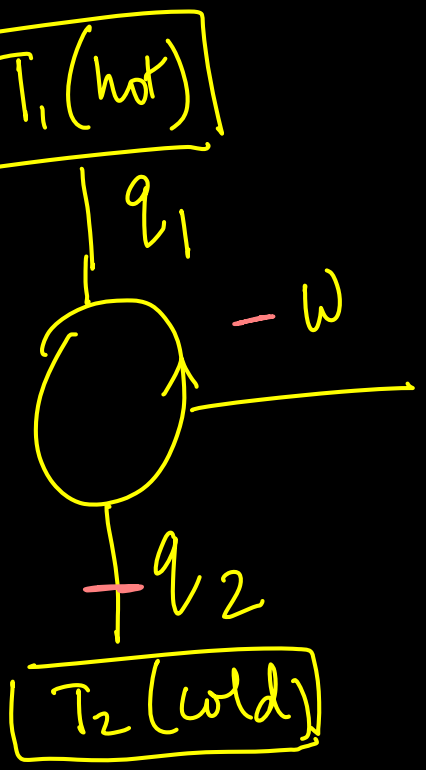
$$\left(\frac{\partial U}{\partial V}\right)_T = \pi_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\left(\frac{\partial H}{\partial P}\right)_T = \eta_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

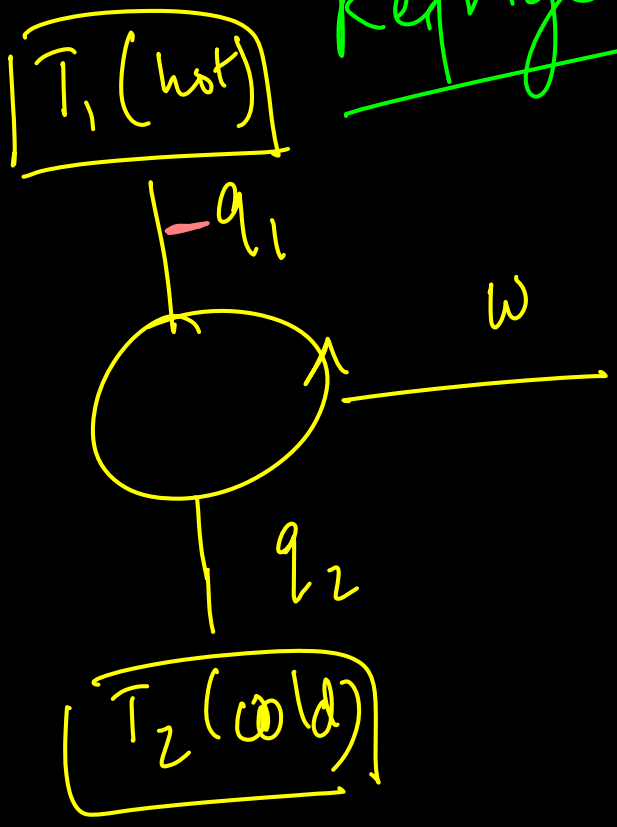
$$dU = dq + dw$$

$$\oint dU = 0$$

Engine



Refrigerator



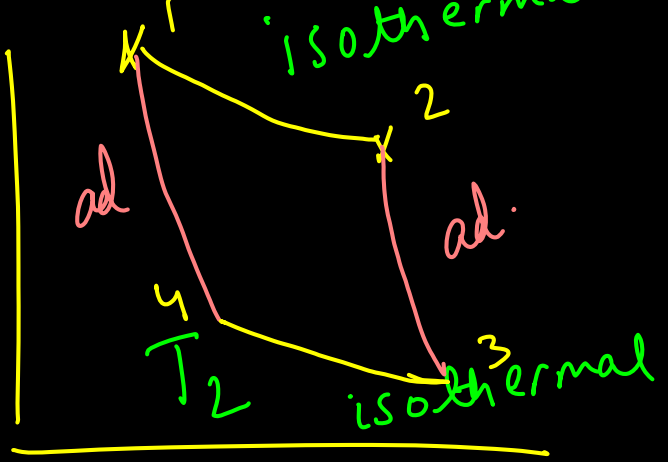
Clausius: All spontaneous processes are irreversible

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

Clausius Inequality

$$\oint \frac{dq_{rev}}{T} = 0 \qquad \oint \frac{dq_{irr}}{T} < 0$$

Reversible Carnot cycle



$1 \to 2$ $\Delta U = q_1 + w_1$

$2 \to 3$ $\Delta U = w_1^{ad}$

$3 \to 4$ $\Delta U = q_2 + w_2$

$4 \to 1$ $\Delta U = w_2^{ad}$

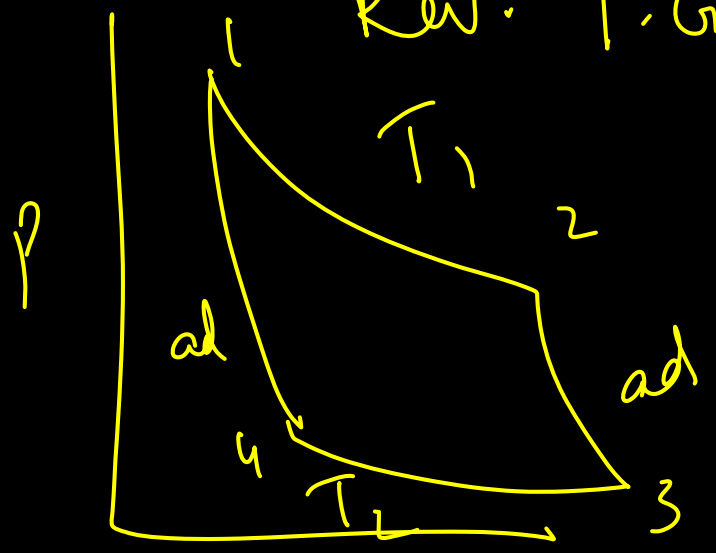
$$\text{Eff. } \varepsilon = \frac{W_{total}}{Q_{input}} = \frac{-(w_1 + w_1^{ad} + w_2 + w_2^{ad})}{q_1}$$

$\oint dU = 0$

$-w = q_1 \varepsilon$

$$\varepsilon = \frac{q_1 + q_2}{q_1} = 1 + \frac{q_2}{q_1} < 100\%$$

Rev. 1. Gr.



1-2 $\Delta U = 0$: $q_1 = -w_1 = RT_1 \ln \frac{V_2}{V_1}$

2-3 $w_1^{ad} = c_V (T_2 - T_1)$

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1}$$

3→4 $\Delta U = 0$ $q_2 = -w_2$

$= RT_2 \ln(V_4/V_3)$

4→1 $q = 0$ $w_2^{ad} = c_V (T_1 - T_2)$

$$T_1/T_2 = \left(\frac{V_4}{V_1}\right)^{\gamma-1}$$

$$\frac{q_2}{q_1} = -\frac{T_2}{T_1}$$

$$\frac{q_2}{T_2} + \frac{q_1}{T_1} = 0$$

$$\oint \frac{dq_{rev}}{T} = 0$$

$$\varepsilon = 1 + \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1}$$

$$T_2 \to 0\ K$$

$$W = \frac{T_2 - T_1}{T_1} q_1 = \frac{-T_2 + T_1}{T_2} q_2$$

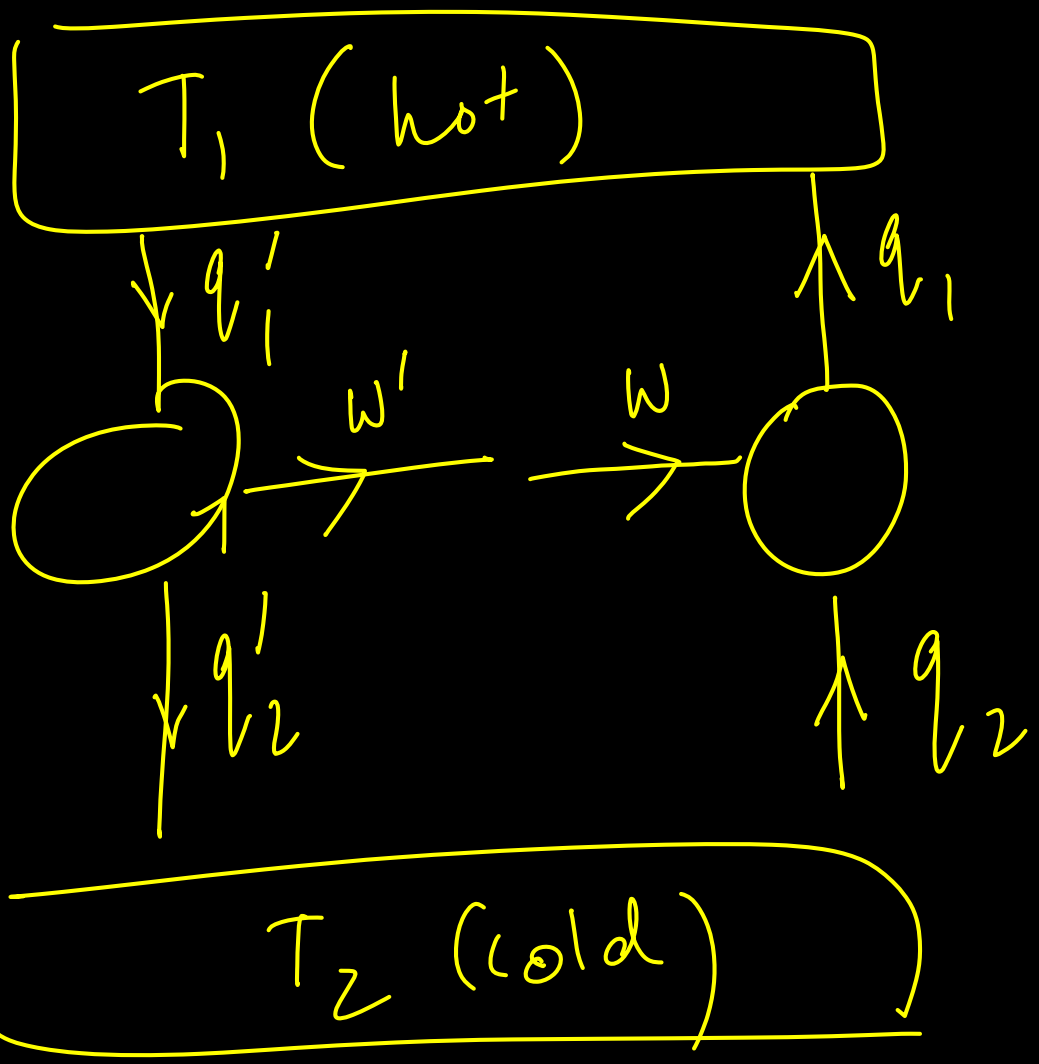
$\varepsilon' > \varepsilon$

Carrot rev.

$\varepsilon' > \varepsilon$

$$\frac{-w'}{q_1'} > \frac{-w}{q_1}$$

$$\Rightarrow \frac{w}{q_1'} > -\frac{w}{q_1}$$



$-w' = w$

$$-\frac{w'}{q_1'} > -\frac{w}{q_1} \qquad \frac{w}{q_1'} > -\frac{w}{q_1} \qquad q_1 < 0 \quad q_1' > 0$$

$$(q_1' + q_1) < 0 \qquad q_1 < -q_1'$$