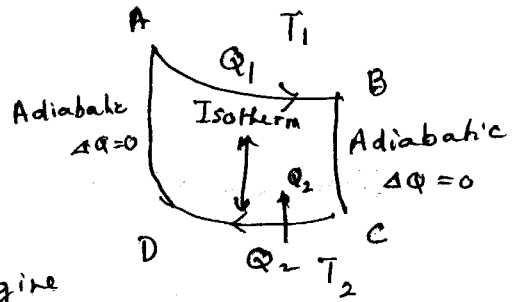


Some revision of essential points with

examples

We will work in the context of Carnot engine



$-\Delta W =$ Work done by the system.

(1) The efficiency of the engine after a cycle is completed is given

$$\Delta Q = \Delta U + \Delta W = \Delta W = Q_1 - Q_2$$

Zero for a cycle

$Q_1 =$ Heat into the system at T_1

$Q_2 =$ Heat out of the system at T_2

For reversible engine

$$\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

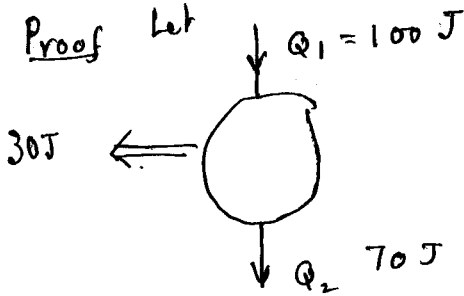
$$= - \frac{Q_{\text{out}}}{Q_{\text{in}}} = \frac{Q_2'}{Q_1}$$

For reversible engine

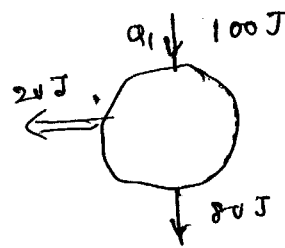
$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

Any irreversible engine will have an efficiency lower than the reversible Carnot engine. If not it will violate II law in either of the forms.

Proof Let



Irreversible



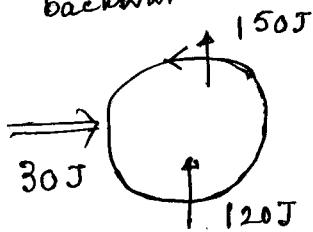
Reversible

Can scale the reversible engine by a factor $\frac{7}{8}$ and run it in the reverse mode. Heat supplied at T_2 is 70 J and heat delivered at $T_1 = 87.5$ J, with 17.5 J of work on the system. Total Balance: Only $\Delta Q = 12.5$ J from T_1 converts to work. [Kelvin Planck violated]

We could have scaled it by $\frac{3}{2}$ and run it
 reversible engine

(40)

backwards.



Total is No work done
 50J from T_2 transferred to
 reservoir at T_1 .
 Violates Clausius.

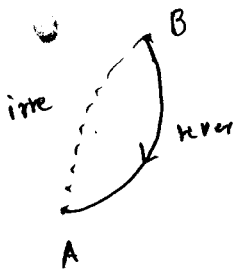
We also had

$$\frac{Q_1}{T_1} + \frac{Q_2'}{T_2} = 0$$

for reversible engine and

$$\frac{Q_1}{T_1} + \frac{Q_2'}{T_2} \leq 0$$

for irreversible engine.



$$\int_A^B \frac{dQ_1}{T} + S(A) - S(B) \leq 0$$

$$\int_A^B \frac{dQ}{T} \leq S(B) - S(A)$$

In fines. $\Delta Q \leq T \Delta S$.

We had introduced three thermodynamic potentials

Enthalpy $H = U + PV$

$$dH = dU + PdV + VdP = \Delta Q + VdP$$

If P is constant

$$dH = d(U + PV) = \Delta Q$$

~~$dH =$~~ If $\Delta Q = 0$ [thermally insulated]

$dH = 0$ and P is constant.

Example was that Joule-Thomson cooling.

Enthalpy

Consider a reservoir + system

Explained
later
in detail

closed Fixed entropy and is a maximum.

$U^s + U^r$ must be a minimum. ; No heat exchange $\Delta Q = 0 \Rightarrow \Delta S^r = 0$

$$d(U^s + U^r) = 0 \quad dU^s + \frac{\partial U^r}{\partial V^r} dV^r = dU^s - P^r dV^r = 0$$
$$= dU^s + P^r dV^s = 0$$

$$d(U^s + P^r V^s) = 0$$

$P^s = P^r$ as Volume can change (mechanical \rightleftharpoons)

$$d(U^s + P^s V^s) = 0$$

Example is that Joule Thomson effect.

Helmoltz Free energy

$$F = U - TS \quad dF = dU - TdS - SdT$$
$$= dU - \Delta Q - SdT$$
$$= -\Delta W_{by} - SdT \quad dU - TdS - SdT$$

$-\Delta W_m > d(U - TS)$ if T is ~~constant~~ constant

$$\Delta W_m \gg \Delta F = F_B - F_A$$

if $\Delta F = F_B - F_A > 0$ then more work than ΔF is needed to take the system from A to B.

if $\Delta F = F_B - F_A < 0$ [$F_A - F_B > 0$]

Then $F_A - F_B \gg -\Delta W_m = \Delta W_{by}$

The maximum work that can be extracted from the system is $F_A - F_B$

Example 1 Use of Perfect gas.

$$U = \frac{3}{2} NRT \quad S = NR \ln \frac{V}{N} + \frac{3}{2} NR \ln T + \text{Const.}$$
$$F = -NRT \ln \frac{V}{N} + Nf(T) = \left[\frac{3}{2} NRT - NRT \ln \frac{V}{N} + \text{Const.} \right]$$

Example 2

(43)

A solid with ~~sp~~ sp. ht ($C_p = C_v = c$)
Mass 1 kg at temperature T_i
Touches a reservoir at a lower temperature
 T_o .

What is the change in entropy.

Heat supplied $c (T_i - T_o)$

No work extracted.

change in entropy, let it be at temp T

and change to $T + \Delta T$

ΔQ given to the reservoir is $[\Delta Q = c \Delta T]$

[Entropy decrease] $= c \frac{\Delta T}{T}$

Entropy increase of the reservoir is $\frac{c \Delta T}{T_o}$

Thus $S(\text{solid}) = c \int_{T_o}^{T_i} \frac{\Delta T}{T} = c \ln \frac{T_i}{T_o}$

Increase for the reservoir $= \frac{c (T_i - T_o)}{T_o}$

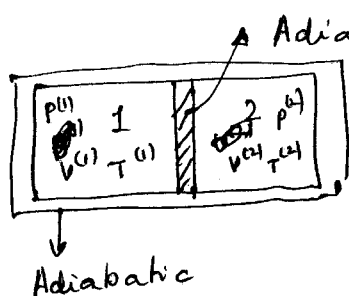
Increase $= c \left[\left(\frac{T_i}{T_o} - 1 \right) + \ln \frac{T_i}{T_o} \right]$ $\frac{T_i}{T_o} = x$

$= c [x - 1 + \ln x]$

$x - 1 + \ln x > 0$

Had we changed the temperature of the solid by using a series of reservoirs we could have made the process reversible.

[A paper by A. Miranda will be circulated.]



one mole on both sides.

What would be $T_f^{(1)}$, $T_f^{(2)}$ when the wall is

allowed to move suddenly.

As there is no contact with outside.

$$S = S^{(1)}(U^{(1)}, V^{(1)}) + S^{(2)}(U^{(2)}, V^{(2)})$$

$$V^{(1)} + V^{(2)} = V = \text{const.}$$

Since each side has $\Delta Q = 0$

$$dU^{(1)} = -p^{(1)} dV^{(1)} \text{ for a small change}$$

$$dU^{(2)} = -p^{(2)} dV^{(2)}$$

Entropy must be maximised.

$$dS = \frac{dU^{(1)}}{T^{(1)}} + \frac{p^{(1)}}{T^{(1)}} dV^{(1)} + \frac{dU^{(2)}}{T^{(2)}} + \frac{p^{(2)}}{T^{(2)}} dV^{(2)}$$

$$= 0 \text{ for any situation!}$$

All one can get is

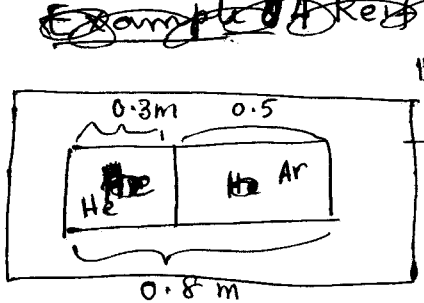
$$U^{(1)} + U^{(2)} = 0, \quad dV^{(1)} = -dV^{(2)}$$

$$dU^{(1)} = -dU^{(2)}$$

$$\frac{\partial U^{(1)}}{\partial V^{(1)}} dV^{(1)} = - \frac{\partial U^{(2)}}{\partial V^{(1)}} dV^{(1)} = \frac{\partial U^{(2)}}{\partial V^{(2)}} dV^{(1)}$$

$$\text{or } -p^{(1)} = -p^{(2)} \text{ at equilibrium.}$$

Need some more modeling to obtain $T_f^{(1)}$, $T_f^{(2)}$.



Example 4 - (Reif Problem)

Partition is conductor

1 litre.

$c_{\text{water}} = 1$
mass of water = 1 kg

He at 5 Atmos, and is 1 mole. Ar at 1 atm. The entire system at temp $T = 298^\circ \text{K}$. Both are perfect gases

The partition allowed to move.

(1) What is the change in temperature of water

(2) How far left has the piston come to rest

(3) What is the increase in entropy of the system.

(1) Let the final temperature be T_f

$$\Delta U_{\text{He}} = \frac{3}{2} R (T_f - 298^\circ)$$

$$\frac{P_{\text{Ar}} V_{\text{Ar}}}{298^\circ} = n_{\text{Ar}} R ; \quad \frac{P_{\text{He}} V_{\text{He}}}{298} = R$$

$$\frac{P_{\text{Ar}}}{P_{\text{He}}} \left[\frac{5}{3} \right] = n_{\text{Ar}} \quad \text{or} \quad n_{\text{Ar}} = \frac{1}{3}$$

$$\Delta U_{\text{Ar}} = \frac{1}{2} R (T_f - 298)$$

$$\Delta U_{\text{water}} = c_v \times 1 (T_f - 298)$$

No exchange with surroundings.

$$\left(\frac{3}{2} R + \frac{R}{3} + c_v \right) (T_f - 298) = 0 \quad \frac{T_f}{298} = 1$$

No change in temperature!

(2) Let the final position be V_f , P_f , $T_f = 298$.

$$P_f V_{\text{He}} = R \times 298 ; \quad P_f V_{\text{Ar}} = \frac{1}{3} R \times 298$$

$$\frac{V_{\text{He}}}{V_{\text{Ar}}} = \frac{1}{3} \quad \frac{V_{\text{He}} + V_{\text{Ar}}}{V_{\text{Ar}}} = \frac{1.8}{0.8} \quad V_{\text{Ar}} = \frac{3}{4} \times 0.8 = 0.6$$

$$V^{Ar} = \frac{V^{He}}{3}$$

$$V^{Ar} + V^{He} = 0.8 \text{ m} \times S$$

$$\left(\frac{1}{3} + 1\right) V^{He} = 0.8 \times S$$

$$V^{He} = 0.6 \times S$$

$S =$ Area of cross section of the container.

$$S_f - S_i = R \ln \left[\frac{0.6}{0.3} \right] + \frac{R}{3} \ln \left[\frac{0.2}{0.5} \right]$$

+ 0 (for water - as it has not been heated)

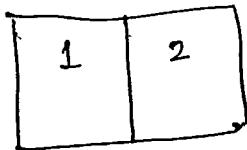
(used $S = N \frac{3R}{2} \ln T + NR \ln V$)

$$S_f - S_i = R \times 0.38 = 3.2 \text{ J/K}$$

[Convert Atmospheres to Pascals]

Comments on Example 3 From A.E. Curzon AJP 37, 404 (1969)

Consider an isolated box containing gas in the two chambers 1 and 2, separated by a partition.



No exchange of matter.

We have

$$dU_1 + dU_2 = 0 \quad (1)$$

$$dV_1 + dV_2 = 0 \quad (2)$$

$$T_1 dS_1 = dU_1 + P_1 dV_1 \quad (3)$$

$$T_2 dS_2 = dU_2 + P_2 dV_2 \quad (4)$$

Let the partition move: Equilibrium when $S_1 + S_2$ is a maximum $d(S_1 + S_2) = 0$

(a) Perfect conductor.

$$dS = \left[\frac{dU_1}{T_1} + \frac{P_1}{T_1} dV_1 \right] + \left[\frac{dU_2}{T_2} + \frac{P_2}{T_2} dV_2 \right]$$

$$(dU_1 = -dU_2) \text{ \& } (dV_1 = -dV_2)$$

$$dS = \left[dU_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + \left[\frac{P_1}{T_1} - \frac{P_2}{T_2} \right] dV_1 \right]$$

dU_1 and dV_1 are independent Thus $T_1 = T_2$ & $P_1 = P_2$.

(b) Perfect insulator. dU_1 and dV_1 are not independent.

Now system 1 $\Delta Q_1 = 0$ and $dS_1 \geq 0$
 2 $\Delta Q_2 = 0$ $dS_2 \geq 0$

Given $dS_1 + dS_2 = 0$ [for \equiv $S_1 + S_2$ must be maximum]

$$dS_1 = dS_2 = 0$$

$$dU_1 = -P_1 dV_1 \quad dU_2 = -P_2 dV_2$$

~~$$dS = \left[\left(\frac{1}{T_1} - \frac{1}{T_2} \right) P_1 dV_1 + \dots \right]$$~~

$$dS_1 = \frac{dU_1}{T_1} + \frac{P_1 dV_1}{T_1} \quad dS_2 = \frac{dU_2}{T_2} + \frac{P_2 dV_2}{T_2}$$

$$dS = \left[\left(\frac{1}{T_1} - \frac{1}{T_2} \right) (-P_1 dV_1) + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dV_1 \right]$$

from (A)

$$= \left(\frac{P_1}{T_2} - \frac{P_2}{T_2} \right) dV_1 = 0$$

$$P_1 = P_2$$

No conclusion about T_1 & T_2