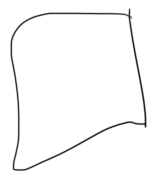


isolated system

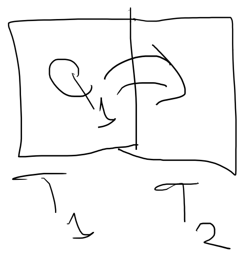
$$\oint \frac{dQ}{T} \leq 0$$

$$\underbrace{(irr)\int_A^B \frac{dQ}{T}}_{=0} + (rev)\int_B^A \frac{dQ}{T} \leq 0$$

$$S(A) - S(B) \leq 0$$

$$\Rightarrow \boxed{S(B) \geq S(A)}$$

Example



$$\Delta S = \frac{-Q_1}{T_1} + \frac{Q_1}{T_2} = Q_1\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\Delta S \geq 0$$

$$T_1 > T_2 > 0 \Rightarrow \frac{1}{T_1} < \frac{1}{T_2} \Rightarrow \frac{1}{T_2} - \frac{1}{T_1} > 0 \Rightarrow Q_1 \geq 0$$

$$T_2 > T_1 > 0 \Rightarrow \frac{1}{T_1} > \frac{1}{T_2} \Rightarrow \frac{1}{T_2} - \frac{1}{T_2} < 0 \Rightarrow Q_1 \leq 0$$

$T_1 > 0 > T_2$ $\qquad T_2 < 0 \Rightarrow \frac{1}{T_2} < 0$

$$\frac{1}{T_1} > 0$$

$$\frac{1}{T_2} - \frac{1}{T_1} < 0 \Rightarrow Q_1 < 0$$

$$dU = T\,dS - P\,dV$$

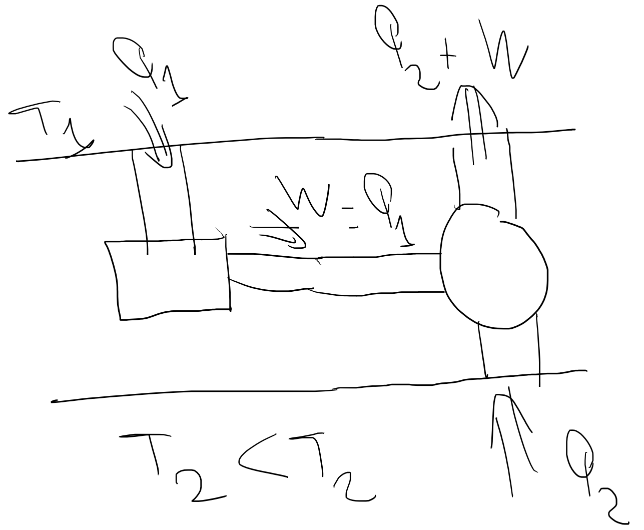
$$\Rightarrow dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V$$

2^{nd} Law: Heat can not flow spontaneously from a colder reservoir to a hotter one.

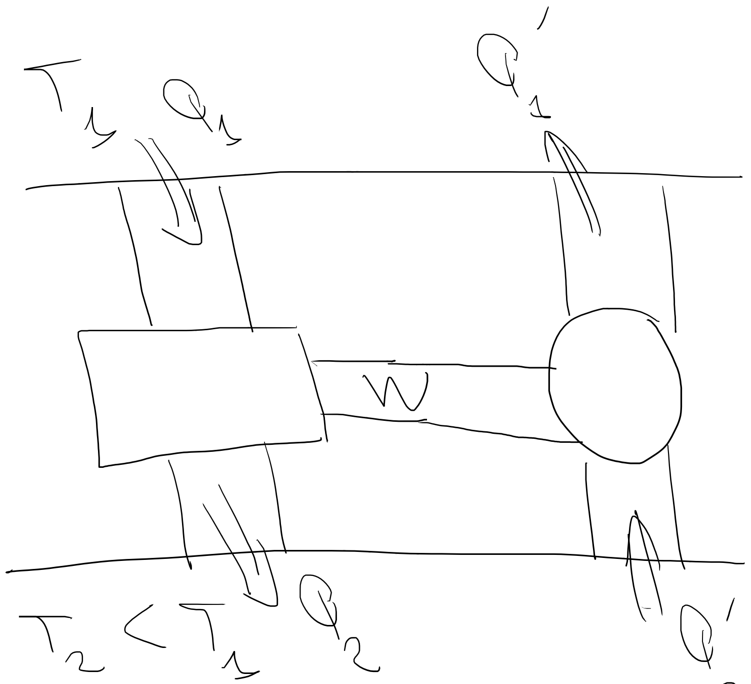
2^{nd} Law: No machine can convert heat completely into work

Assume ∃ a machine that can convert heat completely into work.



can not exist!

No machine can be more efficient than a Carnot engine



$$\frac{W}{Q_1'} = 1 - \frac{T_2}{T_1}$$

$$\frac{W}{Q_1} > \frac{W}{Q_1'}$$

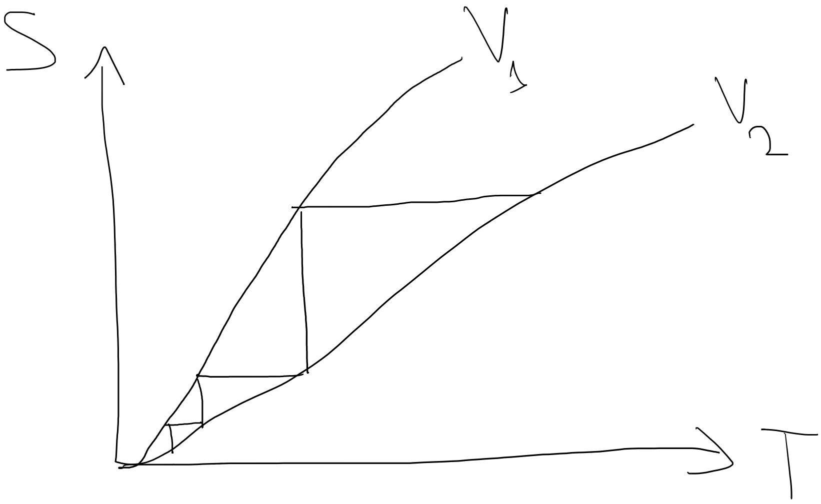
$$\Rightarrow Q_1 < Q_1'$$

more efficient than Carnot engine $\frac{W}{Q_1} > 1 - \frac{T_2}{T_1}$

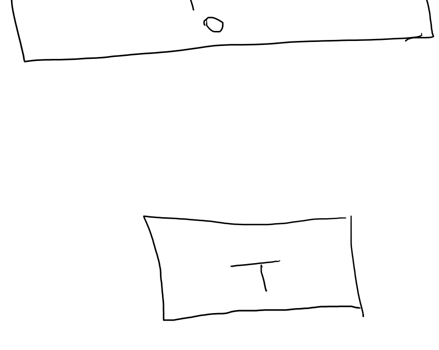
This hypothetical system takes heat from the colder reservoir and dumps it into the hotter reservoir. This can not be!

3^{rd} Law of Thermodynamics

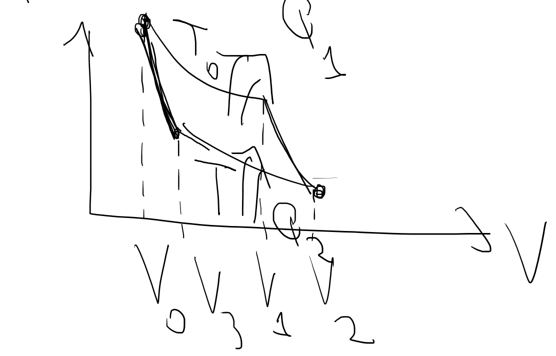
$$S(V, T=0) = 0$$



Example



$T < T_0$



$$\frac{V_0}{V_3} = \frac{V_1}{V_2} \qquad V_1, V_3, Q_1, Q_2$$

$$\frac{Q_1}{Q_2} = \frac{T_0}{T} \qquad V_1 = \frac{V_2}{V_3} V_0 = (V_2 V_0) \frac{1}{V_3}$$

$$Q_1 = Nk T_0 \ln\left(\frac{V_1}{V_0}\right) \qquad V_1(V_0, V_2, T, T_0)$$

$$Q_2 = Nk T \ln\left(\frac{V_2}{V_3}\right) \qquad V_3(V_0, V_2, T, T_0)$$

$$T_0 V_0^{2/3} = T V_3^{2/3} \qquad V_3^{2/3} = \frac{T_0}{T} V_0^{2/3}$$

$$Q_2 = NkT \ln\left(\frac{V_2}{\left(\frac{T_0}{T}\right)^{3/2} V_0}\right)$$

$$= NkT \ln\left(\left(\frac{T}{T_0}\right)^{3/2} \frac{V_2}{V_0}\right) \to 0$$

Heat capacity

$$C = \frac{\Delta Q}{\Delta T} = T \frac{\Delta S}{\Delta T}$$

$$C_x = T\left(\frac{\partial S}{\partial T}\right)_x \Rightarrow \Delta Q = C \Delta T$$

$$S(P,T) \overset{T\to 0}{=} d(P)\,T^{\alpha} + \Theta\left(T^{\beta > \alpha}\right) \quad \alpha > 0$$

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p \overset{T\to\infty}{=} \alpha\, T\, d(P)\, T^{\alpha-1}$$

$$C_p = \alpha\, d(P)\, T^{\alpha} = \alpha S$$

$$\Delta Q = NkT \ln\left(\left(\frac{T}{T_0}\right)^{3/2} \frac{V_2}{V_0}\right)$$

$$\Delta T = \frac{\Delta Q}{C} = \boxed{\frac{NkT \ln\left(\left(\frac{T}{T_0}\right)^{3/2} \frac{V_2}{V_0}\right)}{\alpha S} = \Delta T}$$

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

Refrigerator

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

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

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

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

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

<u>Heater</u>

$$\eta = \frac{Q_2}{W} \geq 1$$