

0. Introduction

- * Physics so far :
 - Deterministic: e.g. Newton's laws of motion, Maxwell's eqn.
differential eqns + initial/boundary conditions
 - Single or few-body systems.

- * Macroscopic systems: # of d.o.f. N is large $N_A \approx 10^{23}$

compare to e.g. # of grains of sand in all beaches
in the world: $\sim 10^{18}$

of stars in our galaxy $\sim 10^{11}$

... .. Universe $\sim 10^{22}$

Thermodynamics: phenomenological description of equil. properties of
macroscopic systems.

Stat Mech: a probabilistic approach to

e.g. obtain macroscopic state variables.

Large $N \Rightarrow$ complexity, emergence of new phenomena:

e.g. macroscopic variables, (temperature)

phases of matter & phase transitions

\hookrightarrow magnetism, superfluidity/superconductivity etc.

* Historically:

heat engine & Industrial Revolution 1840's

Chemistry

Early days of Quantum Mechanics \Leftrightarrow Stat. Mech.

1900 Max Planck, energy quantization + stat. mech. \Rightarrow Black-body radiation

1907 Albert Einstein, 1912 Peter Debye, Heat capacity of solids

1925 Bose & ~~Einstein~~ Einstein, Bose-Einstein statistics,
indistinguishable particles

Bose-Einstein Condensation

1926 Enrico Fermi & Paul Dirac Fermi-Dirac statistics

(1925 Pauli Exclusion principle)

applications

\Rightarrow 1926 Ralph Fowler: white dwarf

1927 Arnold Sommerfeld: electrons in metals

Critical Phenomena & Field Theory

1950's - 1960's 2nd order phase transitions, scale invariance,
universality

1966 Leo Kadanoff "block-spin" real-space renormalization group

1971 Kenneth Wilson: links RG in particle physics & stat. mech.

RG explains universality, scaling hypothesis, leads to a
computational scheme for e.g. critical exponents

Recent Development

Quantum Thermalization: emergence of stat. mech. from isolated, quantum
many-body systems under unitary dynamics. (M. Srednicki 1994)
(M. Rigol. 2008)

I. Thermodynamics

Phenomenological approach, w/o. knowledge of microscopics. Law's of T.D
Experience &
Observations

Systems at equilibrium: properties do not change over observation time

⇕
character of measurements: slow & coarse

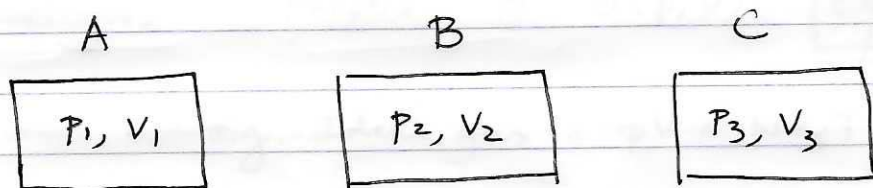
$\sim 10^{23}$ microscopic d.o.f.	"filtered" by macroscopic measurements	Thermodynamic variables vary slowly in space & time
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e.g. P, V , (mechanical) M, B , etc.

thermal?

* 0th Law: If A & B are each in equil w/ a 3rd system C , then they are in equil w/ each other.

⇒ Existence of "temperature".



Bring A & C together until they are in equil.
a constraint

$$F_{AC}(P_1, V_1; P_3, V_3) = 0 \Rightarrow V_3 = f_{AC}(P_1, V_1; P_3)$$

Similarly, for B & C

$$F_{BC}(P_2, V_2; P_3, V_3) = 0 \Rightarrow V_3 = f_{BC}(P_2, V_2; P_3)$$

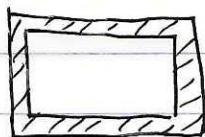
$$\Rightarrow f_{AC}(P_1, V_1; P_3) = f_{BC}(P_2, V_2; P_3)$$

Now, if A & B are also in equil.

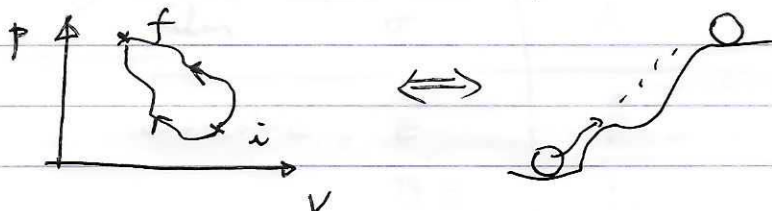
$$F_{AB}(P_1, V_1; P_2, V_2) = 0 \leadsto \text{does not depend on } P_3!$$

1st Law

The amount of work required to change an adiabatically isolated system from state 1 to state 2 is independent of how the work is performed.



- * adiabatic wall: no heat transfer system \Leftrightarrow environment
- diathermic wall: allow heat transfer
- isolated system: no heat transfer + no work



* Internal energy: $\Delta W = U(P_f, V_f) - U(P_i, V_i)$

* Diathermic wall: $\Delta W \neq U(P_f, V_f) - U(P_i, V_i)$
(w) heat exchange)

heat: $\Delta Q = (U_f - U_i) - \Delta W$

amount of energy transfer that cannot be accounted for by the work done.

or, $\Delta U = W + Q$

* Infinitesimal step:

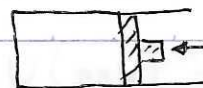
$$dU = \underbrace{\delta W}_{\substack{\text{function of} \\ \text{state.}}} + \underbrace{\delta Q}_{\substack{\text{depends on path} \\ \text{infinitesimal amount, not an exact} \\ \text{differential}}}$$

an expression for δW & δQ ?

* Quasi-static processes: slow enough, effectively in equil.

thermodynamic variables (e.g. P, V) are well-defined during the process.

$$\delta W = -p dV$$



$\delta W > 0$ $dV < 0$
sign \uparrow

more generally, mechanical work

$$\delta W = \sum_i F_i dx_i$$

\nearrow generalized force \searrow generalized displacement

e.g.

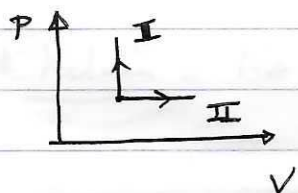
	F_i	x_i
film	σ	A
dielectric	E	\vec{P}
	\vec{H}	M
	intensive	extensive

$\delta Q ? \Rightarrow$ 2nd Law
must be related to
 $T \times ?$

Heat Capacity

$$C \equiv \frac{\delta Q}{dT} \Big|_{\text{path}}$$

gas



• Const. V : $C_V = \frac{\delta Q}{dT} \Big|_V = \left(\frac{\partial U}{\partial T} \right)_V$

• Const P : $C_P = \frac{\delta Q}{dT} \Big|_P = \frac{dU + PdV}{dT} \Big|_P$
 $= \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P$

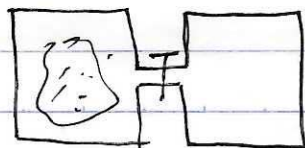
Enthalpy: $H \equiv U + PV$

$C_P = \left(\frac{\partial H}{\partial T} \right)_P$ Chemists love this.

* Ideal gas: Joule's expansion

Isolated system:

measure $T_i, T_f \Rightarrow T_i = T_f$



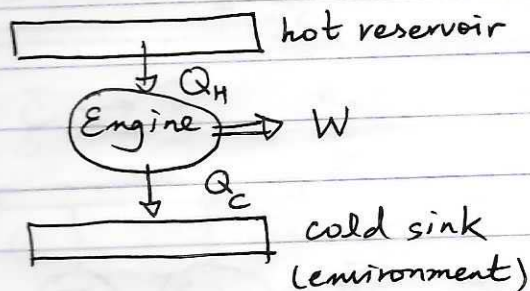
$\Delta Q = \Delta W = 0 \Rightarrow U_i = U_f$

$U = U(p, V) = U(p, V) = U(T)$
 $\leftarrow p \text{ \& } V \text{ changed during expansion}$

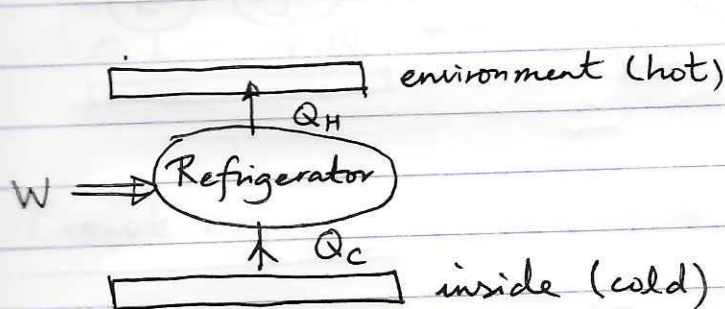
$$C_p - C_v = \frac{pV}{T} = N k_B$$

2nd Law

Industrial Revolution 18th century
heat engine. heat \rightarrow work



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



Performance $\tilde{\eta} \equiv \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C}$
(unconstrained)

2nd Law

* Kelvin: No process is possible whose sole effect is to ~~extract heat from a hot reservoir and convert this entirely~~
complete conversion of heat \rightarrow work.

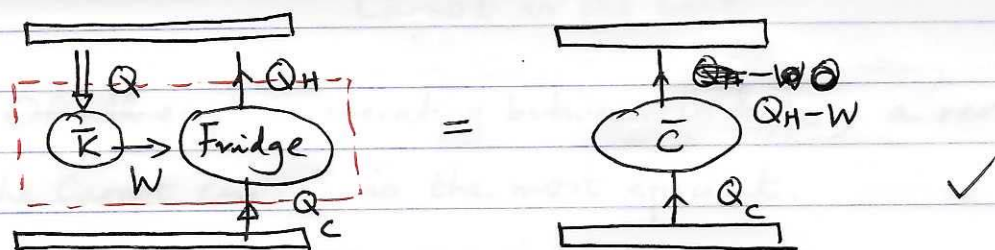
(no perfect heat engine $\eta < 1$)

* Clausius: transfer ^{of} heat from colder to hotter body.
(no ideal refrigerator)

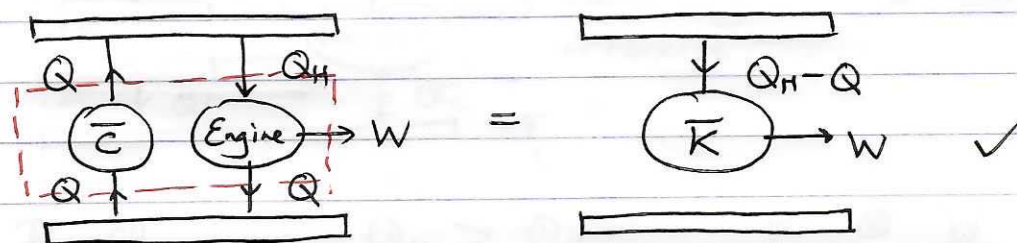
Two statements are equivalent.

$$K \Leftrightarrow C \quad \text{equivalent to} \quad \bar{K} \Leftrightarrow \bar{C}$$

① $\bar{K} \rightarrow \bar{C}$



② $\bar{C} \rightarrow \bar{K}$

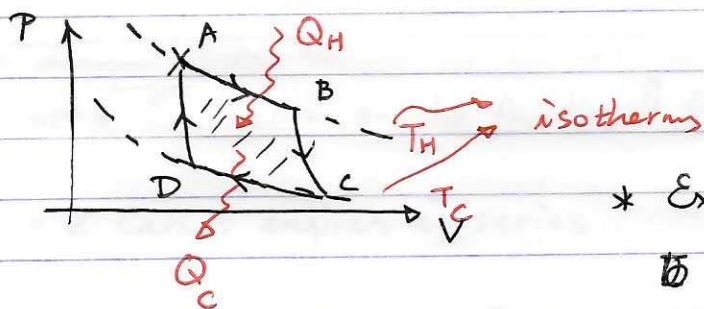


Carnot Engine

Reversible, cycle, operates between two temps. T_H & T_C

↑
"frictionless"

↑
where all heat exchanges happen



BC, DA are adiabatic paths
no heat exchange

* Existence of adiabatic surfaces

$$U = U(p, V)$$

adiabaticity + 1st law: $dU + p dV = 0$

$$\Rightarrow \frac{\partial U}{\partial p} dp + \frac{\partial U}{\partial V} dV + p dV = 0$$

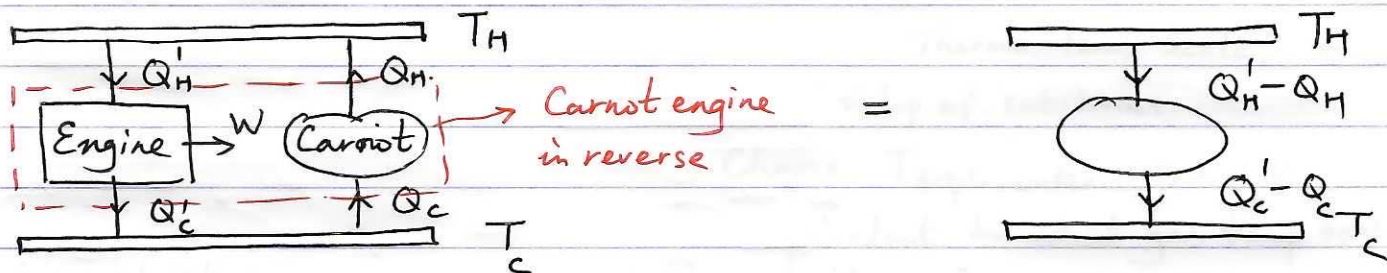
$$\text{or: } \frac{dp}{dV} = - \left(\frac{\partial U}{\partial p} \right)^{-1} \left(\frac{\partial U}{\partial V} + p \right)$$

→ a line

Carnot's Theorem :

Carnot is the best.

Of all engines operating between T_H & T_C , a reversible engine (the Carnot engine) is the most efficient.



By Clausius, $Q'_H > Q_H$,

$$\textcircled{C} \frac{W}{Q'_H} < \frac{W}{Q_H} = \eta_{\text{Carnot}}$$

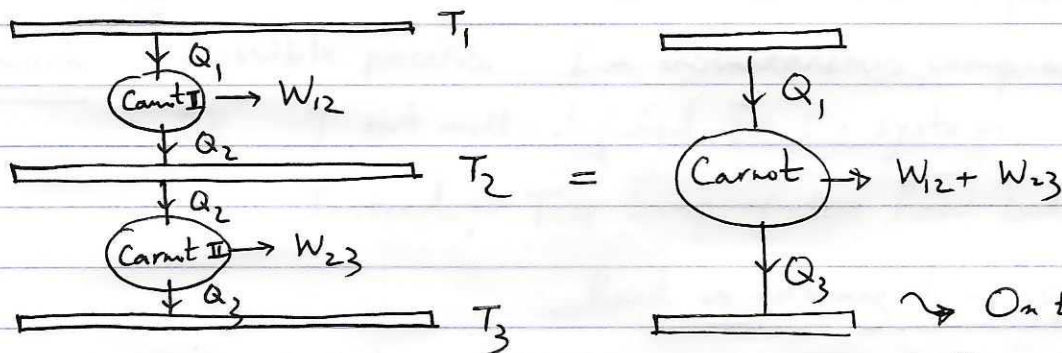
- All Carnot engines have the same efficiency.

↳ ideal gas, realistic gas, liquid, ... any substance $\left\{ \eta(T_H, T_C) \right\}$

Thermodynamic Temperature Scale

need information on the functional form of $\eta(T_H, T_C)$

- 2 Carnot engines in series



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

~ On the other hand

$$Q_3 = Q_1 [1 - \eta(T_1, T_3)]$$

$$Q_3 = Q_2 - W_{23} = Q_2 [1 - \eta(T_2, T_3)] = Q_1 [1 - \eta(T_1, T_2)] [1 - \eta(T_2, T_3)]$$

η satisfies:

$$1 - \eta(T_1, T_3) = [1 - \eta(T_1, T_2)] [1 - \eta(T_2, T_3)]$$

need

$$1 - \eta(T_1, T_2) = \frac{f(T_2)}{f(T_1)} \quad \text{Convention} \quad \frac{T_2}{T_1}$$

Thermo. Temp. Scale,
indep. of substances.

Choose $T_{\text{triple-water}} = 273.16 \text{ K}$
equivalent to ideal gas temp. scale

Clausius' Theorem

\Rightarrow notion of entropy

From Carnot's theorem, any engine operating between T_H & T_C :

$$\eta = 1 - \frac{Q_C}{Q_H} \leq 1 - \frac{T_C}{T_H}, \text{ i.e. } \frac{Q_C}{Q_H} \geq \frac{T_C}{T_H}$$

$$\text{or: } \frac{Q_H}{T_H} + \frac{(-Q_C)}{T_C} \leq 0 \quad \left\{ \begin{array}{l} = : \text{reversible} \\ < : \text{IR} \end{array} \right.$$

For any cyclic process:

$$\oint \frac{dQ}{T} \leq 0 \quad \left\{ \begin{array}{l} = : \text{reversible} \\ < : \text{IR} \end{array} \right.$$

Clausius' Inequality (dQ carries minus sign)

Remark: reversible process: T = instantaneous temp. of system

IR: T not well-defined for the system.

Instead; T = temp. of the heat bath through which heat is exchanged w/ system.

Arbitrary at this point.