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TD 2213 - THERMODYNAMICS

Classical Thermodynamics

Laws of Thermodynamics

The summarise the properties of energy and its transformations.

Concepts were developed in 19th century to develop the efficiency of heat engines, heat pumps, refrigerators.
later touch upon concepts in chemistry & biology.

Each law describes a fundamental thermodynamic property -
- 0 : temperature
- 1 : energy
- 2 : Entropy
- 3 : Absolute 0.

Classical TD deals with bulk matter because that's where the laws are drawn from.

When the concepts are explained from the pov of atoms and molecules, statistical TD was developed.

The part of the universe under consideration - System
the rest is called Surroundings from where we make observations & study the system's properties

A System is defined by its boundaries -
1. Open system - can exchange matter & energy with surrounding
2. <u>Closed</u> system - can exchange only energy & <u>not</u> matter with the surroundings

   based on modes of transfer of energy, its further divided into -

   <u>Adiabatic</u> : • through work - thermally insulated boundary

   *<u>Isothermal</u> : • through transfer of heat - thermally conducting bdary
3. <u>Isolated</u> system : can't exchange work or heat with the surroundings

   This system remains unchanged

   Eg: the universe.

* Under equilibrium conditions, the T of system = T of surroundings

Property of any system is defined by prevailing conditions, described by state variables like T, P, volume, internal energy, etc no. of moles ...

<u>Extensive</u> properties – they depend on the amount of matter present. Eg: mass, volume

<u>Intensive</u> properties – they are independent of the amount of matter present in the system. Eg: T, density.

Gaseous matter

- The P of a gas varies ~~invariably~~ inversely with volume
- Among T, P, V and n, if we know any 3, we can calculate the fourth.

⇒ These variables are interconnected through an eqⁿ of state —

$\boxed{PV = nRT}$ where $R = 8.314\ J\,K^{-1}mol^{-1}$ Universal Gas constant.

This can be derived from Kinetic Theory of Gases based on —

① Gas consists of tiny molecules & volume occupied by a single molecule is negligible compared to the volume occupied by the gas.

② Attractive force between gas molecules is negligible

③ The pressure P of the gas is due to the bombardment of gas particles on the walls of the container.

These assumptions are only valid for Ideal Gases.

Kinetic Gas Eqⁿ : $\boxed{PV = \frac{1}{3} mNc^2}$

m: mass of gas molecule
N: No. of molecules
c: root mean square velocity

$PV = \frac{1}{3} mNc^2 = \frac{2}{3} \cdot \frac{1}{2} mN_A c^2$ where $N = N_A$

$\frac{1}{2} mN_A c^2$: KE of 1 mol of gas molecules $= E$

$\therefore PV = \frac{2}{3} E = RT$

(kinetic)

$\therefore \boxed{E = \frac{3}{2} RT}$ ⇒ Energy of ideal gas depends only on T, independent of P, V & nature of gas.

$E \propto T$ ⇒ $c \propto \sqrt{T}$ ⇒ Speed also only varies with T.

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Lecture 2A

Classical TD focuses more on gases because -

- its the simplest state of matter
- laws of gases are more uniform & better understood.

Absolute '0'T and Joule-Thomson effect cannot be understood without understanding the nature of gases.

Equation of State or Ideal gas equation : $PV = nRT$ - ①

* Boyle's Law $V = \frac{nRT}{P}$ $\Rightarrow$ $V \propto \frac{1}{P}$ at const temperature & no. of moles.

i.e At constant T and n, $PV =$ constant.

* Charle's Law : At constant pressure and no. of moles, $V \propto T$ i.e volume varies with T directly

* Avagadro's law : At constant P and T, the volume occupied by gas is directly proportional to no. of moles

$V \propto n$

According to postulates of kinetic theory of gases, these equations are applicable for ideal / perfect gas.

Real gas systems deviate from this under certain conditions.

Recall : Kinetic gas eq^n : $PV = \frac{1}{3} mNc^2$

This gave us, $E = \frac{3}{2}RT = \frac{1}{2} mN_A c^2$

c: root mean square velocity.

So $E \propto T$ $\Rightarrow$ $\boxed{c \propto \sqrt{T}}$

Pressure - bomardment of gas molecules on the walls of container caused by the translational motion of gase.

Translation KE is independent of P, V and nature of gas.

The molecular motion is thermal motion – random & disorganised

$E = 0$ at $T = 0$

So, molecular motion ceases or stops completely at absolute temp.

Consequence : $P = 0$ at $T = 0$.

Lecture 2B

Real gases deviate from ideal gas equations under conditions which vary from the postulates of Kinetic Theory.

① Volume of a single molecule is negligible compared to the entire volume available.

For Real Gases → ⇒ Entire volume is compressible.

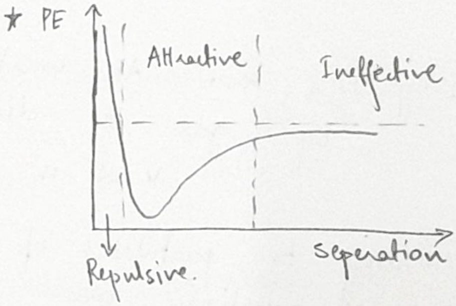
② No inter-particle interactions

→ ⇒ particles will move independent of one another

Conditions under which real gases deviate –

Boyle's Law $V \propto \frac{1}{P}$ (T, n)

Charle's law $V \propto T$ (P, n)



* At very low pressure, the available volume is very high

So volume of each particle can be neglected

⇒ Real gas satisfies Postulate ①

So under conditions of low pressure, the seperation is also very high ⇒ there is essentially no interaction.

Under very low P conditions, P① is satisfied

Compress the gas by increasing pressure, then volume of particle can't be neglected & interactions are also significant because of decreased seperation.

NOT IDEAL.

Similar condition if we decrease T i.e volume decreases

∴ High P, Low T – deviates from ideal gas conditions.

Particle - Particle Interactions

Consider 1 mole of ideal gas a temp T and pressure P with volume V_m°.

Assume that suddenly repulsive interactions dominate i.e. particles get pushed apart i.e expansion of the gas to V_m

So, $\frac{V_m}{V_m^\circ} > 1$ i.e. $Z > 1$

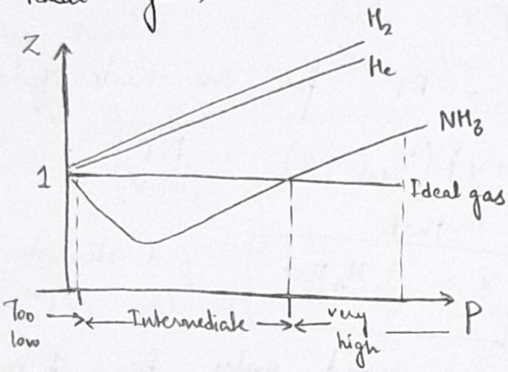
If attractive interaction dominates, it draws molecules together, which means it favors compression $\Rightarrow \frac{V_m}{V_m^\circ} < 1$.

$\therefore Z < 1$

Relative ratio of $\frac{V_m}{V_m^\circ}$ is a measure of the interaction between gas particles given by, $\boxed{\frac{V_m}{V_m^\circ} = Z}$

Z : Compressability factor

For ideal gas, $Z = 1$ under all conditions of T, P.



- NH_3 can be explained based on the potential energy vs seperation graph i.e. we see repulsive interation at very high P.
- At very low P → very large speration → ineffective interaction
- At intermediate P, attraction comes into play. So, $\frac{V_m}{V_m^\circ} < 1$

For H_2 and He, $Z > 1$ because of their compairitively small masses — negligent attractive & dominant repulsive interactions. So $Z > 1$ always.

This discussion is very important to study Joule-Thompson effect.

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Lecture 03

Drawbacks of assumption of Kinetic theory

- Gas particles don't occupy any volume → ideal assumption

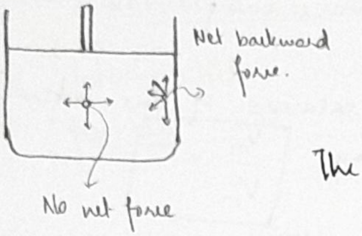
If there's 1 mol of gas in a container, entire volume V that they occupy is compressible.

Real gas particles occupy finite volume.

$V_{ideal} = V_{real} - x$ ① x: correction value

- No interaction b/w gas molecules → ideal assumption

Consider a container containing real gas where attractive forces dominate



$P = \frac{Force}{Area}$ = Bombardment of gas particle on walls on container.

The particle will strike the wall with less vigor and less strength because its pulled back by other particles

$P_{ideal} = P_{real} + y$ ②

We know that $PV = RT$ for one mole of ideal gas.

For real gas, $(P_{real} + y)(V_{real} - x) = RT$

Van der Waals found out that,

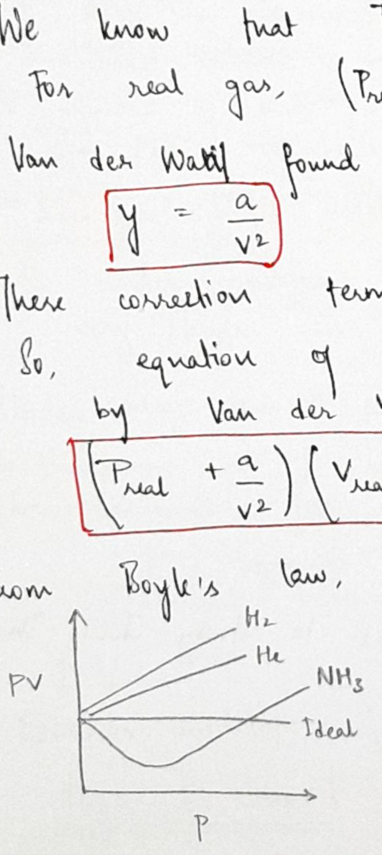
$\boxed{y = \frac{a}{V^2}}$ $\boxed{x = \frac{4}{6} N_A \pi d^3}$ d: diameter of gas particle

* These correction terms are valid only for 1 mole of real gas

So, equation of state for a real gas is given by Van der Waal's equation –

$$\boxed{\left(P_{real} + \frac{a}{V^2}\right)\left(V_{real} - b\right) = RT}$$

From Boyle's law, PV = constant at constant temperature.



Constant temperature curves i.e. isotherms,

* At low 'p' (at a given T), the volume can be high i.e. correction factor b can be g neglected.

$\Rightarrow PV = RT - a/V$

* When pressure is very high, we can neglect 'a' correction term

$\Rightarrow PV = RT + Pb$

* The nature of curve of ammonia can be explained through this

Charle's Law, at a given P, volume increases with T.
If we increase the T, the volume will also increase. ⇒ b can be neglected and a/v^2 also becomes negligible.
So, the equation becomes — $PV = RT$
So, at high T real gases tend to behave ideally
This is because volume will increase, so the postulates of kinetic theory are being satisfied

Van der Waal's eqn also explains the nature of curve of H_2 and He. They have very small mass, so attractive interaction between them is negligible
So $P.(V-b) = RT \Rightarrow PV = RT + Pb$
⇒ At a given T, if we increase the pressure, PV always increases.

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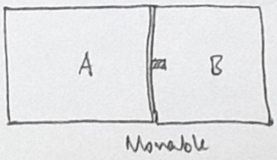
Lecture 04

Zeroth Law of Thermodynamics

Although the fact was known, it was added to Thermodynamics is an afterthought — added in 20th century after 1st & 2nd law had been formulated

This law introduces the concept of temperature



Movable system

Consider two gaseous closed systems seperated by a movable piston that's initially pinned in place

When the pin is removed, if the piston moves towards the left, we can infer that $P_A > P_B$.

If the pin doesn't move, we can infer that $P_A = P_B$.

The technical expression for this 'equality of pressures is 'mechanical equilibrium'.

∴ Pressure is a concept / property that indicates when two systems are in mechanical equilibrium

P is universal indicator of

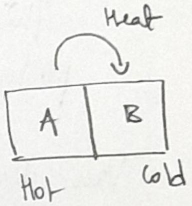
Consider we replace A with another system C. and again we see that nothing happens i.e., $P_C = P_B$

From this we can say that A and C have to be in mechanical equilibrium when you bring them together.

In other words, systems A, B and C have same pressure.

In thermodynamics,

consider that two systems are in contact



If one of them is hotter than other, then heat is transferred from A to B

This transfer energy goes on until A & B reach the same degree of hotness.

Suppose there's <u>no transfer</u> of heat ⇒ A & B have the same degree of hotness.

We can conclude that they are in thermal equilibrium.

Consider that we now replace ~~B~~ A by C and we observe that nothing happened.

∴ We can say that A and C are also in thermal equilibrium.

Statement : If A is in thermal eq with B and B is in thermal eq. with C, then A ~~is~~ will be in thermal equilibrium with C.

Analogous to pressure, temperature is the property of the system that indicates when systems will be in thermal equilibrium.

i.e. if A, B & C have the same temperature, then they are in thermal equilibrium.

* The working principle of thermometer is based on 0th law.

Mercury is used because its a liquid metal and has a very high coefficient of thermal expansion i.e. for 1° rise in T, mercury will expand noticeably compared to many other substances.

Mercury is inside a glass capillary in a thermometer

The temperature between bp and mp of water was divided into 100 different parts and ~~it~~ this is called the Celsius scale.

Its a relative scale and prone to error.

The principle behind ~~0th law~~ * working of thermometer is the 0th law — A: Tongue
B: Glass capillary
C: Mercury.

Absolute temperature scale was proposed by Lord Kelvin.

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Lecture 5A

Kelvin observed that for one mole of gas

$PV_m = RT$ i.e PV_m should go to 0 when $T = 0$.

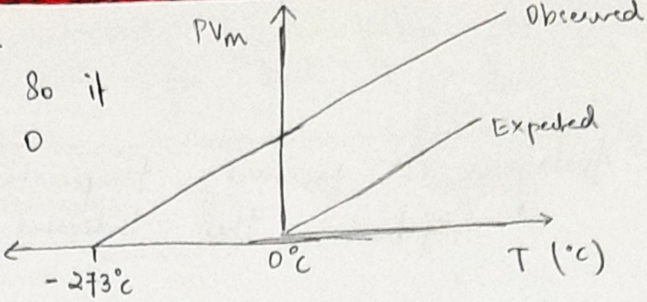
~~Whe~~ We know that at very low P (v. high volume) real gases behave like ideal gases

He carried out expt at very low pressures and plotted PV_m versus T.

Whate he observed -

$PV_m \neq 0$ at 0°C. So it can't be the absolute 0

So he extrapolated the curve to the point where $PV_m = 0$.



The T at which $PV_m = 0$ was found to be ~-273.15°C

i.e at this T, $P = 0$ which means there is no bombardment of gas particles on the wall

i.e. the molecular motion completely ceases

$$\Rightarrow KE = \frac{3}{2}RT = 0.$$

Thus this temperature (-273.15°C) was considered as the absolute 0 of temperature called 0 Kelvin.

The Kelvin scale of T (based on absolute 0) is called the thermodynamic scale of T.

Lecture 5B

First Law of Thermodynamics

- Its an extension of Law of Conservation of Energy - that it can't be created or destroyed, just transformed from one form to another.
- This law clarifies the concept of energy. and understand the notion of "work"

Work - motion against an opposing force is called work

Eg: lifting up an object -

$W = mgh$ where $g = 9.8\ ms^{-2}$

A stretched spring has more capacity to do work than a resting spring. Greater the distance of stretching, greater the capacity to do work.

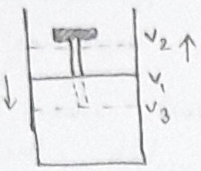
This capacity of system to do work is known as Energy, specifically as Internal energy of the system

Stretching a spring means we're doing work on the system and hence increasing energy.

So, work is a mode of transfer of energy.
The other mode is heat

What is the difference?
The distinction b/w work and heat is made only in the surroundings and not in the system
i.e. system is indifferent to the mode of transfer of energy.

Consider:



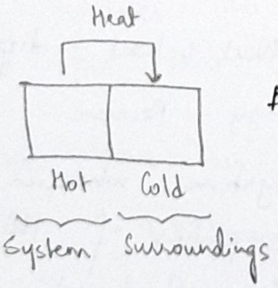
Expansion ⇒ equivalent raising weight by height h
So the system performs work, thus decreasing its own internal energy.

All the atoms of weight are raised uniformly.

In case II, when P is increased, the volume decreases, because of work done on the system. So, the internal energy of system increases.
So all atoms are decreased by some level

* ∴ Work is the transfer of energy by the organised motion or uniform motion of atoms in the surroundings.

Heat



WKT, $KE = \frac{3}{2}RT$

Atoms in hot block will be oscillating more vigorously than atoms in the cold block.
At the point of contact, the atoms vibrating with more vigor will simulate those oscillating with less vigour to move more vigorously.
This has the effect of an energy transfer.

There is no net movement of blocks itself. Thermal motion of atoms is random & unorganised

Heat is the transfer of energy by the unorganised or random motion of atoms in the surroundings.

work : w heat : q Internal energy : U

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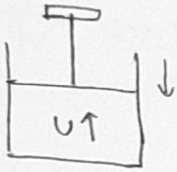
Lecture 06

When heat flows into a system, the internal energy increases and when it flows out, U decreases.

Consider a container where piston is coming down i.e work done on the system increases internal energy.



At a microscopic level, when the piston comes down, it hits the gas particles and accelerates it. That particle randomly collides with other gas particles and energy will be quickly dispersed

When heated, first the thermally conducting wall gets heated up, heats the gas particles near it. They collide with other particles and disperse energy.

Either way, the result inside the system is the same. The mode of transfer matters only in the surroundings.

Analogy : System - bank Work & heat - different currencies
Internal energy - Reserve

U is a property of the system, whereas, work and heat are properties of the path that changes U. i.e. q & w are processes to change U.

Changing U ⇒ Changing the state of the system

Internal energy is a state function i.e independent of the path taken, it only depends on initial and final states

$$\Delta U = U_i - U_f$$

$$\boxed{\Delta U = q + w}$$

Mathematical expression of first law of thermodynamics.

Heat flow into the system (+ve) ; Work done on the system (+ve)
out of the system (-ve) by the system (-ve)

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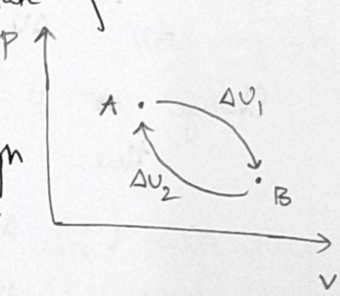
Lecture 07

If internal energy was not a state function —

$$\Delta U_2 > \Delta U_1$$



⇒ When we reach state A, through Path 2, the system is left with more energy

So, if the same cyclic path is traversed, more & more energy will be created even though the system is in same state

⇒ Perpetual motion machine — a machine that can generate more energy, with expenditure of energy.

This violates the cumulative human experience, and the law of conservation of energy.

Suppose we have an adiabatic system i.e. $q = 0$ —

$$\Delta U = q + w$$

$$\Rightarrow \Delta U = w$$

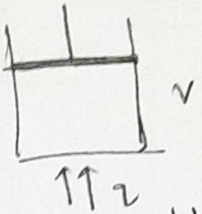
Its internal energy can be changed only by doing work.

For an isolated system, $q = 0$ and $w = 0$.

$\Rightarrow \Delta U = 0$ i.e. internal energy of an isolated system is a constant.

Consider a system with fixed volume — When heated, the heat q will be used to increase the internal energy

i.e $\boxed{\Delta U = q_v}$ → heat at const. volume



Then, we release the pin and make the piston movable, gas is allowed to expand.

Now when heated, the speed of gas particle increases $\Rightarrow$ pressure also increases, and piston moves up

So this is similar to heating at constant pressure

Moving up the piston — work is done and a fraction of energy is used up for it.

$\Rightarrow \Delta U < q_p$

Change in U can't account for heat absorbed at const P.

Here, $w = -mgh$

m: mass of piston
h: distance the piston moves

$\Rightarrow q = \Delta U + mgh$

$W = \text{Force} \times \text{displacement} = (\text{Pressure} \times \text{Area}) \times \text{displacement}$

$\therefore W = P\Delta V$

So, $\boxed{q_p = \Delta U + P\Delta V}$

This $\boxed{q_p = \Delta H}$ i.e. the heat absorbed at constant pressure is known as Enthalpy.

As U, P and V are all state functions, ΔH is also a state function.

Enthalpy is not a thermodynamic property in the strictest sense. It's an accounting trick to keep track of heat absorbed at constant pressure.

Also, invisible tracks the leakage of energy as work.

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Lecture 8A

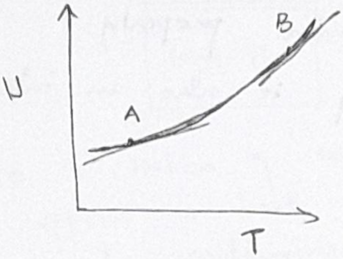
Recall : Heat absorbed constant value, $q_v = \Delta U$

This is done by maintaining a T gradient between the system and surroundings.

Amount of heat transferred varies directly with the magnitude of the gradient

$\Rightarrow$ ΔU will increase greatly.

$\therefore$ Internal energy has more or less, a linear relation with temperature



The slope of tangent at any given T is —

$$\left(\frac{\partial U}{\partial T}\right)_v = C_v$$: Heat capacity at constant volume

$$\Rightarrow \boxed{dU = C_v . dT}$$

From graph $\Rightarrow$ Heat capacity of a system varies with temperature

This can be explained by statistical thermodynamics based on population of various energy levels wrt temperature.

Experimentally, it has been determined that, above room T, for a reasonable range of T, C_v varies slightly

$\Rightarrow$ It is approximately constant.

$\Delta U = q_v$

$$\therefore \boxed{\Delta U = C_v \Delta T}$$

$$\therefore \boxed{C_v = \frac{q_v}{\Delta T}}$$

If $\Delta T = 1°C$, $C_v = q_v$

$\Rightarrow$ Heat capacity is the amount of energy to raise the temp. of system by 1°c.

energy $\downarrow$ supplied as heat at *constant V.*

A system will have large C_v when amt of heat required to raise the T is large

A system can have infinite heat capacity i.e. no increase in T, however much energy is supplied as heat.

Eg. At BP of water, T is constant during phase transition. Energy supplied will be utilised for vaporisation of water & not to raise T.

Heat capacity is an *extensive property* i.e. its a property that depends on the amount of matter present in the system

More matter ⇒ More heat required

But $\frac{C_v}{n}$: molar heat capacity at constant volume is an intensive property

$\frac{C_v}{w}$: Specific heat capacity is also an intensive property.

Unit of C_v : $J K^{-1}$

Water has very high heat capicity.

⇒ Its a good material to use in cooling system

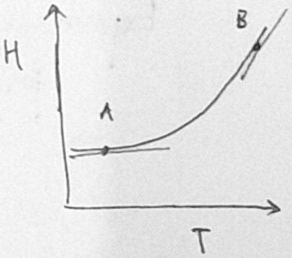
Oceans are slow to heat and slow to cool.

Lecture 8B

Heating system at const. pressure –

$$\Delta H = q_p$$

Experimentally, it has been observed that,



$$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$: Heat capacity at const P.

$$\boxed{dH = C_p dT}$$

C_p varies with T. But above room T. for a reasonable range, C_p is more of less constant.

$$\Rightarrow \Delta H = C_p \Delta T$$

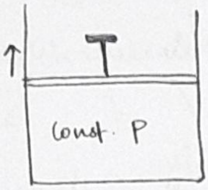
$\boxed{\Delta H = C_p \Delta T}$ $\Rightarrow$ $\boxed{C_p = \frac{q_p}{\Delta T}}$

C_p is the amount of heat energy required at const P. to raise the temperature by 1°c.

C_p is also an extensive property

But molar and specific heat capacity at const. pressure are both intensive properties.

Difference between C_p and C_v



Here, a portion of energy supplied as heat is used for performing the expansion work

Remaining fraction → increasing temperature

All energy provided will be available for increasing T.

$\Rightarrow$ At const P. more energy is required to raise the system by same ΔT than in the case of constant volume

$\therefore C_p > C_v$

For 1 mole of an ideal gas —

$C_p - C_v$ = Expansion work done by 1 mole of gas when heated through 1°c at const. P.

WKT, $W = P\Delta V$

When $T \rightarrow T+1$ $V \rightarrow V+\Delta V$

$P(V+\Delta V) = R(T+1)$ $\Rightarrow$ $P\Delta V = R.$ $\boxed{C_p - C_v = R}$

→ Molar heat capacity of an ideal gas about ~ 8 $JK^{-1}mol^{-1}$ higher at const P than const V

For monoatomic gas, $C_v \approx 12\ JK^{-1}mol^{-1}$

and $C_p - C_v = 8.314\ JK^{-1}mol^{-1}$

∴ The difference is quite significant and must be taken into account.

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Lecture 9A

Many chemical reactions involve consumption and evolution of gaseous species. So expansion work is very important.

Eg: Combustion of octane — releases CO_2

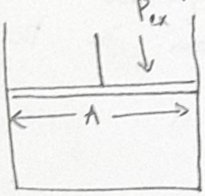
Decomposition of $CaCO_3$ ↗

Expansion work also considers negative change in volume i.e compression.

In physics, work is motion against opposing force

$$dW = -F.dz \quad ①$$

i.e when system moves the object, the internal energy of the system decreases.



If there's constant ext. pressure on a movable piston of area A —

$$\frac{P_{ex}}{\cancel{A}} . A = F \quad ②$$

$$dW = -F\,dz = -P_{ex}\,A.dz$$

$$dW = -P_{ex}\,dV$$ where dV: change in volume during expansion.

~~dV~~ × $V_f - V_i$: final and initial volume.

Total work done —

$$\boxed{W = -P_{ex}\int_{V_i}^{V_f} dV} \quad ⑤$$ - General expression of expansion work

$V_f > V_i$ - expansion $V_f < V_i$ - compression

Lecture 9B

If $P_{ex} = 0$ — opposing force, $F = 0$.

WKT, $W = -P_{ex} \int_{V_i}^{V_f} dV$ i.e $W = 0$. (only for ideal gas ∵ no interactions)

This means that there is free expansion of gas. Expansion of this type occurs when a gaseous system expands in vacuum.

For n moles of ideal gas, the internal energy is independent of the volume occupied by the gas because it has no interactions to overcome
⇒ U is only a fn of temperature.

For a real gas, there can be attractive interactions. So even if $P_{ex} = 0$ (gas expands in vacuum), it'll have to overcome attractive interactions between gas particles. So for a real gas, $w \neq 0$ even for free expansion.

If an ideal gas expands isothermally — U remains constant i.e. $\Delta U = 0$ because it depends only on temperature.

Change in enthalpy : $H = U + PV$ ⇒ $\boxed{\Delta H = \Delta U + \Delta(PV)}$

$\Delta H = \Delta U + \Delta(nRT) = \Delta U + \Delta nRT + nR\Delta T$

$\Delta n = 0$ (fixed no. of moles). $\Delta T = \Delta U = 0$.

∴ $\Delta H = 0$ for isothermal expansion

WKT, $\Delta U = q + w$ ⇒ $\boxed{q = -w}$

∴ During isothermal expansion, work is done at the expense of heat absorbed.

However, the magnitude of work done depends on whether the process is carried out reversibly or irreversibly.

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Lecture 10A

Reversible isothermal expansion

↳ In thermodynamics, its a change that can be reversed by an infinitesimal modification of a variable.

Reversible - something that can change direction.

A reversible change usually happens when the system is in equilibrium with its surroundings.

★ Eg: A & B are in thermal equilibrium.
If T of B is lowered infinitesimally, energy will flow into B
If T of A is raised slightly, then energy will flow out of A.
Here, energy flow as heat occurs reversibly.

★ Consider an ideal gas in a container with ext. pressure P_{ex} ⇒ system is in mechanical equilibrium
If P_{ex} is changed infinitesimally, then the volume of the gas will change inversely (opp. direct)
i.e. P_{ex} reduces ⇒ Gas expands
Here, the gas expands reversibly.

★ Consider situation where $P_{ex} \ll P$ where P is the pressure of gas. If P_{ex} is changed infinitesimally, it will not change the direction of the process.
because system is not in mechanical equilibrium
So, the expansion is said to be happening irreversibly

In isothermal reversible expansion, we must make sure that at every stage, $P_{ex} = P$ i.e. its in mechanical equilibrium at every stage. To do so, we must decrease the pressure infinitesimally.

Generally, $W = -\int_{V_i}^{V_f} P_{ex}\, dV$ Since $P_{ex} = P$ —

$$= -\int_{V_i}^{V_f} P.\, dV = -\int_{V_i} nRT .\frac{dV}{V}$$

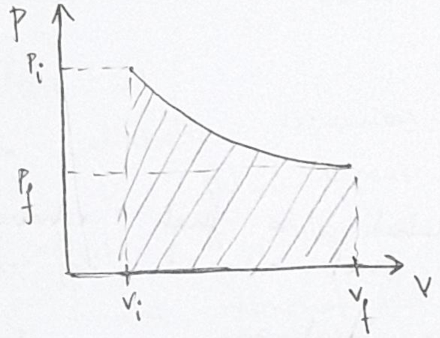
Isothermal ⇒ T is constant ⇒ $W = -nRT \int_{V_i}^{V_f} \frac{dV}{V}$

$$\therefore \boxed{W = -nRT \ln\left(\frac{V_f}{V_i}\right)}$$

Isothermal reversible expansion

In expansion, $V_f > V_i$ ⇒ work will be negative.

In Pressure - Volume indicator diagram,



there, gas expands gradually from P_i to P_f.

How to ensure gradual expansion?

$P_{ex} = P$ at every stage

$P = \frac{nRT}{V}$ P vs $\frac{1}{V}$ - linear

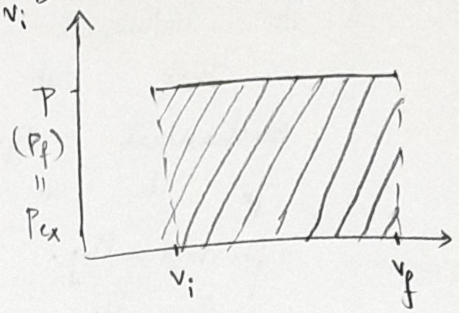
Under these conditions, total work done is the area under the whole curve

If at $t = 0$, I set $P_{ex} = P_f$ — the gas will expand irreversibly. Because under such conditions, $P_{ex} = P_f$ is quite different from P_i. System will not be in mechanical equilibrium with its surrounding. Infinitesimal change in P_{ex} will not affect pressure of the gas.

In that case, expression of work done is –

$$W = -\int_{V_i}^{V_f} P_{ex}.dV = -P_{ex}\int_{V_i}^{V_f} dV$$

$$\therefore \boxed{W = -P_{ex}(V_f - V_i).}$$



Indicator diagram — $P_{ex} \ll P$
P_{ex} is fixed as constant value of P_f.

From graphs, we can see that, ∵ of size of area
$W_{rev} < W_{irr}$

When we set $P_{ex} = P$ at every stage, it ensures that none of the system's pushing power is wasted

We cannot work more work than a reversible process.
If P_{ex} is changed slightly, there's a compression
⇒ System is doing maximum possible work.

When $P_{ex} \ll P$, some of the pushing power of the system is wasted.

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Lecture 10B

Adiabatic system
↳ The boundary is insulated so that exchange of energy as heat is not allowed i.e $q = 0$

Adiabatic expansion of an ideal gas
$$\Delta U = q + w = w$$
Expansion ⇒ work should be done by the gas which means w is negative
⇒ ΔU is -ve ⇒ T also decreases.
⇒ Internal energy of system will decrease.
Work is done at the expense of system's U.

As T decreases, there will be a cooling effect

WKT, $\Delta U = C_v \Delta T$ C_v : heat capacity at const volume

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + R\Delta T \quad \text{(for 1 mole)}$$

$$\Rightarrow \Delta H = C_v \Delta T + R\Delta T = (C_v + R)\Delta T$$

$$\boxed{\Delta H = C_p \Delta T} \quad \because C_p - C_v = R.$$

What about work done?

WKT, $\boxed{\Delta U = w = C_v \Delta T.}$

We can see that, ΔU, ΔH and w all depend on ΔT. We know that maximum work can be extracted from a reversible ~~state~~ reaction.

⇒ ΔT depends on the way adiabatic process is carried out – reversibly or irreversibly.

Max ΔT can be expected if work is done reversibly.

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Lecture 11

In adiabatic expansion, $w = -\Delta U$ i.e work is done at the expense of U i.e a cooling effect is observed

This was demonstrated by JP Joule and William Thomson.

They allowed real gases to expan from a region of high P into vaccum or region of low P * through a porous plug. Apparatus is thermally insulated

Most often, they observed a decrease in temperature.

This is known as Joule-Thomson effect.

They showed that it was due to decrease in kinetic energy which is used to overcome the van der Waals interactions.

* ~5:15 video.

During expansion, avg seperation of gas particles will increase for which energy is required — a part of KE is used for this.

That's why there's a cooling effect.

When gas approaches ideal behaviour, Joule-Thomson

* effect is very small, because theoretically, there are no interparticle attractions to overcome.

If a gas expands in vacuum —

$w = 0 \Rightarrow \Delta U = w = 0 \Rightarrow \Delta T = 0$

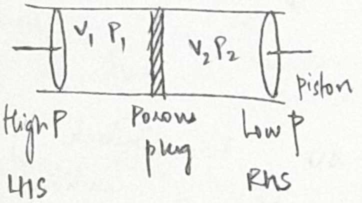
i.e no cooling effect.

For an ideal gas, change in U wrt volume at a constant T, i.e $\left(\frac{\partial U}{\partial V}\right)_T = 0$

∴ U depends only on T.

$\left(\frac{\partial U}{\partial V}\right)_T$: internal pressure of gas ∵ units are $\frac{N}{m^2} = Pa$

Adiabatic box



Gas enclosed in LHS of volume V_1, pressure P_1 is pushed through the porous plug, into the RHS where it expands to volume V_2 at pressure P_2

LHS — doing work on system i.e $w = +ve$

RHS — Gas expanding (system is doing work) $w = -ve$

$W_1 = P_1 V_1$: LHS

$W_2 = -P_2 V_2$: RHS

Net work done by the system —

$w_1 + w_2 = P_1V_1 - P_2V_2 = \Delta U = U_2 - U_1$

As this is an adiabatic system, $q = 0 \Rightarrow \Delta U = w$

$\therefore U_2 - U_1 = P_1V_1 - P_2V_2$

$\Rightarrow U_1 + P_1V_1 = U_2 + P_2V_2$

WKT, $H = U + PV$

$U_1 + P_1V_1 = U_2 + P_2V_2$

∴ $H_1 = H_2$ ⇒ $\Delta H = 0$

⇒ Joule-Thomson effect is a constant enthalpy or an isenthalpic process.

$H = f(T, P)$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

WKT, $\left(\frac{\partial H}{\partial T}\right)_P = C_P$ – heat capacity at const. P

Also, in an isenthalpic process, $dH = 0$

$$\Rightarrow C_P\, dT = -\left(\frac{\partial H}{\partial P}\right)_T dP$$

$$\left(\frac{\partial T}{\partial P}\right)_H \cdot \cancel{dP} = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T \cancel{dP}$$

$$\therefore \boxed{\left(\frac{\partial T}{\partial P}\right)_H = \frac{-1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T = \mu_{JT}}$$

μ_{JT} : Joule-Thomson coefficient.

It depends on the nature of gas and the conditions at which the experiments are carried out.

Summary

$\left(\frac{\partial T}{\partial P}\right)_H$: Positive because dP – -ve (expansion)
dT – -ve (cooling effect)

$\left(\frac{\partial T}{\partial P}\right)_H = 0$ In adiabatic expansion, dP = -ve.
So, dT has to be 0 (i.e. no effect)

$\left(\frac{\partial T}{\partial P}\right)_H = 0$ Negative Here also, dP is -ve. So dT has to be +ve
i.e. gas gets heated upon expansion.

For an ideal gas,

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{1}{C_p}\left[\left(\frac{\partial H}{\partial p}\right)_T\right] = -\frac{1}{C_p}\left[\left(\frac{\partial U}{\partial p}\right)_T + \left(\frac{\partial pV}{\partial p}\right)_T\right] \quad \text{— } ★ \qquad \because H = U + PV$$

$\left(\frac{\partial U}{\partial p}\right)_T = 0$ ∵ U depends only on T

$\left[\frac{\partial}{\partial p}(PV)\right]_T = 0$ At const T, $PV = nRT$ i.e a constant
So this term is also 0.

∴ for the abiabatic expansion of ideal gas,
$\left(\frac{\partial T}{\partial p}\right)_H = 0$ ⇒ no cooling effect

Real gas –

They can have attractive interactions between particles.

★ During expansion, avg seperation should increase, for this, work has to be done against attractive forces of interaction.

Seperation ⇒ position of particles will be different
So the work done is stored as potential energy within the system i.e PE increases
KE will remain constant because it depends on T and T is kept constant.
∴ There is a net increase in internal energy

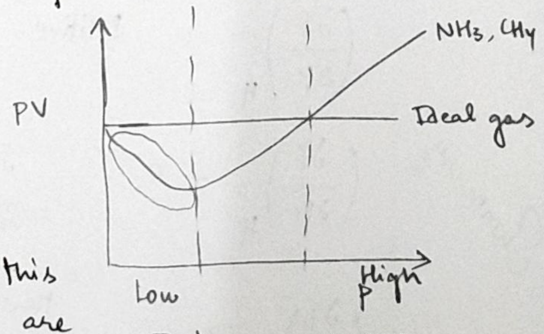
i.e $\left(\frac{\partial U}{\partial p}\right)_T =$ ~~+ve~~ -ve   dU is positive
dp is negative (expansion)

★ 2nd Term : $\left(\frac{\partial (PV)}{\partial p}\right)_T$

In low p region, $\frac{\partial (PV)}{\partial p}$ is -ve

Then, in above ★ eqn, in this case, both terms in bracket are -ve, and there's $-C_p$ outside

a) So, $\left(\frac{\partial T}{\partial p}\right)_H = +ve$ Since dp is already -ve, dT also has to be -ve
∴ COOLING EFFECT.



Isotherm curves

In the high pressure region, $\left(\frac{\partial(PV)}{\partial P}\right)_T$ is +ve. and as P increases it becomes more and more positive

So, at a particular pressure, the two terms in the bracket cancel each other out, so,

$\left(\frac{\partial T}{\partial P}\right)_H = 0$ i.e no cooling effect during adiabatic expansion at this P.

b) Beyond this pressure, $\left(\frac{\partial(PV)}{\partial P}\right)_T$ becomes very +ve

i.e $\left(\frac{\partial T}{\partial P}\right)_H = -ve \Rightarrow \partial T$ will be +ve $\because \partial P$ is always -ve.

c) Temperature increases i.e gas heats up when it expands adiabatically

μ_{JT} = +ve (low P) - Cooling effect

0 (midlevel P) - $\Delta T = 0$

-ve (high P) - Heating effect.

Best Summary

This JT Effect is very useful. Lind - Refrigerator uses JT expansion to liquefy gases!

Gas at high P is expanded through a throttle so it gets cooled, it gets circulated past incoming gas, which gets cooled and enters through the throttle, cools even more and condenses into a liquid.

Lecture 12A

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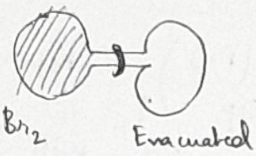
2nd Law of Thermodynamics

First law : when one form of energy is converted to another, the total energy will be conserved

Many processes have a natural tendency to occur in a particular direction.

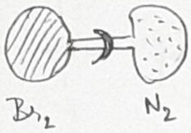
Consider:

①



When stopcock is released, both bulbs will have Br_2 at equal pressure

②



When stopcock is released, both bulbs will have uniform mixture of Br_2 and N_2

The reverse of these two processes never occurs spontaneously i.e having a tendency to occur naturally in a particular direction.

Defn:

No relation with the speed/rate of the processes.

Consider a metal bar with uniform T. For it to become hot at one end and cold at another spontaneously ∵ it wouldn't violate 1st law.

But it will never occur spontaneously. This demands a 2nd law which tells us about whether a reaction will occur in the forward / backward ~~reaction~~ direction spontaneously.

Entropy (s) : thermodynamic property

It tells us whether a reaction can occur spontaneously in a given direction

↳ State function

Entropy is a <u>measure</u> of <u>degree of disorder</u> in a given system.

Eg, When water vaporises, the random motion of H_2O will increase in gas phase ⇒ so does entropy.

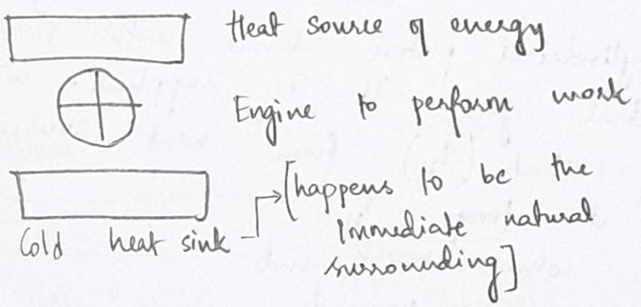
$U \rightarrow$ quantity of energy

$S \rightarrow$ <u>quality</u> of energy ($\uparrow S \Rightarrow \downarrow$ quality)

1st law : $\Delta U = q + w$

Isothermal : $\Delta U = 0$ $\Rightarrow q = -w$ ①

① ⇒ all heat can be converted to work



The engine will absorb energy from heat source, do work and unused energy is released to the heat sink (surroundings)

Wrt steam engine, they found that they could never convert heat completely into work ~~&~~

i.e efficiency << 1.

$$\eta = \frac{\text{Work performed by engine}}{\text{Heat supplied}}$$

So how much of heat can be converted to work ?

For ideal engine, ~~$\eta = 1$~~. we can calculate this and use as reference.

<u>Sadi</u> <u>Carnot</u> developed an engine – Carnot's cycle answers this

Lecture 12B

Carnot engine

Theoretical engine – consists of 1 mole of ideal gas. It was used to determine the max efficiency of theoretical heat engine

Most important specification:

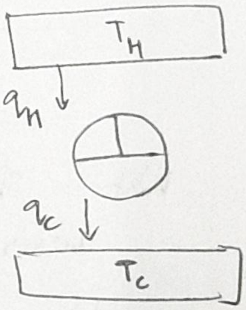
- It must function reversibly – to maximise the work output of the engine to use as theoretical reference.
- It must work in a closed cycle, because at the end of each cycle, the engine will return to it's initial state & hence can perform work again

Carnot cycle: 4 steps of alternating sequence of reversible isothermal & adiabatic changes.

~~When system~~ Recall sign conventions of q & w.

Carnot engine: cylindrical piston device with 1 mole of ideal gas. It is supplied with an amount of heat (q_H) from heat source which is at temp. T_H

The engine does some work, and releases q_c amount of unused heat to the cold heat sink, maintained at temp. T_c



Obviously, $T_H > T_c$

Defn: Carnot suitably paired reversible adiabatic & isothermal changes to make the engine work in a closed cycle, is called Carnot cycle

Each Carnot cycle conists of -

Reversible 1. isothermal expansion - ∵ q_H amt of heat
work is done by system

2. adiabatic expansion - $q = 0$
work is done by system

3. isothermal compsession - work is done on system

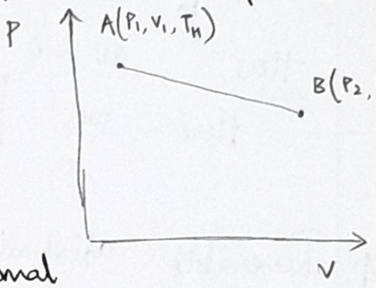
4. adiabatic compression. q_c will be rejected
└ $q = 0$, but work is done on system, which will ↑ U

Lecture 12C

1. Reversible isothermal expansion [AB]

q_H amt. of heat is absorbed (from source at T_H) by the gas and it expands.

Let work done be w_1 at const. Temp T_H.



$$P_1V_1 \xrightarrow{T_H} P_2V_2$$

Isothermal $\Rightarrow$ $q = -w$

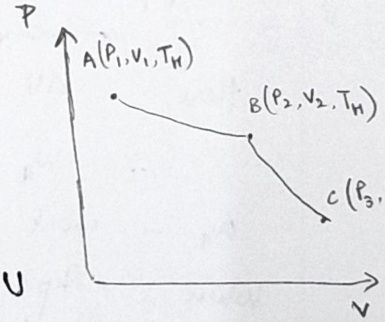
$q_H = -w_1$

Work done during reverssible isothermal expansion : $w = -RT \ln \frac{V_f}{V_i}$

Here, $\boxed{w_1 = -RT_H \ln\left(\frac{V_2}{V_1}\right)}$ $\Rightarrow$ $q_H = RT_H \ln\left(\frac{V_2}{V_1}\right)$

2. Reversible adiabatic expansion. [BC]

Here, heat exchanged, $q = 0$.



$$P_2, V_2, T_H \longrightarrow P_3, V_3, T_c$$

Here, $\Delta U = w$

Work is done at the expense of U which in turn depends on T

Say, work done is w_2

i.e $w\uparrow = U\downarrow \rightarrow \therefore T\downarrow$

$\boxed{\Delta U = C_v \Delta T}$ $\Rightarrow$ $w_2 = C_v \Delta T = C_v (T_c - T_H)$

Lecture 13A

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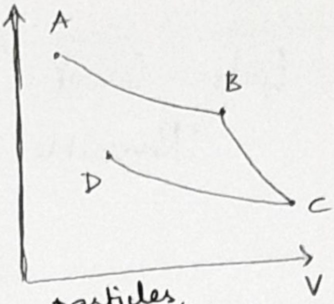
3. Reversible isothermal compression [CD]

there, pressure ↑ & volume ↓



$(C)\ P_3 V_3 T_c \longrightarrow P_4 V_4 T_c\ (D)$

Gas is compressed ⇒ work (w_3) is done <u>on</u> the system

When incoming piston strikes gas particles, gas particles will be accelerated & in turn, avg speed of gas particles will increase.

WKT, $\underset{\text{speed}}{c} \propto \sqrt{T}$

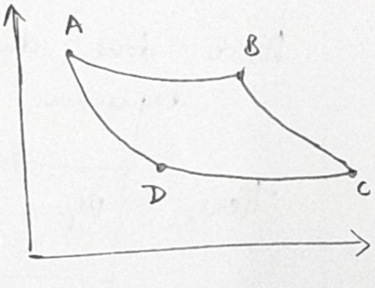
When compressed, T should increase. But to maintain temp, the system will release heat to the cold sink, q_c

there, $\Delta U = 0 \Rightarrow q_c = -w_3$

there too, $\boxed{w_3 = -RT_c \ln\left(\frac{V_4}{V_3}\right)} \Rightarrow q_c = RT_c \ln\left(\frac{V_4}{V_3}\right)$

4. Reversible adiabatic compression (DA)

there, $P_4 V_4 T_c \longrightarrow P_1 V_1 T_H$



When P increases, the temperature increases (∵ $q = 0$ i.e. increased energy can't be released as heat)

$c \propto \sqrt{T}$

there, $\Delta U = w_4$ $\quad \Delta U = C_v \Delta T = C_v (T_H - T_c)$

$\therefore w_4 = C_v (T_H - T_c)$

w_4 – work done on the system

When step 4 is completed, one cycle of the Carnot engine is completed i.e. engine goes back to the initial state

Overall, q_H : heat supplied $\quad q_c$: heat released

What is the net heat absorbed?

Clearly, its. $q_H - q_c$

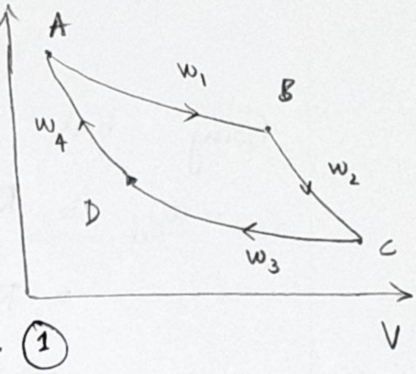
$q_H - q_c$ = net work done by the system

$$\eta = \frac{\text{net work}}{\text{Total heat}} = \frac{q_H - q_c}{q_H}$$

$$\boxed{\eta = 1 - \frac{q_c}{q_H}}$$

Lecture 13B

What is the net work done?



$$w_{net} = w_1 + w_2 + w_3 + w_4$$

$$= -RT_H \ln\left(\frac{V_2}{V_1}\right) + \cancel{C_v\left(T_c - T_H\right)}$$

$$+\left[-RT_c \ln\left(\frac{V_4}{V_3}\right)\right] + \cancel{C_v\left(T_H - T_c\right)}$$

$$w_{net} = -RT_H \ln\left(\frac{V_2}{V_1}\right) + \left(-RT_c \ln\left(\frac{V_4}{V_3}\right)\right)$$ — ①

What's the net work done by the system?

When system does work by system, its taken as -ve convention

Net work done by the system : $-w_{net}$

$$\Rightarrow RT_H \ln\left(\frac{V_2}{V_1}\right) + RT_c \ln\left(\frac{V_4}{V_3}\right)$$

To simplify this, we need a relation b/w $\frac{V_2}{V_1}$ & $\frac{V_4}{V_3}$

For an adiabatic expansion,

$dq = 0$, $dU = dW = C_v dT = -PdV$

$$\boxed{C_v dT = -PdV}$$

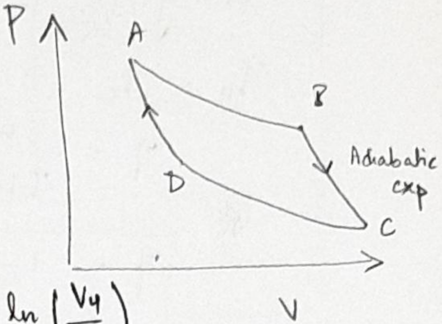
In this case, $T_i \to T_f$ and $V_i \to V_f$

$$C_v dT = -RT\frac{dV}{V} \Rightarrow \int_{T_i}^{T_f} C_v \frac{dT}{T} = \int_{V_i}^{V_f} -R\frac{dV}{V}$$: Total work done

$$C_v \ln\left(\frac{T_f}{T_i}\right) = -R \ln\left(\frac{V_f}{V_i}\right)$$

$$\therefore\ C_v \ln\left(\frac{T_f}{T_i}\right) = R\ln\left(\frac{V_1}{V_f}\right)$$: Adiabatic change

Using this equation, in adiabatic change in Carnot cycle,



$$BC:\ C_v \ln\left(\frac{T_c}{T_H}\right) = R\ln\left(\frac{V_2}{V_3}\right)$$

$$DA:\ C_v \ln\left(\frac{T_H}{T_c}\right) = R\ln\left(\frac{V_4}{V_1}\right)$$

$$\Rightarrow \cancel{R}\ln\left(\frac{V_2}{V_3}\right) = C_v\ln\left(\frac{T_c}{T_H}\right) = -\cancel{R}\ln\left(\frac{V_4}{V_1}\right)$$

$$\Rightarrow \frac{V_2}{V_3} = \frac{V_1}{V_4} \Rightarrow \boxed{\frac{V_1}{V_2} = \frac{V_4}{V_3}}$$

Going back to w_{net} eqn ① —

$$-w_{net} = RT_H\ln\left(\frac{V_2}{V_1}\right) + RT_c\ln\left(\frac{V_4}{V_3}\right)$$

$$= RT_H\ln\left(\frac{V_2}{V_1}\right) - RT_c\ln\left(\frac{V_2}{V_1}\right)$$

$$\therefore\ \boxed{-W_{net} = R\ln\left(\frac{V_2}{V_1}\right)\left[T_H - T_c\right]}$$

$$\eta = \frac{\text{net work}}{\text{heat supplied}} = \frac{w_{net}}{q_H}$$

$$\eta = \frac{R\,\cancel{\ln(V_2/V_1)}\,[T_H - T_c]}{R\,\cancel{\ln(V_2/V_1)}\cdot T_H}$$

$$\therefore\ \boxed{\eta = \frac{T_H - T_c}{T_H}} = \frac{\Delta T}{T_H} = 1 - \frac{T_c}{T_H} = 1 - \frac{q_c}{q_H}$$

∴ Efficiency of engine depends only on T_c and T_H & its independent of the nature of the substances used for the operation

As long as $T_c > 0$, $\eta < 1$ even for a perfect Carnot engine

∴ Only a fraction of heat supplied can be converted to work.

Wasn't this our assumption?

This is the basis for Kelvin's statement of 2nd law:

" In a cyclic process, it's impossible to convert heat entirely into work."

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Lecture 14A

Recall Carnot cycle: Heat is absorbed / released is q_H / q_c during isothermal expansion / compression.

Also, $\eta = 1 - \frac{T_c}{T_H} = 1 - \frac{q_c}{q_H}$

$\Rightarrow \frac{T_c}{T_H} = \frac{q_c}{q_H} \Rightarrow \frac{q_H}{T_H} = \frac{q_c}{T_c}$ when $q_H > q_c$, $T_H > T_c$

Which means, q and T vary along the path.

$\frac{q}{T}$ is a constant!

q - heat exchanged reversibly

So, $\boxed{\Delta S = \frac{q_{rev}}{T}}$ = constant = ΔS : Entropy change of the system

This eq^n is not valid for irreversible change

$\left.\frac{q_H}{T_H} - \frac{q_c}{T_c} = 0\right\}$ for one-cycle of Carnot's engine

Around this closed cycle of reversible changes,

$$\Sigma \frac{q_{rev}}{T} = 0$$

$\Rightarrow \Delta S = 0$ around the closed cycle of reversible changes

$\therefore$ Entropy is a state function

Lecture 14 B

Entropy – measure of degree of disorder in a system

$$\Delta S = \frac{q_{rev}}{T} \quad - ①$$

Even if a process happens to be irreversible, ΔS will have to be estimated using ①

→natural tendency to occur.

Consider the spontaneous expansion of an ideal gas at a constant temp T

$\Rightarrow \Delta U = 0$

It could happen when external pressure is decreased suddenly.

Suppose, its carried out reversibly.

During the expansion, gas will absorb amt $q_{rev,sys}$ of heat from surroundings.

$q_{rev,sur}$ – heat lost by the surroundings

$$q_{sys} = -q_{sur} \quad ②$$

Divide eqn by temperature

$$\frac{q_{sys}}{T} = -\frac{q_{sur}}{T} \Rightarrow \Delta S_{sys} = -\Delta S_{sur}$$

$$\therefore \Delta S_{sys} + \Delta S_{sur} = 0$$

During a reversible, spontaneous process, i.e. no entropy change

$$\boxed{\Delta S_{univers} = 0}$$

If isothermal expansion is carried out irreversibly, q : heat exchanged b/w system & surroundings. we can write,

From Eqn ②,

$$q_{irr,sys} = -q_{irr,sur} \quad - ③$$

Heat gained   Heat lost by surroundings

But surroundings is considered vv vast ⇒ change in surr. due to loss of heat will be negligible

So, for surroundings, it looks like a reversible heat exchange. We can write,

$$q_{irr,\, sur} = q_{rev,\, sur}$$

$$\Delta S_{sur} = \frac{q_{rev,\, sur}}{T} = \frac{q_{irr,\, sur}}{T}$$

For the system (v. small compared to surroundings), it'll feel the irreversible change

- WKT, Maximum change will happen in reversible process than irreversible

$$\Rightarrow \underline{q_{rev,\, sys}} > \underline{q_{irr,\, sys}}$$

From Eqⁿ ③, $q_{rev,\, sys} > -q_{irr,\, sur}$

$$\Rightarrow \frac{q_{rev,\, sys}}{T} > -\frac{q_{irr,\, sur}}{T}$$

$$\Delta S_{sys} > -\Delta S_{sur}$$

$$\therefore \Delta S_{sys} + \Delta S_{sur} > 0$$

$$\boxed{\Delta S_{universe} > 0}$$

Thus, for an irreversible, spontaneous process, total entropy change. In fact, $\Delta S_{uni} > 0$ is a condition for spontaneity!

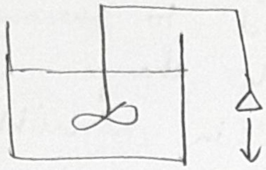
2nd law: Entropy of the universe only increases in the course of any irreversible spontaneous change

Note: There's no prohibition of system or surroundings individually undergoing a decrease in entropy, provided there's a compensating change elsewhere

Part 2

The process of matter changing from one form to another is governed by the laws of thermodynamics.

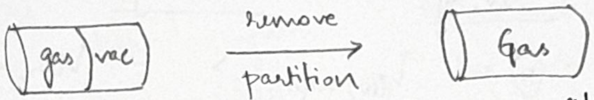
Joule's expt.



When the weight goes down, the paddle spins and water gets heated up.

But in the reverse process, water doesn't cool.

Consider a container with a partition —



But if we reinstate the partition, the reverse process won't occur.

Similarly, heat always flows from hot body to cold.

These are irreversible process and 2nd law tells us, qualitatively & quantitatively, why a process occurs spontaneously & irreversibly and why/when if doesn't.

2nd law also tells us that 100% efficiency in a engine is not possible.

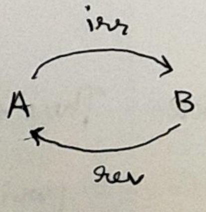
Recall : In Carnot cycle, $\oint \frac{dq_{rev}}{T} = 0$

By definition, $\frac{dq_{rev}}{T}$: entropy. So, $\oint ds = 0$

$$\Rightarrow \Delta S = \oint ds = 0.$$

This is true for any cyclic process.

Consider a cycle that's not reversible :



1st law holds : $dU = dq + dW$

For a cyclic process, $dU = 0$ $dw_{rev} < dw_{irr}$ work done on the system

$$\Rightarrow dq_{rev} + dw_{irr} = dq_{irr} + dw_{rev}$$

So, $dq_{rev} > dq_{irr}$

$$\frac{dq_{rev}}{T} > \frac{dq_{irr}}{T}$$

$$dS > \frac{dq_{irr}}{T}$$

$$\oint dS > \oint \frac{dq_{irr}}{T}$$

For an irreversible cycle $\rightarrow$ $\oint \frac{dq_{irr}}{T} < 0$

$$\therefore \boxed{\oint \frac{dq}{T} \leq 0} \quad : \text{Clausius inequality.}$$

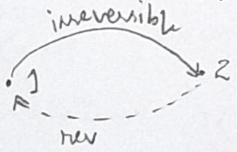
This is known as the mathematical formulation of 2nd law of thermodynamics

The irreversible processes are connected to entropy.

How to calculate entropy?

Eg: 1) Isolated system undergoing some irreversible process.

$$\Delta S_{tot} = \Delta S_{sys} \quad \text{because } \Delta S_{sur} = 0$$



To calculate, we will consider a cycle with rev. & irr. processes

$$\int_1^2 \frac{dq_{irr}}{T} + \int_2^1 \frac{dq_{rev}}{T} < 0$$

$$\int_1^2 \frac{dq_{irr}}{T} - \int_1^2 \frac{dq_{rev}}{T} = \int_1^2 \frac{dq_{irr}}{T} - \int_1^2 dS < 0$$

$$\Rightarrow \int_1^2 dS > \int_1^2 \frac{dq_{irr}}{T} \qquad dq_{irr} = 0$$

$$\therefore \int_1^2 dS > 0$$

Consider placing an ice cube in an isolated container above RT. It will melt.

$\Delta S \quad S_2 - S_1 < 0$

$\Delta S_{backward} < 0$ — ①

Since entropy is a state function,

$\Delta S_{cycle} = 0 \Rightarrow \Delta S_{forward} = - \Delta S_{backward}$

From ①, $\Delta S_{forward} > 0$

Entropy increases in a spontaneous process in an isolated system.

2) System is not isolated. Universe is an isolated system. So, for a —

- reversible process: $\Delta S_{universe} = 0$

  $\therefore \Delta S_{sys} = - \Delta S_{sur}$

- irreversible process: $\Delta S_{universe} > 0$

  $\boxed{\Delta S_{sur} > - \Delta S_{sys}}$

⇒ Entropy of the universe always increases so that
So, all spontaneous processes occur
entropy always increases. 7/4

Lecture

Reversible process: $dw_{rev} > dw_{irr}$: work done by system is max (-ve)

$\Rightarrow dq_{rev} > dq_{irr}$

Work done on the system is minimum (+ve)

$dw_{rev} < dw_{irr}$

$dq_{rev} > dq_{irr}$

Since this is a cyclic process, $dU = 0$

$\Rightarrow dw_{rev} + dq_{rev} + dw_{irr} + dq_{irr} = 0$

Certain things that are not forbidden by other laws of physics donot occur.

Arrow of time -video

Entropy has always been increasing since Big bang

How do we know for sure?

Entropy of the universe is always increasing on an average (not a spatially or temporally local value).

⇒ 2nd law is a statistical law, not well-explained by classical TD

P, V, T – macroscopic variables / macrostates

Position / momentum of each particle – microstate

Statistical Thermodynamics

Its a branch of science that uses microscopic information to obtain macroscopic quantities.

Probabilistic approach is used instead of specifying the properties of each & every particle

Why is entropy increase (on avg) feasible?

From a statistical viewpoint, entropy is nothing but options. ie

We can write 2nd law as –

Every system when left to itself, will on an average, change to a condition of maximum probability i.e max. no. of options ⇒ max. entropy

The system can distribute itself in as many states (arrangements ie microstates) as possible which happens when state goes from cold to hot

$\underline{S \propto W}$

where W : no. of microstates

This relation (phenomenological observations) was discovered by Boltzmann

Consider a system A with W microstates -

$$\underset{A}{\boxed{W}} \quad \underset{A}{\boxed{W}} \xrightarrow{\text{combind}} \boxed{W | W} \; : W^2 \text{ microstates.}$$

$S_A \propto W$

$2 S_A \propto W^2$

$2 S_A \propto \ln(W^2)$

$\therefore S_A \propto \ln(W)$

$$\therefore \boxed{S_A = k_B \ln W}$$

Boltzmann equation. k_B : constant

Stat. TD can calculate entropy, not just ΔS.

"Entropy is not disorder" — disorder is subjective

13/4

Concept of Probability

Every system when left to itself will on an avg change to a condition of maximum probability

$$\text{Probability of } X = \frac{\#\text{ of ways of getting } X}{\text{Total no. of ways}}$$

Probability can be of 2 types -

"AND" : $P(X \,\&\, Y) = P(X) . P(Y)$ Multiplicative

"OR" : $P(X \text{ or } Y) = P(X) + P(Y)$ Additive

1) "AND" : P of getting a 4 ten times in a row?

$$P = \frac{1}{6} \times \frac{1}{6} \times \cdots \frac{1}{6} = \left(\frac{1}{6}\right)^{10} \sim \frac{1}{6 \times 10^7}$$

This is true for independent events

2) P of drawing 2 hearts from a full pack of cards?
(without replacement)

$$P = \frac{13}{52} \cdot \frac{12}{51} \sim 0.0588$$

Outcome of 2nd event is not independent of first.

3) OR : P of rolling a 2 or 3 ?

$$P = \frac{1}{6} + \frac{1}{6} = \frac{1}{3}$$

AND & OR probability can be combined —

4) 2 6-sided dice P of getting a 8 ?

★ 8 — (2, 6) (3, 5) (4, 4) (5, 3) (6, 2)

$$P_8 = \frac{5}{36}$$

★ $$P_8 = \left(\frac{1}{6} \cdot \frac{1}{6}\right) + \left(\frac{1}{6} \cdot \frac{1}{6}\right) + \cdots\cdots + \left(\frac{1}{6} \cdot \frac{1}{6}\right)$$

$$P_8 = 5 \times \frac{1}{36} = \frac{5}{36}$$

This is combining AND and OR probabilities.

5) P of tossing 2 coins s.t. head falls once?
(at least)

(H, H) (H, T) (T, H)

$$P_{H/\_} = \frac{3}{4} = 3 \times \left(\frac{1}{2} \cdot \frac{1}{2}\right)$$

6) P of drawing 2 cards s.t. one card is a heart?

$$P_{\heartsuit} \,\&\, P_{\not\heartsuit} = \frac{\cancel{13}}{\cancel{52}_4} \times \frac{\cancel{39}^{13}}{\cancel{51}_{17}}$$

$$P_{\not\heartsuit} \,\&\, P_{\heartsuit} = \frac{\cancel{39}^{13}}{\cancel{52}_4} \times \frac{13}{\cancel{51}_{17}}$$

$$P_{1\,\text{heart}} = \frac{13}{34} = 0.382$$

P of not getting any heart ?

$P = \frac{39}{\cancel{52}_{4}} \times \frac{38}{\cancel{51}_{17}} \sim 0.559$

Both are hearts — $P = \frac{13}{52} \times \frac{12}{51}$

7) Rolling 2 dices. P(n) → P of getting n

$P(2) = \frac{1}{36}$

$P(3) = 2/36$

$P(4) = 3/36$

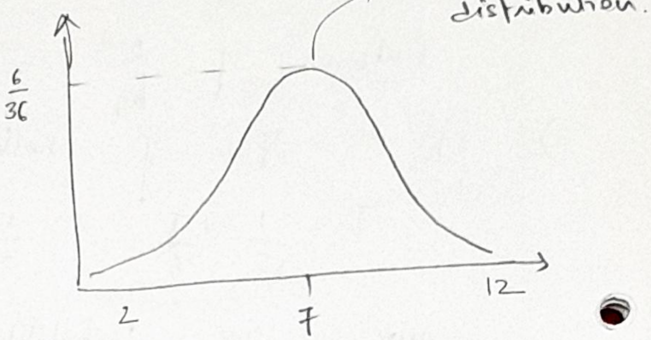
$P(5) = 4/36$

$P(6) = 5/36$

$P(7) = 6/36$

$P(10) = P(4) = 3/36$

$P(12) = P(2) = 1/36$



13/3

Lecture

Why is entropy important?

We need statistical thermodynamics to answer this.

Recall : Bozeman's equation : $S \propto W$

W : max no. of microstates

Probability examples — P & C

20/4

Recorded Lec 3a

Distinguishable balls in distinguishable boxes — permutations

1 ball — 1 box

Balls (> 1) in boxes — Combinations

Choose r balls out of N in one box

$\hookrightarrow {}^{N}P_{R} = {}^{6}P_{3} = \frac{6!}{3!} = 120$ ways

If we don't care about the order of balls chosen

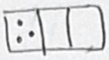
$\rightarrow {}^{N}C_{R} = \frac{N!}{R!\,(N-R)!} = \frac{6!}{3!\,3!} = \underline{\underline{20 \text{ ways}}}$

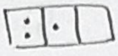
R indistinguishable balls in N distinguishable boxes

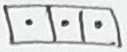
→ $\boxed{{}^{N+R-1}C_{N-1}}$

Both balls and boxes are indistinguishable

→ 3 way







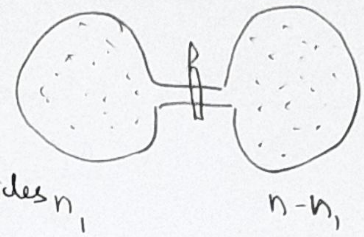
Both are distinguishable ⇒ $3^3 = 27$ ways

R balls N boxes $\boxed{N^R}$ ways

Recorded Lec-3b

Two level system : n distinguishable particles

Consider two bulbs connected with a valve – when open, the particles will start to mix and we'll have n_1, $(n-n_1)$ particles



This is a combinations problem –

$$W = \frac{n!}{n_1!\,(n-n_1)!} = {}^nC_{n_1}$$

Each value of n_1 represents a distribution.

If $n = 8$, $n_1 \in [1,7]$

Total no. of distributions –

$$W_{tot} = {}^8C_1 + {}^8C_2 + \dots {}^8C_7 = 254 \text{ distributions}$$

$n_1 = 4$ is the most probable distribution –

$$W_{MPD} = {}^8C_4 = \frac{8!}{4!\,4!} = 70$$

$$P_D = \frac{70}{254} \; (n_1 = 4) \; ; \; P_A = P_G = \frac{8}{254} \; (n_1 = 1, 7)$$

$S \propto W$ ⇒ Entropy is max for MPD

$\boxed{W \text{ is maximum when } n_1 = \frac{n}{2}}$ – Prove

$W = \frac{n!}{n_1!\,(n-n_1)!}$ for maximising W,

$\frac{\partial W}{\partial n_1} = 0$ Same as $\frac{\partial \ln(W)}{\partial n_1} = 0$

$\ln(W) = \ln(n!) - \ln(n_1!) - \ln([n-n_1]!)$

Considering W is a large no., we can apply the Sterling approximation. — (only when n is large)

$\ln n! = n\ln n - n$

$\Rightarrow \ln(W) = n\ln(n) - \cancel{n} - n_1\ln(n_1) + \cancel{n_1} - (n-n_1)\ln(n-n_1) \cancel{+n} \cancel{-n_1}$

$\ln(W) = n\ln(n) - n_1\ln(n_1) - (n-n_1)\ln(n-n_1)$

$\frac{\partial \ln(W)}{\partial n_1} = -\ln(n_1) - \cancel{n_1}\cdot\frac{1}{\cancel{n_1}} - n\cdot\frac{1}{(n-n_1)} + \ln(n-n_1) + n_1\cdot\frac{1}{(n-n_1)}$

$= -\ln(n_1) + \ln(n-n_1) \cancel{-1} + \frac{\cancel{(n-n_1)}}{\cancel{(n-n_1)}}$ → somehow

$\Rightarrow -\ln(n_1) + \ln(n-n_1) = 0$

$\Rightarrow n_1 = \frac{n}{2}$

When n and n_1 are large, the most probabale distribution is when $n_1 = \frac{n}{2}$

Problem Solving 1

1) 1 mole of ideal gas at 27°c (300 k) is expanded isothermally from 3 atm to 1 atm a) reversibly and b) against const P of 1 atm

Calculate ΔS_{sys}, ΔS_{sur} and Δ_{tot} for each path.

a) Reversible : isothermal

$\Delta S_{sys} = nR\ln\left(\frac{V_f}{V_i}\right) = nR\ln\left(\frac{P_i}{P_f}\right)$

$= R.\ln\left(\frac{3}{1}\right) = R\ln(3)$

↳ $\Delta S_{tot} = 0 \Rightarrow \Delta S_{sur} = -\Delta S_{sys} = -R\ln(3)$.

b) At const. P = 1atm

$$\Delta S = \frac{dq_{rev}}{T} \qquad dq_{rev} = -dw \quad (T \text{ const})$$

$$\Delta S = \frac{P_{ext}(V_f - V_i)}{T} = \frac{P_f V_f}{T}\left(1 - \frac{V_i}{V_f}\right)$$

$$\Delta S = R\left(1 - \frac{P_f}{P_i}\right) = R\left(1 - \frac{1}{3}\right) = \frac{2}{3}R$$

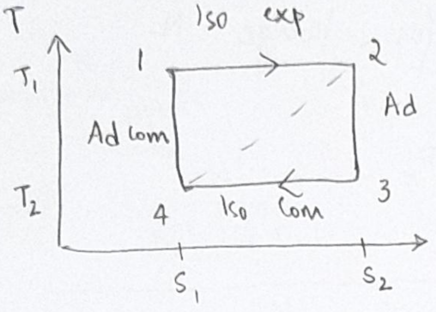
$$\therefore \Delta S_{sys} = \frac{2}{3}R \Rightarrow \Delta S_{surr} = -\frac{2}{3}R$$

This process is irreversible $\Rightarrow \Delta S_{tot} > 0$

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr}$$
$$= R\ln(3) - \frac{2}{3}R$$

By choosing a reversible process.

2)



Carnot cycle

$$\eta = \frac{q_{tot}}{q_{in}}$$

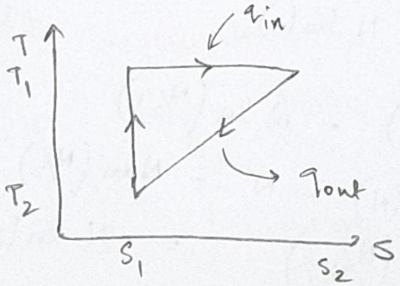
$$q^{(in)}_{\cancel{tot}} = T_1(S_2 - S_1)$$

$$q_{(out)} = T_2(S_1 - S_2)$$

$$\eta = \frac{q_{in} + q_{out}}{q_{in}} = 1 + \frac{q_{out}}{q_{in}} = 1 + \frac{T_2(S_1 - S_2)}{T_1(S_2 - S_1)}$$

$$\eta = 1 - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1}$$

Engine A :



$$q_{in} = T_1(S_2 - S_1)$$

$$q_{tot} = \frac{1}{2}\left(q_{tot} \text{ of Carnot engine}\right)$$

Efficiency. $\eta_A = \frac{q_{out}}{q_{in}} = \frac{1}{2} \frac{(T_2 - T_1)\,(s_1 - s_2)}{T_1\,(s_2 - s_1)}$

$$\eta_A = \frac{1}{2}\left(1 - \frac{T_2}{T_1}\right) = \frac{1}{2}\eta$$

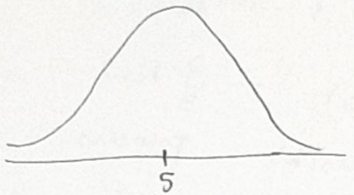
20/4

Lecture 4.

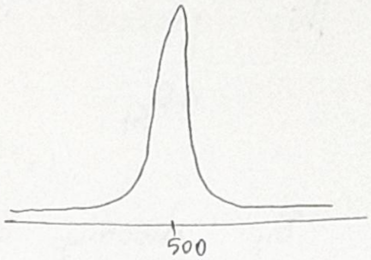
Distribution and microstates

Entropy ⇒ when left to itself, a system will go to a maximum ~~distributio~~ no. of microstates i.e most probable distribution OR maximum probability.

With increasing N, the distribution becomes narrower



N = 10



N = 1000

⇒ $\boxed{W_{MPD} \simeq W_{total}}$ for laarge N. → other distributions don't survive

∴ $S = k_B \ln W_{MPD}$

We can calculate entropy using just W_{MPD}

When N is large —

$$W_{MPD} = \frac{N!}{(N/2)!\,(N/2)!}$$

N coins distributed in 2 boxes (H or T)

$$W_{tot} = 2^N$$

$$\ln W_{tot} = N \ln(2)$$

$$\ln W_{MPD} = \ln(N!) - 2\ln(N/2\,!)$$

$$= N.\ln(N) - N - N\ln(N/2) + N$$

$$= N \ln\left(\frac{N}{N/2}\right) = N \ln(2)$$

$\therefore$ $\boxed{W_{MPD} = 2^N = W_{tot}}$ when N is large

In MPD, no. of microstates for all distributions

energy levels have equal population, no. of microstates are maximum

$S = k_B \ln(W_{MPD})$ — large N.

Multiple level System

N particles are distributed among R energy levels (R > 2).

Eg: N particles in 3 energy levels

No. of ways in which n_1 particles can be placed in 1st energy level, then n_2 particles to be placed in 2nd level

$${}^{N}C_{n_1} \times {}^{N-n_1}C_{n_2} \times {}^{N-n_1-n_2}C_{n_3} \quad \text{where } N = n_1 + n_2 + n_3$$

$$W = \frac{N!}{n_1!\,(N-n_1)!} \times \frac{(N-n_1)!}{n_2!\,(N-n_1-n_2)!} \times \frac{(N-n_1-n_2)!}{n_3!\;0!}$$

$$\boxed{W = \frac{N!}{n_1!\,n_2!\,n_3!}}$$ Multinomial distribution

No. of ways in which n_i particles can be placed in r energy levels

In this case, there is no preference for energy levels i.e. they're considered to be degenerate

Consequence of going from 2 → 3 energy levels;

Say $N = 210$

$\frac{210!}{70!\,70!\,70!} \simeq \underline{10^{97}}$ } 3 energy levels $\quad \frac{210!}{105!\,105!} \simeq \underline{10^{61}}$ } 2 e

*: With increase in no. of accessible states, the entropy will increase ∵ more no. of choices

~~27/4~~
4/5

Lecture 5

Distribution of particles in different energy level $\frac{N!}{n_1!\, n_2!\, n_3!} = W$

For large values of N in the energy levels are equally populated ~~so~~ in most probable distribution

$W_{tot} \sim W_{MPD}$

With increase in no. of energy states, entropy increases.

In these cases, energy levels are degenerate i.e no preferance

Energy levels are not degenerate

Consider distributing 3 units of energy among 3 distinguishable particles.

Boxes : Particles (distinguishable)
Balls : energy (indistinguishable)

A : 1 particle has all 3 units : 3 possibilities

B : 1 particle has 2 units, another has 1 unit : 6 possibilities

C : All particles have 1 unit : 1 possibility

Note that amount of energy remains constant.

$P_A = \frac{3}{10}$ $P_B = \frac{6}{10}$ $P_C = \frac{1}{10}$

(MPD) – no 2 particles have same energy

This is when energy levels are not degenerate

Distribution of indistinguishable energy among distinguishable particles –

$$\boxed{W_{tot} = {}^{r+N-1}C_{N-1}}$$

: Star bar problem

r: energy units

N: particles.

Probability to be in the i^{th} energy level -

$$P_i = \frac{n_i}{n}$$ n : total no. of particles

$$\boxed{P_i = \frac{W_i}{W_{tot}}}$$ where $$\boxed{W_i = {}^{(r-i)+(N-1)-1}C_{(N-1)-1}}$$

r-i : energy units

N-1 : remaining particles

Say, r = 3 - N = 3

For i = 0, $$P_i = \frac{\overset{A}{(2\times3)} + \overset{B}{(1\times6)} + \overset{C}{0}}{3\times10} = \frac{12}{30} = \frac{2}{5}$$

i = 1 $$P_i = \frac{0 + (1\times6) + (3\times1)}{3\times10} = \frac{3}{10}$$

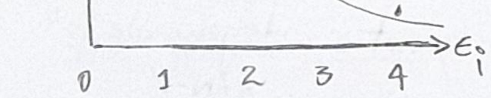
$$W_i = {}^{3+(3-1)-1}C_{(3-1)-1} = {}^{4}C_{1} = 4$$

For i = 0

$$P_i = \frac{W_i}{W_{tot}} = \frac{4}{10} = \frac{2}{5}$$

$$W_i = {}^{(3-1)+(3-1)-1}C_{(3-1)-1} = {}^{3}C_{1} = 3$$

$$P_i = \frac{W_i}{W_{tot}} = \frac{3}{10}$$



As energy increases, P of filling the higher energy levels decrease → Exponentially decaying curve for greater N, r values

MAXWELL - BOLTZMANN DISTRIBUTION

$$\boxed{\frac{n_i}{n} = a e^{-b\epsilon_i}}$$

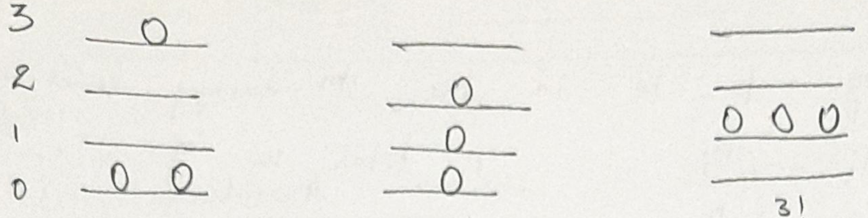
a : Normalisation constant

b : measure of rate of decay

This gives the distribution of distinguishable particles among energy levels.

4/5

Recorded : Star Bar Problem



$r = 3$

$N = 3$

$W_i = \frac{3!}{2!} = 3 \qquad \frac{3!}{1!} = 6 \qquad \frac{3!}{3!} = 1$

$W_{tot} = 10$

r Energy units are indistinguishable ; they're distributed among N distinguishable particles

Energy : $\underset{r}{* \; * \; *}$ Boxes / particles : $\underset{N-1}{\_|\_|\_}$ (Bars)

No. of ways of arranging r $*$ and $N-1$ $|$

Think of it as placing the bars in between stars, i.e placing $(N-1)$ $|$ in $r+N-1$ spaces. So,

$$W_{tot} = {}^{r+N-1}C_{N-1}$$

4/5

Live lecture 6

Recall

- In realistic systems, total no. of particles is v. large
- So, instead of W_{tot}, we can consider distribution that W_{mpd} which is the only survives. $\Rightarrow S \simeq k_B \ln W_{mpd}$
- When energy levels are degenerate, in the mpd, all energy levels are equally populated
- When energy levels are not degenerate,

$$P_i = \frac{n_i}{n} = \frac{W_i}{W_{tot}} \qquad W_{tot} = {}^{r+N-1}C_{N-1}$$

Probability to occupy higher energy levels is low.

Also, $\frac{n_i}{n} = P_i = ae^{-b\epsilon_i}$: Maxwell - Boltzmann distribution

One of our biggest assumption : equal spaing of energy levels.

But what's important is the distribution of particles in mpd.

$$W = \frac{N!}{\prod_i n_i!} \quad - \text{multinomial coefficient}$$

So we maximise W with the constraints —

$$\sum_i n_i = N \qquad E = \sum_i n_i \epsilon_i$$

Total energy is constant. ϵ_i : energy of i^{th} level

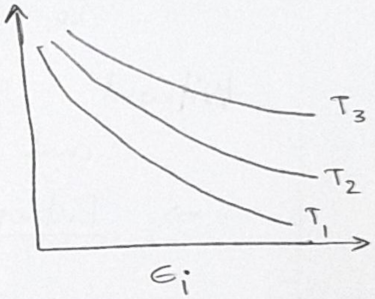
With this, we can show that, in the mpd,

$$\frac{n_i}{n} = \frac{e^{-\beta\epsilon_i}}{\sum_i e^{-\beta\epsilon_i}} \Rightarrow \frac{n_i}{n} = a e^{-\beta\epsilon_i}$$

So, mpd distribution is same as maxwell-boltzman distribution for any ~~ab~~ arbitrary distribution

Furthermore, $\boxed{\beta = \frac{1}{k_B T}}$

So, here, $T_3 > T_2 > T_1$



Also, $n_i \propto e^{-\beta\epsilon_i}$

$$\frac{n_i}{n_j} = e^{-\beta(\epsilon_i - \epsilon_j)}$$

At v.v. high T, $\beta \to 0$ so we can say that ✻ all energy states are equally populated

Also, for degenerate energy states $(\epsilon_i = \epsilon_j)$, then also all energy states are equally populated $(\because n_i = n_j)$.

Consider 1st law of TD : $U = q + w$

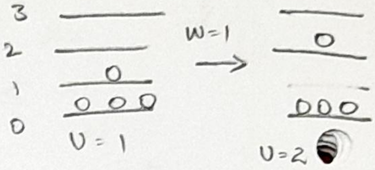
If you want to increase U of system, then you can give –

i) Heat

When system absorbs heat, the distribution of particles in different energy levels changes. (increase in no. of microstates) → $E = \frac{n^2h^2}{mL^2}$ particle in a box

ii) Work (no heat)

When work is done ~~on~~ by the system, volume decreases and energy increases by increasing the energy spacing. But, particle distribution remains the same



Consider a system with constant volume & heat is being supplied step-wise

We can see that the no. of microstates is proportional to the energy supplied

$W \propto E$ and $S \propto W$

So, $S \propto$ ~~entropy~~ energy ?

Without doing work, internal energy increases and W (ie. S) increases.

⇒ Entropy is a monotonically increasing function of energy.

Even classically, $\frac{dq_{rev}}{T} = dS$ $\qquad dE = dq + \cancelto{0}{dw}$

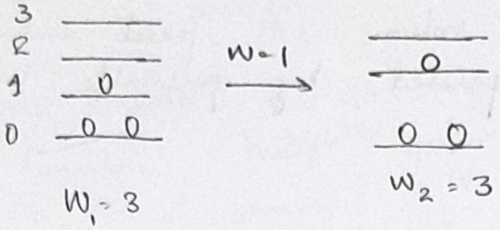
$$dE = dq_{rev} = T.dS$$

$$\therefore \left(\frac{\partial E}{\partial S}\right)_{const\ vol} = T$$

Since T is positive, entropy increases with increase in E.

Heat flows into a system spontaneously because W, S increase

Effect of work on Entropy –



In an adiabatic system, no. of microstates are the same even when work is done by system.

$dq_{rev} = 0$

Recall for adiabatic expansion: $dS = 0$

There, T is decreasing, so it doesn't have energy to access higher energy levels.

It decreases the energy level spacing

In adiabatic compression, energy spacing ~~de~~ increasing but T increases, so this is used as compensation and entropy is maintained.

Note: Classical particles are distinguishable – theis positions & trajectories can be tracked.

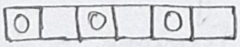
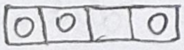
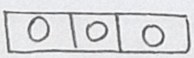
Quantum particles are indistinguishable – fermions (2 in energy state) & bosons (no limit to occupation)

Recording 5a

Estimation of entropy for various processes

Lattice model

The particles are represented as beads which occupy lattice points – 3D space. Each point can hold only 1 particle

	n = 3	Vol	W_i
Indistinguishable particles placed in distinguishable boxes		6	$^6C_3 = 20$
		4	$^4C_3 = 4$
		3	1

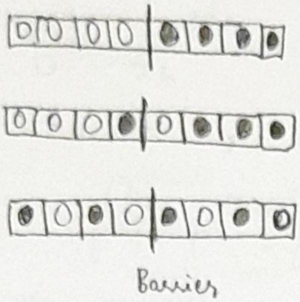
As lattice points (volume) increase, W increases.
So. maximising the volume occupied is the state of maximum entropy

Mixing of Gases

Consider that total volume is fixed and 2 gases are seperated by permeable barrier.

$W = W_{left} \cdot W_{right}$

W



$\frac{4!}{4!} \cdot \frac{4!}{4!} = 1$

$\frac{4!}{3!} \cdot \frac{4!}{3!} = 16$

$\frac{4!}{2!\,2!} \cdot \frac{4!}{2!\,2!} = 36$

The gases mix in such a way that they go to a state which has maximum no. of microstates

Recording 5b

Heat flows from hot to cold body
When heat flows and both systems have same energy (thermal eq.) then the no. of microstates are maximised & entropy increases.
If they don't same energy but are in thermal contact, the total no. of microstates will be lesser.

4/5

Recording 6

Bose-Einstein & Fermi-Dirac statistics.

Quantum particles are indistinguishable.
Bosons – integral spin, Fermions – $\frac{1}{2}$-integral spin
In fermions, no more than 2 electrons can stay in same energy level because of Pauli Exclusion Principle.

For bosons, any no. of particles can have same energy level

→ Bose-Einstein Statistics

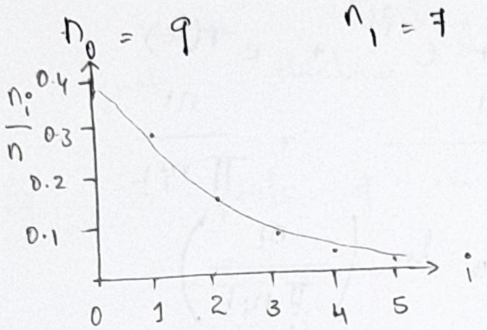
Consider that 5 units of energy (r) is distributed among 4 particles.

This can have 6 different kinds of distribution.

Since bosons are indistinguishable, for all 6 distributions, $w_i = 1 \Rightarrow w_{tot} = 6$

$P_i = \frac{n_i}{n}$ $\quad n = 6 \times 4 = 24$

$n_0 = 9 \quad n_1 = 7 \quad n_2 = 4 \quad n_3 = 3 \quad n_4 = 1 = n_5$



Equation:

$$\frac{n_i}{n} = \frac{1}{ae^{+b\epsilon_i} - 1}$$

The probability of occupying an energy level changes

Boson distribution.

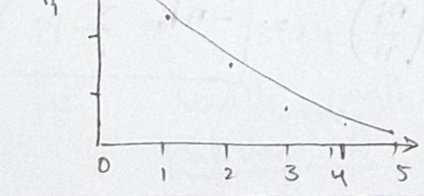
→ Fermi-Dirac statistics

Same, $r = 5$, $n = 4$ but each level can't have more than 2 fermions.

So there are 4 distributions possible with $w_i = 1 \Rightarrow w_{tot} = 4$

$n = 4 \times 4 = 16$

Here, $n_0 = 6 \quad n_1 = 4 \quad n_2 = 3 \quad n_3 = 2 \quad n_4 = 1 = n_5$



Another distribution –

$$\frac{n_i}{n} = \frac{1}{ae^{-b\epsilon_i} + 1}$$

Depending on nature of particles (distinguishable, bosons, fermions) influences the distribution i.e. no. of microstates.

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Live lecture 7

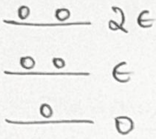
Recall : MPD is the Boltzmann distribution

$$P_i = \frac{n_i}{n} = a e^{-\beta \epsilon_i} \qquad \beta = \frac{1}{k_B T}$$

$$P_i = \frac{e^{-\beta \epsilon_i}}{\left.\sum_i e^{-\beta \epsilon_i}\right\}}$$

Q : Partition function
(Normalisation constant $\because \sum_i P_i = 1$]

Partition function has microscopic information about system



$$Q = e^{-\beta(0)} + e^{-\beta \epsilon} + e^{-\beta(2\epsilon)}$$

$$W = \frac{n!}{n_1!\, n_2! \ldots} = \frac{n!}{\prod_i n_i!}$$

$$S = k_B \ln(w) = k_B \ln\left(\frac{n!}{\prod_i n_i!}\right)$$

$$S = k_B \left[\ln n! - \sum_i \ln(n_i!)\right]$$

$$S = k_B \left[n \ln(n) - \cancel{n} - \sum_i \left(n_i \ln(n_i) - \cancel{n_i}\right)\right]$$

$$S = k_B \left[n \ln(n) - \sum_i n_i \ln(n_i)\right] \qquad \because \sum_i n_i = n$$

$$S = k_B \left[\sum_i n_i \left(\ln(n) - \ln(n_i)\right)\right]$$

$$S = k_B \sum_i n_i \ln\left(\frac{n}{n_i}\right) = -k_B \sum_i n_i \ln\left(\frac{n_i}{n}\right)$$

$$S = -k_B\, n . \sum_i \frac{n_i}{n} \ln\left(\frac{n_i}{n}\right) = \boxed{-n k_B \sum_i p_i \ln(p_i)}$$

Formula for entropy of system

For degenerate systems, $P_i = \frac{e^{-\beta\epsilon}}{Q}$ for any energy level since each level has equal no. of particles, each microstate is equally likely —

$$P_i = \frac{e^{-\beta\epsilon}}{Q} = \frac{1}{W}$$

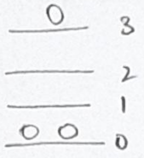
$$S = -nk_B \sum_i \left(\frac{1}{W}\right) \ln\left(\frac{1}{W}\right)$$

$$\therefore S = k_B \ln(W) \quad — ①$$

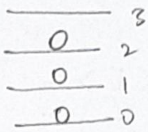
We arrive at the same eq^n

When we have v. large no. of particles, we're dealing with W_{MPD}, so we're just dealing with simpler ① equation

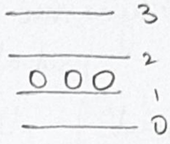
Eg: 3 units of energy among 3 particles



W = 3



W = 6



W = 1

$W_{tot} = 0 \Rightarrow S = k_B \ln(10) = 2.3\ k_B$

$$S = -k_B \sum_i P_i \ln(P_i)$$

$P_0 = \frac{3\times 2 + 1\times 6}{3\times 10} = \frac{4}{10}$ $\quad P_1 = \frac{3}{10}$ $\quad P_2 = \frac{2}{10}$

$P_3 = 1/10$

$$S = -3k_B \left[0.4\ln(0.4) + 0.3\ln(0.3) + 0.2\ln(0.2) + 0.1\ln(0.1) \right]$$

$$S = 3.84\ k_B$$

The results will be more similar when no. of particles is greater.

The main reason for difference is the lack of good statistics.

Another eg: socks color of class
Pencil pointing towards cardinal directions.

Broader / flatter the distribution, higher is the entropy.

Here, total energy is not changed, its just better distributed, like from Big Bang to now.

Entropy will be maximum when energy is distributed in similar manner everywhere.

At eq. every molecule will have same energy i.e flat distribution ⇒ max entropy.

So energy is conserved but not entropy.
We have arrived at this from microscopic view of the world.

Thermodynamic observables are averages of weighted probability.

$$\text{Observed } U = \langle E \rangle = \sum_i E_i P_i$$

$$\langle p \rangle = \sum P_i \, p_i \longrightarrow \text{pressure}$$

$$P_i = \frac{e^{-\beta E_i}}{Q}$$

Through this microscopic information is converted to macroscopic thermodynamic particle.

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Lecture 7a

Free Energy

Just by considering the system alone, its difficult to know whether the process is spontaneous or not.

We need to consider* the entropy of system & surr

* unless the system is isolated.

If we're only considering the system, entropy is not enough of a criteria to judge whether a process is spontaneous.

For this, we use free energy calculations to understand spontaneity.

1st law : $dU = đq + đw$

2nd law : $dS = \frac{dq_{rev}}{T}$

$$dU = T.dS + dw$$

$$\boxed{dU = TdS - PdV}$$ Fundamental Eq^n of Thermodynamics

$U \quad T \quad S \quad P \quad V \rightarrow$ state variables

So the eq^n holds true for reversible or irreversible processes.

$$U \equiv U(S, V, N)$$

For $f(x, y)$ $\quad df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x . dy$

$|||^{ly}$, $\quad dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN$

If we compare with fundamental eq^n,

$$\underline{T = \left(\frac{\partial U}{\partial S}\right)_{V,N}} \qquad \underline{-P = \left(\frac{\partial U}{\partial V}\right)_{S,N}} \qquad \underline{\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}}$$

These are known as equations of state

Recording 76

When we take a derivative, we lose some information about the function.

T, P, μ are intensive properties (don't change with size)

U S V N – extensive variables

Derivative of 2 extensive variables gives intensive variable.

Consider : $T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$ In closed system of const volume

Since T is always positive, entropy is a monotonically increasing function of energy.

From microscopic POV, increasing energy leads to more microstates hence greater entropy

For a multi-component system,

$$U \equiv U(S, V, \{n_i\})$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_i} dV + \underbrace{\sum_i \left(\frac{\partial U}{\partial n_i}\right)_{S,V}}_{\mu_i} dN_i$$

μ_i : chemical potential of i^{th} component.

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

$$dH = TdS - PdV + PdV + VdP$$

$$\therefore \boxed{dH = TdS + VdP}$$

$$\therefore H = H(S, P)$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP \Rightarrow T = \left(\frac{\partial H}{\partial S}\right)_P$$

$$V = \left(\frac{\partial H}{\partial P}\right)_S$$

Lecture 18/5

Fundamental Eqⁿ : $dU = TdS - PdV$

This is valid for any closed system i.e. no mass transfer.

$$\left(\frac{dU}{dT}\right)_V = T\left(\frac{dS}{dT}\right)_V \Rightarrow \boxed{\left(\frac{dS}{dT}\right)_V = \frac{1}{T}C_V}$$

$$\therefore \quad dH = TdS + VdP$$

$$\Rightarrow \boxed{\left(\frac{dS}{dT}\right)_P} = \frac{1}{T}\left(\frac{dH}{dT}\right)_P = \boxed{\frac{1}{T}C_P}$$

3rd Law of Thermodynamics

Planck's statement : As $T \to 0 \Rightarrow S \to 0$ for every pure substance

WKT, $S = k_B \ln(w)$

In a perfect crystal, where every atom is in its position, there's only ~~1~~ way of distribution.

$\Rightarrow w = 1$. as $T \to 0$.

This is possible ~~at~~

But its impossible to reduce the T of any substance to 0K.

Consider we have 1 mole of gas (ideal)

$\Rightarrow PV = RT$

$T_1, V_1 \longrightarrow T_2, V_2$ where $T_2 < T_1$

$$dU = TdS - PdV$$

$$C_V dT = TdS - \left(\frac{RT}{V}\right)dS$$

For spontaneous adiabatic expansion, $\Delta S = C_V \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{V_2}{V_1}\right)$

If $T_2 = 0$, $\ln\left(\frac{T_2}{T_1}\right) = -\infty$

For $\Delta S = 0$, $\ln\left(\frac{V_2}{V_1}\right) = +\infty$ which is impossible

Hence achieving $T = 0\ K$ is impossible

What is equilibrium? What is the direction of Spontaneous change?

For an isolated system, a spontaneous change takes place in a direction where entropy is increasing

All these reactions occur spontaneously. Just sign of ΔS is not sufficient to predict

$$2H_2O_{2\,(l)} \rightleftharpoons 2H_2O_{(l)} + O_{2\,(g)}$$

$\Delta H = -209\ kJ$ $\Delta S = 132\ J\ K^{-1}$

$$3H_{2\,(g)} + N_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$$

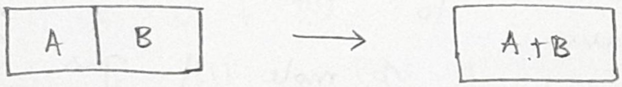
$\Delta H = -92\ kJ$ $\Delta S = -198\ J K^{-1}$

$$NaCl_{(s)} + H_2O_{(l)} \rightleftharpoons sol^n\ (NaCl)$$

$\Delta H = 4 kJ$ $\Delta S = 45\ J\ K^{-1}$

Entropy is not the only criteria to judge the spontaneity of reaction.

Consider Gas A & B



ΔS_{mixing} is positive

$$dS > \frac{dq_{irr}}{T_{surr}} \quad \text{(spontaneous)}$$

$dU = dq + dw$ $dw = -P_{ext}\,dV$

$$\boxed{dU - TdS + P_{ext}dV \leq 0}$$ from above 3 eq^n

This is an eq^n with state variables.

Entropy is harder to measure/work with.

★ For an isolated system, i.e. at const. volume and energy,

$dU = 0$ and $dV = 0$

$TdS > 0$ i.e. $(dS)_{U,V} > 0$

This is the criteria of spontaneity for isolated

There cannot be any accessible state that has entropy greater than the equilibrium state for an isolated system.

★ Consider const. S and V i.e $dS = dV = 0$

$\Rightarrow (dU)_{S,V} < 0$: criteria for spontaneity

$\Rightarrow$ Equilibrium is acheived when energy is minimised (Also true for classical mech)

★ S is const, $P = P_{ext} = \text{const.}$

$dU + PdV < 0$

$d(U + PV) < 0$

$\therefore (dH)_{S, P_{ext}} < 0$: condition of spontaneity ats const. S & P.

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Live lecture 9 - 19th May

To predict spontaneity we have above inequalities based on state variables

At constant T and V -

$dU - TS < 0$

$d(U - TS) < 0$ Take $\boxed{A = U - TS}$

$\therefore \underset{\substack{\downarrow \\ \text{Helmholtz free energy}}}{dA} < 0$

At eq. A is minimised ast const. T & V.

$$A = U - TS \quad \Rightarrow \quad dA = dU - TdS - SdT$$

$$dA = dq_{rev} + dw_{rev} - dq_{rev} - SdT$$

$$dA = dw_{rev} - SdT$$

$$-(dA)_T = -dw_{rev}$$: Max. reversible work done by the system

⇒ At const T, change in A denotes the max. work that can be extracted from system

---

$$A = -TS + U$$

$$A = \sum_i P_i E_i - T\left(-k_B \sum_i P_i \ln P_i\right)$$

$$= \sum_i P_i \left(E_i + k_B T \ln P_i\right)$$

wkt, $$P_i = \frac{e^{-\beta E_i}}{Q} \qquad \beta = \frac{1}{k_B T}$$

$$\Rightarrow \ln P_i = -\beta E_i - \ln Q$$

$$k_B T \ln P_i = -E_i - \frac{\ln Q}{\beta}$$

$$A = \sum_i P_i \left(\cancel{E_i} - \cancel{E_i} \pm k_B T \ln Q\right) = -\left(\underset{\overset{\shortparallel}{1}}{\sum_i P_i}\right) \ln Q \cdot k_B T$$

$$\therefore \underset{\text{Macro}}{\underset{\downarrow}{A}} = -k_B T \underset{\text{Partition fn (micro)}}{\underset{\downarrow}{\ln Q}} \quad \sim \quad \underset{\text{Macro}}{\underset{\downarrow}{S}} = k_B \ln \underset{\text{micro}}{\underset{\downarrow}{W}}$$

$$A = U - TS \qquad dA = dU - TdS - SdT$$

$$dA = TdS - PdV - TdS - SdT$$

$$\therefore \boxed{dA = -PdV - SdT} \quad \Rightarrow \quad P = \left(\frac{\partial A}{\partial V}\right)_T$$

If we know partition fn, through A, we can calculate other macroscopic properties.

$$S = -\left(\frac{\partial A}{\partial T}\right)_V$$

$(dA)_{T,V} < 0$: condition for spontaneity.

What we can easily maintain is T & P

In this,

$dU + PdV - TdS < 0$

$d(U + PV - TS)_{T,P} < 0$

$G = U + PV - TS$

$(dG)_{T,P} < 0$

$\boxed{G = H - TS}$

Gibbs' free energy : criteria for spontaneity at T,P (macrostates that we can control).

At const T, V -

$dU = dq - PdV$

$(dU)_V = dq$

At const volume, change in energy is reflected as heat transfer ⇒ when energy decreases, q is lost to surroundings ⇒ entropy of surroundings increases.

For spontaneity, $dA = dU - TdS_{sys} < 0$

Say WKT, $dS_{sys} < 0$ ⇒ $TdS_{sys} < 0$

For something to occur spontaneously $dA < 0$

for that dU has to be -ve.

For G - $\Delta G = \Delta H - T\Delta S$ $\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr}$

For spontaneity, ΔG -ve ⇒ $\Delta S_{sys} > 0$ ⇒ ΔH has to be negative or $|\Delta H| < |T\Delta S|$

$dH = TdS + VdP$ If $\Delta H < 0$ ⇒ ΔS_{surr} will ↑

$(dH)_P = dq$ If $\Delta H > 0$, $|\Delta H| < T\Delta S$ (High T)

Say, $\Delta S < 0 \Rightarrow -TdS > 0$

For reaction to be spontaneous, $\Delta H < 0$ & $|\Delta H| > |T\Delta S|$

If $\Delta H < 0$, ΔS_{surr} will increase i.e. $\underset{(+)}{|\Delta S_{surr}|} > \underset{(-)}{|\Delta S_{sys}|}$

If $|\Delta H| < |T\Delta S|$ & $\Delta H > 0$, $\underset{(-ve)}{|\Delta S_{surr}|} < \underset{(+ve)}{|\Delta S_{sys}|}$

$$dG_{T,P} = dU + PdV - TdS$$

$$= dU - dq + PdV$$

$$= dW - \underset{\substack{\text{Mechanical} \\ \text{work}}}{dW_{P,V}} = dW_{non\text{-}PV}$$

Gibbs free energy is some chemical work — rearrangement or bringing charges closer

At const T, P : $A \longrightarrow B$

$\Delta G < 0$: $A \rightarrow B$ happens spontaneously

$\Delta G = 0$: Equilibrium

$\Delta G > 0$: reaction occurs spontaneously in other direction

At equilibrium, the ratio of ~~bov~~ reactants and products is given by the equilibrium constant — $K_c = \frac{[B]}{[A]}$

This has biological (biochemical) applications in use of drugs — they bind to certain compounds and reduce $|\Delta G|$

Recording 8a

Legendre Transform

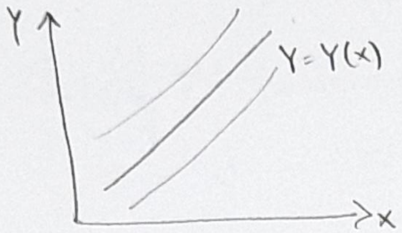
Fundamental eqn : $dU = TdS - PdV + \mu dN$

$$U = U\underbrace{(S, V, N)}_{\text{Extensive variables}}$$

But its easier to control intensive variables!

Can we get a function of intensive variables?

$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T$: But there's a loss of information



$P = \frac{\partial Y}{\partial X} \Rightarrow Y = Y(P)$

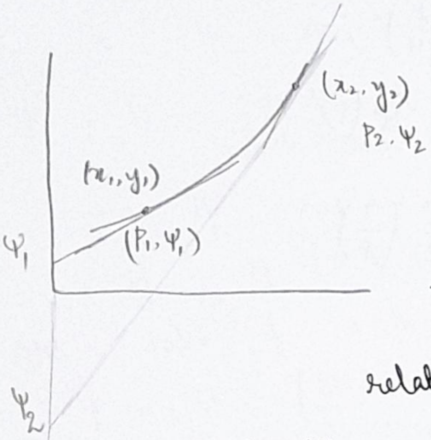
1st order DE

On integration,

$Y_1 = Y(x) + c$

All curves satisfy $Y = Y(P)$ i.e. same value of P, shifted by other values of C

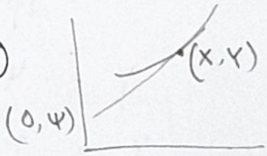
So, $Y = Y(P)$ involves some loss of info that was contained in fundamental relation $Y = Y(x)$.



We can match the $\{X, Y\}$ to $\{\psi, P\}$ where P: intensive variable.

Thus we won't be losing any information.

Recall : $\psi = \psi(P)$ is a fundamental relation in the ψ representation.



$P = \frac{Y - \psi}{X - 0} \Rightarrow \psi = Y - PX$ — ①

$Y = Y(x)$ — ② $P = P(x)$ — ③

$d\psi = \cancel{dY} - dP \cdot X - \cancel{P \cdot dX}$ $P = \frac{dY}{dX}$

$d\psi = -X \cdot dP$

$\therefore X = -\frac{d\psi}{dP}$

$$\therefore \boxed{\psi = Y - \frac{\partial Y}{\partial X} \cdot X}$$

So, by eliminating ψ and P, we can obtain a relation b/w X & Y, like we just did the inverse.

ψ is the Legendre transform of Y.

Eg: $Y = 2\exp(2x) = 2e^{2x}$

$p = \frac{dY}{dx} = 4\cdot e^{2x}$ —① ∴ $Y = \frac{4e^{2x}}{2} = \frac{P}{2}$

$Y = Y(P)$ → No LT.

$\Rightarrow Y = \frac{dY}{dx}\frac{1}{2} \Rightarrow \frac{dY}{Y} = 2dx$

$\ln Y = 2x - \ln C \Rightarrow CY = e^{2x}$

∴ $Y = c'e^{2x}$ —②

There's some loss of info from Eqn ① to ②

Recording 8b

$P = \frac{dY}{dx} = 4e^{2x}$ $x = \frac{1}{2}\ln\left(\frac{P}{4}\right)$ ∵ $P = 4\cdot e^{2x}$

$Y = \frac{P}{2}$

Using LT —

$$\psi = Y - PX$$

$$= 2e^{2x} - \frac{P}{2}\ln\left(\frac{P}{4}\right)$$

$$\psi = \frac{P}{2} - \frac{P}{2}\ln\left(\frac{P}{4}\right) \equiv \psi(P)$$

$$\frac{d\psi}{dp} = \cancel{\frac{1}{2}} - \frac{1}{2}\ln\left(\frac{P}{4}\right) - \frac{\cancel{P}}{2}\left(\frac{1}{\cancel{P}}\right)$$

$$\frac{d\psi}{dp} = -\frac{1}{2}\ln\left(\frac{P}{4}\right)$$

$$Y = \psi + PX$$

$$Y = \frac{P}{2} - \frac{P}{2}\ln\left(\frac{P}{4}\right) + P\left(\frac{1}{2}\ln\left(\frac{P}{4}\right)\right)$$

$$\therefore Y = \frac{P}{2} = \frac{4e^{2x}}{2}$$

No loss of info!

$$\therefore Y = 2e^{2x} \equiv Y(x)$$

LT can be extended to $Y(x_1; x_2)$ also.

there, $\left.\begin{array}{l} P_1 \to Yx_1 \text{ plane} \\ P_2 \to Yx_2 \text{ plane} \end{array}\right\}$ slope planes.

ψ : intercept on Y axis

$$P_1 = \left(\frac{\partial Y}{\partial x_1}\right)_{x_2} \qquad P_2 = \left(\frac{\partial Y}{\partial x_2}\right)_{x_1}$$

$$\psi = Y - P_1 x_1 - P_2 x_2$$

$$\hookrightarrow \psi \equiv \psi(P_1, P_2)$$

Similarly. fundamental eqn : $U = U(S, V, N)$

$$\star \quad \psi = \underbrace{U - \left(\frac{\partial U}{\partial S}\right)_{V,N} \cdot S}\ \cancel{+ \left(\frac{\partial U}{\partial V}\right)_{S,N} \cdot V} \ \cancel{- \left(\frac{\partial U}{\partial N}\right)_{S,V} \cdot N}$$

$\psi = U - TS = A$ i.e. Helmholtz free energy

⇒ A is the partial LT of U that replaces entropy by T as an independent variable

i.e. $\psi = A(T, V, N)$

$$\star \quad \psi = U - \left(\frac{\partial U}{\partial V}\right)_{S,N} V = U + PV = H \quad \text{enthalpy}$$

⇒ H replaces ~~pressure~~ volume by pressure

$H = H(S, P, N)$

Also take it with 2 variables –

$$\star \quad \psi = U - \left(\frac{\partial U}{\partial S}\right)_{V,N} \cdot S - \left(\frac{\partial U}{\partial V}\right)_{S,N} \cdot V = U - TS + PV$$

$\psi = H - TS \underset{\vee}{=} G$: Gibbs free energy

$$\psi = G(T, \textcircled{P}, N)$$

U, A, H, G — Thermodynamic potentials

They can be obtained by taking LT of fundamental eqn.

We can use these to derive different expressions of various quantities.

★ $H \equiv H(S, P, N)$

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P,N} . dS + \left(\frac{\partial H}{\partial P}\right)_{S,N} dP \quad - ①$$

$$H = U + PV$$

$$dH = dU + PdV + VdP = TdS - \cancel{PdV} + \cancel{PdV} + VdP$$

$$dH = TdS + VdP \quad - ②$$

Comparing, $\left(\frac{\partial H}{\partial S}\right)_{P,N} = T \qquad \left(\frac{\partial H}{\partial P}\right)_{S,N} = V$

★ $A = A(T, V, N) \qquad A = U - TS$

$$dA = \left(\frac{\partial A}{\partial T}\right)_{V,N} . dT + \left(\frac{\partial A}{\partial V}\right)_{T,N} . dV$$

$$dA = dU - TdS - SdT \qquad \because \; dU + Pd\cancel{S} = TdS$$

$$\boxed{dA = -PdV - SdT}$$

$$\therefore \; P = -\left(\frac{\partial A}{\partial V}\right)_{T,N} \qquad S = -\left(\frac{\partial A}{\partial T}\right)_{V,N} \quad - \#$$

★ Similarly for $G \equiv G(T, P, N)$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} . dT \qquad dG = \left(\frac{\partial G}{\partial P}\right)_{T,N} . dP$$

$$G = H - TS$$

$$dG = dH - TdS - SdT = T\cancel{dS} + VdP - T\cancel{dS} - SdT$$

$$\therefore \; V = \left(\frac{\partial G}{\partial P}\right)_{T,N} \qquad -S = \left(\frac{\partial G}{\partial T}\right)_{P,N} \quad - \#$$

can be used to calculate entropy by calculating free energy at different temperatures

$$dG = VdP - SdT$$

All thermodynamic properties can be obtained by taking partial derivatives of thermodynamic potentials. ⇒ TD potentials characterize microscopic states

Recording 9

$$dU = TdS - PdV$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V \qquad P = -\left(\frac{\partial U}{\partial V}\right)_S$$

LT of $U(S,V)$ gives — $H = H(S,P)$

$A = A(T,V)$

$G = G(T,P)$

From A, $P = -\left(\frac{\partial A}{\partial V}\right)_T$ $\qquad S = -\left(\frac{\partial A}{\partial T}\right)_V$

H, $T = \left(\frac{\partial H}{\partial S}\right)_P$ $\qquad V = \left(\frac{\partial H}{\partial P}\right)_S$ → very difficult

G, $-S = \left(\frac{\partial G}{\partial T}\right)_P$ $\qquad V = \left(\frac{\partial G}{\partial P}\right)_T$ — not sure

<u>solvation E</u>

They're describing how TD values change only wrt state functions

Consider $G = H - TS$ $\Rightarrow H = G + TS$

$U = H - PV$

$$H = G + T\left(-\left(\frac{\partial G}{\partial T}\right)_P\right)$$

$$U = G - T\left(\frac{\partial G}{\partial T}\right)_P - P\left(\frac{\partial G}{\partial P}\right)_T$$

$$A = U - TS = G - T\left(\frac{\partial G}{\partial T}\right)_P - P\left(\frac{\partial G}{\partial P}\right)_T + T\left(\frac{\partial G}{\partial T}\right)_P$$

$$\therefore A = G - P\left(\frac{\partial G}{\partial P}\right)_T$$

So there potentials can be used to calculate anything

→ $A \equiv A(V,T)$

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial A}{\partial T}\right)_V\right]_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right)_T\right)_V$$

$$\Rightarrow \left[\frac{\partial}{\partial V}(-S)\right]_T = \left[\frac{\partial}{\partial T}(-P)\right]_V$$ From Pg-72

same same

$$\therefore \left[\frac{\partial S}{\partial V}\right]_T = \left[\frac{\partial P}{\partial T}\right]_V \quad ①$$ Equivalent to isothermal expansn
system " fixed volume,
varying T measuring P.

→ For an ideal gas $PV = nRT$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$$

$$\Delta S = nR\int_{V_1}^{V_2} \ln V = nR \ln\left(\frac{V_2}{V_1}\right)$$ at const T

⇒ $G = G(T,P)$

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right]_P = \left[\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P\right]_T$$

$$\therefore ② \left(\frac{\partial V}{\partial T}\right)_P = \left[-\frac{\partial S}{\partial P}\right]_T \qquad ④ \left(\frac{\partial S}{\partial P}\right)_V = \left(-\frac{\partial V}{\partial T}\right)_S$$

So we can measure entropy at const vol by varying T and measuring V at const P.

$$\left[\frac{\partial S}{\partial P}\right]_T = -\left(\frac{\partial V}{\partial T}\right)_P = -\frac{nR}{P}$$

$$\therefore \Delta S = -nR\ln\left(\frac{P_2}{P_1}\right) = nR\ln\left(\frac{P_1}{P_2}\right)$$ at const T

→ From H & U, you can get,

$$② \cancel{\left(\frac{\partial P}{\partial S}\right)_T = -\left(\frac{\partial T}{\partial V}\right)_S} \qquad ③ \left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial P}{\partial T}\right)_S$$

MAXWELL RELATIONSHIP.

Note: To arrive at this, we make use of fact that all TD potentials are exact differentials

Eg: $dU = TdS - PdV$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$ Use maxwell relation ①

For an ideal gas, $PV = nRT$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\cdot\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\cdot\frac{nR}{V} - P = 0$$

$$\left(\frac{\partial U}{\partial V}\right)_T = C_V \eta_J$$ η_J : Joule's coefficient

For an ideal gas, $\left(\frac{\partial U}{\partial V}\right)_T = 0$

* Since $C_V \neq 0$, $\eta_J = 0$.

⇒ Joule's coefficient for an ideal gas = 0
Used to be just an observation, now confirmed

$dH = TdS + VdP$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\cdot\left(\frac{\partial S}{\partial P}\right)_T + V$$ $$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = \frac{-nR}{P}$$

$$= -T\cdot\frac{nR}{P} + V = 0$$

* $\left(\frac{\partial H}{\partial P}\right)_T$: Isothermal Joule-Thompson coefficient.
Its also 0 for an ideal gas.

30/5

Live lecture 10 – 25th May

For an isolated system, $(dU)_{U,V} > 0$

$(dU)_{S,V} < 0$

$(dH)_{S,P_{ext}} < 0$

$(dA)_{V,T} < 0$ } very useful

$(dG)_{P,T} < 0$ }

$dA = dU - TdS$

$dG = dH - TdS$

Through these, we can look at the system and talk about ΔS_{surr}

Fundamental equations –

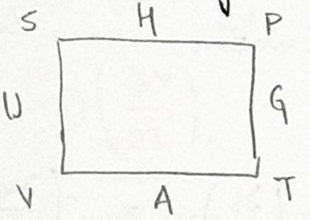
$$dU = TdS - PdV$$
$$dH = TdS + VdP$$
$$dA = -PdV - SdT$$
$$dG = VdP - SdT$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P$$

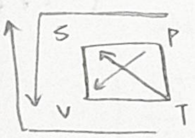
They contain the same information ∵ the 3 same equations have been arrived through Legendre transformatn.

Recall : All TD potentials are exact differentials

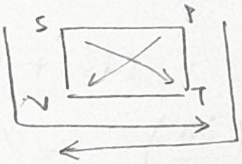
Mnemonic diagram



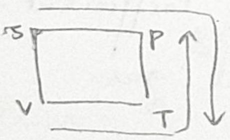
Sun please Turn Violet



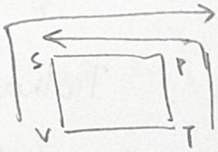
$$-\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S \quad ④$$



$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad ①$$



$$-\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T \quad ②$$



$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S \quad ③$$

S T V P HG A U — Imp

$$\left(\frac{\partial x}{\partial y}\right)_z \qquad 8 \times 7 \times 6 = 48 \times 7 = 336.$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p \qquad C_v = \left(\frac{\partial U}{\partial T}\right)_v = T\left(\frac{\partial S}{\partial T}\right)_v$$

There are a huge no of derivatives and its difficult to measure all. So we'll use a combination of heat capacities & Maxwell's relation to measure things.

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p \qquad \boxed{\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p} \qquad \boxed{K_T = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T}$$

coeff of thermal expansion

Isothermal compressability

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_v$$

Jacobian method

Say, $u \equiv u(x, y)$

$$du = \left(\frac{\partial u}{\partial x}\right)_y dx + \left(\frac{\partial u}{\partial y}\right)_x dy$$

$$v = v(x, y)$$

$$dv = \left(\frac{\partial v}{\partial x}\right)_y dx + \left(\frac{\partial v}{\partial y}\right)_x dy$$

$$\begin{pmatrix} du \\ dv \end{pmatrix} = \underbrace{\begin{bmatrix} \left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x \\ \left(\frac{\partial v}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x \end{bmatrix}}_{\text{Jacobian matrix}} \begin{bmatrix} dx \\ dy \end{bmatrix}$$

Notation

$$\frac{d(u, v)}{d(x, y)} = \text{Determinant of Jacobian matrix}$$

$$= \left(\frac{\partial u}{\partial x}\right)_y \underset{\overset{\shortparallel}{1}}{\left(\frac{\partial v}{\partial y}\right)_x} - \underbrace{\left(\frac{\partial v}{\partial x}\right)_y}_{0 \text{ if } v = y} \left(\frac{\partial u}{\partial y}\right)_x$$

If $v = y$,

$$\boxed{\frac{d(u, y)}{d(x, y)} = \left(\frac{\partial u}{\partial x}\right)_y}$$

So for $\left(\frac{\partial G}{\partial H}\right)_T = \frac{d(G,T)}{d(H,T)}$

By matrix rule, $\frac{\partial(v,u)}{\partial(x,y)} = \frac{-\partial(u,v)}{\partial(x,y)}$

Chain rule, $\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,v)}{\partial(r,s)} \times \frac{\partial(r,s)}{\partial(x,y)}$

Reciprocality $\frac{\partial(u,v)}{\partial(x,y)} = \left[\frac{\partial(x,y)}{\partial(u,v)}\right]^{-1}$

Eg. 1 ST $\left(\frac{\partial U}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T$

WKT, $dU = TdS - PdV$

$$\left(\frac{\partial U}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T$$

Use Maxwell relation ② in Pg 76

$$\therefore \left(\frac{\partial U}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T$$

Eg 2 : $\left(\frac{\partial T}{\partial P}\right)_V = \frac{d(T,V)}{d(P,V)}$ Use chain rule

$$= \frac{-\partial(V,T)}{\partial(P,V)} = \frac{-\partial(V,T)}{\partial(P,T)} \times \frac{-\partial(T,P)}{-\partial(V,P)}$$

$$= -\left(\frac{\partial V}{\partial P}\right)_T \cdot \left(\frac{\partial T}{\partial V}\right)_P$$

$$= VK_T \cdot \left[\left(\frac{\partial V}{\partial T}\right)_P\right]^{-1} = \frac{VK_T}{V\alpha}$$

$$\therefore \left(\frac{\partial T}{\partial P}\right)_V = \frac{K_T}{\alpha}$$

3) $$\left(\frac{\partial G}{\partial S}\right)_V = \frac{\partial(G,V)}{\partial(S,V)}$$

$$= \frac{\partial(G,V)}{\partial(P,T)}\;\frac{\partial(P,T)}{\partial(\partial S,V)} = \begin{vmatrix} \left(\frac{\partial G}{\partial P}\right)_T & \left(\frac{\partial G}{\partial T}\right)_P \\ \left(\frac{\partial V}{\partial P}\right)_T & \left(\frac{\partial V}{\partial T}\right)_P \end{vmatrix} \;\frac{\partial(P,T)}{\partial(S,V)}$$

$$dG = VdP - SdT \Rightarrow \left(\frac{\partial G}{\partial P}\right)_T = \underset{?}{-V} \qquad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial G}{\partial S}\right)_V \Rightarrow \begin{vmatrix} -V & -S \\ -VK_T & V\alpha \end{vmatrix} \;\frac{\partial(P,T)}{\partial(V,T)}\;\frac{\partial(V,T)}{\partial(S,V)}$$

$$= \left(-V^2\alpha + SVK_T\right)\underset{\overset{\parallel}{-\frac{1}{VK_T}}}{\left(\frac{\partial P}{\partial V}\right)_T} \times \underset{\overset{\parallel}{\frac{T}{C_v}}}{\left(\frac{\partial T}{\partial S}\right)_V} = \left(-V^2\alpha + SVK_T\right)\frac{T}{VC_vK_T}$$

$$\therefore \left(\frac{\partial G}{\partial S}\right)_V = \frac{ST}{C_v} - \frac{V\alpha T}{C_v K_T}$$

$$dG = VdP - SdT$$

$$S = \left(\frac{\partial G}{\partial T}\right)_P \qquad V = \left(\frac{\partial G}{\partial P}\right)_T$$

$$G = H - TS \Rightarrow H = G + TS$$

$$U = H - PV$$

So, if we have $G(P,T)$, we can find other TD variables.

$$dG = VdP - SdT + \underset{\downarrow}{\underline{\underline{\sum_i \mu_i dn_i}}}$$

Chemical potential

It plays an important role in multi-component systems

Problem Solving 3

1) PT $C_v = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_v$

WKT, $C_v = \left(\frac{\partial U}{\partial T}\right)_v$

$dA = -PdV - SdT$

$\left(\frac{\partial A}{\partial T}\right)_V = -S$

$\Rightarrow C_V = -T.\left[\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial T}\right)\right]_V$

$U = TdS - PdV$

$C_V = -T\left[\frac{\partial^2 A}{\partial T^2}\right]_V$

$\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$

2) PT $\left(\frac{\partial H}{\partial V}\right)_T = -V^2\left(\frac{\partial P}{\partial T}\right)_V \cdot \left[\frac{\partial (T/V)}{\partial V}\right]_P$

$\left(\frac{\partial (T/V)}{\partial V}\right)_P = \left[\frac{\partial}{\partial V}\left(\frac{T}{V}\right)\right]_P = -\frac{T}{V^2} + \frac{1}{V}\left(\frac{\partial T}{\partial V}\right)_P$

RHS $= -V^2\left(\frac{\partial P}{\partial T}\right)_V\left[\frac{1}{V}\left(\frac{\partial T}{\partial V}\right)_P - \frac{T}{V^2}\right]$ — ①

$dH = TdS + VdP$

$\left(\frac{\partial H}{\partial V}\right)_T = T.\left(\frac{\partial S}{\partial V}\right)_T + V\left(\frac{\partial P}{\partial V}\right)_T$

$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

$\left(\frac{\partial P}{\partial V}\right)_T = \frac{d(P,T)}{d(V,T)} = \frac{d(P,T)}{d(P,V)} * \frac{d(PV)}{\partial(V,T)}$

$= \frac{\partial(T,P)}{\partial(V,P)} \cdot \frac{\partial(P,V)}{-\partial(T,V)}$

$= \left(\frac{\partial T}{\partial V}\right)_P \times -\left(\frac{\partial P}{\partial T}\right)_V$

Substituting this,

$\left(\frac{\partial H}{\partial V}\right)_T = T.\left(\frac{\partial P}{\partial T}\right)_V - V.\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_P$

$= -V\left(\frac{\partial P}{\partial T}\right)_V\left[-\frac{1}{V}T + \left(\frac{\partial T}{\partial V}\right)_P\right]$

Use ① to prove the question

8) PT $\left(\frac{\partial V}{\partial T}\right)_S \Big/ \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{1-\gamma}$ where $\gamma = \frac{C_P}{C_V}$

$= \frac{C_V}{C_V - C_P}$ $U = TdS - PdV$

flip

MR: $C_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = T \cdot \frac{d(S,V)}{d(T,V)} \times \frac{d(T,S)}{d(T,S)}$

$$C_V = T \times \frac{-d(V,S)}{d(T,S)} \frac{\cancel{-}d(S,T)}{\cancel{-}d(V,T)} = -T \cdot \left(\frac{\partial V}{\partial T}\right)_S \left(\frac{\partial S}{\partial V}\right)_T$$

$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ $C_P = \left(\frac{\partial U}{\partial T}\right)_P = T \cdot \left(\frac{\partial S}{\partial T}\right)_P - P \cdot \left(\frac{\partial V}{\partial T}\right)_P$

$$C_V - C_P = T \cdot \left(\left(\frac{\partial S}{\partial T}\right)_V - \left(\frac{\partial S}{\partial T}\right)_P\right)$$

$V = V(T,P) \Rightarrow dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$

$\left(\frac{\partial V}{\partial T}\right)_S = \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_S$ Divide by $\left(\frac{\partial V}{\partial T}\right)_S$

$$1 = \underbrace{\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial T}\right)_S}}_{LHS} + \frac{\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_S}{\left(\frac{\partial V}{\partial T}\right)_S}$$

$$LHS = 1 - \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial T}{\partial V}\right)_S$$

$$= 1 - \frac{d(V,T)}{d(P,T)} \frac{d(P,S)}{d(\cancel{T,}S)} \frac{d(\cancel{T},S)}{d(V,S)} = 1 - \frac{d(V,T)}{d(V,S)} \cdot \frac{d(P,S)}{d(P,T)}$$

$$= 1 - \left(\frac{\partial T}{\partial S}\right)_V \left(\frac{\partial S}{\partial T}\right)_P = 1 - \frac{C_P}{\cancel{T}C_V/\cancel{T}}$$

$\therefore \left(\frac{\partial V}{\partial T}\right)_P \Big/ \left(\frac{\partial V}{\partial T}\right)_S = 1 - \gamma$ Reciprocal will give required solution