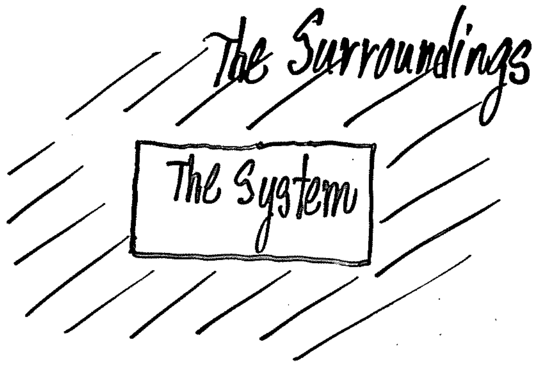
II. Short Review of Thermodynamics

A. Thermodynamic Systems

Typically:

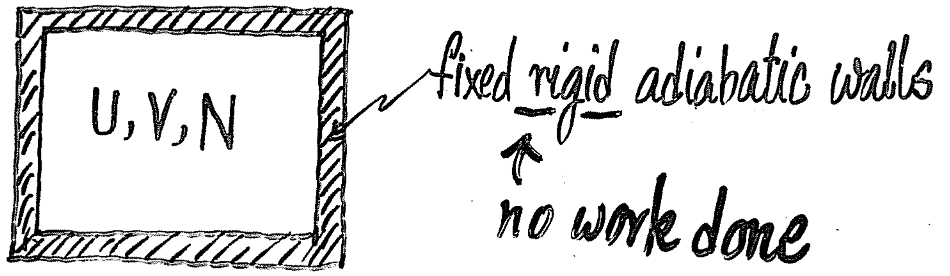


The boundary *may be*:

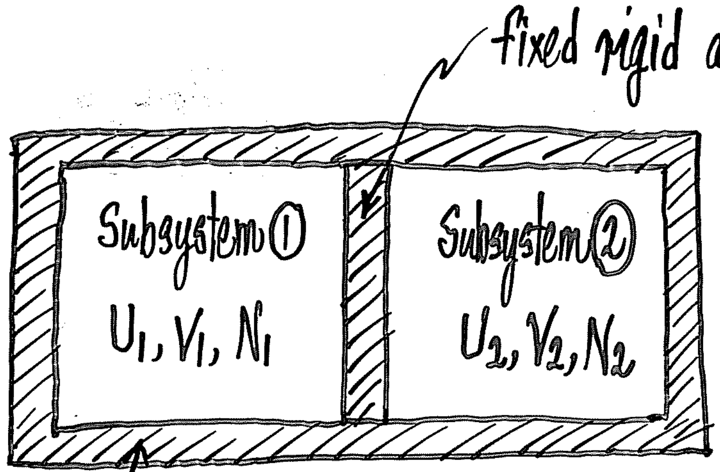
- fixed, rigid (so volume is fixed OR No "exchange" of volume between system and surroundings)
  or movable
- adiabatic (no heat conduction)
  diathermic (allows heat conduction)
- allow (OR not allow) exchange of particles

Isolated System

- System that does NOT exchange energy or particles with the surroundings
- so V, N, U are fixed



Note: The key ideas of stat. mech. are established by considering closed systems. (U and E will be used interchangably)



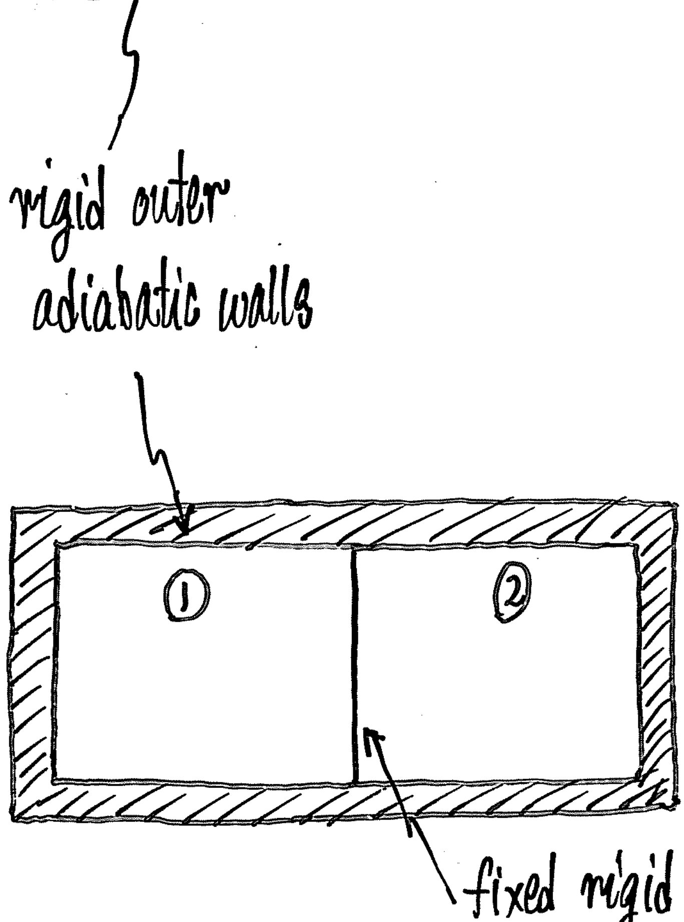
Partition:

fixed: V_1, V_2 fixed

adiabatic: No heat exchange

No holes: No particle exchange

- Subsystem ① and ② are isolated systems
- The whole system (subsystems ①+②) forms an isolated system.



fixed: No change in volume

No holes: No particle exchange

diathermal: heat exchange

- Only $\boxed{①+②}$ forms an isolated system.

B. Description

Thermodynamics is Macroscopic physics
- made no assumptions about atomic structure
- gives relations between thermodynamic variables

- The thermodynamic state or MACROSTATE of a system is described by thermodynamic variables (e.g., p, V, T, n)
- These variables are related by an Equation of State

e.g. Ideal gas law $\quad pV = \underset{\uparrow \text{ \# moles}}{n}RT \quad$ or $pV = NkT$

[In Stat. Mech., we want to derive the equation of state]

Note: The beauty of thermodynamics is that it describes a complicated system ($N \sim 10^{23}$ particles) by only a few variables!

Extensive Variables	Intensive Variables
- depends on the amount of materials in the system ($\propto N$)	- independent of the amount of materials in the system (independent of N)
[e.g., $\underbrace{\text{mass}}_{\text{OR \# moles}}$, U, V, S]	[e.g., p, T, density]

Thermodynamic limit:
$$\begin{cases} N \to \infty, \quad V \to \infty \\ \text{but } \dfrac{N}{V} = \dfrac{\text{\# particles}}{\text{Volume}} = \text{number density} = \text{constant} \end{cases}$$

Conjugated Pairs of Variables:

System	Intensive	Extensive
Gas/Liquid	pressure	volume
Wire	tension	length
Magnetic Material*	Magnetic field	Magnetic dipole moment in sample
"General"	Generalized force variables X_i	Generalized displacement variables x_i
all systems	T	S

Note: the product $X_i x_i$ has the dimension of energy

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* Note: The form of magnetic energy is a non-trivial topic. In thermodynamics, $\vec{B} \cdot d\vec{m}$ is the standard choice and thus the first law is $dU = TdS + \vec{B} \cdot d\vec{m}$. However, in statistical mechanics, $dU = TdS - \vec{m} \cdot d\vec{B}$ is often used. The difference is discussed in C. J. Adkins, "Equilibrium Thermodynamics". Don't worry – physics will guide us through!

C. Laws

Zeroth Law

If { Ⓐ, Ⓑ } is in thermodynamic equilibrium with Ⓒ,

then Ⓐ and Ⓑ must be in equilibrium with each other

Its importance: temperature T

[2 systems in equilibrium have the same temperature]

First Law: Internal energy U

[energy conservation
heat as a form of energy]

$$\underset{\substack{\text{increase}\\ \text{in } U}}{\Delta U} = \underset{\substack{\text{work done}\\ \text{on the system}}}{\Delta W} + \underset{\substack{\text{heat supplied to}\\ \text{the system}}}{\Delta Q}$$

or

$$dU = \delta W + \delta Q$$

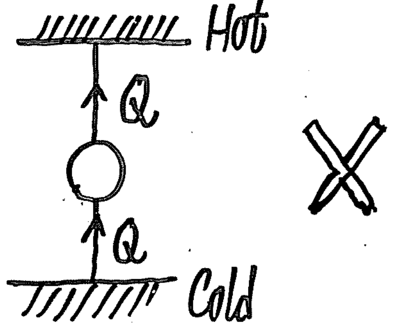
[E.g., for gas-in-a-piston system,
for reversible process, $\delta W_{rev} = -p\,dV$]

U is a $\underbrace{\text{state function}}_{\text{i.e., uniquely determined by thermodynamic state of system}}$

Second Law: Entropy S (Carnot)

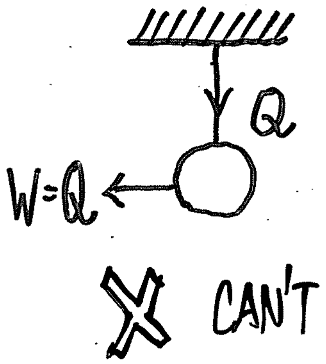
- gives the direction of processes
- an interesting (strange) physics law in that it is a negative statement
  ↳ what cannot happen!

Clausius – No process is possible whose sole result is the transfer of heat from a colder to a hotter body.



CAN'T HAPPEN!

Kelvin-Planck – No process is possible whose sole result is the absorption of heat from a reservoir and conversion of All of this heat into work

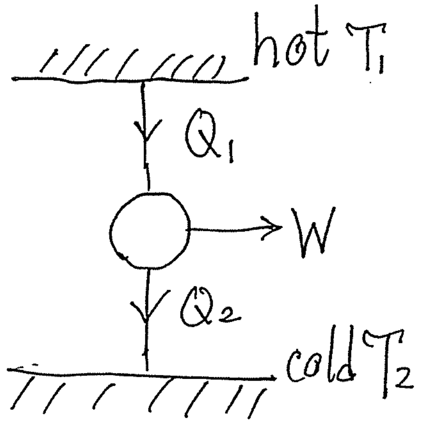


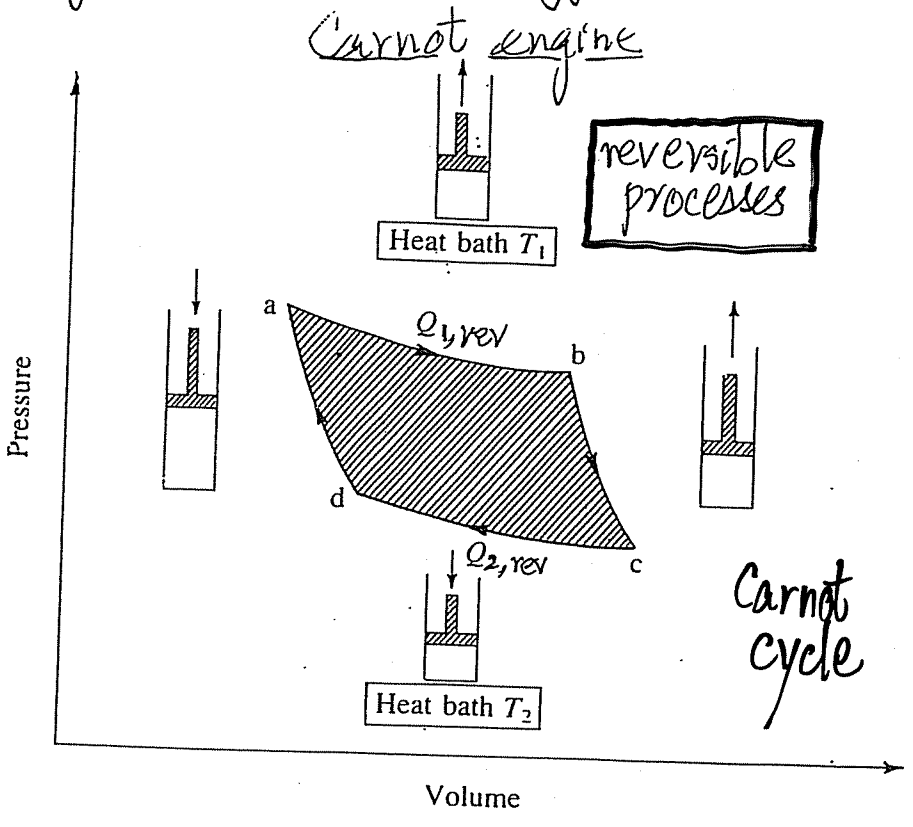
CAN'T HAPPEN!

In addition to a heat source, there must be a heat sink for heat engines to work.

[Carnot: In any engine, how much Q can be turned into W?]

Carnot: "My engine is the most efficient"





Generally,

$$\eta = \frac{W}{Q_1} \equiv \text{efficiency}$$

$$= \frac{Q_1 - Q_2}{Q_1} \quad (1^{st}\ \text{law})$$

$$= 1 - \frac{Q_2}{Q_1}$$

[general, for all engines]

- Carnot engine using gas as working substance
- All 4 steps involve reversible processes.
- η_{Carnot} is the most effective
- Plus all reversible cycles that operate under the same temperatures (T_1 (hot) & T_2 (cold)) are as efficient as Carnot's.

$\therefore \eta_{rev} = \eta_{Carnot}$

highest possible efficiency →

$$\boxed{\eta_{rev} = 1 - \frac{T_2}{T_1}}$$

What else can it be?

Reversible Cycle:

$$\frac{Q_{2,rev}}{Q_{1,rev}} = \frac{T_2}{T_1}$$

OR

$$\underbrace{\frac{Q_{1,rev}}{T_1}}_{\text{take this funny quantity in the process at } T_1} - \underbrace{\frac{Q_{2,rev}}{T_2}}_{\text{put this funny quantity in the process at } T_2} = 0$$

- Over the Carnot cycle [and any reversible cycle]

$$\oint \frac{dQ_{rev}}{T} = 0 \quad \text{for reversible cycle}$$

×

Irreversible Cycle [some irreversible processes involved]

- $\eta_{irrev} < \eta_{rev} \Rightarrow 1 - \frac{Q_2}{Q_1} < 1 - \frac{T_2}{T_1}$

$$\Rightarrow \frac{Q_2}{Q_1} > \frac{T_2}{T_1}$$

$$\Rightarrow \frac{Q_2}{T_2} > \frac{Q_1}{T_1}$$

$$\Rightarrow \frac{Q_1}{T_1} - \frac{Q_2}{T_2} < 0$$

"into" +ve
"out of" −ve

- $\oint \frac{dQ}{T} < 0$ for irreversible cycle

$\therefore \oint \frac{dQ}{T} \leq 0$ for any cycle, with "=" sign holds for reversible cycle.

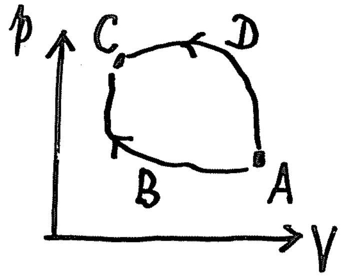
S = entropy = a state function (Clausius)

- $\oint \frac{dQ}{T} \le 0$ for any cycle [Follows from $\eta \le \eta_{carnot} = \eta_{rev}$]
- Equality holds for reversible processes

$$\oint \frac{dQ}{T} = 0 \quad \text{for a reversible cycle}$$

From this, define S by: $\boxed{dS = \frac{dQ_{rev}}{T}}$

for an infinitesimal reversible change



- ADC and ABC are reversible paths

$$\oint dS = 0 = \int_{ABC} dS + \int_{CDA} dS$$

$$\Rightarrow \int_{ABC} dS = -\int_{CDA} dS = \int_{ADC} dS$$

same initial state A and final state C
reversible paths
(true for any reversible path)

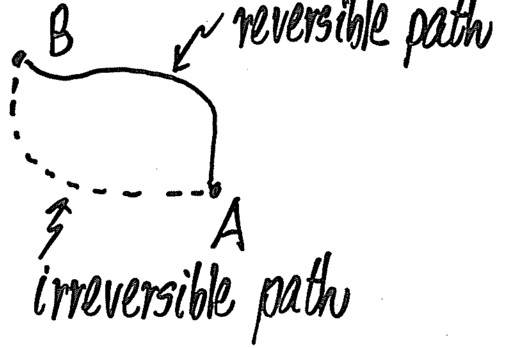
$$S_C - S_A = \int_A^C \frac{dQ_{rev}}{T}$$ (can be evaluated by any reversible path)

S is a function of state

Q: When there is a change in state ⇒ ΔS, how is ΔS relate to dQ in irreversible processes?

$$\oint \frac{dQ}{T} < 0 \quad \text{for irreversible cycle}$$

$$\int_{A(irrev)}^{B} \frac{dQ}{T} + \int_{B(rev)}^{A} \frac{dQ}{T} < 0$$



$$\Rightarrow \int_{A(irrev)}^{B} \frac{dQ}{T} < \underbrace{\int_{A(rev)}^{B} \frac{dQ}{T} = S_B - S_A = \Delta S}$$ [form a irreversible cycle]

OR $\boxed{dS > \frac{dQ}{T} \text{ for an irreversible change}}$ [†] $\frac{dQ}{T} < dS$

c.f. $dS = \frac{dQ_{rev}}{T}$ for a reversible change

- Specializing to isolated systems:

$dQ = 0 \Rightarrow dS \geq 0$ (the inequality specifies the direction in which a physical process will go)

Law of increase of entropy:
The entropy of an isolated system CANNOT decrease

[†] Here, T is the temp. at which the heat is supplied to system

Important Consequence:

For an isolated system:

- if it is not in internal thermodynamic equilibrium, then as it approaches equilibrium, its entropy increases **[Arrow of time!]**†
- if we wait until equilibrium, then the entropy is as large as possible (maximum)

→ S is a maximum (isolated system in equilibrium)
[an extremum condition]

D. The thermodynamic identity

Putting 1st and 2nd laws together

U = internal energy (function of state)

$$\underbrace{dU}_{\text{fn of state}} = \underbrace{dQ + dW}_{\text{not differentials of fn of state (need to specify path)}}$$

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† A criterion on why some processes occur spontaneously [e.g. gas molecules collected to locate at a corner tend to spread uniformly in a room].

$dU = dQ + dW$ (always) [means "for any change"]

$dW = -pdV$ (for reversible changes)

$dQ = TdS$ (for reversible changes)

$$\therefore \boxed{dU = TdS - pdV \quad \text{for reversible changes}}$$

- But, all variables in the equation are functions of state. Integrating the equation to get ΔU is independent of path. All we need is the initial and final states.
- To get ΔU for irreversible changes, since U is a function of state, we can use the same equation and choose a convenient reversible path.

$$\therefore \boxed{dU = TdS - pdV}$$ is the most important equation in thermodynamics!

Remark: Generalizing to system that can exchange particles with its surroundings,

$$\boxed{dU = TdS - pdV + \mu dN}$$

Key relation

often use in Statistical Mechanics

$$\boxed{dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN \quad \text{thermodynamic identity}}$$

$$\therefore \underbrace{S(U,V,N)}$$

if we know $S(\underbrace{U,V,N}_{\text{natural variables of } S})$, then we can calculate [see Appendix]

other thermodynamic variables

$$\boxed{\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} \; ; \; p = T\left(\frac{\partial S}{\partial V}\right)_{U,N} \; ; \; \mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V}}$$

useful relations in microcanonical ensemble in stat. mech.

E. Thermodynamic Potential Functions

$$dU = TdS - pdV$$

↳ $U(S,V) \Rightarrow U$ is NOT the convenient quantity if we want to use T and V as the independent variables

[OR $E(S,V)$ as we will use later]

Helmholtz Free energy (or simply "free energy")

$$F = U - TS$$

This procedure of changing variables is called a Legendre transform.+

It follows:

$$\boxed{dF = -pdV - SdT}$$

$\therefore F(T,V)$ OR $F(T,V,N)$ ← including N

[c.f. $U(S,V)$]

$$\boxed{S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \; ; \; p = -\left(\frac{\partial F}{\partial V}\right)_{T,N}}$$

← useful in canonical ensemble in stat. mech.

Similarly, H = enthalpy $\equiv U + pV = H(S,p)$

G = Gibbs' free energy $= F + pV = G(T,p)$

- The condition for equilibrium (for given V and T) is

F takes on the minimum [an extremum condition]

F. Third Law

- $S(T=0) = 0$ [Nernst]

Ref:

C. J. Adkins, "Equilibrium Thermodynamics" (3rd edition)

+See Appendix

The third law is useful!

Example $dH = TdS + Vdp$

$$dS = \frac{1}{T}dH - \frac{V}{T}dp$$

$H = U + pV$

(Useful for processes at constant pressure)

$\because H(S,p)$

Write: $dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$

gives
$$dS = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_p dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial p}\right)_T - V\right]dp \quad (*)$$
$$= \frac{C_p(T)}{T}dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial p}\right)_T - V\right]dp$$

$$\Rightarrow \boxed{\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p(T)}{T}}$$

$C_p(T)$ can be measured (there are tables!)

$$\boxed{\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_p(T)}{T}dT} \quad (\text{constant } p)$$

The third law gives a zero $S(0K)$ so that

$$\boxed{S(T) = \int_0^T \frac{C_p(T')}{T'}dT'}$$

based on which the Calorimetric way of determining entropies is developed

be aware of $\underbrace{\text{phase transitions from 0K to T}}_{\text{e.g. solid} \to \text{liquid} \to \text{gas}}$

(physical chemistry)

$\therefore$ 3rd law provides a way to calculate $S(T)$.

Summary (Key Points)

- Quick run through of key developments in thermodynamics
- Know what the equation

  $dE = TdS - pdV + \mu dN$ means

- $dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$

  $S(E,V,N)$

  - Knowing $S(E,V,N)$, can calculate T, p, μ

  Isolated system at equilibrium: S is maximized

- $F = E - TS$

  $dF = -SdT - pdV + \mu dN$

  $F(T,V,N)$ [System with N particles in Volume V held at a temp. T (e.g. via contact with a huge heat bath)]

  - Knowing $F(T,V,N)$, can calculate S, p, μ

  System with fixed T, V, N,

  F is minimized at equilibrium.