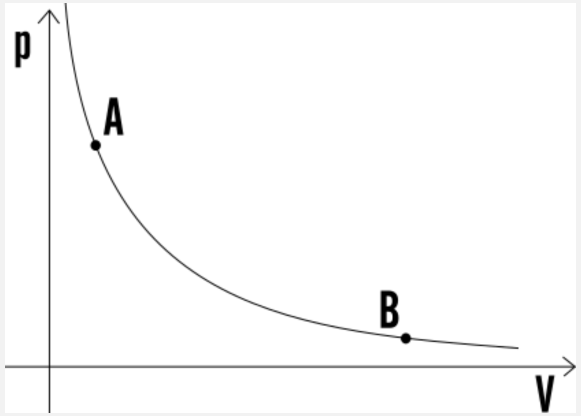
THERMODYNAMICS
MACHINES

University of Teramo

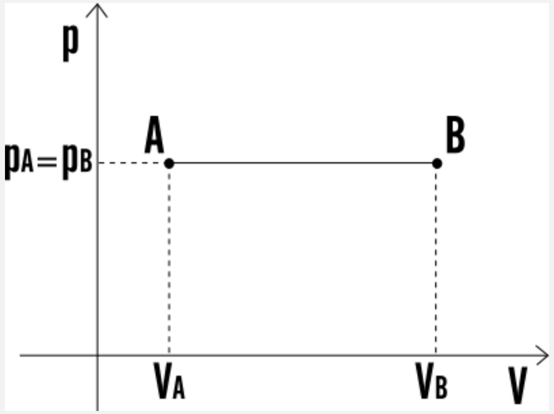
SUMMARY



$$Q_{AB} = nRTln\left(\frac{V_B}{V_A}\right)$$

$$W_{AB} = nRTln\left(\frac{V_B}{V_A}\right)$$

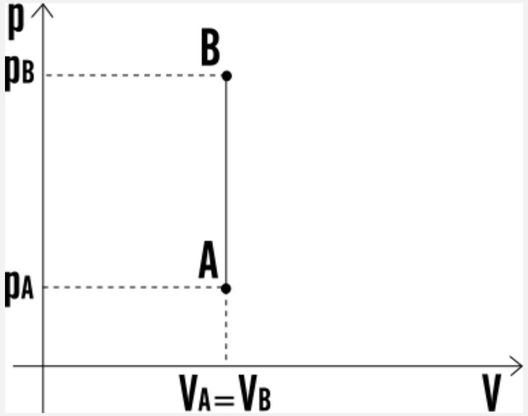
$$\Delta U_{AB} = 0$$



$$Q_{AB} = nc_P(T_B - T_A)$$

$$W_{AB} = p_A(V_B - V_A)$$

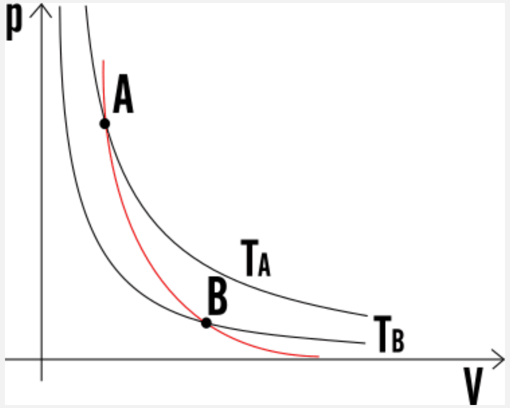
$$\Delta U_{AB} = nc_V(T_B - T_A)$$



$$Q_{AB} = nc_V(T_B - T_A)$$

$$W_{AB} = 0$$

$$\Delta U_{AB} = Q_{AB} = nc_V(T_B - T_A)$$



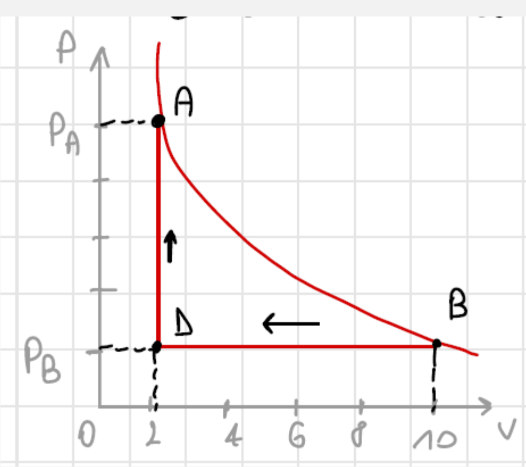
$$Q_{AB} = 0$$

$$W_{AB} = -nc_V\,(T_B - T_A)$$

$$\Delta U_{AB} = -W_{AB} = nc_V(T_B - T_A$$

Example

An ideal gas is slowly compressed at a constant pressure of 2 atm from 10 L to 2 L. In the figure, the transformation is represented as path BD, in which heat is released. Subsequently, heat is supplied to the gas, kept at constant volume, while pressure and temperature are raised (DA), until the temperature returns to its original value ($T_A=T_B$). a) Calculate the total work done by the gas in the BDA transformation and b) the total heat absorbed by the gas.



Example

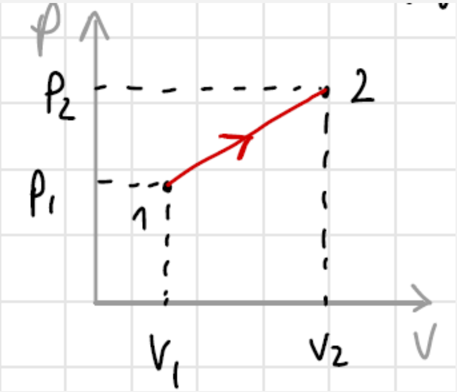
A cylinder divided by a movable piston contains 96 g of O_2 initially at pressure p_i=150 kPa and at temperature T_i=290 K. A) Determine the initial volume of gas.

Subsequently, the gas expands at constant pressure, performing work W=7.2 kJ. B) Calculate its final volume.

Finally, the gas pressure is increased to p_f=300 kPa through an isochoric transformation. C) Determine the work done by the gas in the entire process.

Example

Consider 2 moles of an ideal diatomic gas initially at pressure p_1=2atm and temperature T_1=300K. Starting from this state, the gas follows the reversible expansion shown in the figure, reaching state 2, where $2p_1=p_2$ and $V_2=3V_1$. Determine: a) the volume V_1 and the temperature T_2; b) the internal energy change of the gas $\Delta U_{1,2}$; c) the heat exchanged $Q_{1,2}$



Example

A diatomic gas occupies a volume $V_A=0.03\ m^3$ and has a pressure $p_A=3x10^5$ Pa. Keeping the volume constant, the gas is cooled to 180 K and brought to a pressure $p_B=p_A/3$. Finally, through an isobaric transformation, a volume V is reached$_C$=$V_A/3$.

I want to find T_A, T_C, Q_{AB}, Q_{BC}, Q_{CA}, U_{AB}, U_{BC}, U_{CA}, L_{CA}. Draw the transformations on the pV.

Example

Two moles of an ideal monatomic gas go from initial state A to final state C through an isobaric expansion AB, followed by an adiabatic expansion BC. The temperature at A and C is the same and equals $T_A=T_C=18°C$; $p_A=2x10^5$ Pa; $V_B=2V_A$. Calculate: a) the value of the thermodynamic variables p, V, T at the three points; b) the amount of heat exchanged in the transformations from A a C. Draw the graph of the transformation on the pV.

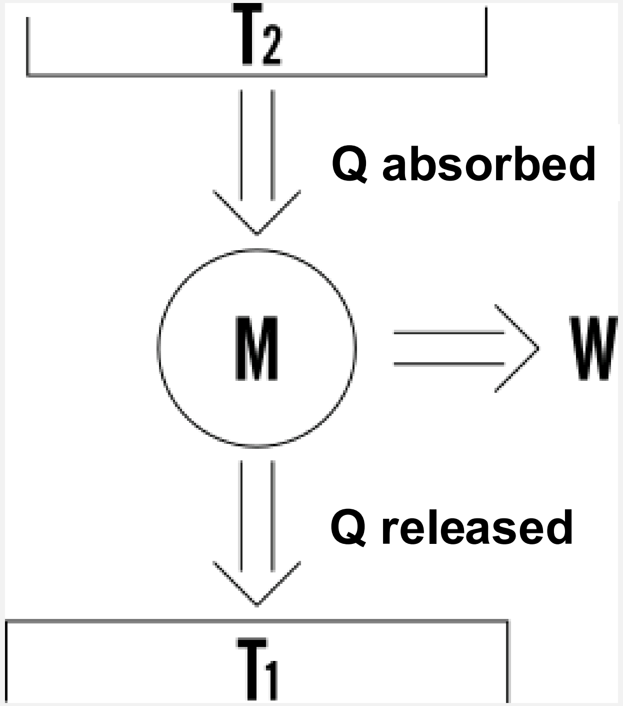
Alone!

Example

An ideal monatomic gas occupies in state A a volume V_A=5 L at atmospheric pressure and temperature T_A=300 K. It is heated at constant volume up to state B at pressure p_B=3atm. Then it expands isothermally up to state C at pressure p_C=1 atm, and finally is compressed isobarically up to the initial state A. a) Draw on the pV the graph of the transformation undergone by the gas and calculate the number of moles n of which the gas consists and the thermodynamic coordinates (p, V, T) of states A, B and C; b) calculate the heat Q, the work L and the internal energy change ΔU for the transformations AB, BC, CA and for the entire cycle.

Alone!

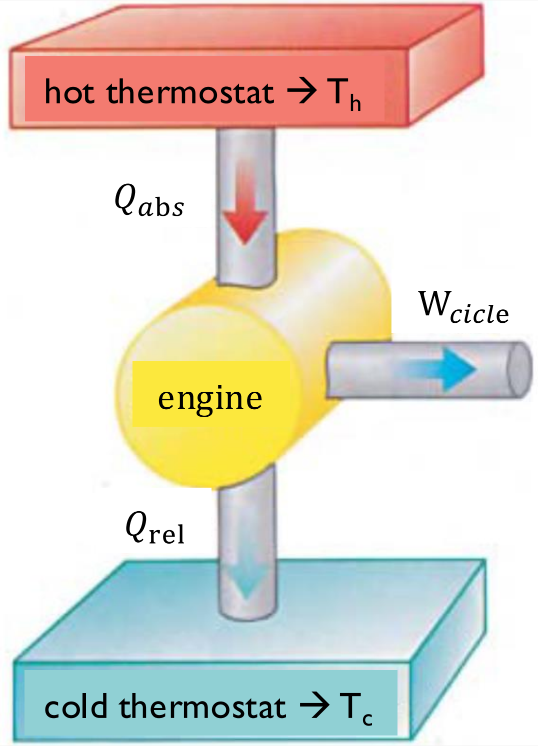
HEAT ENGINES



A high-temperature source transfers a quantity of heat Q to the system to perform work, and the same system then transfers a quantity of heat to the second thermal source at a lower temperature

A heat engine must necessarily operate on a cycle.
For a cycle, the first law of thermodynamics states:
$\Delta U = \Delta Q - W \rightarrow \Delta Q = W$

HEAT ENGINES



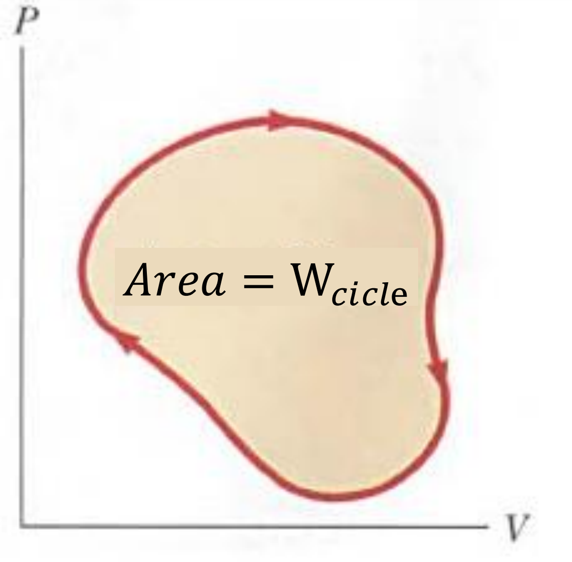
Absorb Q_{abs} , release Q_{rel} and perform work W_{cicle}

If $W_{cicle}>0$ HEAT ENGINE

If $W_{cicle}<0$ REFRIGERATOR

$$Q_{cicle} = Q_{abs} + Q_{rel} = Q_{abs} - |Q_{rel}| \qquad \Delta U_{cicle} = 0 \quad W_{cicle} = Q_{cicle}$$

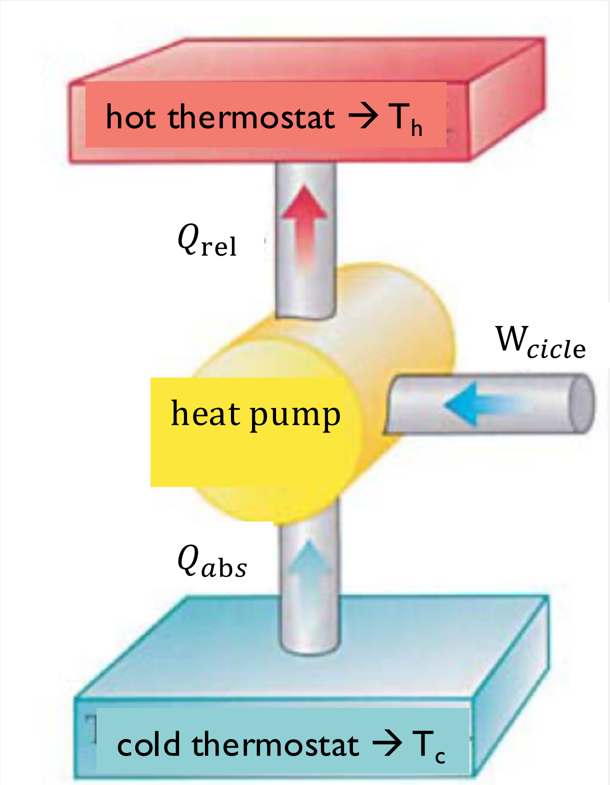
$$W_{cicle} = Q_{cicle} = Q_{abs} - |Q_{rel}|$$



EFFICIENCY is defined as:

$$\eta = \frac{W_{cicle}}{Q_{abs}} = \frac{Q_{abs} - |Q_{rel}|}{Q_{abs}} = 1 - \frac{|Q_{rel}|}{Q_{abs}} < 1$$

REFRIGERATORS



In a refrigerator:

$$Q_{cicle} = Q_{abs} + Q_{rel} = Q_{abs} - |Q_{rel}| \qquad \Delta U_{cicle} = 0 \qquad W_{cicle} = Q_{cicle}$$

$$W_{cicle} = Q_{cicle} = Q_{abs} - |Q_{rel}|$$

The Coefficient of Performance (COP) is defined as:

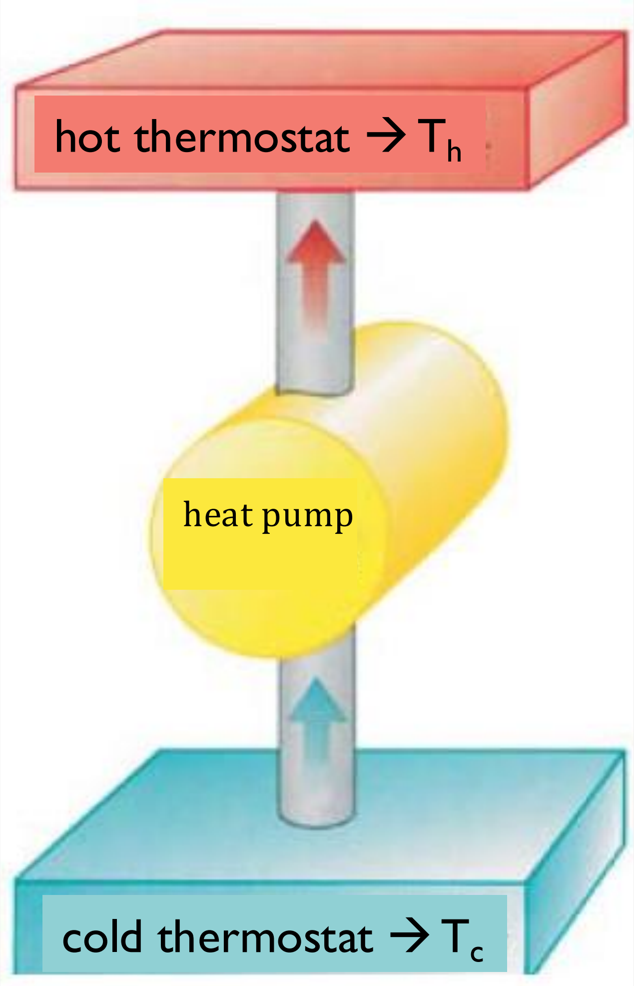
$$COP = \frac{Q_{abs}}{|W_{cicle}|} = \frac{|Q_{rel}| - |W_{cicle}|}{|W_{cicle}|} = \frac{|Q_{rel}|}{|W_{cicle}|} - 1 > 0$$

Why is it >0?

$L_{ciclo} = Q_{ASS} - |Q_{ced}|$

$|W_{cicle}| = -Q_{abs} + |Q_{rel}|$ hence $|W_{cicle}| < |Q_{rel}|$

CLAUSIUS STATEMENT

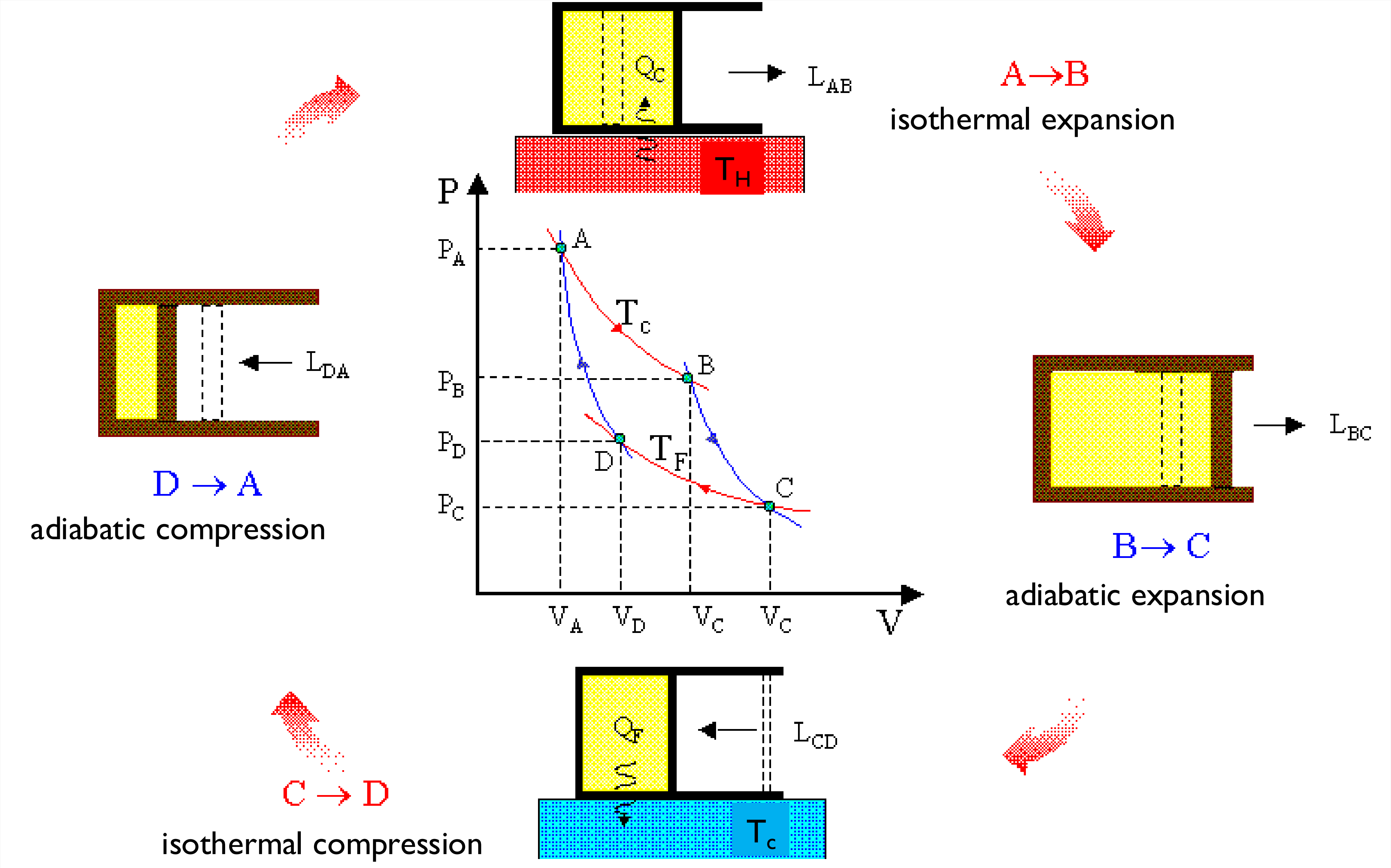


It is impossible to build a machine whose sole result is the transfer of heat from a cold body to a hot body:

This means it is impossible to have $COP = 1$

CARNOT ENGINE

$L = W$



A→B
isothermal expansion

B→C
adiabatic expansion

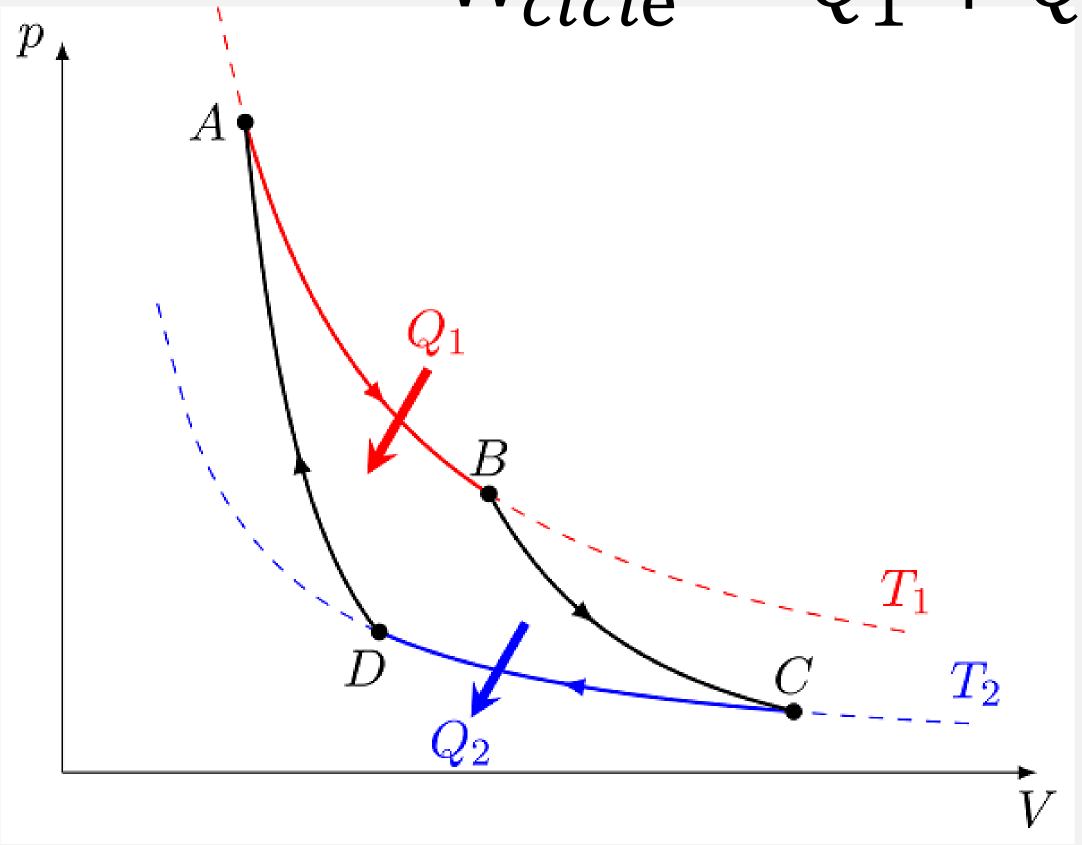
C → D
isothermal compression

D → A
adiabatic compression

CARNOT ENGINE

$\Delta U = 0$

$$W_{cicle} = Q_1 + Q_2$$



$$W_{AB} = nRT_1 \ln\left(\frac{V_B}{V_A}\right) = Q_{AB} = Q_1 > 0$$

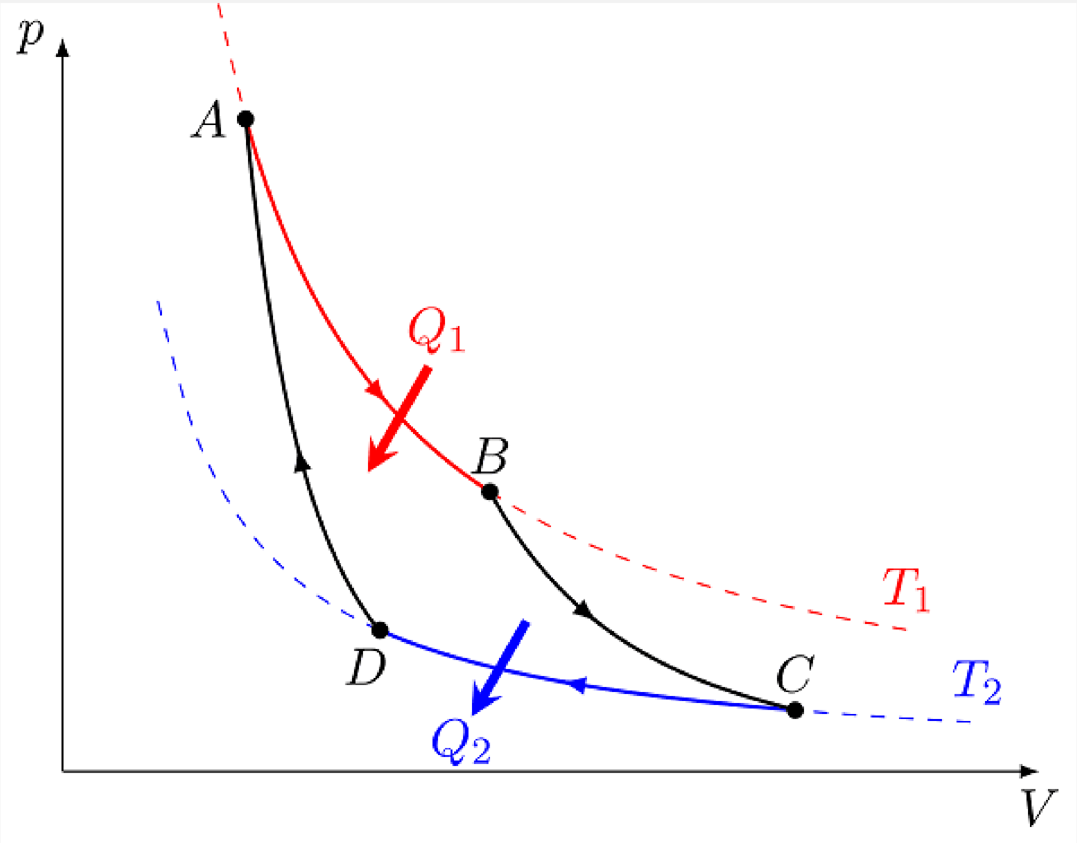
$$Q_{BC} = 0 \quad L_{BC} = -\Delta U_{BC} = -nc_V(T_C - T_B) = nc_V(T_B - T_C)$$

$$W_{CD} = nRT_2 \ln\left(\frac{V_D}{V_C}\right) = Q_{CD} = Q_2 < 0$$

$$Q_{DA} = 0 \quad W_{DA} = -\Delta U_{DA} = -nc_V(T_A - T_D) = nc_V(T_D - T_A)$$

$$\eta = \frac{W_{cicle}}{Q_{abs}} = 1 - \frac{|Q_{rel}|}{Q_{abs}} = 1 - \frac{\cancel{nR}T_2 \ln\left(\frac{V_C}{V_D}\right)}{\cancel{nR}T_1 \ln\left(\frac{V_B}{V_A}\right)} = 1 - \frac{T_2 \ln\left(\frac{V_C}{V_D}\right)}{T_1 \ln\left(\frac{V_B}{V_A}\right)}$$

CARNOT ENGINE



$$W_{AB} = nRT_1 \ln\left(\frac{V_B}{V_A}\right) = Q_{AB} = Q_1 > 0$$

$$Q_{BC} = 0 \quad L_{BC} = -\Delta U_{BC} = -nc_V(T_C - T_B) = nc_V(T_B - T_C)$$

$$W_{CD} = nRT_2 \ln\left(\frac{V_D}{V_C}\right) = Q_{CD} = Q_2 < 0$$

$$Q_{DA} = 0 \quad W_{DA} = -\Delta U_{DA} = -nc_V(T_A - T_D) = nc_V(T_D - T_A)$$

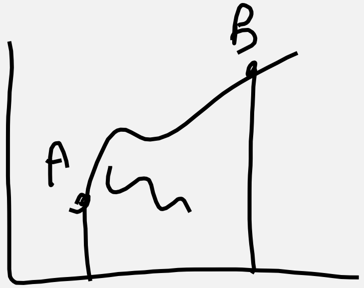
$$\eta = \frac{W_{cicle}}{Q_{abs}} = 1 - \frac{|Q_{rel}|}{Q_{abs}} = 1 - \frac{nRT_2 \ln\left(\frac{V_C}{V_D}\right)}{nRT_1 \ln\left(\frac{V_B}{V_A}\right)} = 1 - \frac{T_2 \ln\left(\frac{V_C}{V_D}\right)}{T_1 \ln\left(\frac{V_B}{V_A}\right)}$$

$$\begin{cases} T_1 V_B^{\gamma-1} = T_2 V_C^{\gamma-1} \\ T_1 V_A^{\gamma-1} = T_2 V_D^{\gamma-1} \end{cases}$$

$$\left(\frac{V_B}{V_A}\right)^{\gamma-1} = \left(\frac{V_C}{V_D}\right)^{\gamma-1} \quad \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

$$\eta = 1 - \frac{T_2}{T_1} < 1$$

ENTROPY



Let us start from an infinitesimal reversible thermodynamic transformation

$$Q - W = \Delta U \qquad \underbrace{\delta Q - \delta W = dU} \qquad \delta Q = nc_V dT + pdV$$

It is not a state function

$$\frac{\delta Q}{T} = \frac{nc_V dT}{T} + \frac{nR\overset{?}{\cancel{T}}dV}{\cancel{T}V} \qquad \int_A^B \frac{\delta Q}{T} = \int_{T_A}^{T_B} \frac{nc_V}{T} dT + \int_{V_A}^{V_B} \frac{nR}{V} dV = \boxed{nc_V \ln\left(\frac{T_B}{T_A}\right) + nR\ln\left(\frac{V_B}{V_A}\right)}$$

is a state function

WE THEREFORE DEFINE ENTROPY:

$${}_{rev}\int_A^B \frac{\delta Q}{T} = S(B) - S(A) = \Delta S_{AB}$$

Variazione di entropia

ENTROPY

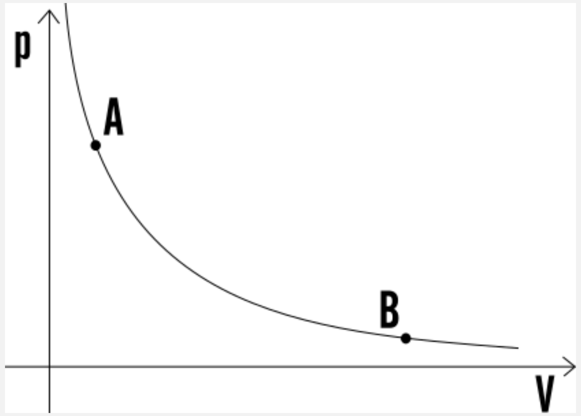
$$\Delta S_{AB} = nc_V \ln\left(\frac{T_B}{T_A}\right) + nRln\left(\frac{V_B}{V_A}\right)$$

$${}_{rev}\int_A^B \frac{\delta Q}{T} = S(B) - S(A) = \Delta S_{AB}$$

REVERSIBLE TRANSFORMATIONS

ISOTHERMAL	**ISOBARIC**	**ISOCHORIC**	**ADIABATIC**
$Q_{AB} = \mathrm{W}_{AB} = nRTln\left(\frac{V_B}{V_A}\right)$	$Q_{AB} = nc_P(T_B - T_A)$ $\frac{dQ}{T} = \frac{nc_P dT}{T}$	$Q_{AB} = nc_V(T_B - T_A)$ $\frac{dQ}{T} = \frac{nc_V dT}{T}$	$Q_{AB} = 0$
$\Delta S_{AB} = nRln\left(\frac{V_B}{V_A}\right)$	$\Delta S_{AB} = nc_V \ln\left(\frac{T_B}{T_A}\right) + nRln\left(\frac{V_B}{V_A}\right)$	$\Delta S_{AB} = nc_V \ln\left(\frac{T_B}{T_A}\right)$	$\Delta S_{AB} = 0$

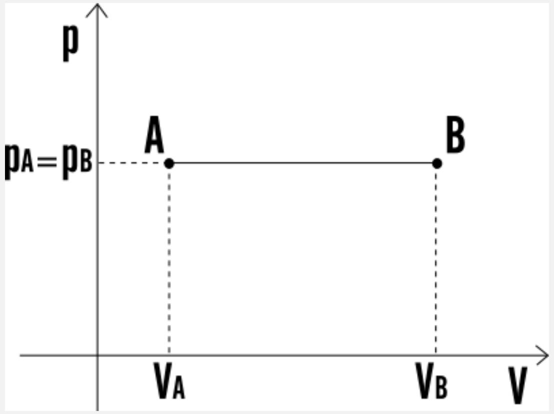
SUMMARY



$$Q_{AB} = nRTln\left(\frac{V_B}{V_A}\right)$$

$$L_{AB} = nRTln\left(\frac{V_B}{V_A}\right)$$

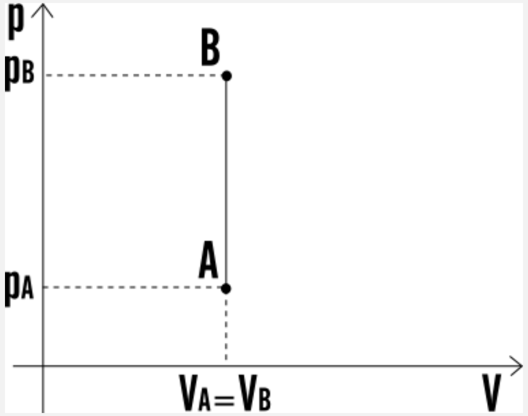
$$\Delta U_{AB} = 0$$



$$Q_{AB} = nc_P(T_B - T_A)$$

$$L_{AB} = p_A(V_B - V_A)$$

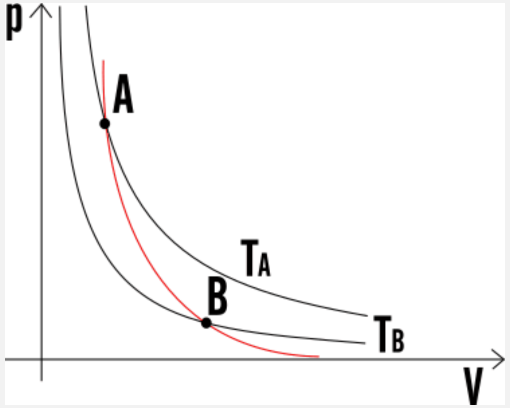
$$\Delta U_{AB} = nc_V(T_B - T_A)$$



$$Q_{AB} = nc_V(T_B - T_A)$$

$$L_{AB} = 0$$

$$\Delta U_{AB} = Q_{AB} = nc_V(T_B - T_A)$$



$$Q_{AB} = 0$$

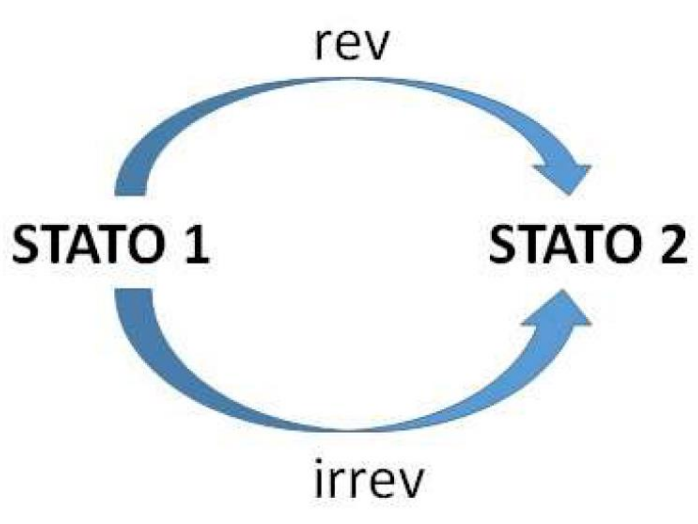
$$L_{AB} = -nc_V\ (T_B - T_A)$$

$$\Delta U_{AB} = -L_{AB} = nc_V(T_B - T_A)$$

ENTROPY

$$\Delta U = Q_{rev} - L_{rev} = Q_{\text{non rev}} - \mathrm{W}_{\text{non rev}} \qquad Q_{rev} - \underbrace{Q_{\text{non rev}} = \mathrm{W}_{rev} - \mathrm{W}_{\text{non rev}}}$$

$$\longrightarrow \mathrm{W}_{rev} > \mathrm{W}_{\text{non rev}} \qquad \mathrm{W}_{rev} - \mathrm{W}_{\text{non rev}} > 0 \qquad \underbrace{Q_{rev} - Q_{\text{non rev}}} > 0$$



$$\frac{Q_{rev}}{T} - \frac{Q_{\text{non rev}}}{T} > 0 \qquad \frac{Q_{rev}}{T} > \frac{Q_{\text{non rev}}}{T} \qquad \int_A^B \frac{\delta Q_{rev}}{T} \geq \int_A^B \frac{\delta Q}{T}$$

$$\boxed{\Delta S_{AB} \geq \int_A^B \frac{\delta Q}{T}}$$

Clausius Inequality

The entropy of an isolated system can never decrease: it remains constant in a system of reversible transformations and increases whenever an irreversible transformation takes place