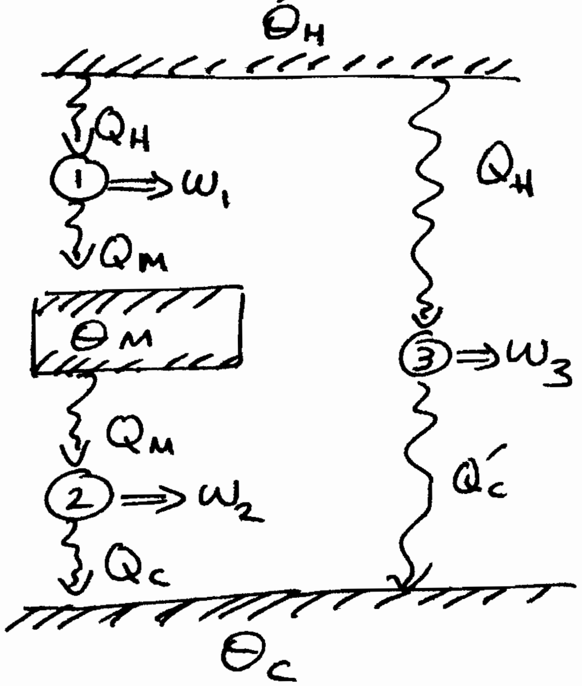
All reversible engines operating between given θ_H, θ_c with same $|Q_c|$ have the same $|W|$, $|Q_H|$

$\therefore$ The ratio $\dfrac{|Q_H^{rev}|}{|Q_C^{rev}|} = f(\theta_H, \theta_c)$ $\left\{ \begin{array}{l} \text{A } \overline{\text{UNIVERSAL}} \\ \text{Function} \end{array} \right\}$

Moreover, from a "cascade" of reversible engines,



For any θ_M

$|Q_c| = |Q_c'| \Rightarrow$

$$\frac{|Q_M|}{f(\theta_M, \theta_c)} = \frac{|Q_H|}{f(\theta_H, \theta_c)} \Rightarrow$$

$$\frac{|Q_H|}{f(\theta_H, \theta_M) f(\theta_M, \theta_c)} = \frac{|Q_H|}{f(\theta_H, \theta_c)}$$

$$\Rightarrow f(\theta_H, \theta_c) = f(\theta_H, \theta_M) f(\theta_M, \theta_c)$$

Two possibilities : $f(\theta_H, \theta_c) = \dfrac{g(\theta_H)}{g(\theta_c)}$ $\left[\text{or } \dfrac{g'(\theta_c)}{g'(\theta_H)} \right]$

$g(\theta) = T$ defines the thermo namic temperature T, to be shown in § .1 to be equivalent to the ideal-gas temperature $T = P\underline{V}/R$

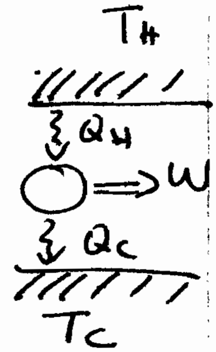
[$g'(\theta) = 1/k_B T \equiv \beta$ is used in statistical mechanics]

Now, the ratio at the top of p. 5 can be written as:

$$\frac{|Q_H^{rev}|}{|Q_c^{rev}|} = \underbrace{\frac{T_H}{T_C} \Rightarrow \frac{Q_H}{-Q_C}}_{\text{using proper signs from system's (engine's) point-of-view}} = \frac{T_H}{T_C} \Rightarrow$$

$$\Rightarrow \boxed{\frac{Q_H}{T_H} + \frac{Q_C}{T_C}}$$

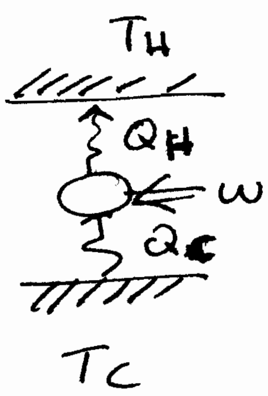
Efficiency of reversible (Carnot) engine:



$$\eta^{rev} \equiv \frac{-W}{Q_H^{rev}} = \frac{Q_H^{rev} - Q_c^{rev}}{Q_H^{rev}} = \frac{T_H - T_C}{T_H}$$

$$|W| = \eta |Q_H|$$

For refrigeration cycle, one uses work to remove heat from the interior of a device or building; Coefficient-of-performance ζ (zeta):



$$\zeta = \frac{|Q_c|}{|W|} = \frac{Q_c}{-Q_c - Q_H} = \frac{Q_C}{-Q_C + \frac{T_H}{T_C} Q_C}$$

$$\Rightarrow \zeta = \frac{T_C}{T_H - T_C} \quad \text{can be } > 1 \text{ !}$$

Another possibility is operation as a "heat pump" to warm a building by transferring heat from the cold outside air. In that case,

$$\zeta = \frac{-Q_H}{W} = \frac{-Q_H}{-Q_C - Q_H} = \frac{Q_H}{Q_H - \frac{T_C}{T_H} Q_H} \Rightarrow \zeta = \frac{T_H}{T_H - T_C}$$

(can also be >1)

Example 3.2

Maximum J for air conditioner $\theta_{in} = 68°F$
$\theta_{out} = 104°F$

$$J^{rev} = \frac{Q_c}{W} = \frac{T_c}{T_H - T_c} = \frac{293\ K}{(313-293)K} = 14.6$$

$\boxed{\text{Entropy}}$

We have just showed that for reversible processes,

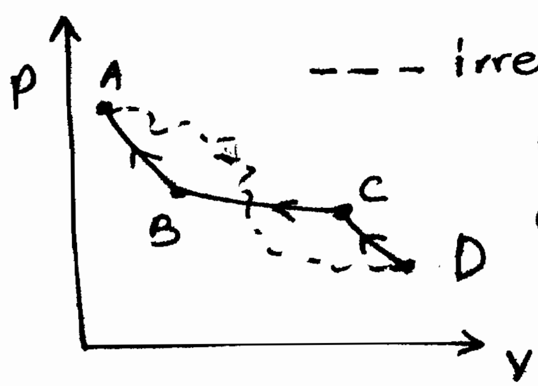
$$\left.\frac{Q_H^{rev}}{T_H} + \frac{Q_c^{rev}}{T_c} = 0 \ \right\} \text{for complete engine "cycle"}$$

This suggests the possibility of defining a new thermodynamic quantity (state function) related to the reversible heat exchanged:

$$dS = \frac{\delta Q^{rev}}{T} \qquad \Delta S = S_B - S_A = \int_A^B \frac{\delta Q^{rev}}{T}$$

Key Property of S : $\Delta S = 0$ for reversible processes
(often used as alternative statement of second law) $\Delta S > 0$ for spontaneous (irreversible) ones in isolated systems

Proof



--- irreversible path $A \to D$

$B-C$ isothermal
$A-B, C-D$ adiabatic
reversible process $D \to A$

$$U_A - U_D = Q^{rev}_{D\to A} + W^{rev}_{D\to A} = T(S_A - S_D) + W^{rev}_{D\to A} \quad ①$$

For irreversible process $A \to D$ (closed, isolated system) $Q=0$

$$U_D - U_A = W^{irr}_{A\to D} \quad ②$$

$$① + ② \Rightarrow \quad T(S_A - S_D) + W^{rev}_{D\to A} + W^{irr}_{A\to D} = 0$$

If $W^{irr}_{A\to D} + W^{rev}_{D\to A} < 0$ (work output)

$T(S_A - S_D) = Q^{rev}_{D\to A} > 0$ (heat absorbed)

$\Rightarrow$ violates Kelvin-Planck postulate!

Therefore, $W^{irr}_{A\to D} + W^{rev}_{D\to A} > 0$

($=0$ would be reversible both ways)

$\therefore \quad S_A - S_D < 0 \Rightarrow \boxed{S_D > S_A}$ for irreversible process $A \to D$

Final state has higher entropy!

Also, $\boxed{W^{irr}_{A\to D} > W^{rev}_{A\to D}}$

If work is produced $+W^{rev}_{A\to D} < 0$
Irreversible work is <u>less</u> in absolute magnitude (more positive)
If work is needed, Irreversible work required is <u>more</u>. $\Rightarrow$ **Reversible processes are "the best"**