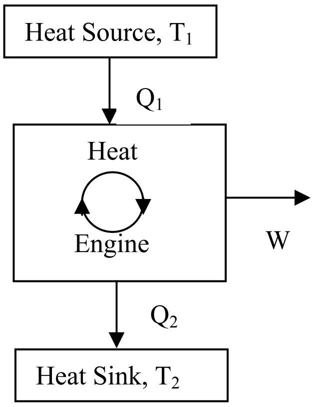
Second Law

1st Law : When a system undergoes a complete cycle, the **net** heat supplied is equal to the **net** work done.

2nd Law: Although the net heat supplied is equal to the net work done, the **gross** heat supplied must be greater than the net work done; some heat must always be rejected by the system.

Heat Engine: System operating in a complete cycle and developing net work from a supply of heat.



Q_1: Heat supplied from the source

Q_2: Heat rejected to the sink

W: Work done by the system

1st: (Net heat supplied) = (Net work done)

$\sum dQ = \sum dW$ or $Q_1 - Q_2 = W$

2nd: (Gross heat supplied) > (Net work done)

$Q_1 > W$

Thermal Efficiency:

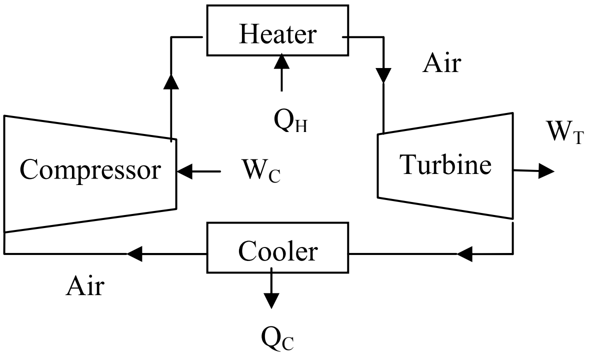
$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} < 1$$

$T_1 > T_2$ A temperature difference, no matter how small, is necessary before net work can be produced in a cycle.

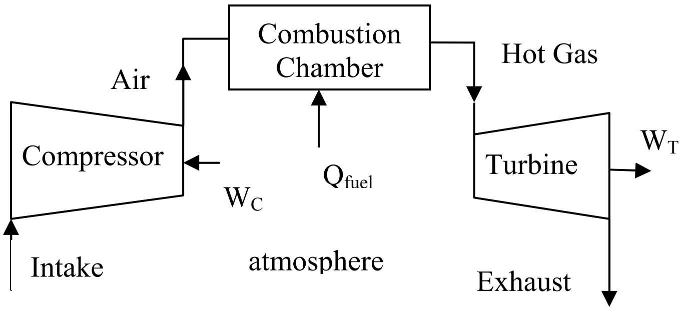
2nd Law It is impossible for a heat engine to produce net work in a complete cycle if it exchanges heat only with bodies at a single temperature.

There is nothing in the first law to indicate that the internal of the sea could not be converted into mechanical energy or work. The second law dictates that a second reservoir of energy at a lower temperature is essential before work can be developed.

Gas turbine plants:



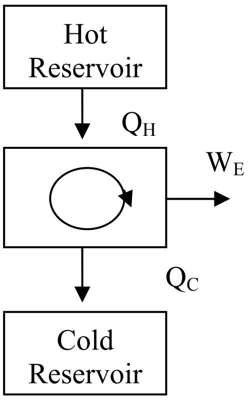
Closed Cycle



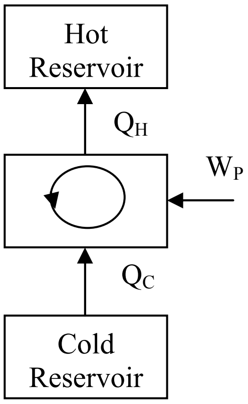
Open Cycle

Heat engine & Heat pump:

Heat Engine



Heat Pump



Heat Pump

Q_C: Supplied from CR

Q_H: Rejected to HR

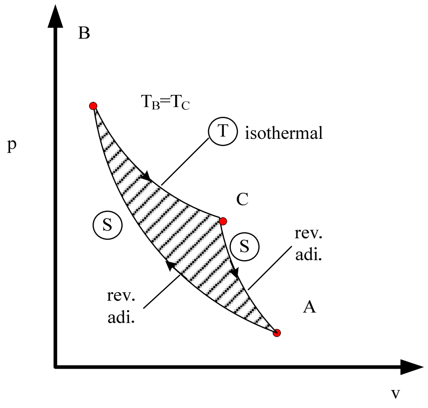
1st: $Q_H = Q_C + W$

2nd: $W > 0$

Work input is essential for heat to be transferred from cold to hot reservoir.

Entropy:

1st internal energy 2nd entropy



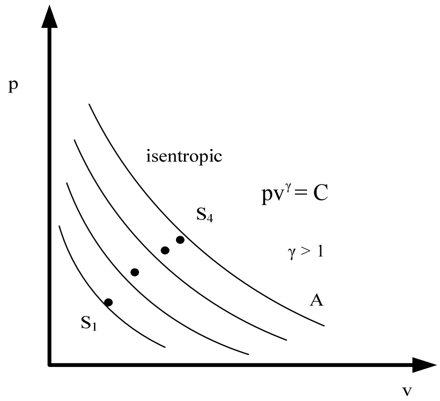
AB: rev. adi. ($q = 0$) (S)

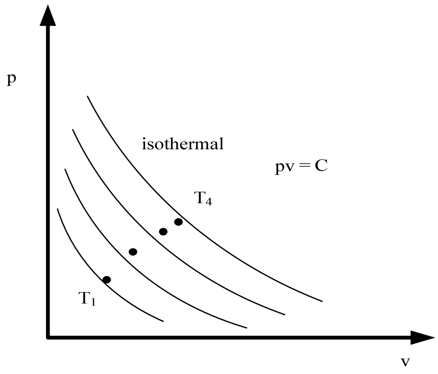
BC: rev. (T)

CA: rev. $q = 0$ (S) isentropic

System undergoes a cycle and develops net work which drawing heat from a reservoir at one fixed dT.

→ Impossible ∴ violates 2nd law.





A rev. adi. Process occupies a unique line on a pv diagram representing one value of entropy. (S) non flow energy equation for a rev. process:

$$\frac{dq}{T} = \frac{du+pdv}{T} = \frac{C_v dT + RT\frac{dv}{v}}{T} = \frac{C_v dT}{T} + R\frac{dv}{v} = 0$$

Adiabatic process: dq = 0

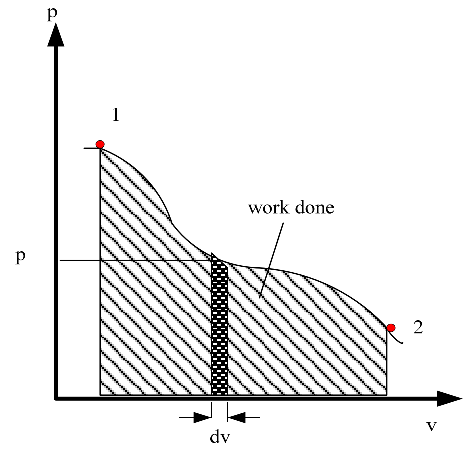
$$\left.\begin{array}{l} \frac{dq}{T} = 0 \text{ for a rev. adi. process} \\ \frac{dq}{T} \neq 0 \text{ for any other process} \end{array}\right\} \quad \begin{array}{l} ds = \frac{dq}{T} \\ \text{for all working substances} \end{array}$$

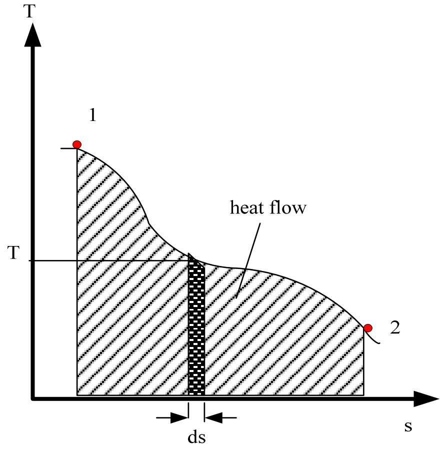
dq: heat added reversibly

$$S_2 - S_1 = \int_1^2 \frac{dq}{T}\left[\frac{kJ}{kgK}\right] \quad \text{specific entropy}$$

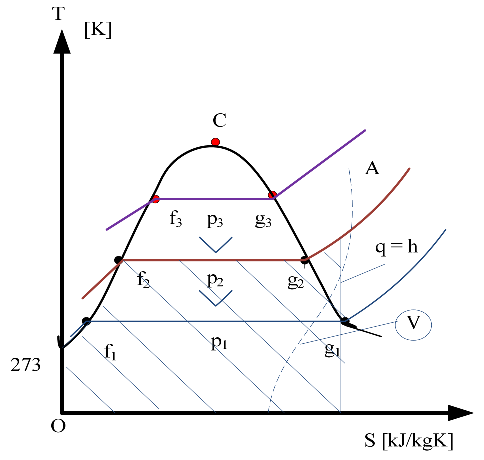
S = ms entropy of mass m of a fluid

$$dq = Tds \qquad q = \int_1^2 Tds \;\leftrightarrow\; W = \int_1^2 pdv$$





T-S diagram (vapor):



S =0 at .01◦C for H_2O but at –40 ◦C for refrigerants

dryness fraction or quality = x

$$x = \frac{S - S_f}{S_{fg}}$$

$$S = S_f + xS_{fg}$$

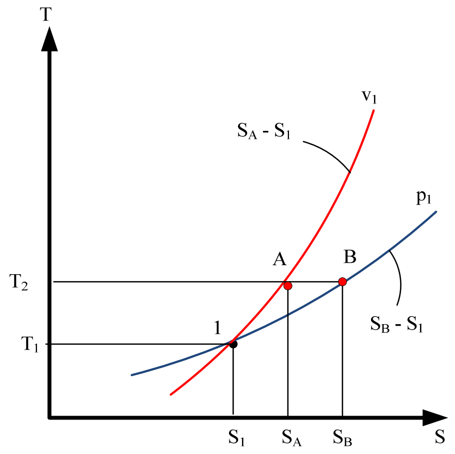
$$h = h_f + xh_{fg}$$

$$h = u+pv$$

$$dh = du+pdv+\cancelto{0}{vdp} = dq$$

h_A: shaded area

T-S diagram (perfect gas):



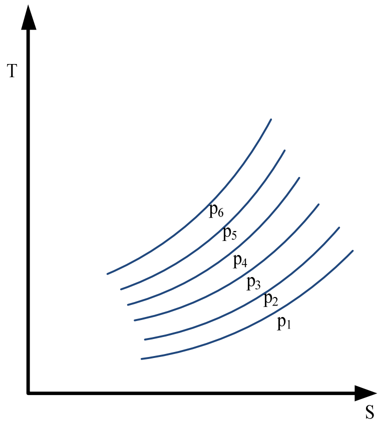
$$S_A - S_1 = \int_1^A \frac{dQ}{T}$$

$$\left(dQ = C_v dT\right)$$

$$= \int_1^A \frac{C_v dT}{T}$$

$$= C_v \ln\frac{T_A}{T_1} = C_v \ln\frac{T_2}{T_1}$$

$$S_B - S_1 = \int_1^B \frac{C_P\ dT}{T} = C_P\ \ln\frac{T_B}{T_1} = C_P\ \ln\frac{T_2}{T_1}$$



$$C_p > C_v$$

$$\therefore\ S_B - S_1 > S_A - S_1 \quad \text{or} \quad S_B > S_A$$

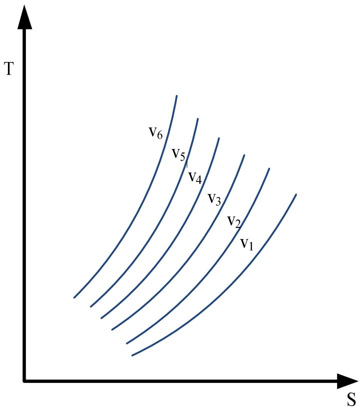
$$Pv = RT$$

$$p\uparrow \rightarrow T\uparrow \rightarrow v\downarrow$$

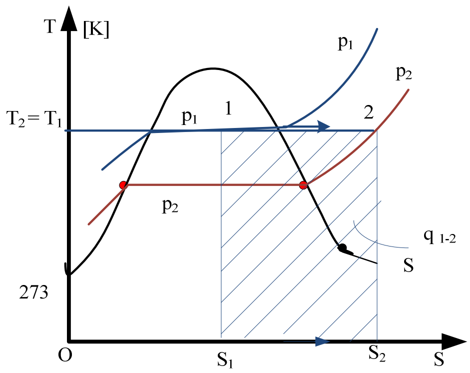
$$p\downarrow \rightarrow T\downarrow \rightarrow v\uparrow$$

$$P_6 > P_5 > P_4 > P_3 > P_2 > P_1$$

$$v_6 < v_5 < v_4 < v_3 < v_2 < v_1$$



Rev. Isothermal process (vapor):



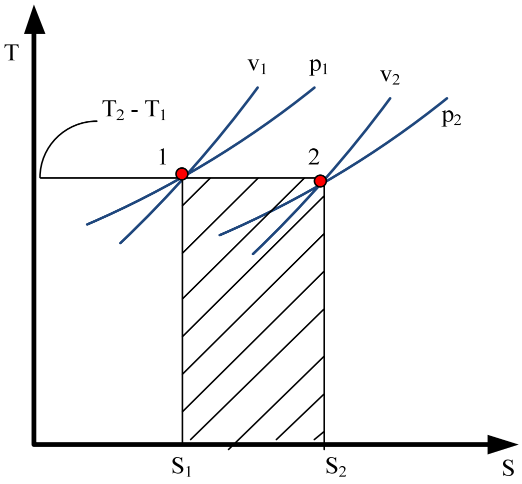
(T) expansion of wet steam into the superheat region

$$q_{1\text{-}2} = T_1\left(S_2 - S_1\right)$$

$$= T_2\left(S_2 - S_1\right)$$

heat supplied during the process

Rev. (T) process (PG):



$$
\begin{aligned}
q_{1\text{-}2} &= T\left(S_2 - S_1\right)\\
dq &= du + pdv\\
&= C_v dT + pdv \;\left[\text{Joule's Law: } du = C_v dT\right]\\
&= pdv \;\left[C_v dT = 0,\ \because (T)\right]\\
&= RT\,\frac{dv}{v}\left[\because pv = RT\right]
\end{aligned}
$$

$$
S_2 - S_1 = \int_1^2 \frac{dq}{T} = R\int_1^2 \frac{dv}{v}
$$

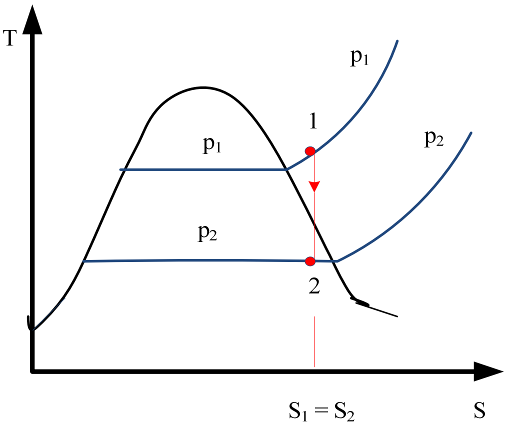
$$
= R\ \ln\frac{v_2}{v_1} = R\ \ln\frac{p_1}{p_2}
$$

$$
q_{1\text{-}2} = T\left(S_2 - S_1\right) = RT\ \ln\frac{v_2}{v_1} = RT\ \ln\frac{p_1}{p_2}
$$

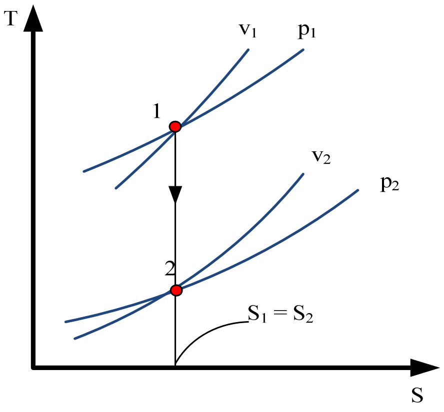
Recall $q_{1\text{-}2} = W_{1\text{-}2} = RT\ \ln\frac{p_1}{p_2} = p_1 v_1 \ln\frac{p_1}{p_2}$

Rev. adi. process (vapor) (S):

Superheated steam expanding into the wet region, or two-phase mixture.



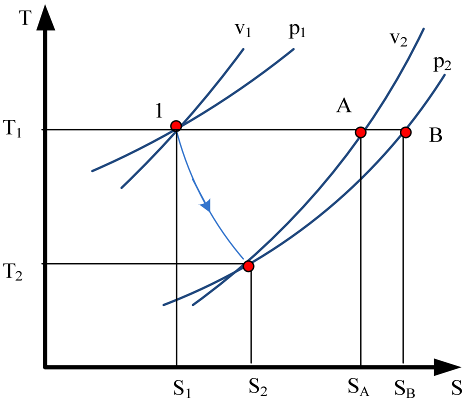
Rev.adi. pocess (PG) (S)



$pv^{\gamma} = \text{const}$

γ : specific heat ratio or isentropic index

Polytropic process:



General case for PG $p_1V_1^n = p_2V_2^n$

$$dS = \frac{dq}{T}$$

$$dq = du + pdv$$

$$= C_v dT + RT\frac{dv}{v}$$

$$dS = C_v\frac{dT}{T} + R\frac{dv}{v}$$

$$T_1 > T_2$$

$$S_2 - S_1 = C_v \ln\frac{T_2}{T_1} + R\ln\frac{v_2}{v_1} = \underset{(a)}{R\ln\frac{v_2}{v_1}} - \underset{(b)}{C_v \ln\frac{T_1}{T_2}}$$

(a) Change of S in (T) process from v_1 to $v_2 = S_A - S_B$

(b) Change of S in (v) process from T_1 to $T_2 = S_B - S_2$

$$S_2 - S_1 = (S_A - S_1) - (S_A - S_2) \quad \text{for } 1 \to A \to 2$$

Likewise,

$$S_2 - S_1 = (S_B - S_1) - (S_B - S_2) \quad \text{for } 1 \to B \to 2$$

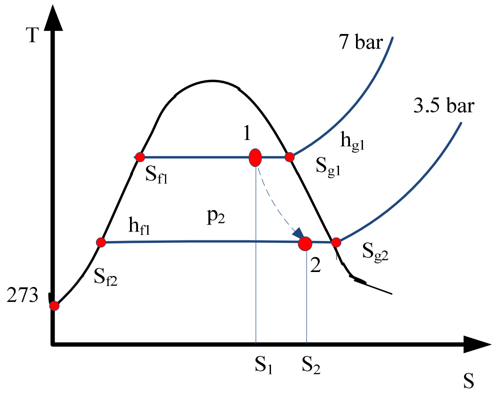
$$S_B - S_1 = R\ln\frac{p_1}{p_2} \text{ at (T)}, \qquad S_B - S_2 = C_p \ln\frac{T_1}{T_2} \text{ (p)}$$

$$S_2 - S_1 = R\ln\frac{p_1}{p_2} - C_p\ln\frac{T_1}{T_2}$$

$$= C_p\ln\frac{T_2}{T_1} + R\ln\frac{p_1}{p_2}$$

Irreversibility:

Steam at 7 bar, dryness fraction 0.96 is throttled down to 3.5 bar. ΔS?



$$S_1 = S_{f1} + x\,S_{fg1}\left[S_{fg1} = S_{g1} - S_{f1}\right]$$

$$= 1.992 + 0.96 \times 4.717$$

$$= 6.522 \text{ kJ/kgK}$$

$h_1 = h_2$ for throttling

$$h_2 = h_1 = h_{f1} + x\,h_{fg1}\left[h_{fg1} = h_{g1} - h_{f1}\right]$$

$$= 697 + 0.96 \times 2067 = 2682 \text{ kJ/kg} < h_{g2} \to \text{still wet steam}$$

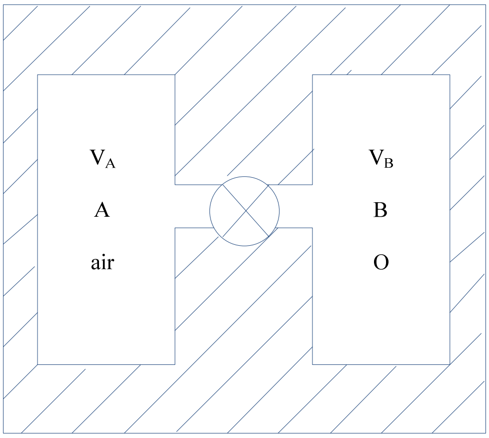
$$x_2 = \frac{h_2 - h_{f2}}{h_{fg2}} = \frac{2682 - 584}{2148} = 0.977$$

$$S_2 = S_{f2} + x_2 S_{fg2} \left[S_{fg2} = S_{g2} - S_{f2} \right]$$

$$= 1.727 + 0.977 \times 5.214 = 6.817 \text{ kJ/kgK}$$

$$\therefore S_2 - S_1 = 6.817 - 6.522 = 0.295 \text{ kJ/kgK}$$

The process is shown dotted. The area under the line does not represent heat flow. Throttling assumes no heat flow, but S changes (irreversible).

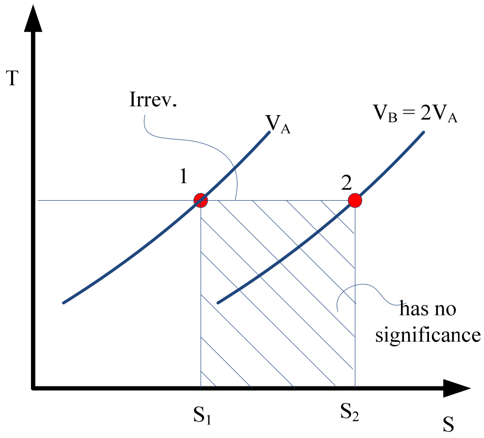


$V_A = V_B$, $T_1 = T_2$, isothermal process

$$S_2 - S_1 = R \ln \frac{V_2}{V_1} = 0.287 \ln \frac{2V_A}{V_A}$$

$$= 0.287 \times \ln 2 = 0.199 \text{ kJ/ kg K}$$

Two vessel of equal volume are connected by a valve. Both vessels are well lagged. V_A contains air, V_B is vacuum. The valve is opened and the air is allowed to fill both vessels.



$dW=0$, yet $dV = 2V_A - V_A$

$$= V_A$$

$dW = pdV$ does not hold

$dQ = 0$, yet $\Delta S > 0$

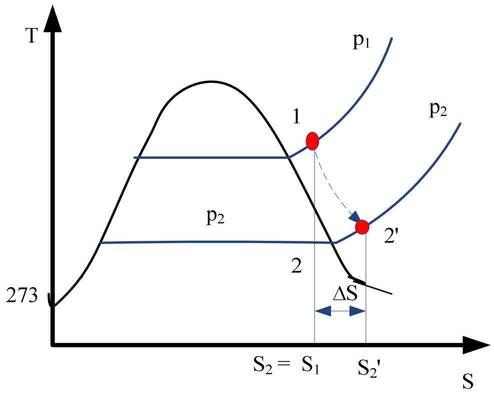
$dS = \frac{dQ}{T}$ does not hold.

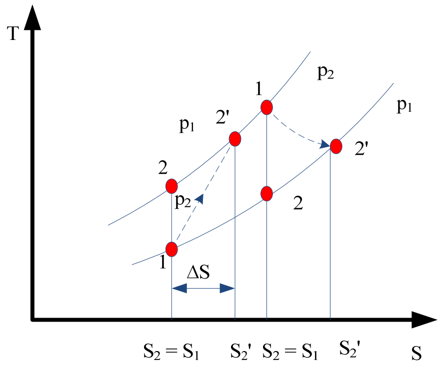
2nd: The entropy of a thermally isolated system must either increase or remain the same.

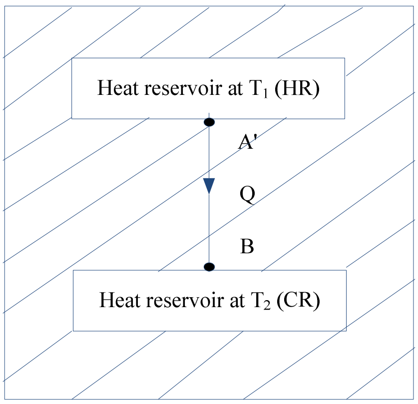
S remains same in a reversible adiabatic process.

S increases in an irreversible adiabatic process.

ΔS is a measure of irreversibility of the process.







Continuous $\Delta T = T_1 - T_2$ between A&B.

Heat transferred reversibly from HR to A

Heat transferred reversibly from B to CR

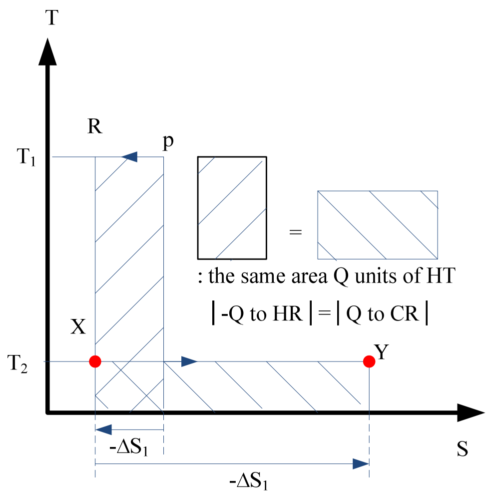
T_1& T_2 remain constant ($\Delta S \to 0$ when $T_1 \to T_2$)

$$\left.\begin{array}{ll} \text{Heat supplied to CR:} & +\ Q \\ \text{Increase of entropy of CR:} & +\ \frac{Q}{T_2} \\ \text{Heat supplied to HR:} & -\ Q \\ \text{Increase of entropy of HR:} & -\ \frac{Q}{T_1} \end{array}\right\} \quad \Delta S = \frac{Q}{T_2} - \frac{Q}{T_1} > 0 \quad (\because T_1 > T_2)$$

($T_{system} - T_{surroundings}$) must be infinitely small during a reversible process (≈ 0).

$\Delta S_{system} > 0$ when the heat flow process is irreversible

$= 0$ when the heat flow process is reversible



$\Delta S_{system} = -\Delta S_1 + \Delta S_2 > 0$

The entropy of CR must always increase more than the entropy of HR decrease => the entropy of the combined system must increase.

The P-R & X-Y processes are reversible, then the irreversibility is caused by the Q process between A & B.

ΔS: A measure of the irreversibility and the degradation of energy.

1st: Energy can never be destroyed.
2nd: Energy can only become less useful and never more useful.

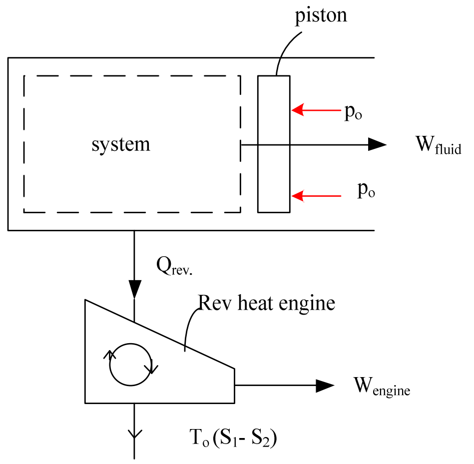
Systems tend naturally to states of lower grade energy.

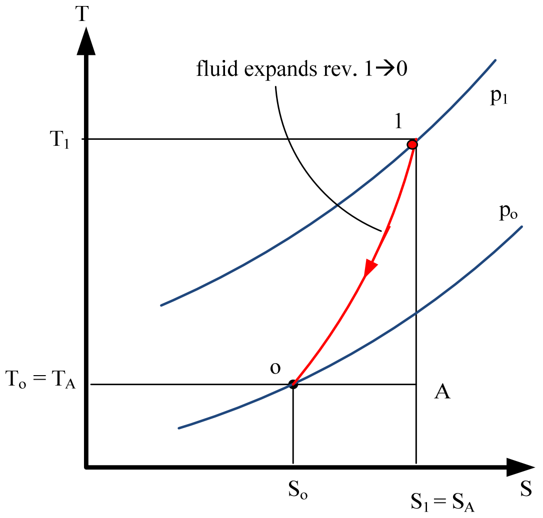
2nd: Implies a direction or a gradient of usefulness of energy. Work is more useful than heat; the higher the temperature of a reservoir of energy, the more useful is the amount of energy available.

$$T_{HR}\uparrow \rightarrow E_{useful}\uparrow \text{ given CR or the atmosphere}$$

Availability: The theoretical maximum amount of work which can be obtained from a system at p_1& T_1 when operating with a reservoir at p_0& T_0.

(a) **Non flow system:** fluids expands rev. 1 → 0





W_{engine} = Heat supplied – Heat rejected = $Q - T_0 (S_1 - S_0)$

= Heat rejected by fluid

$-Q = (U_0 - U_1) + W_{fluid}$ Or, $W_{fluid} = (U_1 - U_0) - Q$

$W_{fluid} + W_{engine} = (U_1 - U_0) - Q + Q - T_0 (S_1 - S_0)$

$$= (U_1 - U_0) - T_0 (S_1 - S_0)$$

The work done by the fluid on the piston is less than the total work done by the fluid, since there is work done on the atmosphere at p_0.

Work done on atmosphere = $p_0 (V_0 - V_1) = W_{atmosphere}$

Maximum work available = $W_{fluid} + W_{engine} - W_{atmosphere}$

$$= (U_1 - U_0) - T_0 (S_1 - S_0) - p_0 (V_0 - V_1)$$

$$W_{max} = (U_1 + p_0 V_1 - T_0 S_1) - (U_0 + p_0 V_0 - T_0 S_0)$$

$$= a_1 - a_0$$

$a = U + p_0 V - T_0 S$: non-flow availability function

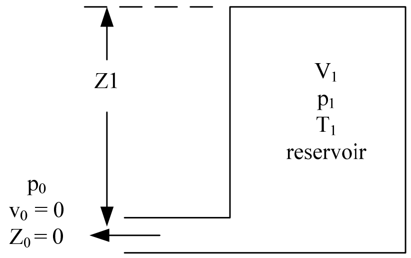
(b) Steady flow system:

$$W_{max} = \left(h_1 + \cancelto{0}{\frac{V_1^2}{2}} + \cancelto{0}{gZ_1} \right) - h_0 - T_0 (S_1 - S_0)$$

$$= (h_1 - T_0 S_1) - (h_0 - T_0 S_0)$$

$$= b_1 - b_0$$

$b = h - T_0 S$: steady flow availability function



Effectiveness: ε

It is a better measure of the usefulness of the process to compare the useful output of the process with the loss of availability of the system. The useful output of a system is given by the increase of availability of the surroundings.

$$\varepsilon = \frac{\text{increase of availability of surroundings}}{\text{loss of availability of system}}$$

$$= \frac{\text{increase of availability of system}}{\text{loss of availability of surroundings}} \quad \text{for compression or heating process}$$