment shows increase of greater magnitude, so that the total change in entropy is always +ve.

"No natural process can ever show a decrease in the total entropy of system + environment."

This is another statement of 2nd law of thermodynamics. Let us consider this statement of 2nd law for the following cases.

Free Compression:

The reverse process of free expansion is called free compression.

The change in entropy is given by

$$\Delta S = nR \ln \frac{V_f}{V_i}.$$

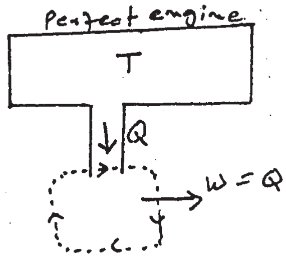
In free compression $V_f < V_i$, so $\ln \frac{V_f}{V_i}$ is -ve. So ΔS is -ve which means that entropy decreases. But this violates the 2nd law according to which entropy of system + environment is always +ve.

In free compression, there is no change in entropy of environment like free expansion.

So the 2nd law of in terms of entropy denies the process of free compression.

The Kelvin Plank Form of 2nd Law

Because all engines operate in cycles. So entropy change for the system in complete cycle is zero.



In a perfect engine the environment (source) releases heat Q at temp. T and its entropy change is $= -\frac{Q}{T}$, a -ve quantity.

The total entropy change of system + environment is therefore -ve in a perfect heat engine which violates the IInd law in terms of entropy.

So the IInd law denies the possibility of perfect engine.

So according to Kelvin

"Heat of a simple source can't be converted into work".

This is Kelvin Planck form of IInd law.

The Clausius Form of 2nd Law

In a perfect refrigerator there is no change entropy of the system in one complete cycle but the environment (cold body) releases heat (-Q) at temp T_L and absorbs heat Q at temp T_H.

$\therefore$ The total change entropy of the environment is

$$\Delta S = \frac{Q}{T_H} - \frac{Q}{T_L} = Q\left(\frac{1}{T_H} - \frac{1}{T_L}\right)$$

Because $T_H > T_L$.

So ΔS is -ve which violates the IInd law in terms of entropy. So IInd law denies the possibility of perfect refrigerator.

"So according to Clausius, perfect refrigerator is not possible"

This is called Clausius form of IInd law.

The Arrow of Time:

All the natural processes are taking place in such direction that the change in entropy of system + environment is always +ve. i.e if any process the entropy of system decreases then there is large increase in the entropy of environment s.t the total entropy change is +ve.

THE END