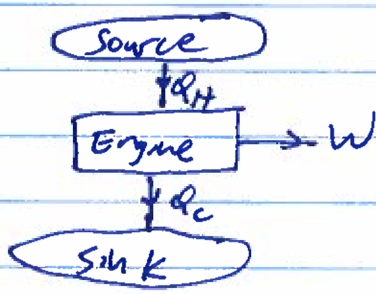
Kardar 1.4

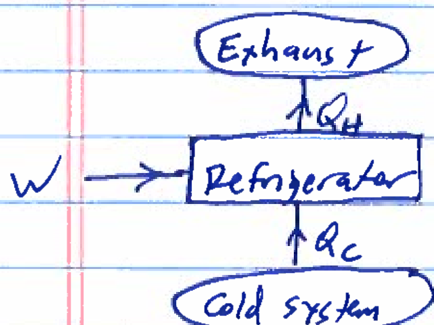
The Second Law

A *heat engine* takes in heat Q_H from a heat source, converts a portion of it to *work* W, and dumps the remaining heat Q_C into a heat sink.



Efficiency $\eta \equiv \dfrac{W}{Q_H} = \dfrac{Q_H - Q_C}{Q_H} \leq 1$

A *refrigerator* is like an engine running backwards.



Merit of performance

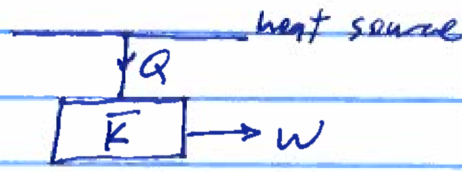
$$\omega \equiv \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C}$$

The first law rules out perpetual motion machines of the first kind, i.e. engines that would produce work w/o consuming energy. The second law rules out perpetual motions of the second kind, e.g. an engine that does work by converting water to ice

There are various equivalent formulations of the second law.

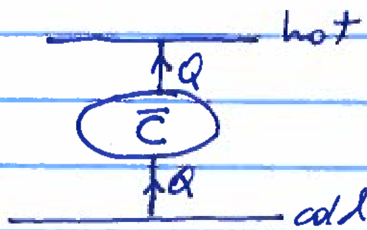
Kelvin's Statement: No process is possible whose sole result is the complete conversion of heat into work.

→ There are no perfect engines.



Engine that violates Kelvin's statement

Clausius's Statement: No process is possible whose sole result is the transfer of heat from a colder to a hotter body. ⇒ No perfect refrigerator

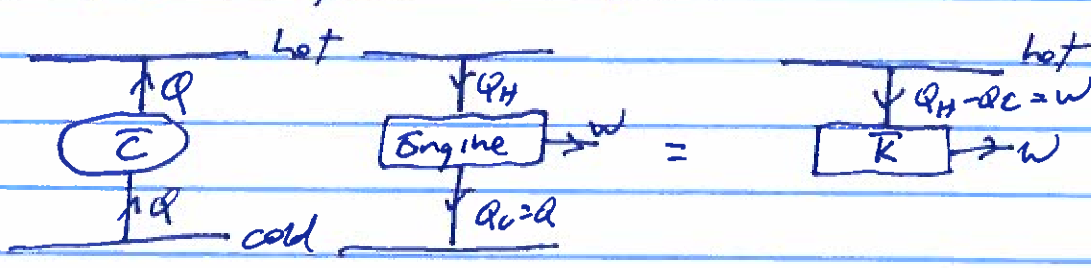


Refrigerator that violates Clausius's statement.

Equivalence of Kelvin's and Clausius's Statements:

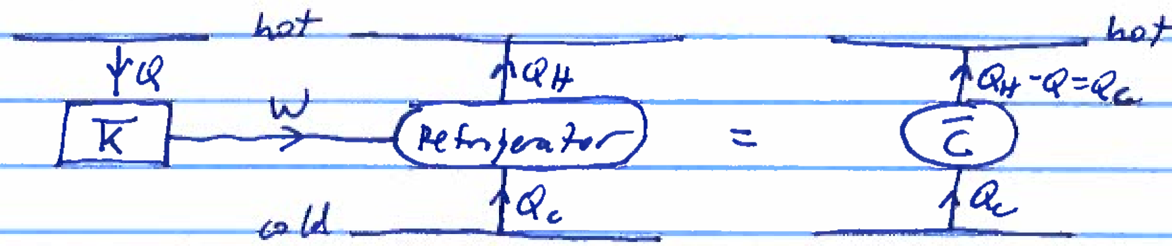
Not Clausius → Not Kelvin:

Consider a combined system of a $\bar{C}$ refrigerator and a heat engine that dumps the same amount of heat Q_c as the refrigerator intakes:

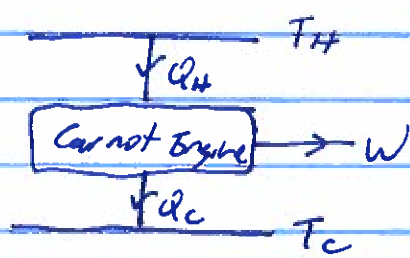


Not Kelvin → Not Clausius:

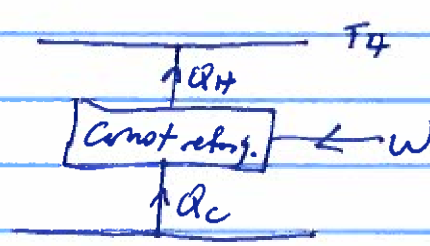
Consider a combined system of a $\bar{K}$ engine and a refrigerator.



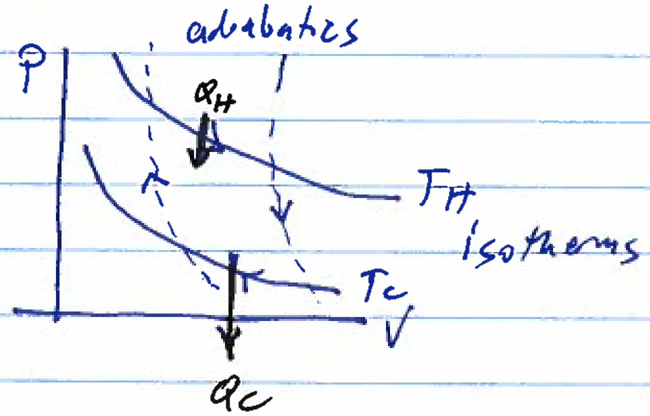
Kardar 1.5 Carnot Engines - Any engine that is reversible, runs in a cycle (i.e. returns to the same state), with all heat exchanges at a source temp T_H and a sink temp T_C.



Reversible: can be run backwards by reversing inputs and outputs



Time reversibility → quasi-static



Carnot cycle for ideal gas

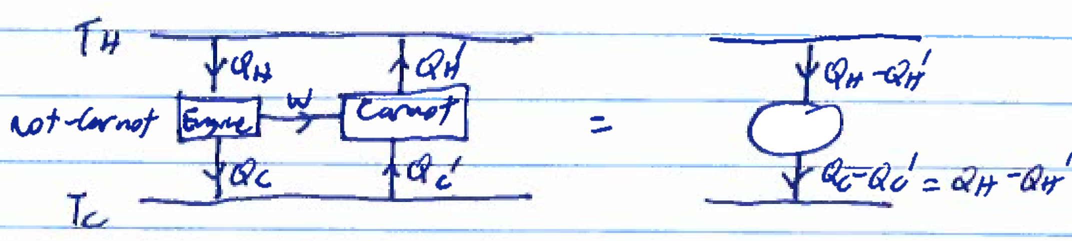
Ideal Monatomic Gas: $E = \frac{3}{2} N k_B T = \frac{3}{2} PV$

Quasi-static path: $đQ = dE - đW = d(\frac{3}{2}PV) + PdV$
$$= \frac{5}{2} P dV + \frac{3}{2} V dP$$

Adiabatic: $đQ = 0 \Rightarrow \frac{dP}{P} = \frac{5}{3}\frac{dV}{V} \Rightarrow PV^{\gamma} = \text{const.}$ with $\gamma = 5/3$

Carnot's Theorem: No engine operating between two reservoirs at temps T_H and T_C is more efficient than the Carnot engine operating at those temps.

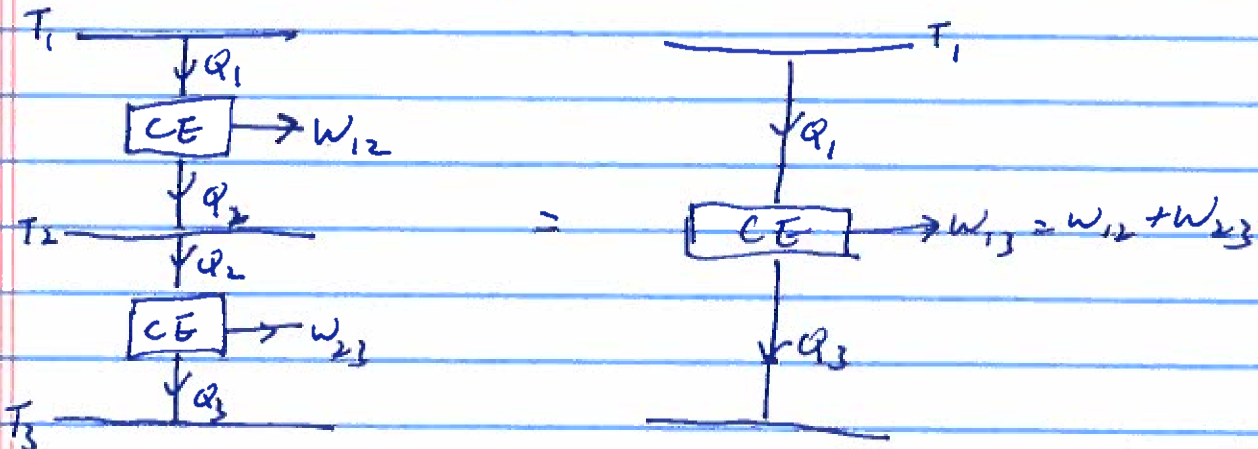
Proof (from Clausius's statement):
Use a regular engine to run a Carnot engine in reverse:



Clausius $\rightarrow Q_H - Q_H' > 0 \rightarrow Q_H \geq Q_H'$
$W/Q_H \leq W/Q_H' \Rightarrow \eta_{carnot} \geq \eta_{non\text{-}carnot}$.

Corollary of Carnot's Theorem: All Carnot engines have the same universal efficiency $\eta(T_H, T_C)$, since each can be used to run any other one backwards.

Carnot thermodynamic temperature scale:



$$Q_2 = Q_1 - W_{12} = Q_1\left(1-\eta(T_1,T_2)\right)$$

$$\left\{\begin{array}{l} Q_3 = Q_2 - W_{23} = Q_2\left(1-\eta(T_2,T_3)\right) = Q_1\left(1-\eta(T_1,T_2)\right)\left(1-\eta(T_2,T_3)\right) \\ Q_3 = Q_1 - W_{13} = Q_1\left(1-\eta(T_1,T_3)\right) \end{array}\right.$$

$$\to \left(1-\eta(T_1,T_3)\right) = \left(1-\eta(T_1,T_2)\right)\left(1-\eta(T_2,T_3)\right)$$

$\Rightarrow$ Can write $1-\eta(T_1,T_2) = \dfrac{f(T_2)}{f(T_1)} \equiv \dfrac{T_2}{T_1}$

Defines temp. scale T up to proportionality constant

$$1-\eta(T_1,T_2) = \frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

$$\Rightarrow \boxed{\eta(T_H,T_C) = 1 - \frac{T_C}{T_H}}$$

$\to$ fix w/ $T_{\text{water-3point}} = 273.16$

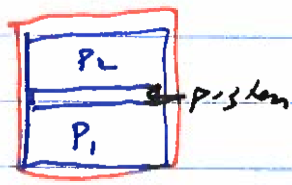
- Agrees w/ ideal gas temp.

ardar 1.6

Entropy

$$dE = \sum J_i dx_i + đQ$$

Equilibrium between two systems → same J_i



Equilibrium → $P_2 = P_1$

Thermal equilibrium between two systems → same temp T

⇒ Suggests $đQ = T\,d(\text{Something})$

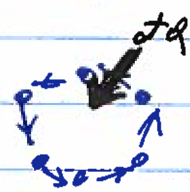
The (something) will be the entropy of the system.

Clausius's Theorem: For any cyclic transformation (not necessarily reversible),

$$\boxed{\oint \frac{đQ}{T} \leq 0}$$, where $đQ$ is the heat exchanged at temp T.

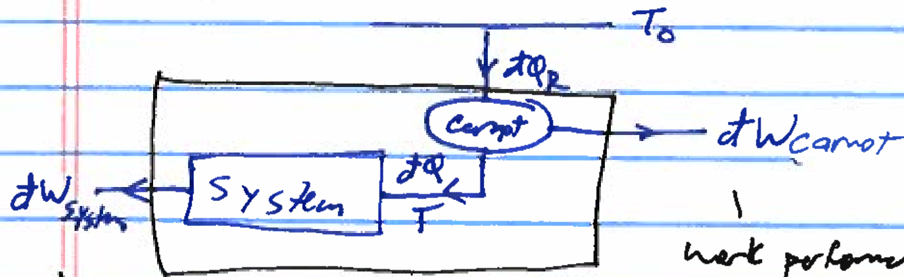
The system need not be in equilibrium throughout the cycle, but, it is helpful to consider certain equilibrium points along the cycle.

Proof:



To define the temp T relevant for Clausius's theorem when the system is out of equilibrium, consider $đQ$ as the output of a carnot engine at the appropriate sink temp T, and source temp T_0.

- Can have different Carnot engines, but w/ same source temp T_0.



work performed by auxiliary Carnot engine

work performed by system

Carnot engine! Heat from reservoir $\boxed{đQ_R = T_0 \dfrac{đQ}{T}}$

Net effect of complete cycle:

Heat $Q_R = \oint đQ_R$ extracted from reservoir

work $W = Q_R = \oint đW_{system} + \int đW_{\substack{carnot\\engine}}$

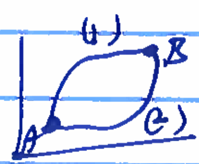
Kelvin's statement $\rightarrow$ $Q_R = W \leq 0$

$$\oint đQ_R = T_0 \oint \frac{đQ}{T} \leq 0 \Rightarrow \boxed{\oint \frac{đQ}{T} \leq 0} \text{ since } T_0 > 0$$

Consequences of Clausius's Theorem:

1) For a reversible cycle, if the cycle is run in reverse,

$$\oint \frac{đQ_{rev}}{T} \leq 0 \text{ and } -\oint \frac{đQ_{rev}}{T} \leq 0 \Longrightarrow \oint \frac{đQ_{rev}}{T} = 0.$$



$$\int_A^B \frac{đQ_{rev}^{(1)}}{T} = \int_A^B \frac{đQ_{rev}^{(2)}}{T} \quad \text{independent of path.}$$

2) This allows us to define a <u>state function</u> S = entropy, such that

$$S(B) - S(A) = \int_A^B \frac{đQ_{rev}}{T}$$

$$\boxed{đQ_{rev} = TdS}$$ for reversible processes

3) From the First Law,

$$\boxed{dE = đQ + đW = TdS + \sum_i J_i dx_i}$$

☆ This is a relation between functions of state, so it is equally valid for reversible and irreversible transformations.

4) Number of <u>independent variables</u> required to describe a thermodynamic system = (# conjugate pairs (J_i, x_i)) + 1.

Using $\{E, x_i\}$ as coordinates, $dE = TdS + \sum_i J_i dx_i$

$$\rightarrow \boxed{\left.\frac{\partial S}{\partial E}\right|_{x_i} = \frac{1}{T}}, \quad \boxed{\left.\frac{\partial S}{\partial x_i}\right|_{E, x_j \neq x_i} = -\frac{J_i}{T}}$$

5) Entropy is at a maximum in equilibrium.

Consider a cycle composed of an irreversible change from $A \to B$ and a reversible change from $B \to A$.

$$\int_A^B \frac{dQ}{T} + \int_B^A \frac{dQ_{rev}}{T} \leq 0$$

$$\Rightarrow \quad \int_A^B \frac{dQ}{T} \leq S(B) - S(A)$$

For a differential transformation from $A \to B$, $\boxed{dS \geq \frac{dQ}{T}}$

For Adiabatic processes $dQ = 0 \Rightarrow \boxed{\delta S \geq 0}$

Example: Gas initially confined to one side of a box, then allowed to expand to fill the box.
In the process, $\delta S \geq 0$.