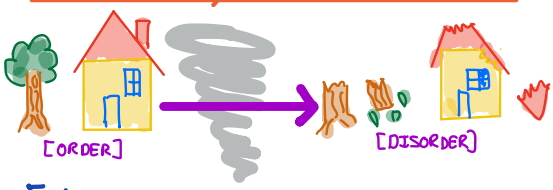
Heat Death, The Fimbulwinter



41. Fills the foreshore
with dead men,
reddens reigns abode
with red gore;
black was sunshine
the summer after,
the weather unsafe.
Understand ye yet, or what?
-Völuspá, Poetic Edda, Odin visits a seeress who narrates the events before Ragnarök

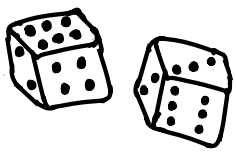
54. "First, there is a winter called the Fimbul-winter, when snow drives from all quarters, the frosts are so severe, the winds so keen and piercing, that there is no joy in the sun. There are three such winters in succession, without any intervening summer."
-Glyfaginning, Prose Edda, Hár replies to Gangleri's questions on preludes to Ragnarök (extract)

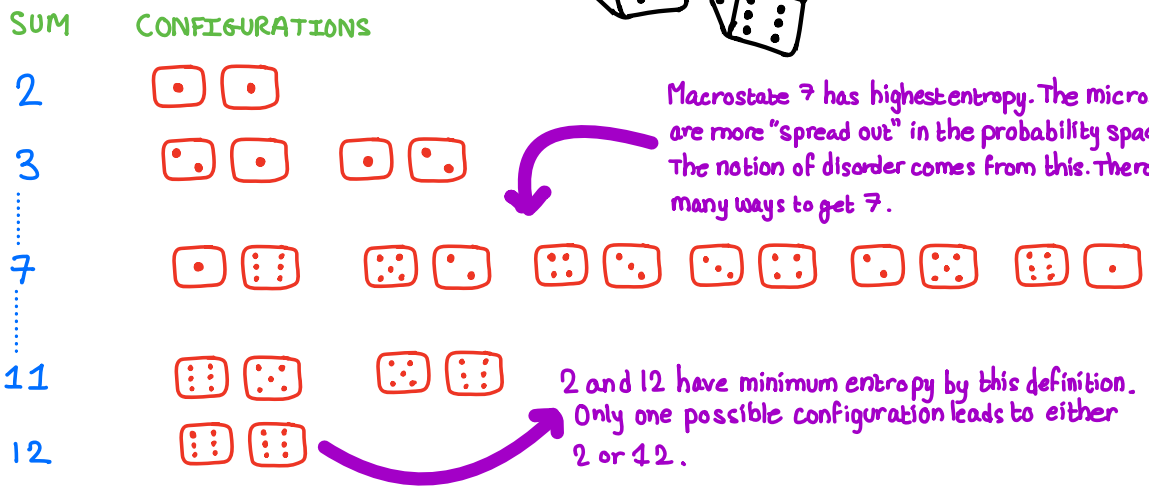
Entropy

Entropy is often introduced as a measure of "disorder". Let us explore a less "classical" definition of entropy as a measure of the number of microstates consistent with a given macrostate. $[S = k_B \ln \Omega]$

Let's play a game where 2 dice are tossed and we are told only the sum of the 2 faces after a throw. The possible sums $2, 3, 4, 5, \ldots, 12$ would be the macrostates and the combinations possible to get a sum, the microstates. e.g. We can get a sum of 3 for (1,2) and (2,1).

The macrostate correspond to the "large-scale" and observable part of the system and the microstate, the small-scale configurations which we can only infer.





Macrostate 7 has highest entropy. The microstates are more "spread out" in the probability space for 7. The notion of disorder comes from this. There are many ways to get 7.

Note: The mean corresponds with 7.
: The microstates are equiprobable.

2 and 12 have minimum entropy by this definition. Only one possible configuration leads to either 2 or 12.

Interpretation for a gas.

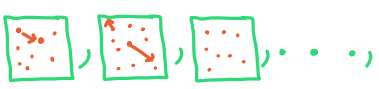
Consider a box containing an ideal gas. It has a specific pressure, volume, temperature and number of molecules. This is the picture of the gas as a whole. The (macrostate of the) gas is defined by the variables (P,V,T,N).

Zooming in on the gas, in the microscopic picture, we see a huge number of molecules constantly bumping into the walls of the container and into themselves. One important attribute of these molecules is their velocities. The distribution of molecular velocity ressembles a normal distribution. Few with very low or very high and most at the mean.

The moving molecules make up the internal energy U of the gas. By elasticity of molecular collisions (and conservation of Energy), 2 molecules knocking into each other simply exchange their velocities. -1ε for 1 molecule and $+1\varepsilon$ for another does not change the average.

↘ The temperature of the gas is a measure of the average velocity of molecules.

While fixing a given state, (P,V,N,T), we now ask ourselves how many such different configurations are possible which leave the state fixed.



The number of microscopic configurations (microstates) consistent with ONE Macrostate is the entropy of the system!

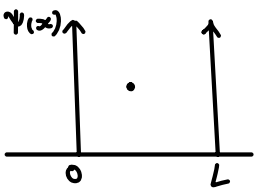
If we slowly cause a small disturbance to the gas by changing (P,V,N,T), eventually the gas will stabilise at a new equilibrium. We will again see the typical behaviour of gases. The equilibrium positions corresponds to max entropy for that state.

Microscopic View

Classical Thermodynamics originally started as an investigation on Steam Engines. The birth of this field led to the industrial era. Analysis of macroscopic behaviour of systems was enough for engineers to improve engines. Watt refined the steam engine, Otto and Diesel pioneered the first model of automobile engines.

For the engineers, the classical model was enough to work with. However for scientists, many concepts remained unexplained. When considering atoms in the microscopic view, the Classical Mechanics started to be somehow lacking. A new mechanics was needed for the small particles ; Quantum Mechanics.

A particle in a 1D box

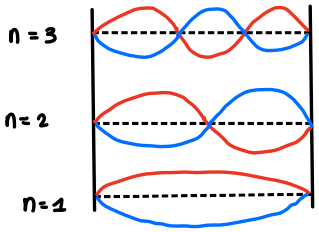


Principal quantum number

$$E_n = \frac{n^2 h^2}{8 m L^2} \quad (n = 1, 2, 3, \ldots)$$

Length of box

Energy of the particle

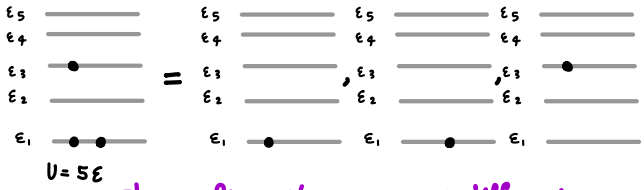


↑ higher Energy (Shorter λ - can pack more cycles in same length)

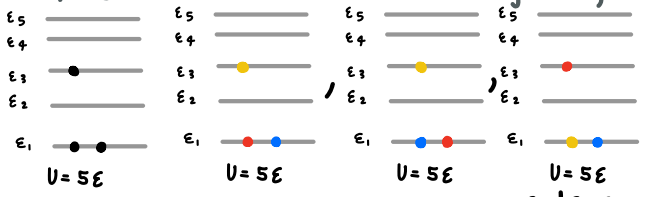
Particle can have only these energies.

material objects are postulated to have wave-like properties. $\lambda = \frac{h}{mv}$ (de Broglie relation)

We shall simplify our diagram as follows :
1) Consider only 3 particles
2) Abstract the energy levels



Now, this state of 5ε can have different configurations,



and so on...

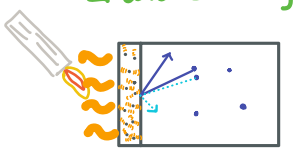
The configurations represent different permutations. Classically, we see this as particles of same mass hitting into each other (elastically) and simply exchanging velocities (kinetic energy). 20 ml of water contains more than 10^{3C} particles. If we got so many arrangements with 3 particles, think about one billion billion billion billion particles! Imagine for a glass of water.

Adding Energy to the System

There are a lot of ways to do so : 1) Pumping more particles into the system 2) Crushing the System
3) Placing the system over a candle 4) Passing a force field through

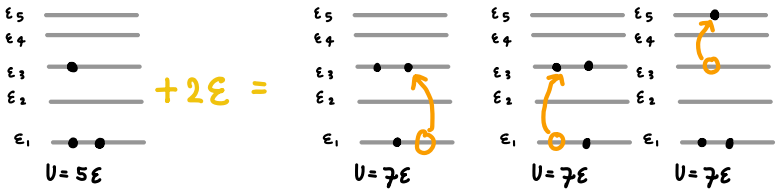
Let's look at 2 and 3. They represent energy transfer as Work (2) and Heat (3).

HEAT



Heating up the walls cause the molecules there to vibrate VIOLENTLY in a RANDOM fashion. The gas molecules moving randomly too, knock into the wall molecules. They bounce back with additional energy but randomly attributed. Vibrations in wall are too wild to give all colliding molecules same energy. Some that collide may get a lot while others, little.

Let's transfer 2ε of Energy as heat and see the result



The absorption of energy by gas molecules is random. Each has a chance of catching 2ε. Each separate state has its own set of permutations.

We see that after heating, we have access to more permutations.

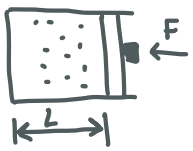
This is why heat is associated with Entropy.
Cooling is heating another object.
The system particles drop down restricting no. of microstates accessible.

This is same as the dice game. When we got a 5, it could have been (2+3), (3+2), (1+4) or (4+1). 5 has a higher entropy than 3 which could only be (1+2) or (2+1).

The movement of heat goes on for a while. At a point both bodies have access to the same number of microstates. (The energy levels are universal). This must mean that the 2 bodies become indistinguishable in a thermodynamic sense. The 2 bodies are said to be in thermodynamic equilibrium and this occurs at a certain temperature. Heat flow stops.

WORK

Let's now look at Work. Consider a simple gas-piston setup. We expend energy as we make a macroscopic force F act on the gas to compress it. By conservation of energy, the gas must store this added energy (which disrupts its initial equilibrium).



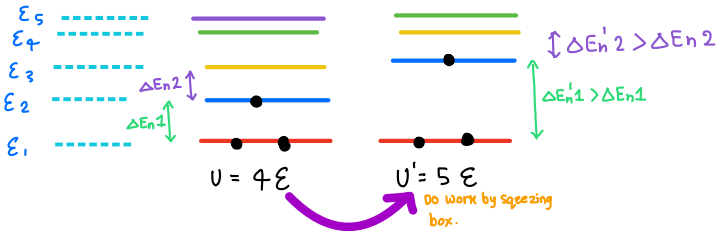
We see that expended energy to compress the gas.

$$\uparrow E_n = \frac{n^2 h^2}{8mL^2} \downarrow$$

We see that decreasing the length increases the gap between the energy levels.

$$\underbrace{(E_n - E_n')}_{\Delta E_n} = \frac{n^2 h^2}{8m}\left(\frac{1}{L^2} - \frac{1}{L'^2}\right) \Rightarrow \Delta E_n \propto \frac{1}{\underbrace{\Delta L}}$$

Work is a little different. It BROADENS the gaps between the energy levels.



population distribution

We see that work cause no change in the energy distribution when the particles collide with each other and exchange velocities. The number of permutation is same at initial and final equilibrium. Work causes no change in entropy.

In our 3D world, we are not limited to only length. The wave function for the particle in a box becomes:

$\psi_{n_x,n_y,n_z} = A \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right)$. It is the product of 3 1D considerations. It is a 3D Standing wave.

The 3 terms (for ideal particle) represent the 3 degrees of freedom for Kinetic energy in x, y, z.

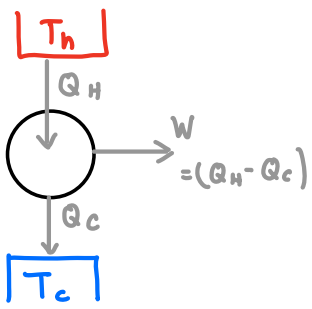
When we do work on a system, we exert a macroscopic force in a particular direction ($W = F \cdot ds$) e.g. the x direction. Transferring this energy to the gas corresponds to energizing the x d·o·f in all particles. To reject back the work, all particles, get rid of the energy added in their x d·o·f. The reverse occurs. The piston which pushed the gas in the x direction is pushed back by the gas particles. The energy released from the x d·o·f corresponds to a macroscopic force which push back the piston.

Owing to its intrinsic mechanism, heat transfers energy randomly. A particle getting energy in the x d·o·f could as likely get it in y or z degrees of freedom. Real gases are not restricted to these, they can rotate or vibrate too. When we want work done (in a particular direction), we most likely desire all particles to give up Energy in the concerned d·o·f to get a macroscopic force out put. But heat does not energize only one kind of degree of freedom (unlike work).

The is a certain number of energized x d·o·f, certain number of y and same for z. If our piston needs to move in the x direction, we can only use energy from the (few) x degree of freedom. The rest (y and z d·o·f) represent unavailable work. There is still energy which we got from heat, but by its nature a portion of it cannot push the piston. This is why thermal energy is seen as a LOW GRADE energy form. When it is injected into a system, not all of it can be used to do useful work. Work when injected into a system can be used by the System to do other work. Work from electrical, kinetic and Chemical is seen as HIGH GRADE.

LEAD to (some) GOLD

Trying to turn low grade stuff to high grade seems like the work of engineers. The French army engineer Sadi Carnot proposed an (ideal) mechanism nowadays known as the Carnot Cycle. It is a cycle built to get work from heat.



Even operating in ideal conditions, the engine does not reach full efficiency. Some of the energy unavailable to do work must be rejected in the cold reservoir, decreasing efficiency.

$$\eta_{Carnot} = 1 - \frac{Q_C}{Q_H}$$

The Arrow of Time

There are many processes in nature which seems to occur in only one direction despite the reverse being in accord with the laws of physics.

Take for example: Dropping an egg on the floor

We never observe the egg magically reconstituting and jumping up from the floor. This is because that process is associated with a decrease in entropy!

When the egg hits the floor, we can see that there is an increase in distribution of mass through space. The mass of the object before falling was concentrated in a small area, the egg. This spreading of mass is an increase in entropy.

Now, when the egg hits the floor, some of its kinetic energy is converted to thermal energy in the floor (heat released). Like we previously saw, heat is associated with entropy change. Conversion of work to heat means entropy increased. Friction between shards and air also releases heat.

Suppose the reverse is to occur; there was no physical laws forbidding the air and ground molecules concentrating to their prior single degree of freedom. Classically, the molecular collisions reverse transfering kinetic energy to molecules in air which push back the shards to the original location. As physical reconstitution reaches completion, the ground molecules align and push the egg back up.

This is very unlikely! Statistics shows this. A new law was needed in physics to account for this. It is the very famous Second Law of Thermodynamics; $dS_{univ} \geq 0$ (Entropy of universe always increases). Another way of saying this is time progresses in direction of increasing entropy.

Now, one might sit down and bring all the pieces together. He might even give the reconstituted egg a kick up. But in doing so, the person expends his energy and sweats (releasing heat) and increases S_{univ} even more. He could get a machine which does not sweat; but it releases heat by friction ($\uparrow S_{univ}$ even more). He could also build a heat engine to convert the heat from the egg impact to work to push it up. But inefficiency of these engines release some heat by its operating principle and by internal friction (real case). Realizing the desired reconstituted egg propulsion increases S_{univ} even more. There is no winning from this.

Work can be done to decrease entropy in one area but on the universal scale, entropy increased. This is the principle of the refrigerator, it moves heat from colder region to hotter to keep food cold. Naturally, heat flows from hot to cold as it increases entropy. The friction in compressor and coolant increases entropy more than that movement of heat. $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$. When $\uparrow \Delta S_{surr} > \downarrow \Delta S_{sys} \Rightarrow \Delta S_{univ} > 0$. All processes are limitted by the laws of Thermodynamics!

The Heat Death

As we saw, all processes result in the entropy of the universe increasing. Eventually, this reaches a maximum value and we then say that the universe itself is in thermodynamic equilibrium. Everywhere is thermodynamically indistinguishable. The whole universe is at the same temperature. Since it is very large, the even distribution of thermal energy results in a cold, eternal winter.

There is no gradient. Heat exchange is not possible and neither are heat engines to extract work. Everywhere in the universe is uniform

Gravity → Entropy?

Bringing objects together

non-elastic

Cause Entropy to ↑.

The universe reaches thermodynamic equilibrium at maximum entropy. Everywhere is even. Everywhere is cold. All the energy in the universe has been distributed in the large region. All forms of energy became heat

Work cannot be done as it requires a disturbance. But everywhere is the same. There can be no external work as it is the whole universe which is in equilibrium. There is no heat flow as everywhere is at the same temperature. Heat engines do not work.

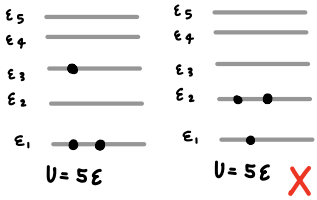
Long before the heat death, the following events concerning us would occur.
If climate change continues as it does so, ecological catastrophe could ensue. Mass migrations and mass extinctions become more likely.

As the Earth's core cools down, it loses its magnetic shield and Sun Coronal Mass ejections quickly rip apart our atmosphere.

Then it is the turn of the Sun to cool down and in the process of becoming a white dwarf incinerate us.

The piston simultaneously energises all the gas molecules by the same amount. The disturbance created in the gas represents the energy added. If we give the system enough time, eventually the system will reach a new equilibrium (molecular interactions even out disturbance). Else, the system can return back to its original state by rejecting the work input.

Now, this state of 5ε can have different configurations,



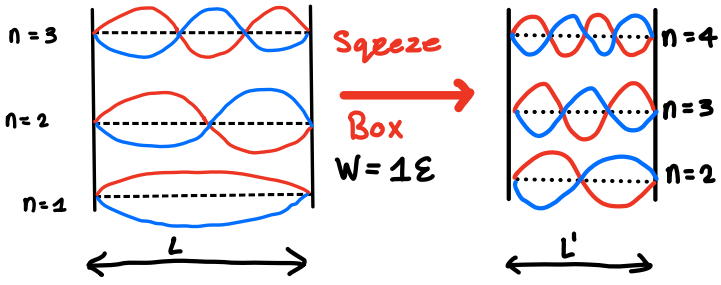
It is also worth remembering that each molecule can take the place of another (permutations). This gives rise to a large number of ways to arrange. 20 ml of water has about 10^{26} particles of water. If we got so many arrangements from 3 particles, imagine with one billion billion billion billion particles! Now think for a glass of water.

$Q = n\varepsilon$ thermal wavelength λ wave interference

Like dice game.

$10\varepsilon \rightarrow 3\varepsilon, 1\varepsilon, 5\varepsilon$

Microstate ⇔ Possibility.



$$\psi(x,y,z) = X(x)\,Y(y)\,Z(z)$$

$$\Rightarrow \psi_{n_x n_y n_z}(x,y,z) = A \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right)$$

$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left(\left(\frac{n_x}{l_x}\right)^2 + \left(\frac{n_y}{l_y}\right)^2 + \left(\frac{n_z}{l_z}\right)^2\right)$$

Some Energy must always be added to disturb the equilibrium.

Can heat only activate rotation & Vibration?

What about non-quadratic dof? Other types of work activate those too.

Link no. Microstates to random energization of d.o.f in particles.

Physical meaning of Entropy

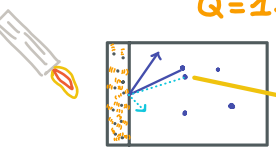
Entropy first appeared as a concept in the field of Thermodynamics. In this, the modes of transfer of Energy in form of heat and work are studied in details. They transfer energy by distinct mechanisms. Heat flow always accompanies entropy change.

For simplicity, consider this 1D box filled with ... We want to transfer 1 additional unit

HEAT

Q = 1J

5 ideal gas particles. The particles move randomly and the internal energy U depends solely on the temperature; ultimately on the average velocity of the molecules. ($PV = NKT$, $U = \frac{3}{2}PV$). Assume each particle has 1 J of energy. (1J) (1J) (1J) (1J) (1J)



2 particles close together likely have different fates.

- Heating up the box cause the wall molecules to vibrate RANDOMLY.
- Gas particles collide with the wall and receive some energy.

(1J) (1J) (1J) (1J) (1J) = 5 J
+ + + + +
0·3J 0·1J 0·05J 0·2J 0·35 = 1 J
(1.3J) (1.4J) (1.05J) (1.2J) (1.35J) = 6 J

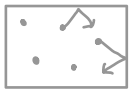
We see the energy gained from heat is more "spread out".

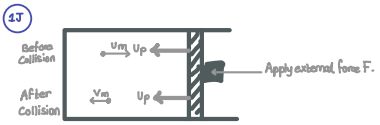
We see more disorder in Energy distribution.

- Collisions cause random distribution of molecular velocity.

The problem of Irreversibility.

of energy to the gas.





WORK

$W = 1\,J$

Elastic collisions $V_i = V_f$

rel. Vel before = $U_p - (-U_m) = U_p + U_m$

rel. vel after = $-(U_p - V_m) = V_m - U_p$

$\Rightarrow V_m = U_m + 2U_p$

- Energy is spend for an external macroscopic force to act on the system. By Conservation of Energy, this external energy is converted to internal energy.
- We see that after collision, the (x-component) velocity increases ($+2U_p$) for ALL molecules. The higher velocity results in increased internal energy.

* (All molecules get mU_p^2 additional Energy)

(1J) (1J) (1J) (1J) (1J) = 5J
+0·2 +0·2 +0·2 +0·19 +0·21 = 1J
(1.2) (1.2) (1.2) (1.19) (1.21) = 6J

We see more order in energy distribution from (reversible) work.

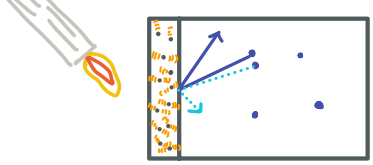
→ In contrast to heat, there is no dispersion in molecular energy.

Algebras: The Reunion of Broken Parts.

If an alien sends you travelling through space and time into dark empty space, before dying look at your entropy-meter. Now $S_{univ} \approx 10^{103}\,K_B$. By looking at the value, you will know if you are in the past or future. Always keep your entropy-meter on you. Being lost in space does not always need for you to be lost in time!

Transferring Energy: Thermodynamics studies 2 common method of Energy Transfer; Heat & Work.
Heat is generally referred as microscopic Energy transfer while Work is macroscopic.
Heat exchange is usually associated with change in System Entropy.

HEAT



When we crank up the heat on one wall of the container, the wall molecules start to vibrate wildly! This jiggling is highly unpredictable (RANDOM).

It must be greater or that process would not be statistically feasable by universe

At thermodynamic equilibrium, the Equipartition Theorem states that all the d·o·f quadratic in energy are equally filled. No work can be done. Imaging pushing a ball up then down, left then right. No net work is done. To get work, we must disturb the equilibrium. We input some energy. To resolve the disturbance, we make it go through a mechanism to take in energy from only one degree of freedom. The machine will take that energy from that particular dof and the system will go back to equilibrium.

↳ It might be a new one as when we changed (disturbed) the sys. we could have changed states.

also, dof could be electrical nuclear, magnetic or rotational

#006fff

Also, the input Energy could be by heat or work,

work would be like 2 piston connected to gas & locking pushing one energizes the ∝ microstate & rejection pushes the other piston. (No change in state same equilibrium).

Heat in line carnot cycle

Mechanism absorb a particular d·o·f

System returns back to eq.

∴ Carnot cycle Analysis.

DOF are independent

Rotating ball does not make it fall less fast.

Projectile Motion: x does not influence y.

↳ Usual Parabolic Shape.

All the energy can be taken by many machinery

e.g. Piston in x, y & z

Rotating Plane for rotating particles or something like that

Vibration for something else.

But when we want only x the others appear useless!

↓

Is there a restriction on this?

Consider case of ideal gas only.

Prove this!

The degrees of freedom all get filled in thermodynamic Equilibrium!

↘ Mechanism of the distribution.

↘ How do degrees of freedom get filled?

Like how does Motional Energy get into the Electric degree of freedom.

or empty space.

If closed in box, measure entropy before & after time travel

$U = \sum$ Microscopic Energy.

Look for Webpage on
$W = qV$
Work, Entropy & Electricity
It looked like ChemLibre text.

egg hit floor.
Work done on floor, U_{floor} increase but is disturbed.
To reach Thermodynamic equilibrium, since is has NO mechanism to expel the additional Energy as work, it releases it by heat.

(or it settles to eq by distributing that random Energy ↑ΔS)

Study therm. eq again in terms of work

E. Level Expand, compress

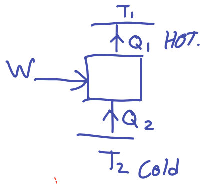
Sin(x) Sin(x) Sin(x) DoF & bounce Energy.

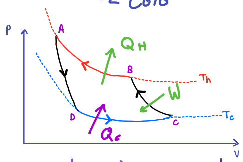
E_K = Work

For heat transfer there must be 2 reservoirs
else the system will absorb heat, reach same T as source & heat (Transfer) will stop!

Refrigerator Cycle

Reverse of CARNOT CYCLE





Start at C (lower T)

①' C to B
Adiabatic Compression
$\Delta Q = 0$
$\Rightarrow \Delta U = -P\Delta V$
Temperature of coolant rises
No heat exchange $\Rightarrow$ Isentropic

For ideal gas U is function of T only (E_k only)
V becomes important when considering E_p (squeeze together $\Rightarrow \uparrow E_p$)
$\left(U = \frac{3}{2} nRT\right)$

②' B to A
Isothermal Compression
$\Delta T = 0 \Rightarrow \Delta U = 0$
$\Rightarrow \Delta Q = \Delta W$
Temperature remains constant
U gained by compression work is equal to U lost as Q (rejected heat)
S decreases in system.

③' A to D
Adiabatic Expansion
$\Delta Q = 0$, $\Delta U = -P\Delta V$ $\quad U = \frac{3}{2} nRT$
Gas expands paid by decrease in U
T coolant drops below refrigerator
No heat exchanged $\Rightarrow$ Isentropic

④' D to C
Isothermal Expansion
$\Delta T = 0 \Rightarrow \Delta U = 0 \Rightarrow \Delta Q = -P\Delta V$
Gas expands w/o decrease in T/U.
Q is injected from refrigerator
S increases in system.

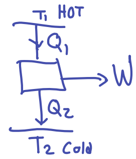
Temp. represents U.
Temp is affected by Q & W.

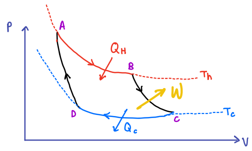
Temp. is average E_k not total.

More heat loss than what is collected (friction)!

Heat Engine Cycle

CARNOT CYCLE





Start at A (Higher T)

① A to B
Isothermal Expansion
$\Delta T = 0 \Rightarrow \Delta U = 0 \Rightarrow \Delta Q = -P\Delta V$
Heat Q from hot reservoir cause work via gas expansion.
Temperature does not change ($\Delta U = 0$)
S increases in system

② B to C
Adiabatic Expansion
$\Delta Q = 0 \Rightarrow \Delta U = -P\Delta V$
Expansion against atmosphere is paid by U.
T decreases
No heat transfer $\Rightarrow$ Isentropic

③ C to D
Isothermal Compression
$\Delta T = 0 \Rightarrow \Delta U = 0 \Rightarrow \Delta Q = -P\Delta V$
U gained by compression work equals to U lost as Q rejected in cold reservoir
S decreases in system.

④ D to A
Adiabatic Compression
$\Delta Q = 0 \Rightarrow \Delta U = -P\Delta V$ (Expansion cause U to increase)
Temperature rises
No heat exchanged $\Rightarrow$ Isentropic

Adiabatic & Isothermal Processes

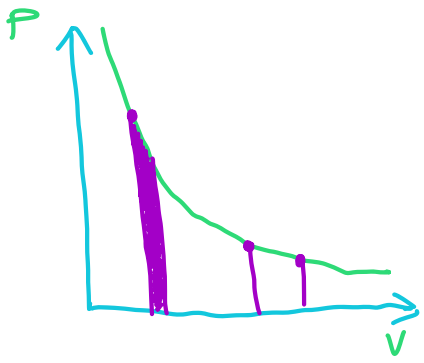
A – B : Isothermal Expansion
Hot reservoir provides heat to system (+ IE as Heat) due to (from res.)
: + S

B – C : Adiabatic Expansion (Reversible)
Reservoir shut off
Expansion continues at cost of internal energy (– IE as Work)
Gas cools.
: S = Constant.

C – D : Isothermal Compression
Surroundings do work on gas
Gas cools down due to heat rejection in cold reservoir (– IE as heat)
: – S

D – A : Adiabatic Compression (Reversible)
Reservoirs shut off.
Surroundings compress gas, heating it up (+ IE as Work) from Surr.
Gas Ends up in same state prior to cycle
: S = Constant

Carnot Cycle



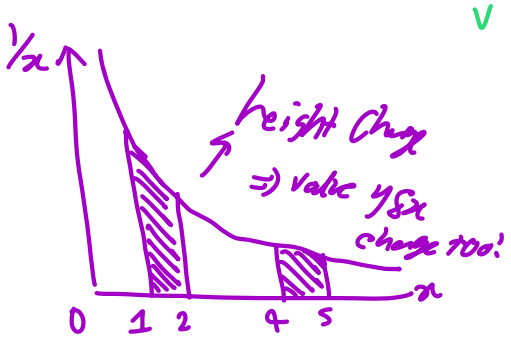
① Isothermal Expansion $T = \text{Constant} \Rightarrow \Delta Q = -P\Delta V$

The HEAT is providing Energy for the expansion of the gas.

Entropy Increases (HEAT Transfer)

① Since we do not allow Temperature to change, the internal Energy remains the same.

Temperature : Value representing the no of ways in which a unit of Energy can be distributed.



Isothermal : keep feeding random Energy to mechanism.

↓ ↳ the x d.of get used up but is replenished.

the Entropy increases in the process.

Why temperature stays constant?

Entropy ↑ ← increases more difficult to add to a ring d.o.f

Relate to equilibrium between each point

Principle of Operation: ① Isothermal Expansion of the gas inside.

The system is placed on a hot reservoir T_h and allowed to expand. The process is isothermal meaning that $\Delta U = 0 \Rightarrow \boxed{\Delta Q = -P\Delta V}$

Why sys. at eq does no work?

The system is not spending a dime. It is drawing heat Energy to make as if it is moving the piston.

↑

But like all processes, this comes at a price!

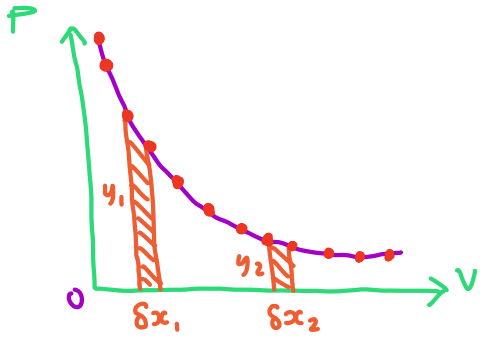
Piston is a macroscopic mechanism which capture x dof molecules hit it often.

Let's take a closer look at what is happening!

↑

Why do they not bounce the new Energy added between themselves but give it to work? Equilibrium thing

Start with system before heat input. It does no work to move the piston as it is in thermodynamic equilibrium. All dof internally cancel each other. (a molecule of gas with x-energy gives it to one who lacks and the bounce it between themselves $\epsilon = \frac{KT}{2}$ - Equipartition theorem).



Now let's pump heat into our system (one segment). Randomly, it adds more energy to the x, y and z d.o.f. x d.o.f has a way to get rid of that energy, it gives it to the piston to do work. Note that not all molecules get x energy. Those who randomly get an excess of it give it to the piston before sharing their x energy with other molecules. The y & z energies which get added randomly get shared.

?!

Does not look fine Analyse this more!

E.T states that all d.o.f have same Energies meaning that x^{dof} keeps some for itself to share to reach same new higher d.o.f value. New thermodynamic Equilibrium is reached.

Heat has increased Entropy meaning that there is relatively fewer d.o.f for that work.

Now as the x d.o.f are spent, it is replaced by more by randomness of heat. But there's a catch! Entropy has increased and heat has more ways to get energy into non-x d.o.f compared to x. This makes work less viable at higher Entropy.

Consider E. Losses in work expansion contraction

Think of This!

eq. could be same as old or new

Note that it is the process of doing work which brings to equilibrium.

2 Observations:

① Each point on the graph represents thermodynamic Equilibrium.

Moving from one point to another must be done slowly so as to predictively disturb the system (quasi-static)

② The work is done when moving between the equilibrium points. (We disturb the system by changing pressure or volume and the system responds by exchanging energy in form of heat or work to get back to equilibrium). At a fixed point (thermodynamic equilibrium, NO energy exchange occurs.

↗ fixed heat bath

Is the System in Carnot Cycle in equilibrium? When system releases Energy, it expends its U. when it gets, it takes from Environment. Exchanges can take place via heat or work.

We see by comparing $y_1\delta x_1$ & $y_2\delta x_2$ that as the isothermal compression goes on, less work is being obtained. This is due to rising Entropy increasing #microstates which results in less and less kind of only 1 d.o.f for work

↳ How heat does it?

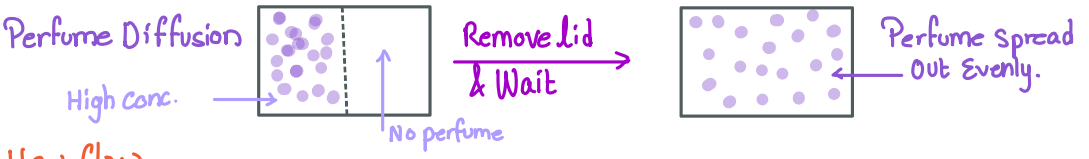
② Adiabatic Expansion

We now Cut off the heat & Seal the system.

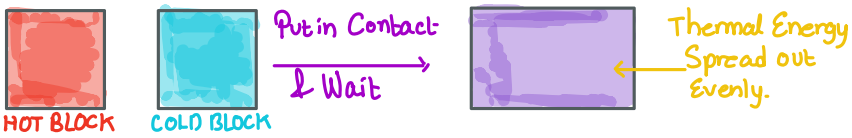
$$\Rightarrow \Delta U = -P\Delta V$$

TO Explain this Properly,
We MUST analyse what actually occurs at thermodynamic Equilibrium.

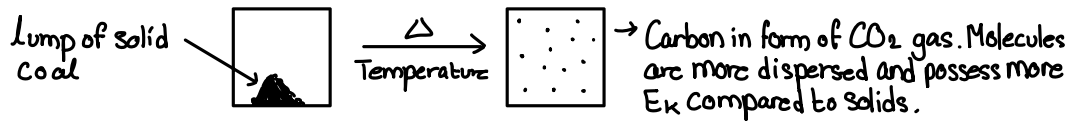
(i) Perfume Diffusion



(ii) Heat flow



(iii) Combustion of Coal : $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta S^{\ominus} = +2.9\ J mol^{-1} K^{-1}$



Work can be done to decrease entropy in one area but on the universal scale, entropy increased. This is the principle of the refrigerator, it moves heat from colder region to hotter to keep food cold. Naturally, heat flows from hot to cold as it increases entropy.

↳ Sound analogy

or $\Delta S = \frac{\Delta Q}{T}$