1st Law: $\Delta E = \Delta Q + \Delta W$

Or: $dE = \bar{d}Q + \bar{d}W$

Positive work for work done *on* the system.
$\Delta Q \equiv$ change in heat

if $\Delta Q = 0$ then adiabatic

Heat capacities:

$$c_V \equiv \left.\frac{\bar{d}Q}{\bar{d}T}\right|_V \qquad c_P \equiv \left.\frac{\bar{d}Q}{\bar{d}T}\right|_P$$

$$c_V \equiv \left.\frac{\partial E}{\partial T}\right|_V$$

For an ideal gas only: $c_P - c_V = nR$

For reversible, adiabatic: $PV^g = const$ $\qquad g \equiv \frac{c_P}{c_V}$

van der Waal's gas equation: $\left(P + \frac{an^2}{V^2}\right)(V - b) = nRT$

In a cycle: $\oint_c dE = 0$

Zeroth Law:

If two bodies are in thermal equilibrium with a third, then they are in thermal equilibrium with each other.

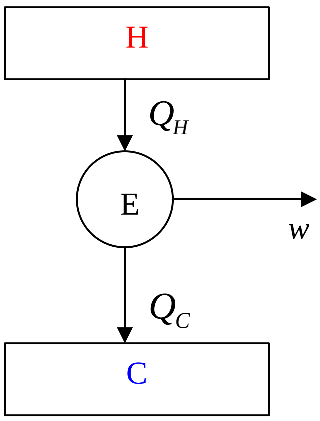
Heat Engines:

- run in cycles… thus $\Delta E = 0$

w = work done BY system $\qquad W$ = work done ON system

ΔQ_H absorbed from "hot" source.
ΔQ_C emitted to "cooler" reservoir.

Engine does work… thus $w > 0$

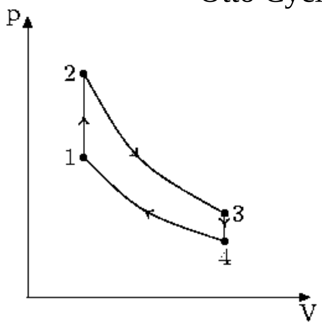


$$w = Q_H - Q_C$$

$$h_E \equiv \frac{w}{Q_H} = 1 - \frac{Q_C}{Q_H} < 1$$

$$h \equiv \frac{\text{input}}{\text{useful output}}$$

Otto Cycle:



Q_H goes into system along 1 → 2
Q_C leaves system along 3 → 4
4 →1 & 2 → 3 are adiabats… thus $\Delta Q = 0$ here

Now:

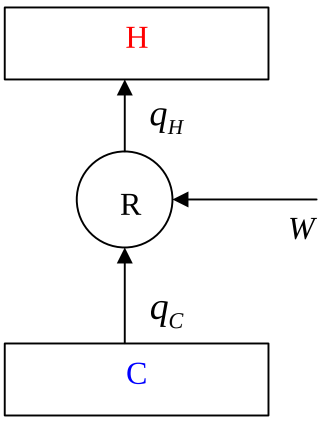
$$c_V \equiv \left.\frac{đQ}{đT}\right|_V \qquad c_P \equiv \left.\frac{đQ}{đT}\right|_P$$

Hence: $Q_H = c_V\left(T_2 - T_1\right)$

Similarly: $Q_C = -c_V\left(T_4 - T_3\right) = c_V\left(T_3 - T_4\right)$

Thus, the efficiency is: $\eta_E \equiv 1 - \dfrac{Q_C}{Q_H} = 1 - \dfrac{T_3}{T_2}$

Refrigerator:



$$W = Q_H - Q_C$$

$$\eta_R \equiv \frac{q_C}{W}$$

$$\eta \equiv \frac{\text{input}}{\text{useful output}}$$

Heat pump a similar setup to a refrigerator, except the "useful output" is q_H , so the efficiency term changes:

$$\eta_P \equiv \frac{q_H}{W}$$

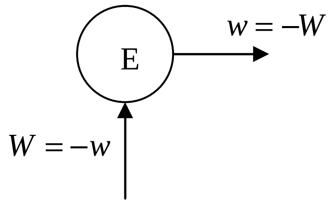
Kelvin-Planck Statement:

It is impossible to construct an *engine*, operating in a cycle, which produces *no effect other* than the extraction of heat from a reservoir and the performance of an equivalent amount of heat.

Clausius' Statement:

It is impossible to construct a *refrigerator* operating in a cycle, which produces *no effect other* than the transfer of heat from cooler to a warmer body.

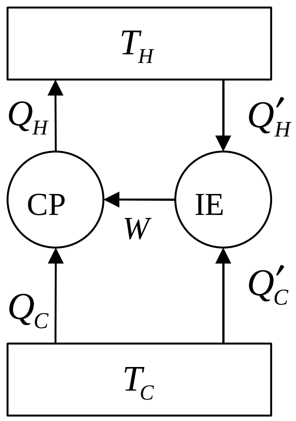
Conventions:



w +ve ➔ work done BY engine
W +ve ➔ work done ON engine

Carnot cycles:

- Carnot engine $\equiv$ reversible engine operating between two reservoirs.
  Thus, process must be isothermal or adiabatic.



CP = Carnot pump
IE = irreversible engine
$Q'_H \geq Q_H$

And, by 1st law: $W \equiv Q_H - Q_C = Q'_H - Q'_C$

The efficiency of an ideal gas-Carnot cycle:

$$\bar{d}Q = dE - \bar{d}W$$

And: $\bar{d}W^{rev} = -pdV$ $\qquad E = E(T)$

Suppose four paths: a → b → c → d → a (a closed cycle)

Along a → b & c → d are isotherms;
Q_H input along c/d $\qquad Q_C$ output on a/b
Along b → c & d → a are adiabats.

Now, $dE = 0$ along any isotherm. Hence, along isotherms:

$$đQ = pdV = \frac{nRTdV}{V}$$

$$c \to d \quad Q_H = \int_c^d đQ = nRT_H \ln\left(\frac{V_d}{V_c}\right)$$

$$a \to b \quad Q_C = nRT_C \ln\left(\frac{V_a}{V_b}\right)$$

Hence, the efficiency:

$$h_{CE} \equiv 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$

Thus: $\frac{Q_C}{T_C} = \frac{Q_H}{T_H}$ for Carnot engines.

- the max efficiency that can be achieved from an engine operating between two fixed reservoirs.

Clausius' Theorem: $\oint_c \frac{đQ}{T} \leq 0$

Equality for reversible… $\oint_c \frac{đQ^{rev}}{T} = 0$

Entropy: $\frac{đQ^{rev}}{T} \equiv S$ S a state variable

- thus independent of path!!

In isolated systems: $dS \geq 0$ entropy can never decrease.

$dS = 0$ for any reversible, adiabatic process.

Spontaneous changes are ALWAYS irreversible

$$\Delta S_{system} + \Delta S_{surroundings} = 0$$

For irreversible entropy problem, as S is a state variable, can choose any path. Hence, choose a reversible path. Hence:

$$\Delta S = \oint_c \frac{đQ^{rev}}{T}$$

Thermodynamic Relations:

Fundamental Thermodynamic Relation		$dE = TdS - pdV$	(for a gas)
Enthalpy	$H \equiv E + pV$	$dH = TdS + VdP$	$H(S,P)$
Helmholtz Free Energy	$F \equiv E - TS$	$dF = -pdV - SdT$	$F(V,T)$
Gibbs Free Energy	$G \equiv E - TS + pV$	$dG = -SdT + Vdp$	$G(T,p)$