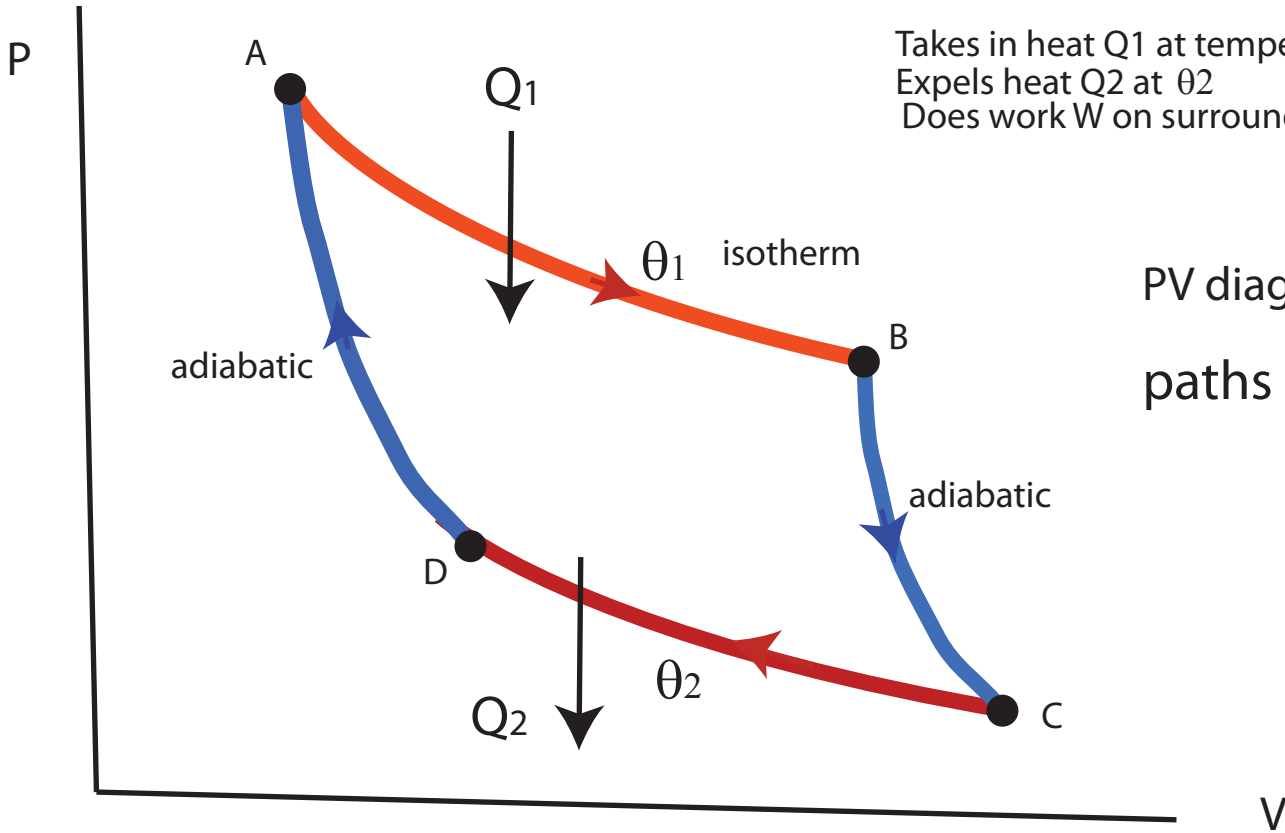


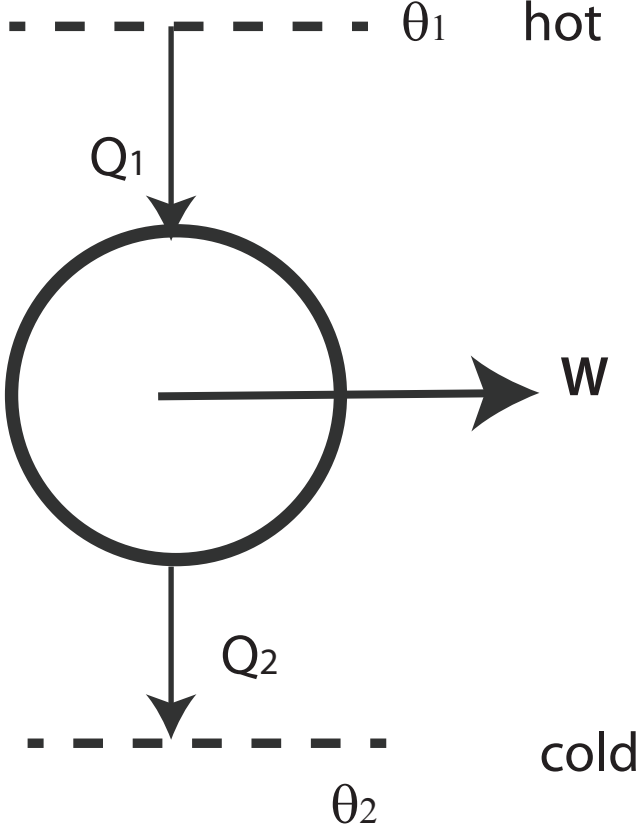
**Carnot cycle**



Takes in heat  $Q_1$  at temperature  $\theta_1$   
Expels heat  $Q_2$  at  $\theta_2$   
Does work  $W$  on surroundings

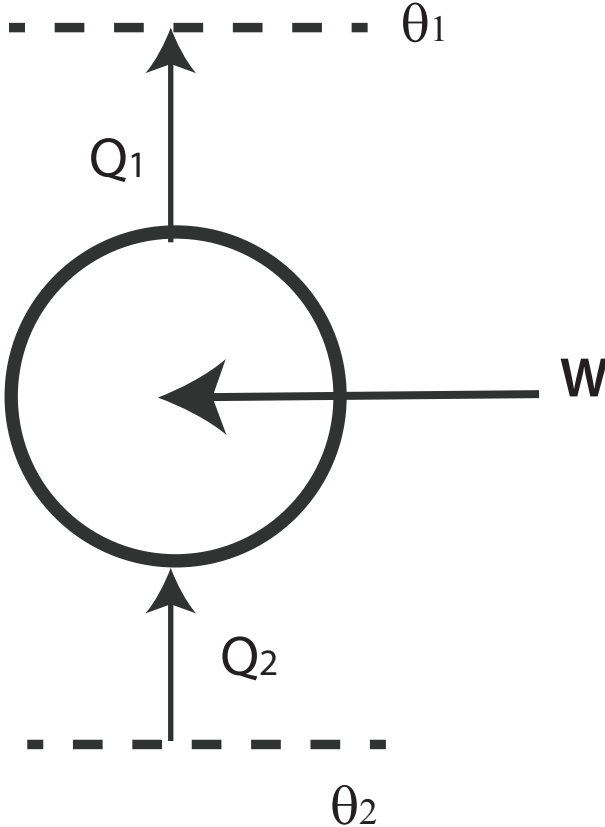
PV diagram  
paths reversible

**Symbolic diagram**

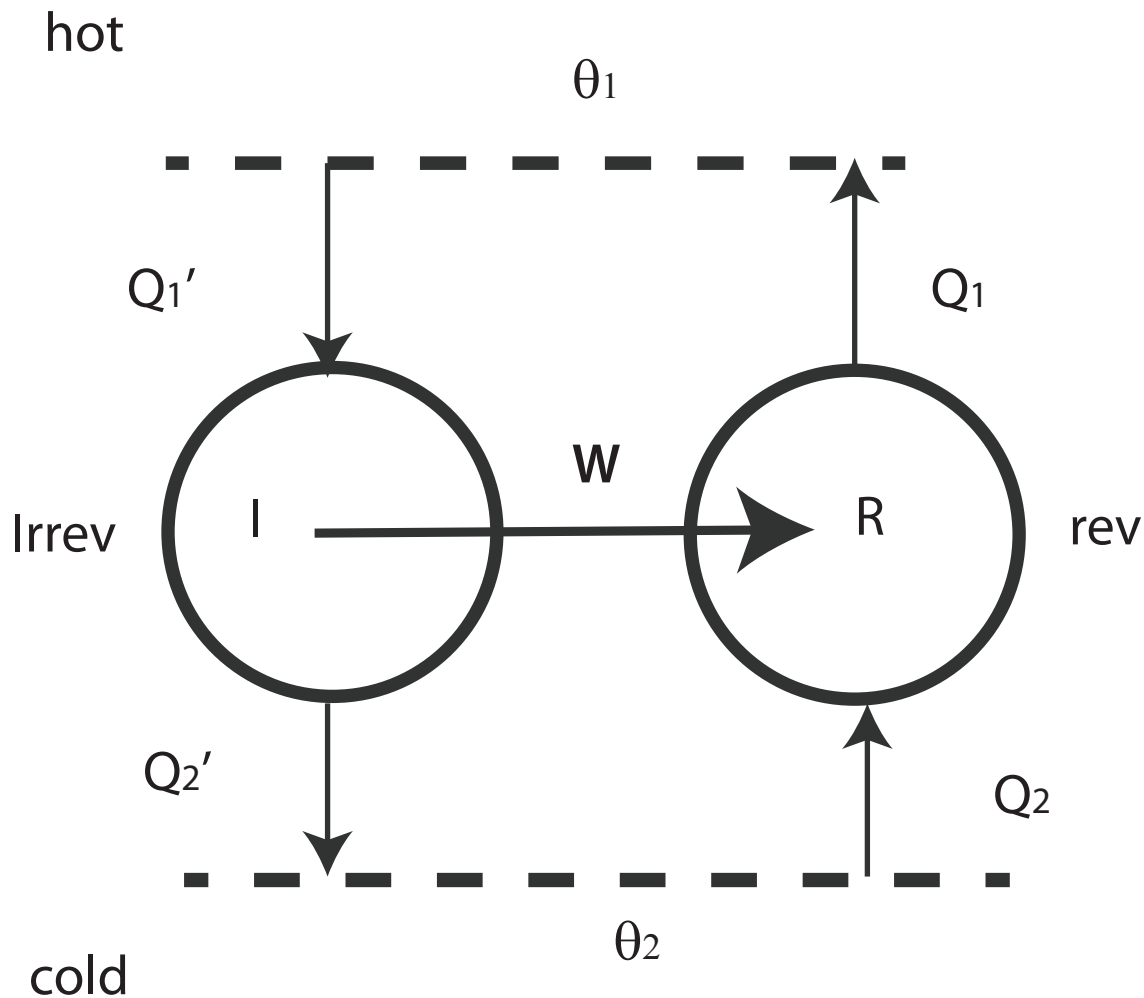


Efficiency  
 $\eta = W/Q_1$   
 $= 1 - Q_2/Q_1$

Refrigerator (reverse of Carnot on page 1)



## One engine drives the other



If I is irreversible can show no irreversible cycle more efficient than Carnot cycle.

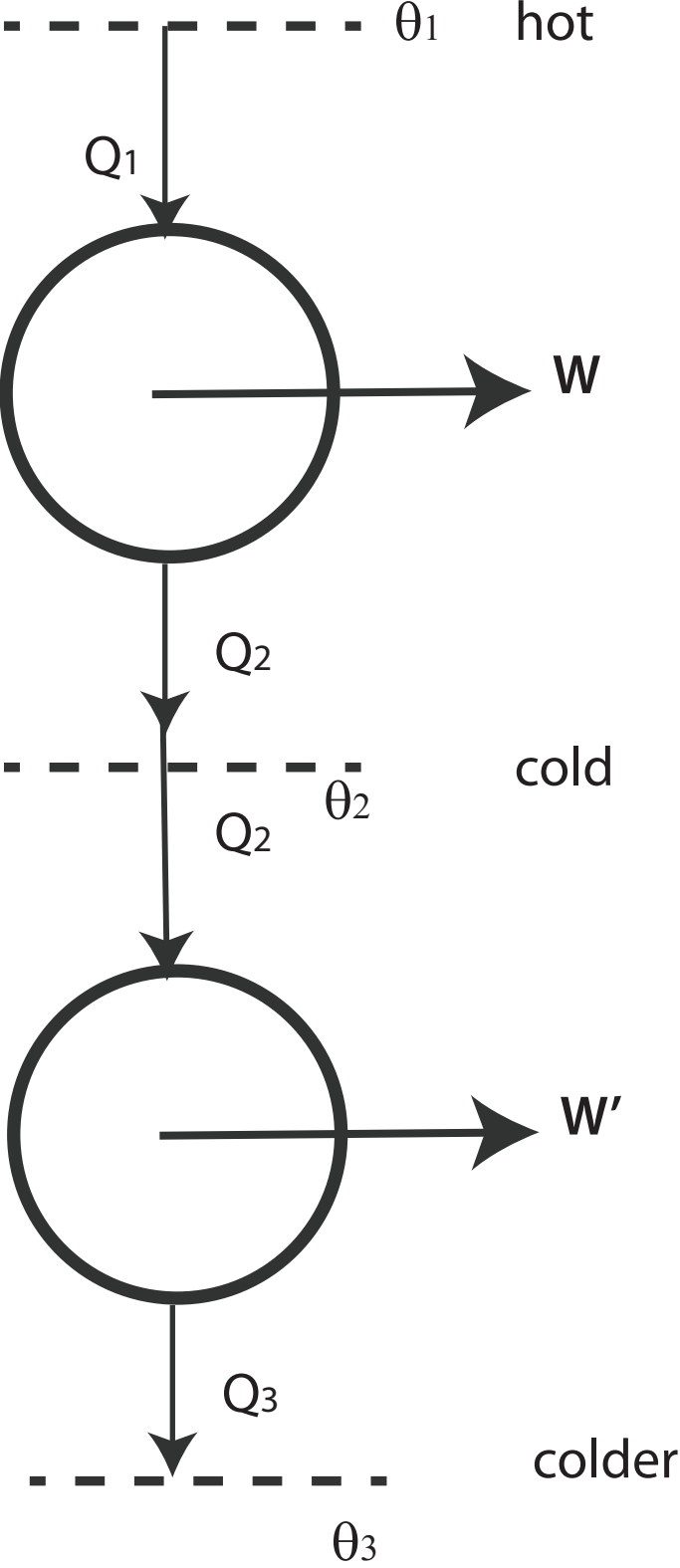
If  $\eta(\text{irrev}) > \eta(\text{rev})$ , then  $Q_1' < Q_1$ ,

Nonsense as implies net heat would flow to hot reservoir

Now make both cycles Carnot cycles. Must have  $Q_1' = Q_1$ .  
Efficiencies must be universal function of  $\theta_1$  and  $\theta_2$  ONLY

THUS  $Q_1/Q_2 = f(\theta_1, \theta_2)$

Now place two Carnot cycles in series



**For two Carnot cycles in series (previous page)**

$$\frac{Q_1}{Q_3} = \frac{Q_1}{Q_2} \frac{Q_2}{Q_3} \text{ and thus } f(\theta_1, \theta_3) = f(\theta_1, \theta_2)f(\theta_2, \theta_3)$$

Must have  $f(\theta_1, \theta_2) = \frac{\varphi(\theta_1)}{\varphi(\theta_2)}$  Hence  $\frac{Q_1}{Q_2} = \frac{\varphi(\theta_1)}{\varphi(\theta_2)}$

DEFINE  $T = \varphi(\theta)$  and thus  $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$

Now need to show T is the familiar Absolute T in Kelvin using ideal gas laws.

$$Q_1 = \int_A^B PdV = nR\theta_1 \ln \frac{V_A}{V_B} \quad Q_2 = nR\theta_2 \ln \frac{V_C}{V_D}$$

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} = \frac{\theta_1 \ln \frac{V_A}{V_B}}{\theta_2 \ln \frac{V_C}{V_D}}$$

For adiabatic path BC,  $P_B V_B^\gamma = P_C V_C^\gamma$  or  $\theta_1 V_B^{\gamma-1} = \theta_2 V_C^{\gamma-1}$  (used  $P_B V_B = nR\theta_1$ )

Similarly, for path DA  $\theta_1 V_A^{\gamma-1} = \theta_2 V_D^{\gamma-1}$ . Hence  $\ln \frac{V_B}{V_A} = \ln \frac{V_C}{V_D}$  and  $\frac{T_1}{T_2} = \frac{\theta_1}{\theta_2}$

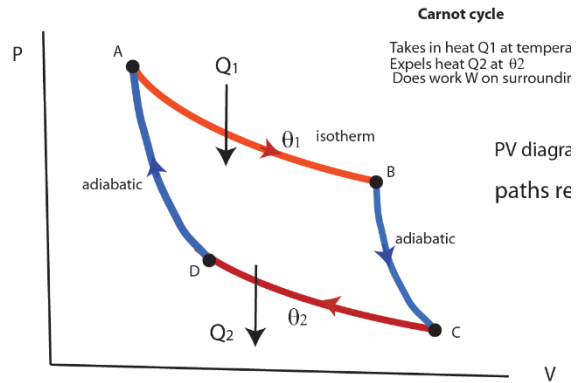
**This implies  $T = \text{constant } \theta$ . We choose constant =1, and  $T = \theta$ .**

Now adopt normal convention for sign of Q. Q positive for heat given to system from reservoir, thus for above reversible processes

$$\frac{-Q_2}{Q_1} = \frac{T_2}{T_1} \text{ or } \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0, \text{ and for tiny reversible steps } \frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} = 0$$

Or  $\oint \frac{dQ}{T} = 0$ . Hence  $\oint_A^B \frac{dQ}{T}$  is independent of path

The entropy is a function of state  $S(B, A) = \oint_A^B \frac{dQ}{T}$ . Only differences in S are well defined. History leaves no imprint on system.



First law:  $dU = TdS - PdV$

Heat capacities. Constant volume:  $C_V = T \left( \frac{\partial S}{\partial T} \right)_V$

Constant pressure:  $C_P = T \left( \frac{\partial S}{\partial T} \right)_P$  If know  $C_P$  as function of T

$$S(T_F) = S(T_I) + \int_I^F C_P \frac{dT}{T} \quad \& \quad \text{if } C_P \text{ is constant } S(T_F) = S(T_I) + C_P \ln \frac{T_F}{T_I}$$

Need to know  $S(0)$ .

New VERY useful function

HELMHOLTZ Free Energy

$$F = U - TS$$

$$dF = dU - TdS - SdT \quad \text{Use } dU = Tds - PdV$$

$$dF = -SdT - PdV$$

$$S = - \left( \frac{\partial F}{\partial T} \right)_V \quad \text{and} \quad P = - \left( \frac{\partial F}{\partial V} \right)_T$$

F function of state, deduce Maxwell relation  $\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V$

$$\text{used } \frac{\partial}{\partial V} \left( \frac{\partial F}{\partial T} \right) = \frac{\partial}{\partial T} \left( \frac{\partial F}{\partial V} \right).$$

Another free energy functional is the GIBBS Free Energy

$$G = H - TS \quad H \text{ is the enthalpy for which we had } dH = dQ(\text{rev}) + VdP$$

$$\text{Thus } dG = TdS + VdP - TdS - SdT = -SdT + VdP = \left( \frac{dG}{dT} \right) dT + \left( \frac{dG}{dP} \right) dP$$

Whence another Maxwell relation  $\left( \frac{\partial V}{\partial T} \right)_P = - \left( \frac{\partial S}{\partial P} \right)_T$

## Law of increase of S

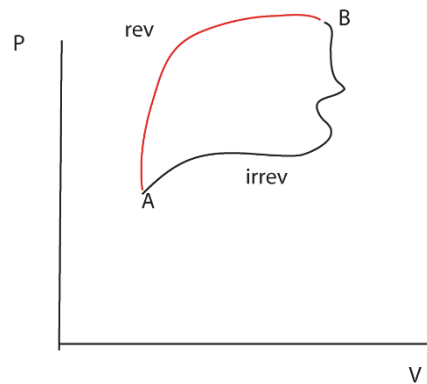
Consider two paths between A and B: one reversible, other irreversible

The efficiencies obey  $\eta_{rev} > \eta_{irrev}$

$$\text{or } 1 - \frac{(-Q_2)}{Q_1} > 1 - \frac{(-Q_2')}{Q_1'}$$

$$\text{For Carnot } \frac{(-Q_2)}{Q_1} = \frac{T_2}{T_1}$$

$$\text{Thus } \frac{(-Q_2')}{Q_1'} > \frac{T_2}{T_1} \quad \text{or} \quad \frac{dQ_1'}{T_1} + \frac{dQ_2'}{T_2} < 0$$



$$\oint \frac{dQ_{irrev}}{T} < 0$$

$$\int_a^b \frac{dQ_{irrev}}{T} < \int_a^b \frac{dQ_{rev}}{T} = S(b, a)$$

$$\text{Clausius inequality } \frac{\delta Q_{irrev}}{T} < \delta S$$

$$\text{Thermally isolated system } \delta Q_{irrev} = 0$$

THUS  $\delta S > 0$  Law of increase of entropy

All changes in isolated system lead to increase in S,

OR keep S unchanged if process is reversible.