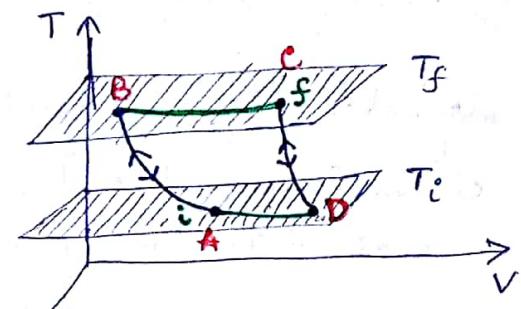
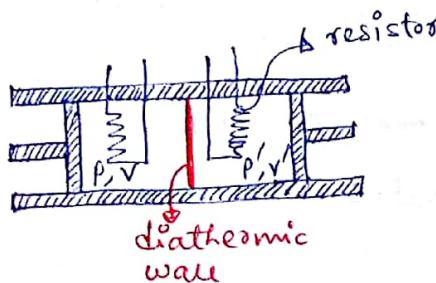


Using Curie's law $M = C \frac{H}{T}$

$$W = \mu_0 \int_{M_i}^{M_f} \frac{MT}{C} dM = \frac{\mu_0 T}{2C} (M_f^2 - M_i^2)$$

$$= \mu_0 \int_{H_i}^{H_f} H \frac{C}{T} dH = \frac{\mu_0 C}{2T} (H_f^2 - H_i^2)$$

Adiabatic Work



System can undergo adiabatic work with surroundings ① moving pistons quasistatically (slowly) $W = - \int P dV$

② non-quasistatic (free expansion) \Rightarrow fast so that velocity of molecules do no work at piston. Also work can be done by dissipating electrical energy on resistors

Path ABC from $i \rightarrow f$, AB is reversible quasistatic adiabatic compression between two isothermal planes. BC correspond to adiabatic irreversible dissipation of electrical energy to keep $T = \text{constant}$, as energy can be added to resistor but cannot be extracted.

There are many such other path (e.g. ADC), meaning adiabatic work is same along all paths.

1st law of Thermodynamics: If a system is changed from initial state to final state by adiabatic work, the work done is same for all adiabatic path connecting two states.

$$W_{i \rightarrow f} (\text{adiabatic}) = U_f - U_i = dU \quad (\text{perfect differential})$$

U = internal energy function

But if system change state nonadiabatically, then to conserve energy, Q heat is to be added to system (+ive)/subtracted (-ive)

from the system, $U_f - U_i = Q + W$.

for infinitesimal process, $dU = dQ + dW$ & if its quasi static
then dU & dW can be expressed in thermodynamic coordinates.

for hydrostatic system $dU = dQ - PdV$

wire $dU = dQ + \gamma dL$

surface film $dU = dQ + \sigma dA$

paramagnetic Rod $dU = dQ + \mu_0 H dM$

When $U = U(V, T)$, $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

$$\therefore dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV \quad \text{--- (1)}$$

$$\Rightarrow \frac{dQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \frac{dV}{dT}$$

(i) $V = \text{constant}$, $\left(\frac{dQ}{dT}\right)_V = \boxed{\left(\frac{\partial U}{\partial T}\right)_V} = C_V$

(ii) $P = \text{constant}$, $\left(\frac{dQ}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \left(\frac{\partial V}{\partial T}\right)_P$

$$\Rightarrow C_P = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] V \beta \quad \beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$$

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_P - C_V}{V \beta} - P}$$

Cyclic process $dU = 0$, $dQ = PdV$. heat = work.

Also, from equation (1) $dQ = C_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV$

for ideal gas, no potential energy, free expansion do not affect heat.

$PdV = 0$, $dQ = 0$ at constant temperature $dT = 0$, $\left(\frac{\partial U}{\partial V}\right)_T dV = 0$.

$\therefore \left(\frac{\partial U}{\partial V}\right)_T = 0 \Rightarrow$ internal energy is independent of volume.

$\therefore \boxed{dQ = C_V dT + PdV}$ for ideal gas.

Equation of state $PV = nRT \Rightarrow PdV + VdP = nRdT$ infinitesimal
quasi static process

$$\therefore dQ = (C_V + nR)dT - VdP$$

$$\Rightarrow \frac{dQ}{dT} = C_V + nR - V \frac{dP}{dT}, P \text{ constant}$$

$$\boxed{C_P = C_V + nR}$$

$$\text{Also } \delta S = C_p dT - V dP$$

Elasticity of perfect gas

Isothermal bulk modulus $E_T = -V \left(\frac{\partial P}{\partial V} \right)_T$

Adiabatic bulk modulus $E_g = -V \left(\frac{\partial P}{\partial V} \right)_g$.

For isothermal change $PV = RT = \text{constant}$

$$PdV + VdP = 0 \Rightarrow \left(\frac{\partial P}{\partial V} \right)_T = -\frac{P}{V}.$$

For adiabatic change $PV^\gamma = \text{constant}$, $\gamma PV^{\gamma-1} dV + dP V^\gamma = 0$

$$\therefore \left(\frac{\partial P}{\partial V} \right)_g = -\frac{\gamma P}{V}. \quad \therefore \boxed{\frac{E_g}{E_T} = \gamma.}$$

Second law of Thermodynamics

This is an extension of first law with a direction of the process \rightarrow experimental development of engines.

Reversibility & Irreversibility

reversibility = system + surroundings from changed state can restore back to initial configuration without change of universe.
The opposite to that is irreversible process.

2nd law \rightarrow Carnot's finding in ideal engine \rightarrow Clausius

statement \rightarrow Kelvin's statement \rightarrow birth of "entropy".

Conversion of work to heat

In previous examples, we saw how heat can be generated indefinitely at the expense of work. To study the converse process, there may be 1 or more than 1 (series of) processes.

At first it appeared that isothermal expansion may be suitable for conversion of heat into work, but it's not indefinite. Thus a cycle is required that can be taken back & forth.

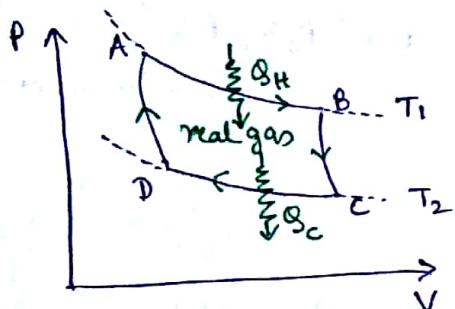
If in a cycle Q_H amount of heat is absorbed & Q_C ($Q_C < Q_H$) amount of heat is radiated & W amount of work is needed then the mechanical device is a "Heat Engine." Efficiency of such engine is defined as

$$\eta = \frac{\text{work output}}{\text{Heat input}} = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H}$$

Hot reservoir of infinite heat capacity is "source" & cold reservoir is called "sink."

Carnot cycle

It's maximum efficient engine (nearly ideal)



AB, CD = isothermal

BC, DA = adiabatic

Consists of four reversible steps.

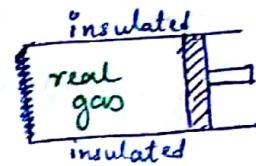
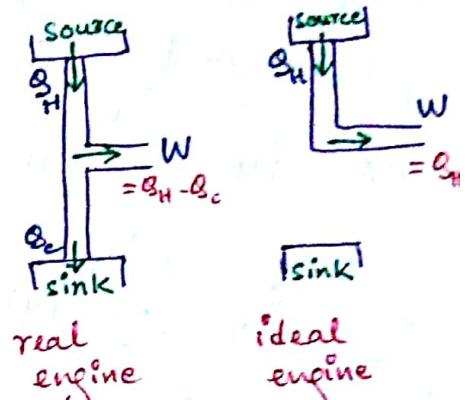
(1) Isothermal expansion A → B :

Cylinder is placed in contact with a heat reservoir at temperature T_1 & gas expands isothermally from (P_1, V_1, T_1) to (P_2, V_2, T_1) . Q_H amount of heat taken from source & W_1 amount of work done "by" the gas.

(2) Adiabatic expansion B → C : The gas is allowed to expand adiabatically in insulated environment. The temperature falls to T_2 & volume changes to V_3 . $Q=0$ and work done "by" the gas is W_2 .

(3) Isothermal compression C → D : The gas at very low pressure is now reversibly compressed in sink at temperature T_2 from volume V_3 to V_4 . Heat rejected to sink is Q_C & work done by the gas is $-W_3$ (-ive because work done "on" gas).

(4) Adiabatic compression D → A : Now the system is adiabatically restored to initial state from $V_4 \rightarrow V_1$, $T_2 \rightarrow T_1$. $Q=0$, work done



real engine

ideal engine

A → B :

B → C :

C → D :

D → A :

Work done by the gas

Work done on the gas

Heat added to the gas

Heat rejected by the gas

Temperature of source

Temperature of sink

Initial pressure

Initial volume

Final pressure

Final volume

Work done

Efficiency

Heat rejected

Heat added

Temperature of cylinder

Volume of cylinder

by the gas is $-W_4$ (-ive because workdone "on" the gas).

from first law of thermodynamics $\oint_C dU = 0$

$$\Rightarrow \oint_C dQ - \oint_C dW = 0 \Rightarrow Q_H + 0 - Q_C + 0 = W_1 + W_2 - W_3 - W_4$$

\therefore Work done by engine = difference of heat absorbed & rejected.

$$\text{Now } Q_H = \int_{V_1}^{V_2} pdV = RT_1 \ln \frac{V_2}{V_1} = W_1.$$

$$Q_C = - \int_{V_3}^{V_4} pdV = RT_2 \ln \frac{V_3}{V_1} = W_3$$

But for isothermal processes $P_1 V_1 = P_2 V_2, P_3 V_3 = P_4 V_4$

for adiabatic processes $P_2 V_2^\gamma = P_3 V_3^\gamma, P_4 V_4^\gamma = P_1 V_1^\gamma$

Multiplying, $P_1 V_1 P_2 V_2^\gamma P_3 V_3^\gamma P_4 V_4^\gamma = P_2 V_2 P_3 V_3^\gamma P_4 V_4 P_1 V_1^\gamma$ (independent events)

$$\text{or } (V_2 V_4)^\gamma-1 = (V_3 V_1)^\gamma-1$$

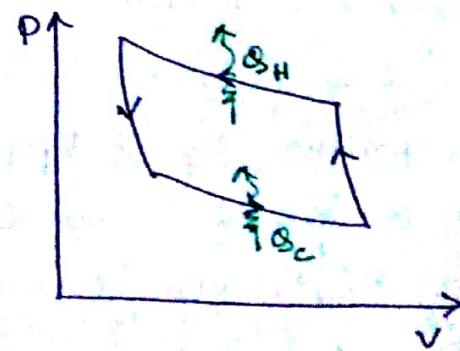
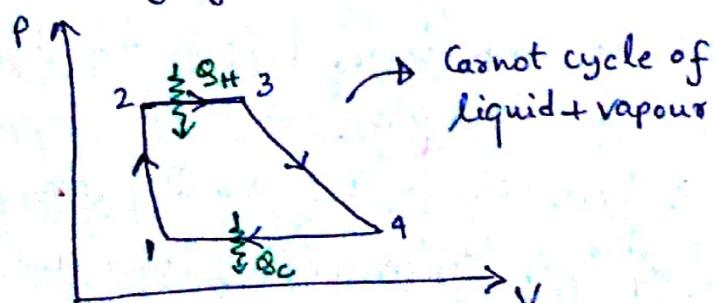
$$\text{or } V_2/V_1 = V_3/V_4$$

$$\therefore \text{Efficiency } \eta = \frac{Q_H - Q_C}{Q_H} = \frac{R(T_1 - T_2) \ln(V_2/V_1)}{RT_1 \ln(V_2/V_1)} \\ = \frac{T_1 - T_2}{T_1} \neq 100\%$$

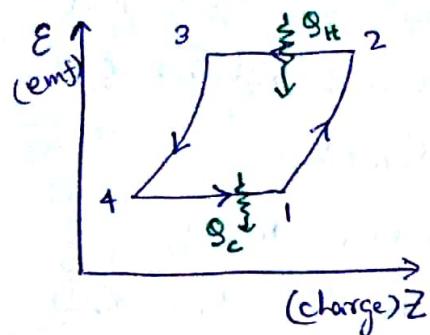
$$\therefore \boxed{\frac{Q_H}{T_1} = \frac{Q_C}{T_2}}$$

We can also reverse the cycle from any point of the indicator diagram.

In that case Q_C heat is removed from sink & Q_H is delivered to source & work must be done to the system. The system is then works as a refrigerator.



- $1 \rightarrow 2$ reversible adiabatic compression to temperature T_H
 $2 \rightarrow 3$ reversible isothermal isobaric vaporization
 $3 \rightarrow 4$ reversible adiabatic expansion temperature falls to T_C
 $4 \rightarrow 1$ reversible isothermal isobaric condensation



- $1 \rightarrow 2$ reversible adiabatic flow of charge from - to + to temperature T_H .
 $2 \rightarrow 3$ reversible isothermal flow of charge from + to -
 $3 \rightarrow 4$ reversible adiabatic flow of charge to temp. T_C
 $4 \rightarrow 1$ reversible isothermal flow of charge

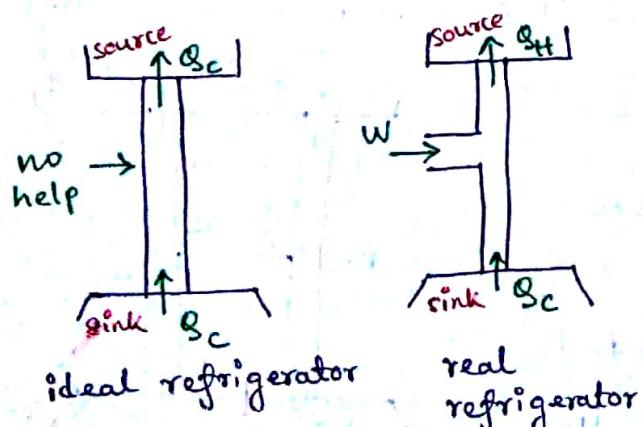
Second law of Thermodynamics

Kelvin's Statement It is impossible by any inanimate object to derive mechanical work from any portion of the matter by cooling it below the temperature of the coldest of the surrounding objects.

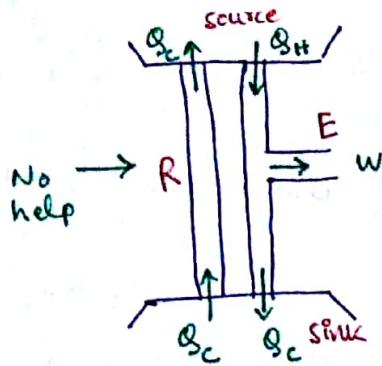
Plank's Statement It is impossible to fabricate an engine working in a complete cycle to produce no effect other than raising a weight & cooling of a hot reservoir.

P-K Statement \rightarrow It is impossible to produce an ideal engine.

Clausius Statement It is impossible for a self-acting machine unaided by any external agency to convey heat from one body at lower temperature to another at a higher temperature. Heat cannot by itself transit from a colder to a warmer body or it is impossible to construct an ideal refrigerator.



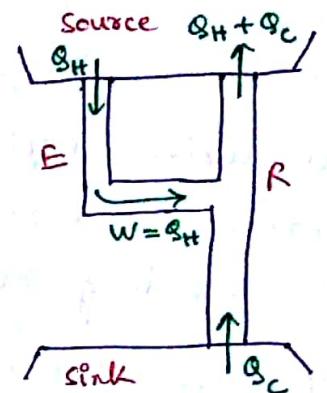
Equivalence of Kelvin-Plank & Clausius statement



Suppose we disobey Clausius's statement & make an ideal refrigerator R that transfers Q_C from sink to source without any work. But engine E draws Q_H from source & returns Q_C to sink & delivering work $Q_H - Q_C$.

∴ Combined R-E system form a self-acting device drawing $Q_H - Q_C$ heat from hot reservoir & convert fully this heat into work without change in sink → violation of K-P statement.

Consider again an ideal engine E that rejects no heat to sink & violate K-P statement. Q_H heat is fully converted to work W which is feeded to a refrigerator R to extract Q_C heat from sink. Again E-R forms a self-acting device that transfers Q_C from sink to source without any change elsewhere → violation of Clausius statement.



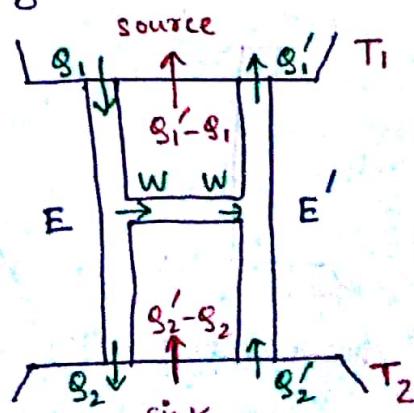
1st law of Thermodynamics = conservation of energy

2nd law of Thermodynamics = directionality (may not be true always)

Carnot's theorem

Efficiency of all reversible engines operating between same two temperatures is equal & no irreversible engine can have a better efficiency compared to the reversible engine between same two temperatures.

Clausius & Kelvin showed that this theorem is a consequence of the 2nd law of thermodynamics. η is independent of working substance & depends only on T_1, T_2 .



Proof: Suppose engine E & E' working between T_1 & T_2 differ in working substance or initial pressure or length of stroke. E runs forward & E' run backward (refrigerator). The system is so made that work done by E is exact amount of work needed for E' to function. Suppose η (efficiency) of E $>$ η' of E'.

$\therefore \frac{Q_1 - Q_2}{Q_1} > \frac{Q'_1 - Q'_2}{Q'_1}$. By construction work done per cycle be $W = W'$ $\Rightarrow Q_1 - Q_2 = Q'_1 - Q'_2$

$$\therefore W = W' \Rightarrow Q_1 - Q_2 = Q'_1 - Q'_2$$

$$\therefore \frac{1}{Q_1} > \frac{1}{Q'_1} \quad \text{as } Q'_1 > Q_1 \quad \text{and } Q'_2 > Q_2 \text{ to satisfy } W = W'$$

Therefore hot source gains heat $Q'_1 - Q_1$ and cold sink loses heat $Q'_2 - Q_2$ and no work is done by the combined E + E' system. We've transferred heat from a cold to hot body without performing work is direct contradiction to Clausius statement.

$$\therefore \eta \neq \eta'$$

Similarly, by reversing the engine E backward & E' forward we can prove that $\eta' \neq \eta$. So the only possibility is

$$\boxed{\eta = \eta'}$$

For irreversible engine we can show by the same procedure that $\eta_{irr} \neq \eta_{rev}$ but due to irreversibility we cannot show $\eta_{rev} \neq \eta_{irr}$
 $\therefore \eta_{irr}$ is either equal to or less than η_{rev} .

$$\therefore \boxed{\eta_{rev} \geq \eta_{irr}}$$

Kelvin scale / Absolute scale / Thermodynamic scale of temperature

Using Carnot engine, temperature can be defined in term of energy & the scale so obtained is independent of nature of any particular substance. Efficiency of all reversible engine is a function of two temperatures only

$$\eta = \frac{W}{Q_1} = f(T_1, T_2) = \frac{Q_1 - Q_2}{Q_1} \Rightarrow \frac{Q_1}{Q_2} = \frac{1}{1-f(T_1, T_2)} = F(T_1, T_2).$$

Suppose we have three reversible engines working between the temperature (T_1, T_2) , (T_2, T_3) & (T_1, T_3) , then

$$\frac{Q_1}{Q_2} = F(T_1, T_2), \quad \frac{Q_2}{Q_3} = F(T_2, T_3)$$

$$\therefore \frac{Q_1}{Q_3} = F(T_1, T_2) F(T_2, T_3) = F(T_1, T_3).$$

This can satisfy if & only $F(T_1, T_3) = \frac{\psi(T_1)}{\psi(T_3)}$

∴ For any reversible engine we can write $\frac{Q_1}{Q_2} = \frac{\psi(T_1)}{\psi(T_2)}$

Now if $T_1 > T_2$, $Q_1 > Q_2$ and therefore $\psi(T_1) > \psi(T_2)$

∴ $\psi(T)$ is a monotonically increasing function of temperature

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

So we have defined a new scale of temperature whose ratio depends on heat absorbed & heat rejected in a reversible engine.

$T=0^\circ$ in this scale is when $Q_2=0$ & ∴ $W=Q_1$ & $\eta=100\%$ (ideal engine). T cannot be less than this as $Q_2 < 0$ means engine would be drawing heat both from source & sink which is impossible due to direct violation of 2nd law. ∴ $T=0$ is the lowest attainable temperature when one gets an ideal engine.

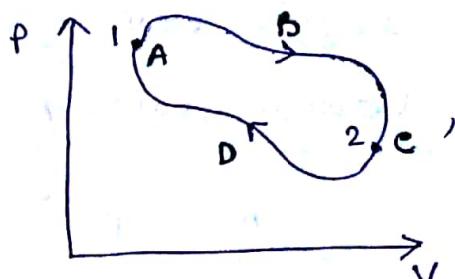
Entropy In any reversible process, if heat Q is added at temperature T and rejects Q' heat at temperature T' , then $\frac{Q}{T} = \frac{Q'}{T'}$.

$$\therefore \frac{Q}{T} - \frac{Q'}{T'} = 0 \quad \text{or} \quad \sum \frac{Q}{T} = 0 \quad (Q = +\text{ive heat absorbed} \\ = -\text{ive heat rejected})$$

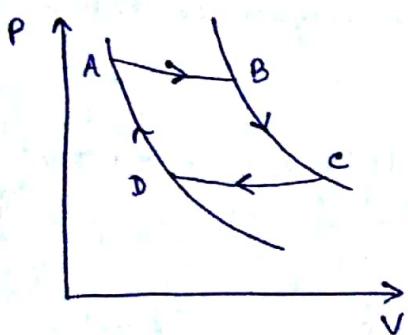
Any reversible transformation is made of a number of infinitesimal reversible isothermal & adiabatic processes. \therefore for any reversible cyclic process ABCD $\oint_C \frac{dQ}{T} = 0$. This is called "Clausius Theorem".

We can define a thermodynamic function "entropy" $dS = \frac{dQ}{T}$ that has the property

$$\oint_{ABCD} \frac{dQ}{T} = 0 \quad \therefore \oint_{ABC} \frac{dQ}{T} + \oint_{CDA} \frac{dQ}{T} = 0$$



$\therefore \oint_{ABC} \frac{dQ}{T} = \oint_{ADC} \frac{dQ}{T}$. This means that $\int \frac{dQ}{T}$ is independent of the path and depends only on the initial & final point 1 & 2.
 $\therefore dS = \frac{dQ}{T}$ is an exact differential. Unit cal/K.



To understand property of dS , consider a reversible cycle constituted by two adiabatic AD & BC & two isothermals AB & CD.

For AD & BC, $dQ = 0 \therefore dS = 0$. & hence

$$\int_A^B \frac{dQ}{T} = \int_D^C \frac{dQ}{T}.$$

Point A & B may be taken anywhere on the adiabatic AD & BC, still the integral will remain same as $dQ = 0$ for adiabatic process. Hence it follows that if we pass from one adiabatic to other, $\int^2 \frac{dQ}{T}$ increases by a definite amount independent of the manner of transformation. We can choose any standard state n & then $\int_n^A \frac{dQ}{T}$ on a reversible path depends only on state n & A. If my standard reference state n is fixed, integral is a function of state A only.

and termed as S_A & can be different if we choose different n .

Thus the entropy is undetermined to the extent of an additive constant that represents entropy of an arbitrarily chosen standard state with respect to state with zero entropy.

$\therefore S_A = S_n + \int_n^A \frac{ds}{T}$. S_n = entropy at state n which according to law of thermodynamics S_n cannot be determined & absolute value of entropy cannot be found out. But change of entropy between states A & B can be accurately determined,

$$S_A - S_B = S_n + \int_n^A \frac{ds}{T} - S_n - \int_n^B \frac{ds}{T} = \int_B^A \frac{ds}{T}$$

This is valid for equilibrium states only & for nonequilibrium states can approach equilibrium by irreversible process in which entropy increases.

Also $ds = dU + PdV$ is an inexact differential as $\int (dU + PdV)$ requires a knowledge of path. But $ds = \frac{ds}{T}$ is perfect or exact differential.

Exact differential (ds)	= Inexact differential (ds)	\times Integrating factor (YT)
--------------------------------	------------------------------------	---

Example $df = 3xydx + 2x^2dy$ = inexact $\frac{\partial^2 f}{\partial x \partial y} \neq \frac{\partial^2 f}{\partial y \partial x}$

But $\boxed{xy} df = d\phi = 3x^2y^2dx + 2x^3ydy = d(x^3y^2) =$ exact.

I.F.

Caratheodory's Principle In the immediate neighbourhood of any arbitrary initial state, there exists neighbouring states which are not accessible from the initial state along adiabatic paths.

Entropy of an ideal gas

If an ideal gas of $m \text{ gm}$ at temperature T & volume V is given heat δQ , then change in entropy is $ms = \int \frac{dU + PdV}{T}$

$$\text{Now } dU = mC_V dT, \quad P = \frac{mRT}{MV}$$

$$\therefore ms = m \left\{ C_V \int_{T_1}^{T_2} \frac{dT}{T} + \frac{R}{M} \int_{V_1}^{V_2} \frac{dV}{V} \right\} \text{ for } (P_1, V_1, T_1) \rightarrow (P_2, V_2, T_2)$$

In general for monoatomic gas $C_V \neq C_V(T)$ & so

$$ms = m \left\{ C_V \ln T + \beta_M \ln V \right\} + \text{constant} \quad \therefore S = S(T, V).$$

To obtain $S = S(T, P)$, we use $C_P - C_V = \beta_M$.

$$\therefore ms = m(C_P - \beta_M) \ln T + \frac{mR}{M} \ln V + \text{constant}$$

$$= mC_P \ln T - \frac{mR}{M} \ln (T_V) + \text{constant} \quad [PV = \frac{mRT}{M}]$$

$$= mC_P \ln T - \frac{mP}{M} \ln (\frac{PM}{mR}) + \text{constant} \quad T_V = \frac{PM}{mR}$$

$$ms = mC_P \ln T - \frac{mP}{M} \ln P + \text{constant}.$$

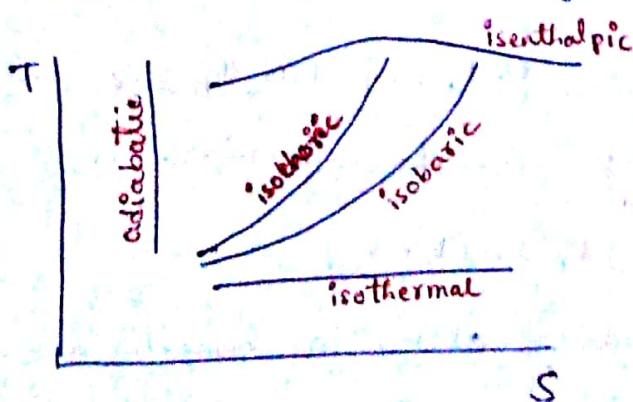
Isothermal system for isothermal change of state of gas $dU = 0$

$$\therefore ds = \frac{pdv}{T} \text{ and using } PV = NRT$$

$$= \frac{N R dv}{V} \quad \therefore S = N R \ln \left(\frac{V_2}{V_1} \right)$$

Adiabatic system for adiabatic change $\delta Q = 0$ & so $ds = 0$. No change in entropy of the system (isentropic process).

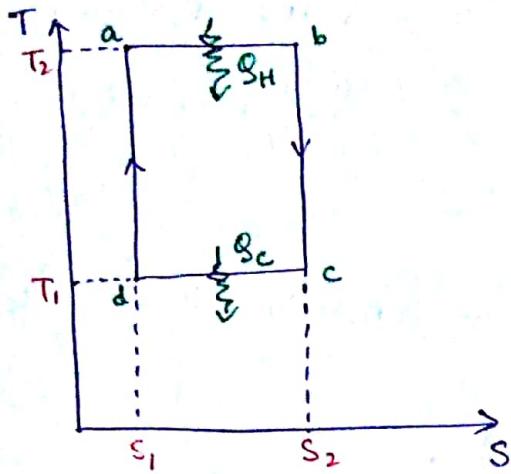
In free expansion of a perfect gas into an empty vessel in a thermally insulated environment, gain in entropy is $\Delta S = \int \frac{pdv}{T} = R \ln \frac{V_2}{V_1}$.



$$\text{In a reversible procen } Q_R = \int_i^f T ds$$

So the heat is the area under a curve in $T-S$ plane.

Carnot's cycle in TS diagram



The Carnot cycle in TS diagram is a parallelogram.

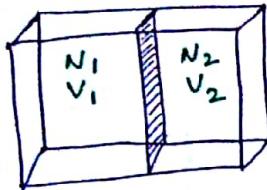
$$Q_H = T_2 (S_2 - S_1)$$

$$Q_C = T_1 (S_2 - S_1) \text{ and } dS = 0 \text{ for bc and da lines.}$$

$$\therefore \text{Efficiency } \eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H}$$

$$= \frac{(S_2 - S_1)(T_2 - T_1)}{T_2 (S_2 - S_1)} = 1 - \frac{T_1}{T_2}$$

Gibbs' Paradox



Consider an ideal gas of N particles in a container with volume V . A partition divides N_1 & N_2 particles & volume V_1 & V_2 such that

$$N = N_1 + N_2, \quad V = V_1 + V_2 \quad \text{and} \quad n = \frac{N_1}{V_1} = \frac{N_2}{V_2} \quad (\text{equal number density})$$

$$\begin{aligned} \text{Using } S &= C_V \ln T + R \ln V + \text{constant} \\ &= \frac{3}{2} R \ln T + R \ln V + \text{constant} \\ &= \frac{3}{2} N_1 k_B \ln T + N_1 k_B \ln V + \text{constant} \end{aligned}$$

firstly, $T \rightarrow 0, S \rightarrow -\infty !!$ violating 2nd law of thermodynamics

Secondly, $S \propto N$ for a given $V !!$ This expression from classical framework is not right. This also leads to gives paradox \Rightarrow

$$\text{In the partitioned state } S_1 = \frac{3}{2} N_1 k_B \ln T + N_1 k_B \ln V_1 + \text{cont.}$$

$$S_2 = \frac{3}{2} N_2 k_B \ln T + N_2 k_B \ln V_2 + \text{cont.}$$

The partition is now removed & gas comes to well-mixed state.

$$S = \frac{3}{2} (N_1 + N_2) k_B \ln T + (N_1 + N_2) k_B \ln (V_1 + V_2)$$

Now its monoatomic gas of identical atoms, so removing the partition shouldn't increase entropy as particles are indistinguishable.

$\Delta S = S - (S_1 + S_2) = 0$ But here we find

$$\begin{aligned}\Delta S &= (N_1 + N_2) k_B \ln(V_1 + V_2) + \frac{3}{2} (N_1 + N_2) k_B \ln T - \\&\quad N_1 k_B \ln V_1 - \frac{3}{2} N_1 k_B \ln T - N_2 k_B \ln V_2 - \frac{3}{2} N_2 k_B \ln T \\&= N_1 k_B [\ln(V_1 + V_2) - \ln V_1] + N_2 k_B [\ln(V_1 + V_2) - \ln V_2] \\&= N_1 k_B \ln \frac{V_1 + V_2}{V_1} + N_2 k_B \ln \frac{V_1 + V_2}{V_2} \neq 0.\end{aligned}$$

This paradox cannot be resolved in classical MB statistics & need statistical physics, namely quantum stat mech where atoms are indistinguishable (leads to Sackur-Tetrode formula of entropy in ideal gas) taking Stirling's approximation ($\ln N! = N \ln N - N$). Now, if we correct S accordingly,

$$S = N k_B \ln \left(\frac{V}{N} \right) + \frac{3}{2} N k_B \ln T + \text{constant}$$

$$\begin{aligned}\text{Then } S - (S_1 + S_2) &= (N_1 + N_2) k_B \ln \left(\frac{V_1 + V_2}{N_1 + N_2} \right) - N_1 k_B \ln \frac{V_1}{N_1} - N_2 k_B \ln \frac{V_2}{N_2} \\&= N_1 k_B \ln \frac{V}{N} - N_1 k_B \ln \frac{V_1}{N_1} + N_2 k_B \ln \frac{V}{N} - N_2 k_B \ln \frac{V_2}{N_2} \\&= N_1 k_B \ln \left(\frac{N N_1}{N V_1} \right) + N_2 k_B \ln \left(\frac{N N_2}{N V_2} \right)\end{aligned}$$

$$\text{But } n = \frac{N}{V} = \frac{N_1}{V_1} = \frac{N_2}{V_2} \quad (\text{no. density is constant})$$

$$\therefore \ln \left(\frac{N N_1}{N V_1} \right) = \ln \left(\frac{n}{n} \right) = \ln(1) = 0$$

$$\ln \left(\frac{N N_2}{N V_2} \right) = 0. \quad \therefore \underline{\Delta S = 0}$$

Gibb's paradox thus gets resolved.

Entropy increase in Irreversible process

Consider an irreversible process in which temperature of a body at T_1 is increased to T_2 by coupling to a reservoir at T_2 . The initial & final state of the body is same & its irreversible as heat flow from reservoir to body cannot be reversed. But change in entropy of the body is same for both reversible or irreversible process as its not path dependent.

Suppose pressure remains constant, then change in entropy of the body

$$\therefore \Delta S_{\text{body}} = \int_{T_1}^{T_2} C_p \frac{dT}{T} = C_p \ln\left(\frac{T_2}{T_1}\right) > 0 \text{ as } T_2 > T_1.$$

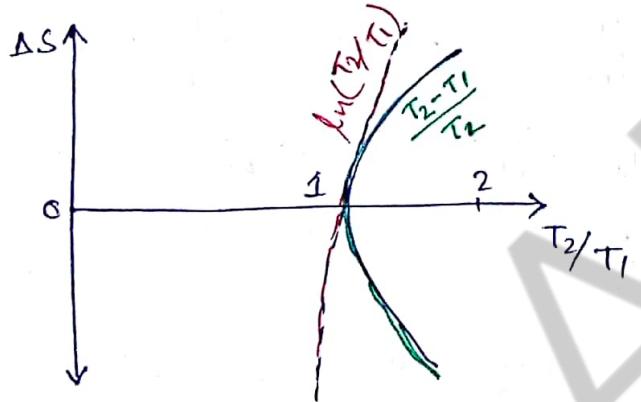
The reservoir temperature T_2 remains constant, so change in entropy is same for reversible isothermal process (heat flowing into reservoir) & irreversible isothermal process (heat only flowing out)

Heat flow into the body $\therefore \delta Q = C_p(T_2 - T_1)$ & this is the heat came out from reservoir, so decrease in entropy of reservoir

$$\therefore \Delta S_{\text{reservoir}} = -\frac{\delta Q}{T_2} = -\frac{C_p(T_2 - T_1)}{T_2}$$

Total change of entropy of the composite system

$$\Delta S = \Delta S_{\text{body}} + \Delta S_{\text{reservoir}} = C_p \left[\ln\left(\frac{T_2}{T_1}\right) - \frac{T_2 - T_1}{T_2} \right]$$



$$\text{for } T_2 > T_1, \ln\left(\frac{T_2}{T_1}\right) > \frac{T_2 - T_1}{T_2}$$

\therefore Increase in entropy of the body is always greater than decrease of entropy of reservoir & \therefore entropy of universe always increases in irreversible process.

Even when the body is at higher temperature than reservoir the situation is reversed but entropy of universe increases. So whenever heat flows across finite temperature difference (~~reversible~~ ~~irreversible~~), entropy of universe increases. For reversible process entropy remains constant.

$$S_f = S_i \text{ for reversible}$$

$$S_f > S_i \text{ for irreversible}$$

This principle of increase in entropy can be termed as 2nd law of thermodynamics. Clausius restated that 1st law is energy of the universe remains constant & 2nd law is entropy of universe tends to be the maximum.

Entropy flow & entropy production

Consider heat conduction along a copper wire that are held between two reservoirs at T_1 & T_2 ($T_1 > T_2$). If heat current or rate of flow of heat is I_Q then in unit time, hot source decreases its entropy by I_Q/T_1 , sink increases entropy by I_Q/T_2 & copper wire at steady state suffers no change in entropy. So $\Delta S_{\text{universe}} = \frac{I_Q}{T_2} - \frac{I_Q}{T_1} > 0$.

We can see it from the perspective of wire that the hot source lost entropy to the wire & there is a flow of entropy into the wire of I_Q/T_1 per unit time. The sink gained entropy so there was a flow of entropy out of the wire. I_Q/T_2 .

$$\text{Entropy production in wire } \frac{dS}{dt} = \frac{I_Q}{T_2} - \frac{I_Q}{T_1} = I_Q \frac{T_1 - T_2}{T_1 T_2}$$

if $T_1 = T + \Delta T$, $T_2 = T$, $T_1 T_2 \approx T^2$

$$\therefore \frac{dS}{dt} = I_Q \frac{\Delta T}{T^2} = I_Q \frac{\Delta T}{T} = I_S \frac{\Delta T}{T}$$

↓
entropy
production

- Ques. 1. A reversible engine in Carnot cycle between 100°C & 0°C does work $1200 \text{ kg-centre}/\text{cycle}$. Find the amount of heat drawn from source. $J = 4.18 \times 10^7 \text{ ergs/cal}$.

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_1 - Q_2}{T_1 - T_2} = \frac{W}{T_1 - T_2} \quad W = mgh$$

$$\therefore Q_1 = \frac{WT_1}{T_1 - T_2} = \frac{1200 \times 10^3 \text{ m} \times 980 \times 373}{100 \times 4.18 \times 10^7} = 10494 \text{ cal.}$$

2. A body of constant heat capacity C_p at temperature T_i is put in contact with reservoir at T_f . At constant pressure, body comes to equilibrium. Show that entropy change of universe is $C_p[x - \ln(1+x)]$ where $x = -\frac{T_f - T_i}{T_f}$.

$$\text{Gain in entropy of the body } \Delta S_{\text{body}} = \int_{T_i}^{T_f} \frac{C_p dT}{T} = C_p \ln\left(\frac{T_f}{T_i}\right)$$

$$\text{Loss of entropy of reservoir } \Delta S_{\text{reservoir}} = -\frac{\delta Q}{T_f} = -\frac{C_p(T_f - T_i)}{T_f}$$

$$\therefore \text{Total change in entropy of the universe } \Delta S = C_p \ln \frac{T_f}{T_i} - C_p \frac{T_f - T_i}{T_f}$$

$$= (C_p \ln(1+x) + C_p x) = C_p(x - \ln(1+x))$$

3. According to Debye's law, the molar heat capacity at constant volume of Diamond varies with temperature as

$C_V = 3R \frac{4\pi^4}{5} \left(\frac{T}{H}\right)^3$. What is the entropy change in units of R of a diamond of 1.2 gm when it's heated at constant volume from 10 to 350K. Atomic weight of carbon is 12 gm & $H = 2230 \text{ K}$.

$$\Delta S = \frac{1.2}{12} \int_{10}^{350} \frac{C_V dT}{T} = \frac{1.2}{12} 3R \frac{4\pi^4}{5} \frac{1}{H^3} \int_{10}^{350} T^2 dT$$

$$= 0.03 R.$$

4. m gms of water at T_1 is isobarically & adiabatically mixed with an equal mass of water at T_2 , so that they attain a common final temperature T_c . Show that entropy change of the universe is $2mC_V \ln \frac{(T_1+T_2)}{\sqrt{T_1 T_2}}$. What would be the loss of available energy?

T_c will attend when $mC_V(T_1 - T_c) = mC_V(T_c - T_2)$

$$\text{or } T_c = \frac{T_1 + T_2}{2}. \quad \Delta S_1 = mC_V \int_{T_1}^{T_c} \frac{dT}{T} = mC_V \ln \frac{T_c}{T_1}$$

$$\Delta S_2 = mC_V \int_{T_2}^{T_c} \frac{dT}{T} = mC_V \ln \frac{T_c}{T_2}$$

$$\Delta S_{\text{universe}} = \Delta S_1 + \Delta S_2 = mC_V \ln \frac{T_c^2}{T_1 T_2} = mC_V \ln \left(\frac{T_c}{\sqrt{T_1 T_2}}\right)^2$$

$$= 2mC_V \ln \frac{T_1 + T_2}{2\sqrt{T_1 T_2}}$$

If T_0 is the lowest attainable temperature, then unavailable amount of energy is $S_{\text{unattain}} = T_0 \Delta S_{\text{universe}} = 2mC_V T_0 \ln \frac{T_1 + T_2}{2\sqrt{T_1 T_2}}$.

- HW
- The equation of state of a new matter is $pV = AT^3$, $A = \text{constant}$. Internal energy of this matter is $U = BT^n \ln(V/V_0) + f(T)$. Using first law of thermodynamics, find B and n .
 - Suppose an engine works between two reservoirs at T_1 & T_2 ($T_2 > T_1$) until both reservoirs attain final temperature T_c . Show that $T_c > \sqrt{T_1 T_2}$. What is the maximum amount of work obtainable from this engine?

Entropy & Unavailable energy

Suppose that Q amount of heat is extracted from a reservoir at temperature T_1 & it is desired to convert this heat into work as much as possible. If T_0 is the temperature of sink, then using a reversible engine, $W_{\max}^r = Q(1 - \frac{T_0}{T_1})$.

Consider an irreversible conduction of heat Q along a metal bar under finite temperature gradient from a region at temperature T_1 to a region at temperature T_2 . After conduction has taken place, Q amount of heat is available at lower temperature T_2 or the maximum amount of available work is $W_{\max}^{irr} = Q(1 - \frac{T_0}{T_2})$. As $T_1 > T_2$, so maximum work obtained in W_{\max}^{irr} is less than W_{\max}^r .

\therefore The amount of energy that is unavailable for work is,

$$E = Q(1 - \frac{T_0}{T_1}) - Q(1 - \frac{T_0}{T_2}) = T_0 Q (\frac{1}{T_2} - \frac{1}{T_1}) = T_0 \Delta S$$

where ΔS is the entropy change of the universe due to the irreversible process. Since irreversible process is continually happening in nature, so energy is continually becoming unavailable for work. This is known as "Principle of degradation of energy".

Thus according to this principle, we are always losing available energy & then a day will come when we will have no available energy for work. This is called "heat death" of the universe.

Disorder & entropy

Whenever work is dissipated within the system because of friction, viscosity, inelasticity, electric resistance or magnetoo hysteresis, the molecules are more disordered. We learned that irreversible process is associated with an increase in entropy of the universe. Thus, entropy must be related with the disorder.

Disorder of a system depends on the number of microstates accessible to the system. This is called "Thermodynamic probability" (Ω) & we can write $S = f(\Omega)$. To obtain the functional form, consider two systems having thermodynamic probability Ω_1 and Ω_2 with entropies $S_1 = f(\Omega_1)$ and $S_2 = f(\Omega_2)$ respectively.

If these systems are mixed then the total entropy is $S = S_1 + S_2$ and the total number of microstates of the system will be

$$\Omega = \Omega_1 \Omega_2 \quad \therefore S_1 + S_2 = f(\Omega_1 \Omega_2)$$

$$\therefore f(\Omega_1) + f(\Omega_2) = f(\Omega_1 \Omega_2)$$

$$\begin{aligned} \therefore \frac{\partial f(\Omega_1)}{\partial \Omega_1} + 0 &= \frac{\partial f(\Omega_1 \Omega_2)}{\partial \Omega_1} = \frac{\partial f(\Omega_1 \Omega_2)}{\partial (\Omega_1 \Omega_2)} \frac{\partial (\Omega_1 \Omega_2)}{\partial \Omega_1} \\ &= \Omega_2 \frac{\partial f(\Omega_1 \Omega_2)}{\partial (\Omega_1 \Omega_2)} \end{aligned}$$

$$\text{Multiplying with } \Omega_1, \quad \Omega_1 \frac{\partial f(\Omega_1)}{\partial \Omega_1} = \Omega_1 \Omega_2 \frac{\partial f(\Omega_1 \Omega_2)}{\partial (\Omega_1 \Omega_2)}$$

$$\text{Similarly, } 0 + \frac{\partial f(\Omega_2)}{\partial \Omega_2} = \frac{\partial f(\Omega_1 \Omega_2)}{\partial \Omega_2} \Rightarrow \Omega_2 \frac{\partial f(\Omega_2)}{\partial \Omega_2} = \Omega_1 \Omega_2 \frac{\partial f(\Omega_1 \Omega_2)}{\partial (\Omega_1 \Omega_2)}$$

$$\therefore \Omega_1 \frac{df(\Omega_1)}{d\Omega_1} = \Omega_2 \frac{df(\Omega_2)}{d\Omega_2} \quad \therefore \Omega \frac{df(\Omega)}{d\Omega} = \text{constant (K say)}$$

$$\therefore df(\Omega) = K \frac{d\Omega}{\Omega} \quad \therefore f(\Omega) = K \ln \Omega + C$$

But if $\Omega = 1$, $f(\Omega) = 0$ as the system is in perfect ordered state.

$$\therefore C = 0. \quad S = K \ln \Omega$$

Entropy and Information

Since the disorder of a system is related to the available information, therefore the entropy of a system should also have a relation with information.

Suppose we are called upon to guess a person's first name. The number of choices of names of men & women is huge. So there is a great disorder without any information. But given an information that the person is a man, the number of choices of names is reduced. Information is reduced further that man is a physicist and this reduces the disorder. The disorder in choosing names is further reduced if given an information that the physicist is a Nobel laureate. \therefore Fewer the number of ways a particular state of a system is achieved, the greater is the information.

A measure of the information when the number of choices is reduced from Ω_0 to Ω_1 is $I = K \ln \frac{\Omega_0}{\Omega_1} = S_0 - S_1$. The bigger the reduction, the bigger the information. Also, $S_1 = S_0 - I$.

\therefore Entropy measures the lack of information about the exact state of a system.

Entropy & 2nd law of Thermodynamics

The 2nd law provides proper direction to all natural processes while the Kelvin-Planck statement gives a direction for the conversion between

heat and work, Clausius statement gives a direction for heat flow between two bodies at different temperature. Combining the 2nd law can be defined in terms of entropy as

"A natural irreversible process will always proceed in a direction in which the entropy of universe increases. In a reversible process, entropy does not change."

This means in approaching equilibrium, the entropy of the universe must increase. $S_f - S_i = \int_i^f \frac{dq}{T}$. The principle of unavailable energy is a replacement of Kelvin-Planck's statement of 2nd law since both suggest a definite rejection of heat energy if some work is to be obtained from heat. The concept of entropy with reference to disorder shows that the direction of all natural processes are governed by probability laws. This 2nd law is a statistical law which is defined as the probability of a process to occur is more if the direction of the process gives an increment in entropy of the universe.

Practical Engines

We learned, engine is a device that converts heat into work. Practical engines are of two types. (a) Internal-combustion engine (Gasoline & Diesel engine)

(b) External-combustion engine.

(Steam & Stirling engine)

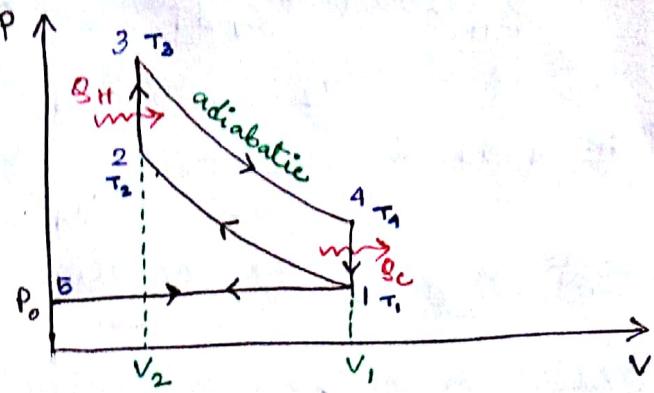
In internal combustion engine, burning of fuel & oxygen with air take place in confined combustion chamber to rise P, & T of the system. In external combustion engine, high temperature surroundings transfer heat to the combustion chamber.

Otto Cycle & Gasoline Engine

The cycle involves performance of 6 processes, 4 of which require "stroke" (vertical motion) of the piston

1. Intake stroke:

A mixture of gasoline vapour and air is drawn into the combustion chamber at constant pressure by the succession of the piston, represented by $5 \rightarrow 1$, & according to equation $P_0 V = n R T_1$, P_0 = atmospheric pressure, V = vol. of chamber, T_1 = temperature of air outside & n moles of atom.



2. Compression stroke: The mixture is compressed in quasistatic adiabatic stroke until its pressure & temperature rise considerably. No friction & no loss of heat at the cylinder wall. $1 \rightarrow 2$ process is represented as. $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

3. Ignition or combustion: Process $2 \rightarrow 3$ represents quasistatic isochoric increase of temperature from T_2 to T_3 where combustion takes place very rapidly by an electric spark.

4. Power stroke: The hot combustion product expands and push the piston out. $3 \rightarrow 1$ represents quasistatic adiabatic proc so that temperature falls down to T_4 with equation $T_3 V_2^{\gamma-1} = T_4 V_1^{\gamma-1}$

5. Valve Exhaust: The combusted product at the end of power stroke are still at a higher pressure and temperature than outside. An exhaust valve allows the gas mixture to escape, that is $1 \rightarrow 5$.

6. Exhaust Stroke: The piston pushes all the remaining combustion product out of the chamber by exerting a sufficiently large pressure $1 \rightarrow 5$ represents this isobaric exhaust.

If the specific heat C_V of the gas mixture is constant then heat absorbed in process $2 \rightarrow 3$ is

$Q_H = \int_{T_2}^{T_3} C_V dT = C_V(T_3 - T_2)$, and the heat rejected in $1 \rightarrow 1$ is $Q_C = - \int_{T_1}^{T_4} C_V dT = C_V(T_4 - T_1)$. Thus the thermal efficiency of the gasoline engine is $\eta = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_4 - T_1}{T_3 - T_2}$

Also for the two adiabatic processes we know

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}, \quad T_4 V_1^{\gamma-1} = T_3 V_2^{\gamma-1}$$

$$\therefore (T_1 - T_1) V_1^{\gamma-1} = (T_3 - T_2) V_2^{\gamma-1} \Rightarrow \frac{T_1 - T_1}{T_3 - T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

$$\therefore \eta = 1 - \left(\frac{1}{r}\right)^{\gamma-1} \quad \text{where } r = \frac{V_1}{V_2} \text{ is the compression ratio.}$$

In actual gasoline engine $r \leq 10$. If r is large then temperature of the gasoline-air mixture upon compression is huge enough to cause combustion before the advent of spark. This is called "Preignition". Taking $r=9$, $\gamma=1.4$, we obtain

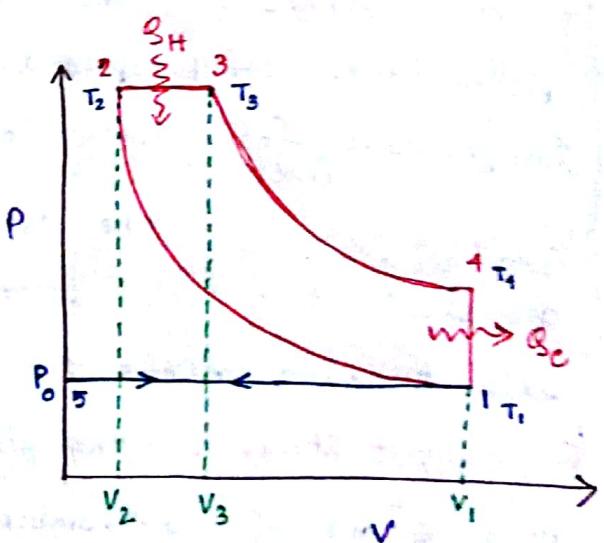
$\eta = \underline{\underline{67\%}}$. In actual engine however due to turbulence, heat conduction etc, the efficiency is less than 67%.

Diesel Engine

Rudolf Diesel in 1897 designed this air-standard Diesel cycle where only air is admitted on intake stroke. The air is compressed adiabatically until temperature reaches high to ignite oil after compression stroke. Combustion stroke happens

isobarically & piston moves out. Process 4,5,6

happen like the Otto cycle. Only change is $2 \rightarrow 3$ is horizontal.



Quasistatic isobaric heat absorption ($2 \rightarrow 3$) $Q_H = \int_{T_2}^{T_3} C_p dT = C_p(T_3 - T_2)$

and valve exhaust releases (1→1) Q_c heat as in Otto engine,

$$Q_c = - \int_{T_1}^{T_2} C_v dT = C_v(T_1 - T_2). \text{ Thus the thermal efficiency of an idealized diesel engine is } \eta = 1 - \frac{Q_c}{Q_H} = 1 - \frac{T_1 - T_1}{\gamma(T_2 - T_2)}.$$

We want to calculate the ratio in terms of adiabatic expansion ratio $\rho = \frac{V_1}{V_2}$ and combustion expansion ratio $e = \frac{V_3}{V_2}$. So we have to evaluate $\frac{T_1 - T_1}{T_3 - T_2}$ in that.

for path 1→2, adiabatic

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

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

for path 2→3 isobaric

$$\frac{T_3}{V_3} = \frac{T_2}{V_2}$$

$$\Rightarrow T_3 = T_2 \frac{V_3}{V_2} = T_2 e$$

for path 3→4, adiabatic

$$T_4 V_4^{\gamma-1} = T_3 V_3^{\gamma-1}, \text{ as } V_1 = V_4$$

$$\Rightarrow T_4 = T_3 \left(\frac{V_3}{V_1} \right)^{\gamma-1} = T_3 \left(\frac{V_3}{V_2} \right)^{\gamma-1} \left(\frac{V_2}{V_1} \right)^{\gamma-1} \\ = T_3 e^{\frac{\gamma-1}{\rho^{\gamma-1}}} = T_2 e^{\frac{\gamma-1}{\rho^{\gamma-1}}}$$

$$\therefore \eta = 1 - \frac{1}{\gamma} \left[\frac{T_2 e^{\frac{\gamma-1}{\rho^{\gamma-1}}} - T_2}{T_2 e - T_2} \right] = 1 - \frac{1}{\gamma} \frac{1}{\rho^{\gamma-1}} \left[\frac{e^{\frac{\gamma-1}{\rho^{\gamma-1}}} - 1}{e - 1} \right]$$

$$\text{if } e = 5, \gamma = 1.4, T_1 = 300K, T_2 = 990K, \eta = 59\% \quad \underline{\underline{=}}$$

Efficiency of Diesel engine < Efficiency of Otto engine

Q1 1. find the efficiency of a Carnot's engine working between the steam point and the ice point.

$$T_1 = 100^\circ C = 373K, T_2 = 0^\circ C = 273K.$$

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{273}{373} = \frac{100}{373}. \quad \therefore \% \text{ efficiency} = \frac{100}{373} \times 100 \\ = 26.81\%$$

2. find the efficiency of a Carnot's engine working between $127^\circ C$ and $27^\circ C$. It absorbs 80 cals of heat. How much heat is rejected?

$$T = 400\text{K}, T_2 = 300\text{K}, \eta = 1 - \frac{T_2}{T_1} = 1 - \frac{300}{400} = 0.25$$

$$\% \eta = 25\%, W = \eta Q_1 = 0.25 \times 80 = 20 \text{ cals}$$

$$\text{Heat rejected } Q_2 = Q_1 - W = 80 - 20 = 60 \text{ cals.}$$

HW 1. A Carnot engine has an efficiency of 30% when the sink temperature is 27°C . What must be the change in temperature of the source to make its efficiency 50%?

2. An inventor claims to have developed an engine working between 600K and 300K to deliver an efficiency of 52%. Is this claim valid? [Hint: use Carnot's theorem].

3. Two Carnot engines X & Y are operating in series. X receives heat at 1200K & rejects to a reservoir at temperature $T\text{K}$. The 2nd engine Y receives the heat rejected by X & in turn rejects to a heat reservoir at 300K . Calculate the temperature T for the situation when, reservoir at 300K . Calculate the temperature T for the situation when,

(i) The work outputs of two engines are equal.

(ii) The efficiency of two engines are equal.

4. A Carnot's refrigerator takes heat from water at 0°C and discards it to a room temperature at 27°C . 1kg of water at 0°C is to be changed into ice at 0°C . How many calories of heat are discarded to the room? What is the work done by the refrigerator in this process?

What is the coefficient of performance ($P = \frac{Q_2}{Q_1 - Q_2}$) of the machine? [$1 \text{ Cal} = 4.2 \text{ Joule}$].

Third law of Thermodynamics : Nernst's Heat Theorem

In 1906, Nernst proposed a general principle on atomic heat of solids at low temperature. The third law of thermodynamics states that the heat capacities of all solids tend to zero as the absolute zero of temperature is approached & the internal energies and entropies of all substances become equal there, approaching their common value

asymptotically tending to zero. In terms of entropy, at absolute zero temperature, the entropy tends to zero & the molecules of a substance are in perfect order.

We cannot have less than zero K temperature because if $T_2 < 0\text{K}$ then efficiency $\eta = 1 - \frac{T_2}{T_1} = 1 + \frac{T_2}{T_1} > 1$. So we cannot make more than 100% efficient engine.