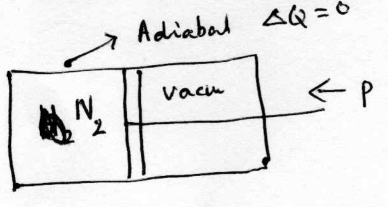
2|a

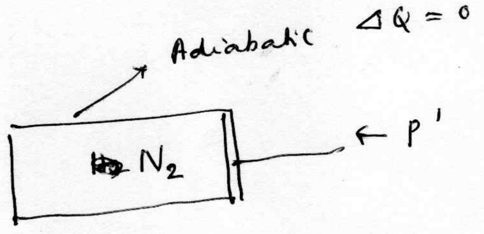
Carnot noticed the following.

In an adiabatic process one can go from an equilibrium position A and B but it was not possible to do so from B to A in some cases.

For example



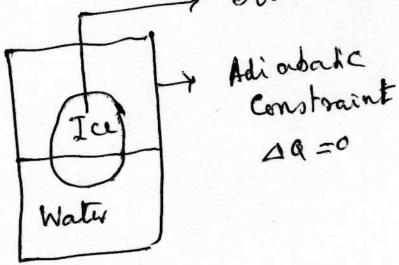
State A



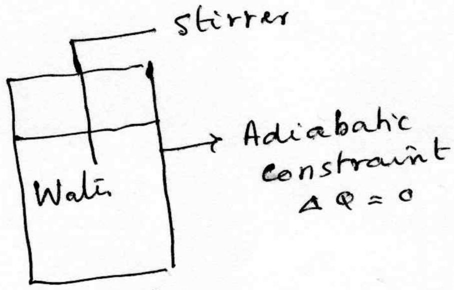
State B

Here by slowly decreasing the force on the piston one can go from state A to B quasi-statistically. The reverse is also possible. One can do work on the gas by pushing the piston and get to the original state. ~~If~~ all this is done quasi-statically the work done from taking the system from B to A matches that done by the system in going from A to B

Now consider a system of a glass [beaker ~~container~~ filled with ice & water as shown



State A



State B.

One can by stirring the beaker one can melt the ice and state is B. However, there is no way adiabatically to reach from B to A.

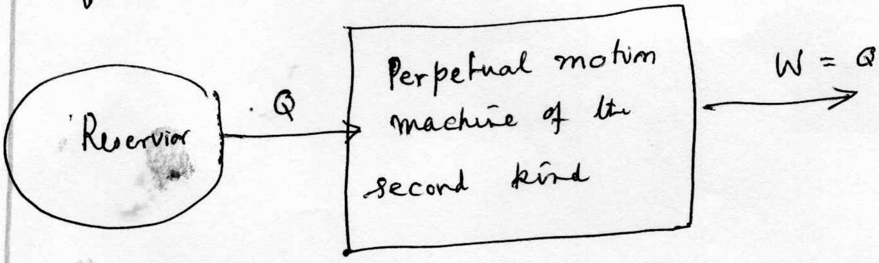
The second law (restated) [original formal definition is now done with physical inputs]

Kelvin-Planck statement

It is impossible to construct a cyclically operating device such that it produces no other effect than the absorption of energy as heat (from a single reservoir) and performs an equivalent amount work.

(*)

(See page 23)



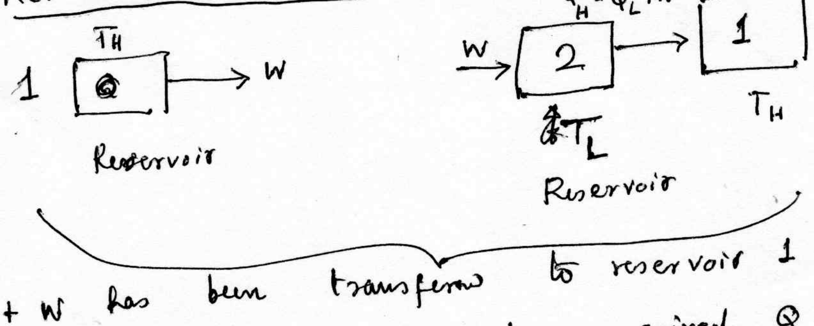
Not possible.

Clausius statement

It is impossible to construct a device that, working cyclically, will produce no other effect than the transfer of energy in the form of heat for a low temperature body to a high temperature body.

Equivalence of the two formulations.

Let Kelvin-Planck statement be false. Then we have



Net effect

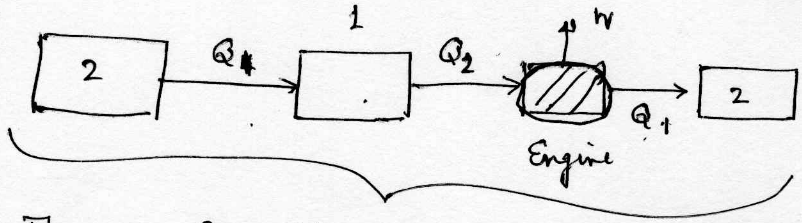
$Q_L + W$ has been transferred to reservoir 1

Thus the reservoir 1 has received Q_L without any change in the surroundings.

Violates Clausius statement.

Let Clausius state be false

Can supply heat Q_1 from a reservoir 2 to 1



Thus $Q_2 = W + Q_1$

Entire system reservoir 1 has converted $(Q_2 - Q_1)$ as mechanical work and reservoir 2 is bac

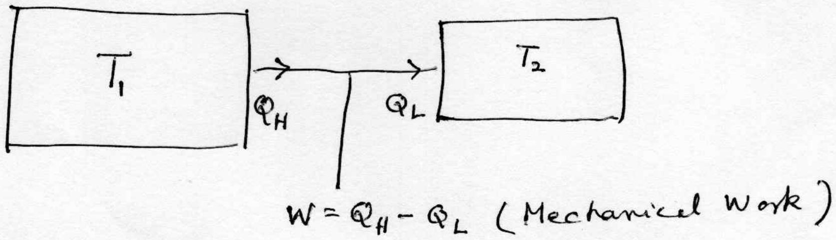
to the original state.

Violation of Kelvin-Planck statement.

For page 22

The following process is allowed in a cyclic process.

$T_1 > T_2$



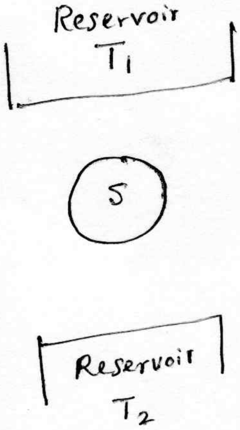
We have used this "engine", in the arguments.

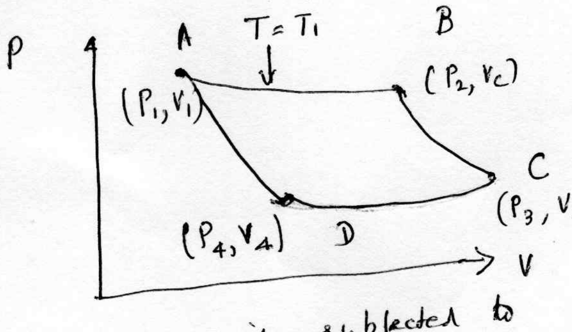
Reversible Carnot Engine

The main motivation was to find how to extract mechanical work from heat.

He introduce the Carnot Engine which represents a cycle of operations and can be used repeatedly

His cycle consits of a working substance at temperatu T_1, by making it in equilibrium with a heat reservoir at temperature T_1. [Reservoirs are considered as very large compared to the working system and any change brought about by the working system on it is negligible]. Then its volume is increased from V_1 to V_2 ~~isothe~~ isothermally at temperature T_1 [From A to B in the figure]





Then the system ~~undergoes~~ is subjected to an adiabatic taking it to the state C (P_3, V_3), at temperature T_2. As isothermal Contraction brings it to state D (P_4, V_4)

All these are done quasi-statistically and is reversible.

All reversible Carnot engines (RCE) have the same efficiency

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{W}{Q_1}$$

Q_1 heat absorbed by the system in AB
Q_2 heat given by " in CD
W = Work done by the system in the cycle ABCD.

<u>Proof</u> Assume the contrary. Let the efficiencies of two resersible Carnot cycle C & C′ be η & η', $\eta' < \eta$.

Then $\eta' = \dfrac{Q_1 - Q_2'}{Q_1}$. implies $Q_2' > Q_2$ [We can always scale the operations such that the heat absorbed from the hot reservoir (T_1) to be Q_1]

Now run the more effecient reservoir C in the reverse and C′ in the forward direction. The sum total is heat has been taken from reservoir with temperature T_2 $(Q_2' - Q_2)$ and no heat has been taken from the reservoir of temperature T_1. The difference $Q_2' - Q_2$ occurs in the form of work. This directly contradicts Kelvin-Planck statement, of the second law.

Since the efficiency of RCE is independent of the substance, we can calculate it using perfect gas as the working substance.

(one mole)

<u>For AB</u>

$$P_1 V_1 = R T_1$$
$$P_2 V_2 = R T_1$$

~~For~~

<u>For BC</u>

$$\Delta Q = C_V\, dT + p\, dV = 0$$
$$C_V\, dT + \frac{RT}{V}\, dV = 0$$
$$\text{or} \quad d\left[C_V \ln T + R \ln V\right] = 0$$
$$\left(\frac{C_V}{R} \ln T + \ln V\right) = \text{Const}$$
$$\text{or} \quad \frac{C_V}{R} \ln \left(\frac{PV}{R}\right) + \ln V = \text{Const}$$
$$\text{or} \quad \frac{C_V}{R} \ln P + \left(\frac{C_V}{R} + 1\right) \ln V = \text{Const}.$$
$$\text{or} \quad P V^{(C_V + R)/C_V} = P V^{\gamma} = \text{Const}.$$

when $\gamma = \frac{C_v + R}{C_v} = \frac{C_p}{C_v}$ is the ratio of the two specific heats.

Thus For BC $\quad P_2 V_2^{\gamma} = P_3 V_3^{\gamma} \quad (1)$ $\quad P_3 V_3 = R T_2$

$P_4 P_4 =$

For CD $\quad P_4 V_4 = P_3 V_3 = R T_2 \quad (2)$

For DA $\quad P_4 V_4^{\gamma} = P_1 V_1^{\gamma} \quad (3)$

Heat supplied to the system in AB by reservair at T_1

$$Q_{in} = \int_{V_1}^{V_2} p\,dV = RT_1 \int_{V_1}^{V_2} \frac{dV}{V} = RT_1 \ln \frac{V_2}{V_1}$$

Heat the system delivers to the reservoir at T_2

$$Q_{out} = \int_{V_4}^{V_3} p\,dV = RT_2 \ln \frac{V_3}{V_4}$$

$$Q_{in} - Q_{out} = \Delta W \;; \quad \eta = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{T_2}{T_1} \frac{\ln\left(\frac{V_3}{V_4}\right)}{\ln\left(\frac{V_2}{V_1}\right)}$$

From (1)

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1} \quad (4)$$

From (3)

$$T_2 V_4^{\gamma-1} = T_1 V_1^{\gamma-1} \quad (5)$$

From (4) & (5)

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

Thus $\quad \eta = \underline{\underline{1 - \frac{T_2}{T_1}}}$

with T in Kelvin]

$$\frac{Q_{in}}{T_1} = \frac{\Delta Q_1}{T_1} = R \ln \frac{V_2}{V_1}, \quad \frac{Q_{out}}{} = \frac{\Delta Q_2}{T_2} = \ln \frac{V_3}{V_4}$$

$$\frac{\Delta Q_1}{T_1} = \frac{\Delta Q_2}{T_2} \quad \text{or} \quad \frac{\Delta Q_1}{T_1} - \frac{\Delta Q_2}{T_2} = 0$$

Any other engine (which is not reversible) can

not have an efficiency greater than RCE.

Proof Suppose an engine exists. Run this in

the forward direction & RCE in the reverse

direction. We violate Kelvin-Planck statement.

Thus for a fixed Q_{out} (ΔQ_1) Q'_{in} [for (ΔQ_2)

any other engine must be more. Thus

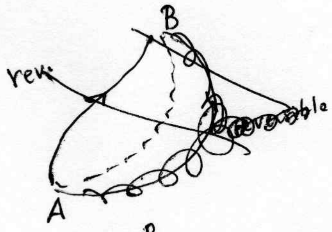
$$\frac{\Delta Q_1}{T_1} - \frac{\Delta Q_2'}{T_2} \leq \frac{\Delta Q_1}{T_1} - \frac{\Delta Q_2}{T_2} = 0$$

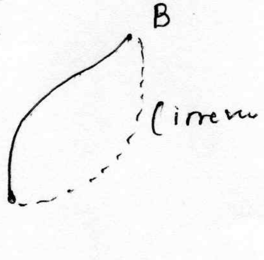
Define entropy change dS as $\displaystyle\int_A^B \frac{dQ}{T}$ (reversible) $= dS$ [with sign Convention]

[

Then $\displaystyle\oint_{rev} \frac{dQ}{T} = 0$ or $\displaystyle\oint dS = 0.$

[Sign $dQ > 0$ for given to the syst.





$$\int_{irre.}^{B} \frac{dQ}{T} + \int_B^A \frac{dQ}{T} < 0$$

$$_{irr}\int_A^B \frac{dQ}{T} + S_A - S_B < 0 \quad \text{or} \quad S_B - S_A > {}_{irr}\int_A^B \frac{dQ}{T}$$

For a closed system $\underline{dQ = 0}$

Thus $S_B \geq S_A$

when one goes from B to A. The entropy of a closed system increases spontaneously.

— · —

We will now use these concepts and some "mathematical gymnastics" for studying various physical systems. [Callan chapter 3]

Start with

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)$$

$$\frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda S)}\Bigg]_{(\lambda V, \lambda N)} \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda V)}\Bigg|_{\lambda S, \lambda N} \overset{\frac{\partial(\lambda V)}{\partial\lambda}}{\downarrow} + \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial \lambda N} \frac{\partial(\lambda N)}{\partial \lambda}$$

$$= U(S, V, N)$$

$$\frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda S)}\Bigg|_{(\lambda V, \lambda N)} S + \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda V)}\Bigg|_{\lambda S, \lambda N} V + \frac{\partial U}{\partial(\lambda N)}\Bigg| N = U$$

Let $\lambda = 1$

$$\frac{\partial U(S, V, N)}{\partial S} S + \frac{\partial U}{\partial V}(S, V, N) V + \frac{\partial U}{\partial N} N = U$$

$$U = +TS - PV + \mu N \quad \text{Ⓐ}$$ [Euler relation]

or $$S = \left(\frac{1}{T}\right) U + \left(\frac{P}{T}\right) V - \left(\frac{\mu}{T}\right) N$$

The Gibbs- Duhem Relation

μ, T, P for a single component are not independent.

$$dU = TdS - PdV + \mu dN$$

$\cancel{dp = ( ) d\left(\frac{U}{N}\right) ( ) T d\left(\frac{S}{N}\right) +}$ $\cancel{= \frac{S}{N} dT - \frac{V}{N} dp + d\mu = 0}$

S, U, V, N

From (A) $dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu$

We also have $TdS = dU + PdV - \mu dN$

Thus $0 = SdT - VdP + Nd\mu$

or $d\mu = -\left(\frac{S}{N}\right) dT + \left(\frac{V}{N}\right) dP$

Thus a single component μ is ~~fixed~~ not independent.

One can integrate this equation provided we know the equations of state or the fundamental ~~func~~ equation

Example Callan 3.2-1

Let $U = \lambda \frac{S^3}{NV} \xrightarrow{\hspace{2em}}$ Fundamental equation $\qquad \lambda = \frac{V_0 \theta}{R^2}$ = Constant.

Then
$$\mu = \left.\frac{\partial U}{\partial N}\right)_{S,V} = -\frac{\lambda S^3}{N^2 V}$$
$$T = \left.\frac{\partial U}{\partial S}\right)_{N,V} = \frac{3\lambda S^2}{NV}$$
$$P = -\left.\frac{\partial U}{\partial V}\right)_{S,N} = \frac{\lambda S^3}{NV^2}$$

Three equations and we can eliminate S, N, V to obtain the relation

$$\left(\frac{T}{3}\right)^3 = -\lambda \mu P$$

Suppose we know the three equations of state

$$T = T(S,N,V) = \cancel{T\left(\frac{S}{N},\frac{N}{N}\right)}\; T\left(\frac{S}{N},\frac{V}{N}\right)$$

$$P = P(S,N,V) = \cancel{P\left(\frac{S}{V},\frac{N}{V}\right)}\; P\left(\frac{S}{N},\frac{V}{N}\right)$$

$$\mu = \mu(S,N,V) = \cancel{\mu\left(\frac{S}{V},\frac{N}{V}\right)}\; \mu\left(\frac{S}{N},\frac{V}{N}\right)$$

Then Euler equation

$U = TS - PV + \mu N$ gives the fundamental equation.

Suppose we know two, say T & P

Then the equation

$$d\mu = -\left(\frac{S}{N}\right) dT + \frac{V}{N}(dP)$$

can be integrated and μ is ~~dep~~ determined upto a constant.

Example Perfect gas.

We use $PV = NRT$, $U = \frac{3}{2} NRT$.

$$\frac{1}{T} = \frac{3}{2}\frac{R}{(U/N)} \; ; \quad \frac{P}{T} = \frac{R}{(V/N)}.$$

$$\frac{\mu}{T}\left(\frac{U}{N},\frac{V}{N}\right)$$

$$N\,d\mu - V\,dP = -S\,dT$$

$$\frac{1}{T}\left(d\mu - \frac{V}{N}dP\right) = -\frac{S}{N}\frac{dT}{T} \quad \left[\text{from } TS = U + PV - \mu N \text{ we write}\right]$$

$$= -\frac{1}{NT^2}(U + PV - \mu N)\,dT$$

$$d\left(\frac{\mu}{T}\right) \mp \mu\, d\left(\frac{1}{T}\right) - \frac{V}{NT}\, dP = -\frac{1}{NT^2}\left(U + PV - \mu N\right) dT$$

$$d\left(\frac{\mu}{T}\right) = \underbrace{\mu\, d\left(\frac{1}{T}\right) + \frac{V}{NT}\, dP - \frac{1}{NT^2}\, U dT - \frac{PV}{NT^2}\, dT + \frac{\mu}{T^2}\, dT}_{\text{Cancel .}}$$

$$= \frac{V}{N\cancel{T}}\left[\frac{dP}{T} - \frac{P}{T^2}\, dT\right] + u\, d\left(\frac{1}{T}\right)$$

$$= \frac{V}{N}\, d\left(\frac{P}{T}\right) + u\, d\left(\frac{3}{2}\frac{NR}{U}\right)$$

$$= v\, d\left(\frac{NR}{V}\right) + u\, d\left(\frac{3}{2}\frac{R}{u}\right)$$

$$= R\, v\, d\left(\frac{1}{v}\right) + \frac{3}{2} R\, u\, d\left(\frac{1}{u}\right)$$

$$= R\, d \ln \frac{1}{v} + \frac{3}{2} R \ln\left(\frac{1}{u}\right)$$

$$= -R\, d \ln v - \frac{3}{2} R \ln u .$$

$u_0 = \frac{3}{2} R T_0$

or $$\frac{\mu}{T} - \frac{\mu_0}{T_0} = -R \ln \frac{v}{v_0} - \frac{3}{2} R \ln \frac{u}{u_0}$$

$$S_0 = \frac{U_0 + P_0 V_0 - \mu_0 N_0}{T_0} \Rightarrow \frac{S_0}{N_0} = \frac{u_0}{T_0} + R - \frac{\mu_0}{T_0}$$

$$\frac{S}{N} - \frac{S_0}{N_0} = \left(\frac{u}{T} - \frac{u_0}{T_0}\right) + \left(R - R\right) - \left(\frac{\mu}{T} - \frac{\mu_0}{T_0}\right)$$

$$= \left(\frac{3}{2}R - \frac{3}{2}R\right) + 0 - \left(\frac{\mu}{T} - \frac{\mu_0}{T_0}\right)$$

$$= R \ln \frac{v}{v_0} + \frac{3}{2} R \ln \frac{u}{u_0} .$$

Note

$$\left.\frac{\partial U}{\partial S}\right)_{N,V} = \cancel{\frac{2}{3}}\, \frac{1}{\left.\frac{\partial S}{\partial U}\right)_{N,V}} = \frac{1}{\frac{3}{2} R \cdot \left(\frac{1}{U}\right)} = \frac{2}{3}\frac{U}{R}$$

when L.H.S $\to 0$, $U \to 0$ and $S \to \infty$ [Postulate IV

(or Third law of thermodynamics is violated.