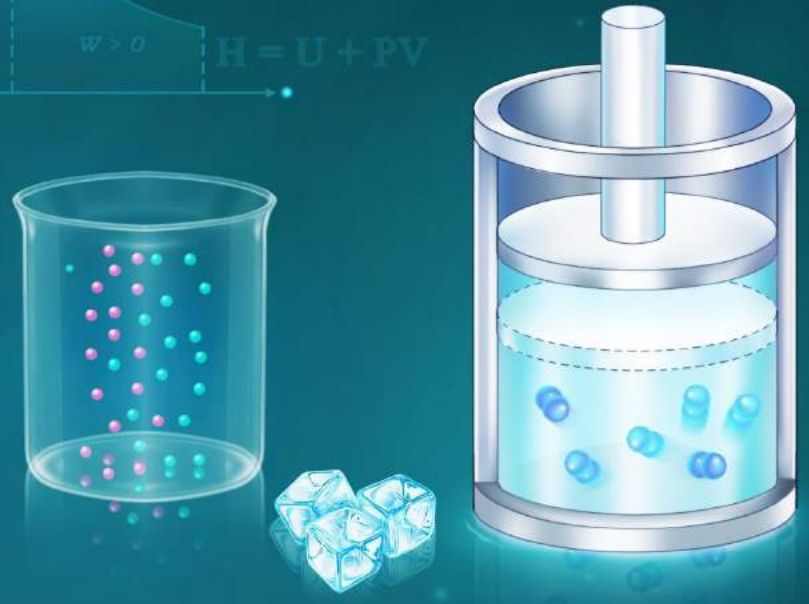
Welcome to

Aakash + BYJU'S LIVE

Thermodynamics



THERMODYNAMICS

Heat

Movement

Various forms of energy are **interrelated**

Can be **transformed** from one form to another

Thermodynamics

Branch of science which deals with different forms of **energy** & their interconversion

Deals with matter in **bulk**

Thermodynamics

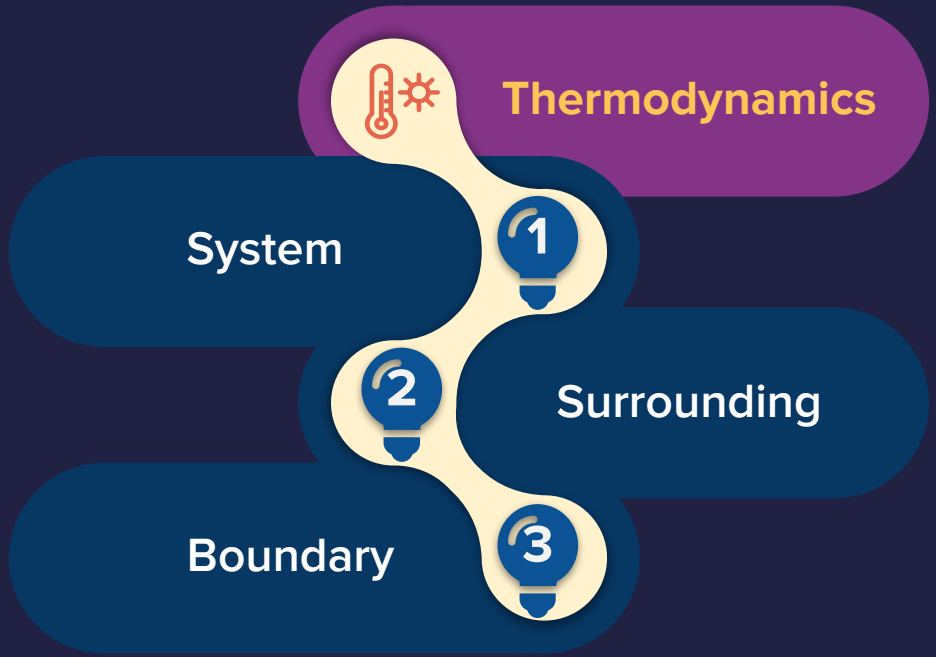
Properties associated with bulk are called **macroscopic properties**

Why Do We Need to Study Thermodynamics?

To understand,

1. What drives a chemical reaction?
2. Energy changes involved in a chemical reaction
3. Extent of completion of a reaction
4. Criteria to predict the feasibility of the process

Terms Used in Thermodynamics



System

Part of the universe under **observation or thermodynamic investigation**

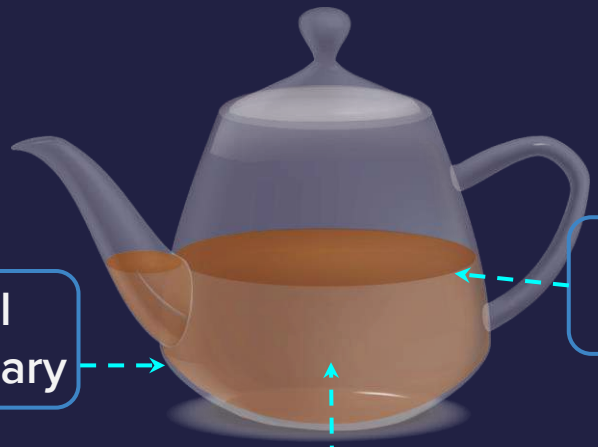
Includes everything else in the universe other than the system

Surrounding

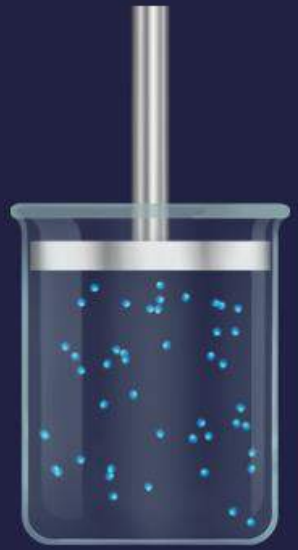
Boundary

A real or imaginary layer **separating the system from its surroundings**

Allows us to **control & keep track** of all the movements of matter & energy



Boundary



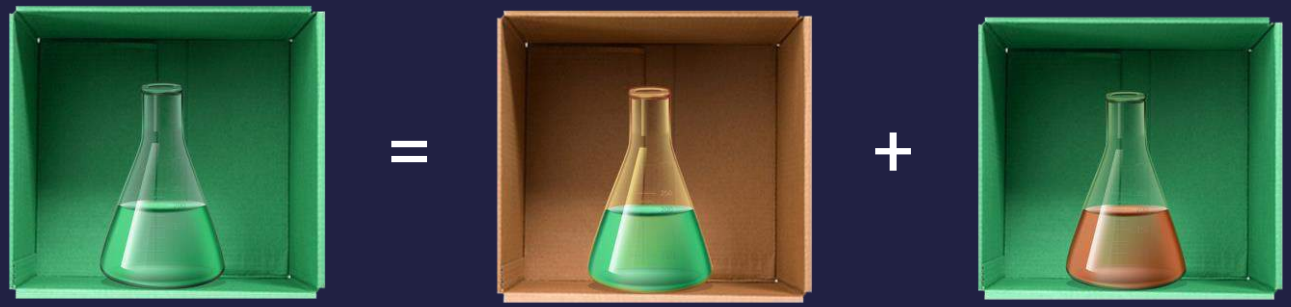
Flexible Boundary

Rigid Boundary

Boundary

Diathermic	Adiabatic
Conducting (**Heat**)	Non conducting (**Heat**)

What is Universe?



Universe	=	System	+	Surrounding

Types of Systems

	OPEN	CLOSED	ISOLATED
			
Matter exchange	✓	✗	✗
Energy exchange	✓	✓	✗

State of the System

Condition in which
the **system** is **present**

State is defined by **measuring the observable properties** of the system

P

V

T

n

State Functions

Values **depend only upon the state of the system**

Does not depend upon the path by which this state has been attained

Pressure, volume, temperature, ...

Path Functions

Depends on the path by which the system has achieved a particular state

Can’t have any definite (particular) value in any particular state of the system

Heat, work

Quick Contrast!

State function	Path function
Independent of the **path taken**	**Dependent** on the **path taken**
Depends only upon the state of the system	Depends upon how that state of the system has been achieved
Multiple paths result in the **same value**	**Multiple paths** may result in **different values**
E.g.: Temperature (T), Pressure (P), Enthalpy (H), Internal energy (U) etc.	E.g.: Heat (q), Work (W)

Macroscopic Properties

Intensive Properties

Macroscopic Properties

Extensive Properties

Intensive

Independent of the **mass** or the **size of the system**

Dependent on the **mass** or the **size of the system**

Extensive

Remember!

Ratio of two extensive properties is an intensive property

Intensive property → Density = $\frac{\text{Mass}}{\text{Volume}}$

Mass ← Extensive property

Volume ← Extensive property

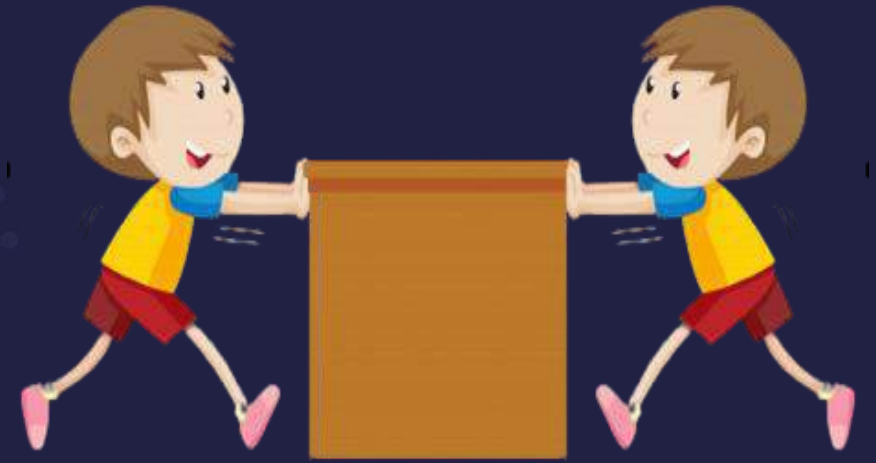
Thermodynamic Equilibrium

No change in any observable or measurable property of a system with time

Thermodynamic Equilibrium

- Mechanical
- Thermal
- Chemical

Mechanical Equilibrium



No pressure gradient with time

Thermal Equilibrium and Chemical Equilibrium

Thermal Equilibrium

No temperature gradient with time

Chemical Equilibrium

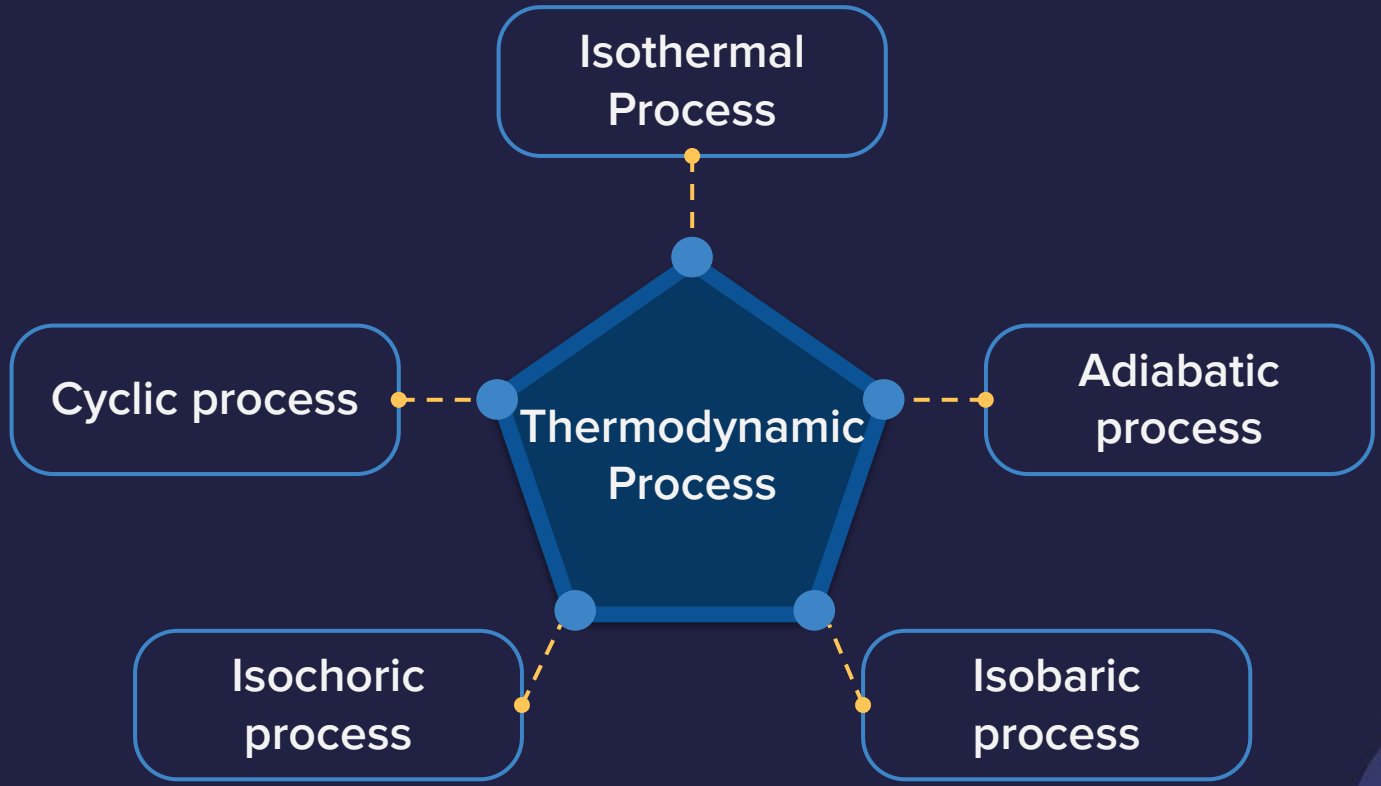
No concentration gradient of any of the species in the system

Thermodynamic state parameters are only defined when the system is in a **thermodynamic equilibrium**

Thermodynamic Process

Process by which a system **can change its state from one state of thermodynamic equilibrium to another**

Thermodynamic Processes



Isothermal Process

dT = 0

Thermodynamic process
in which the **temperature**
remains constant throughout

Adiabatic Process

q = 0

Thermodynamic process in which the **heat exchange** between the system & the surrounding is **not possible**

Heat exchange

Isobaric and Isochoric Process

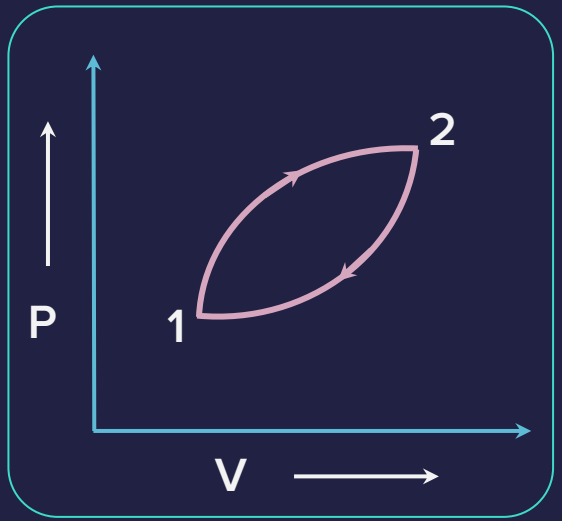
dP = 0

Thermodynamic process occurring at **constant pressure** is **Isobaric Process.**

dV = 0

Thermodynamic process occurring at **constant volume** is **Isochoric Process.**

Cyclic Process

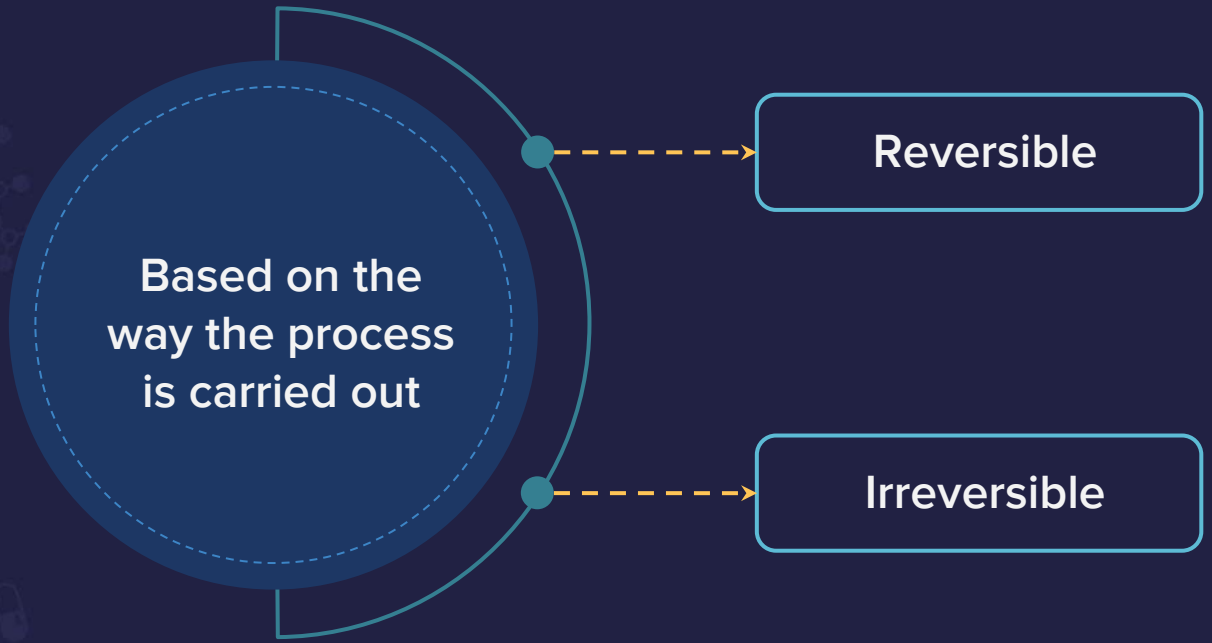


A system undergoes a series of change and comes back to the initial state

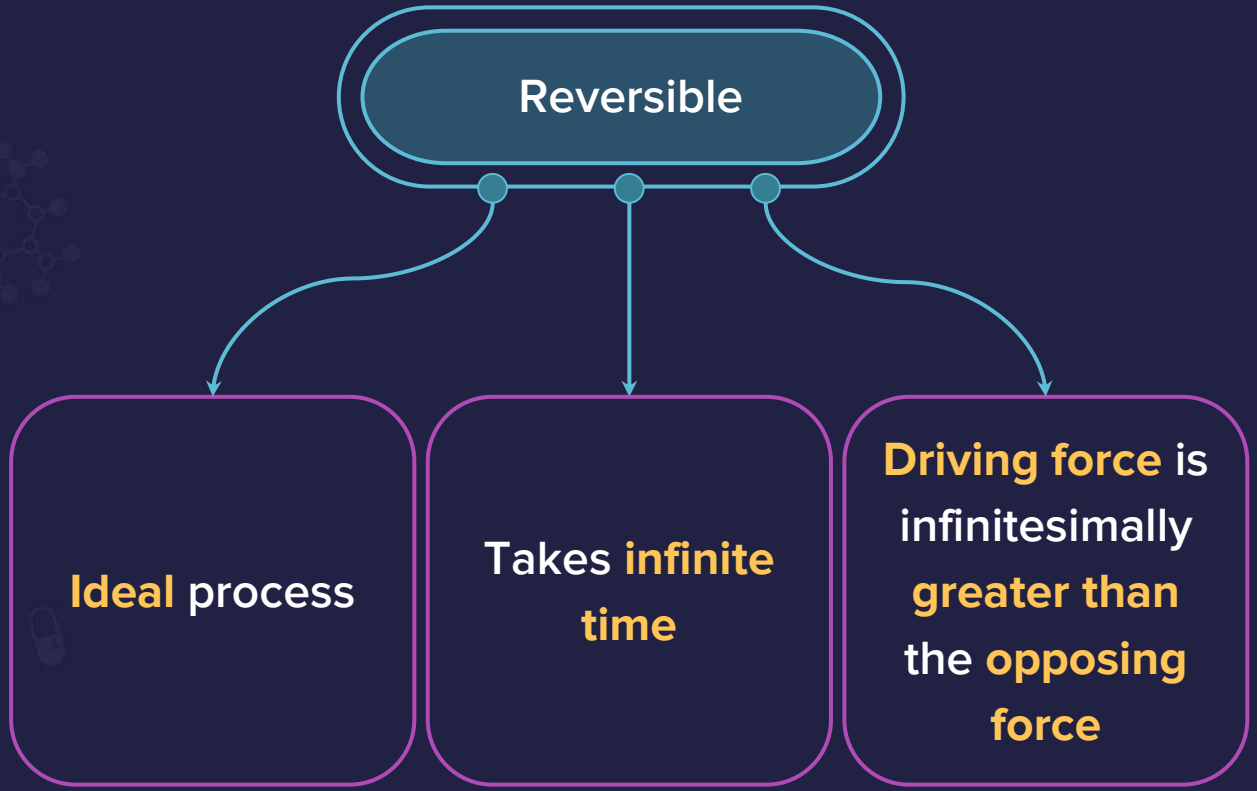
$\Delta H = 0$

$\Delta U = 0$

Thermodynamic Processes



Reversible Process



Reversible Process

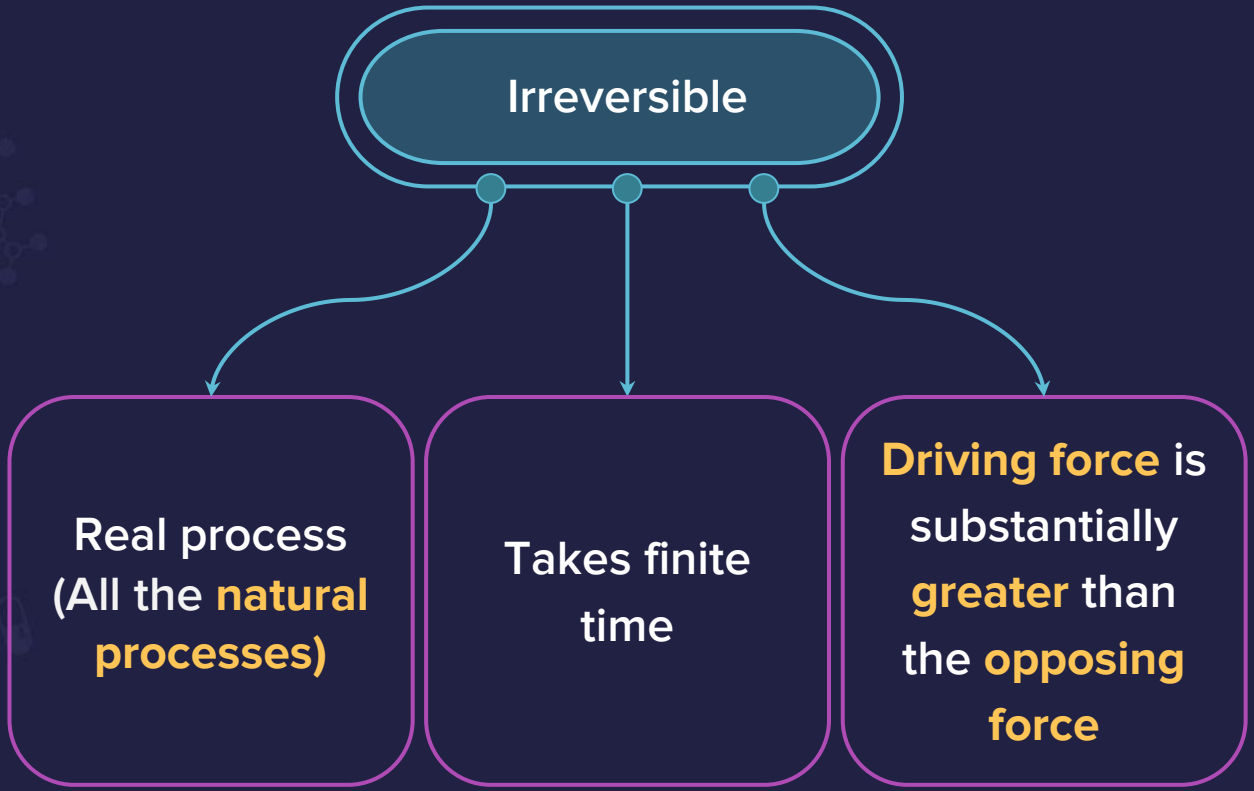
System is **always in thermodynamic equilibrium** at every stage of the process

Carried out **infinitely slowly** through a series of equilibrium states

At any moment, the direction of the process can be **reversed** by an infinitesimal change

System & surroundings can be **restored** back to their original state

Irreversible Process



Irreversible Process

System **may be in thermodynamic equilibrium** state at some finite number of intermediate stages only

Carried out in **finite steps**

Process that goes from the initial to the final state in **finite steps**

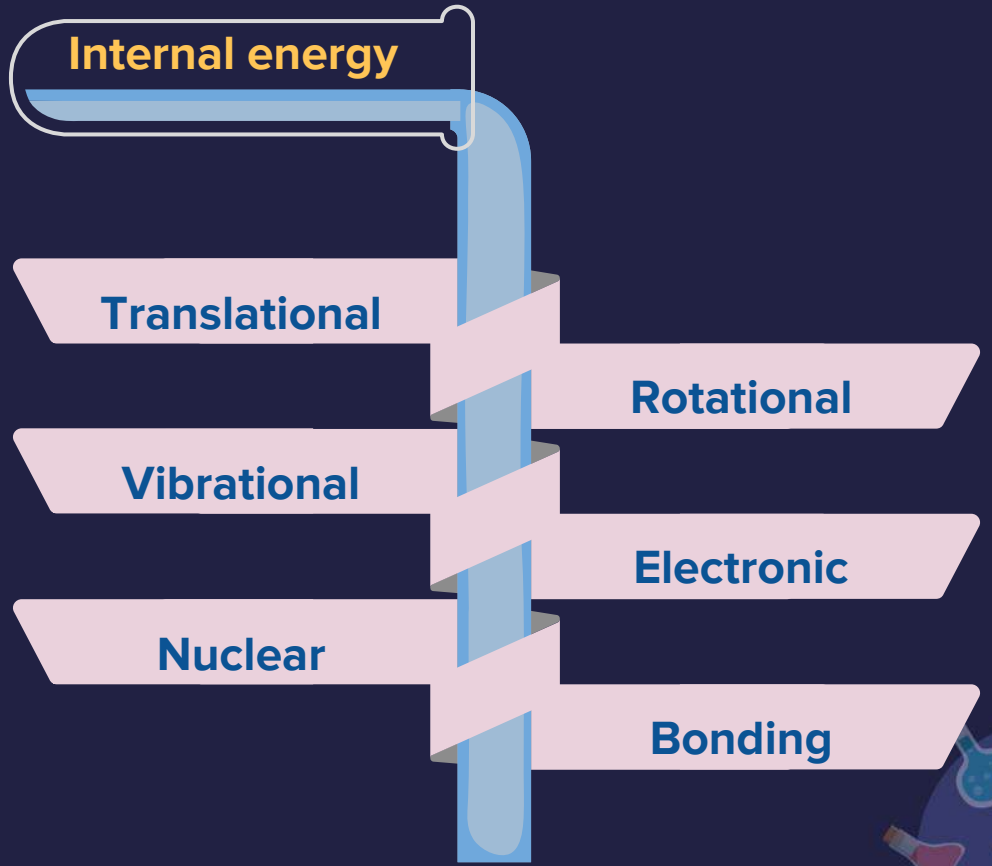
Reversal of driving force **does not restore** the system & surroundings back to their original state

Internal Energy (U)

Every system having some **quantity of matter** is associated with a **definite amount of energy,** called internal energy

Extensive property

State function



Internal Energy

Total energy contained **within the system**

$$U_{Total} = U_{Translational} + U_{Rotational} + U_{Vibrational} + U_{Electronic} + U_{Nuclear} + U_{Bonding} + \dots$$

Can't be measured

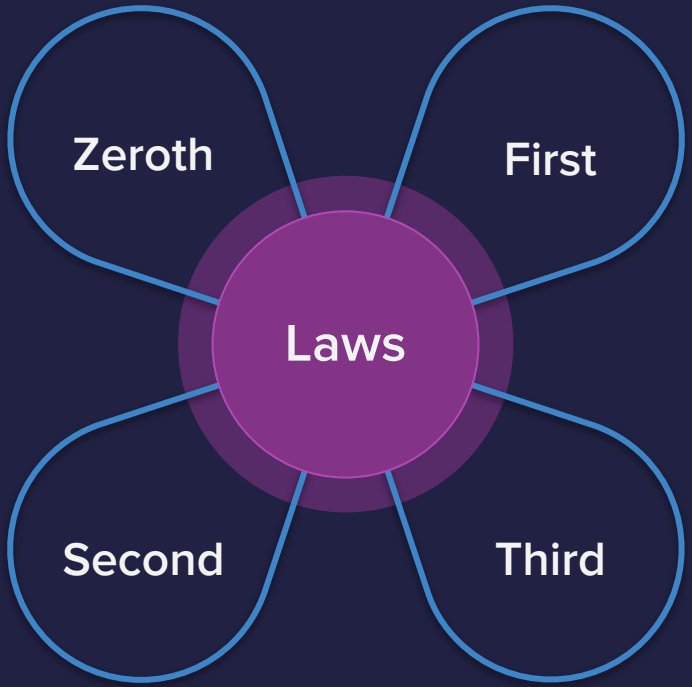
Change in Internal Energy (ΔU)

$$\Delta U = U_{final} - U_{initial}$$

Can be measured

Can be **zero, positive or negative**

Laws of Thermodynamics

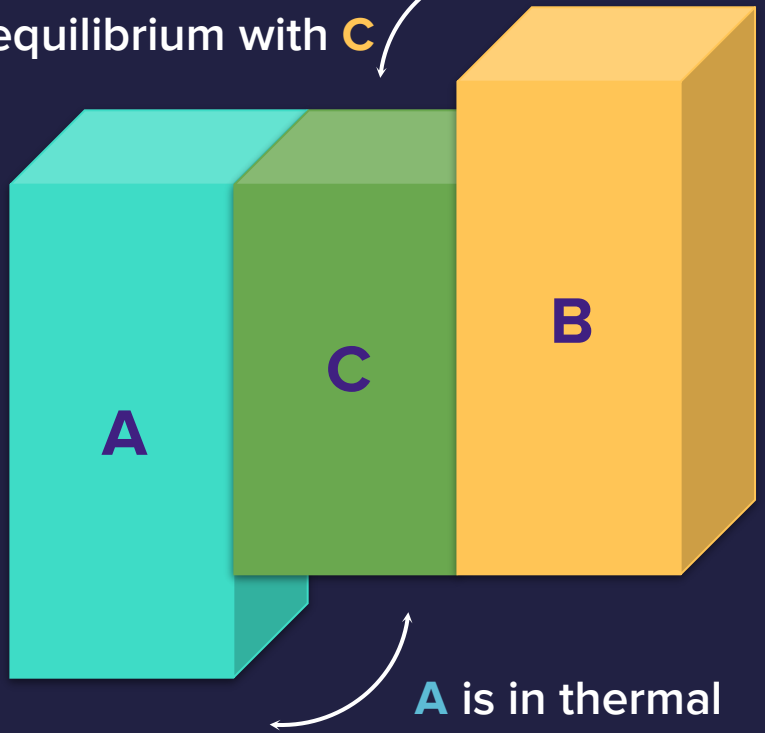


Zeroth Law of Thermodynamics

If two bodies **A & B** are in thermal equilibrium with another body **C**, then **A** and **B** are also in **thermal equilibrium** with each other

Zeroth Law of Thermodynamics

B is in thermal equilibrium with C



Therefore, A and B are in thermal equilibrium

A is in thermal equilibrium with C

First Law of Thermodynamics

Energy can **neither be created nor destroyed** but can be converted from one form to another

Total energy of an isolated system is **always conserved**

System can exchange energy with its surroundings by

- Heat
- Work

Heat (q)

Heat is the **Energy transferred** across a boundary as a result of **temperature difference** between **system & surroundings**

Flow of energy from **high T** to **low T**

Work (W)

Work is the motion **against** an **opposing force**.

$$dW = \vec{F} \cdot \vec{dx}$$

F	Force
dx	Displacement

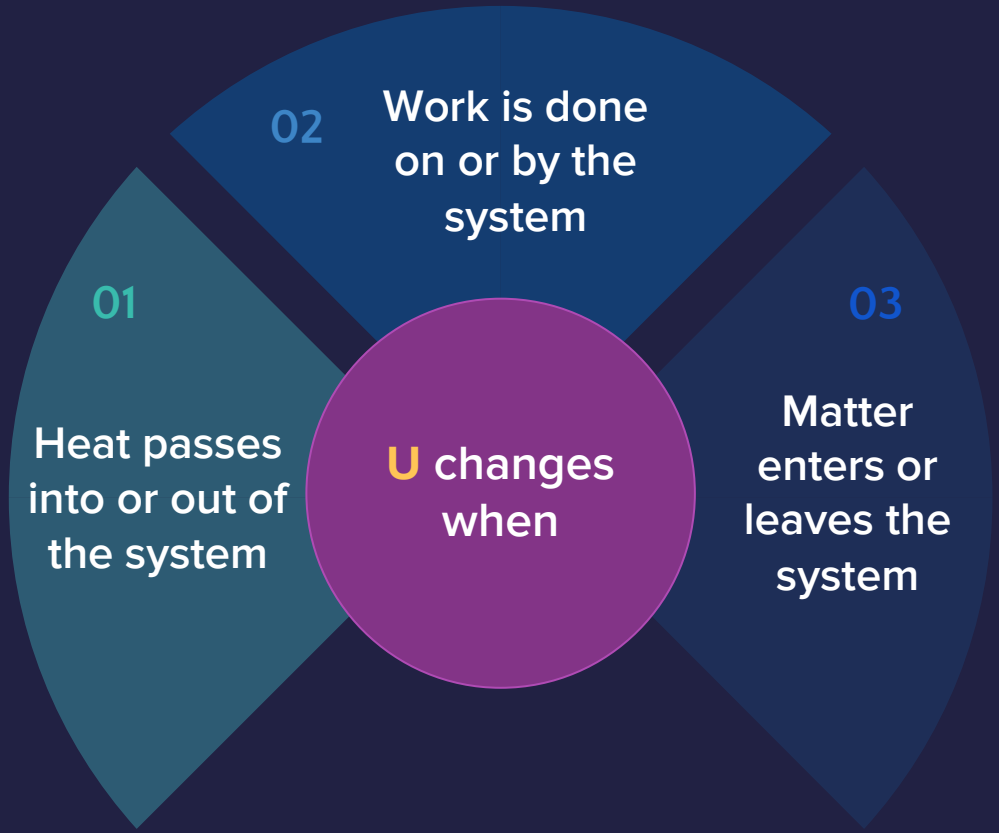
Heat (q) & Work (W)

Both are mode of transfer of energy

Path function

SI Unit : Joule (J)

First Law of Thermodynamics



Mathematical Expression for the Ist Law

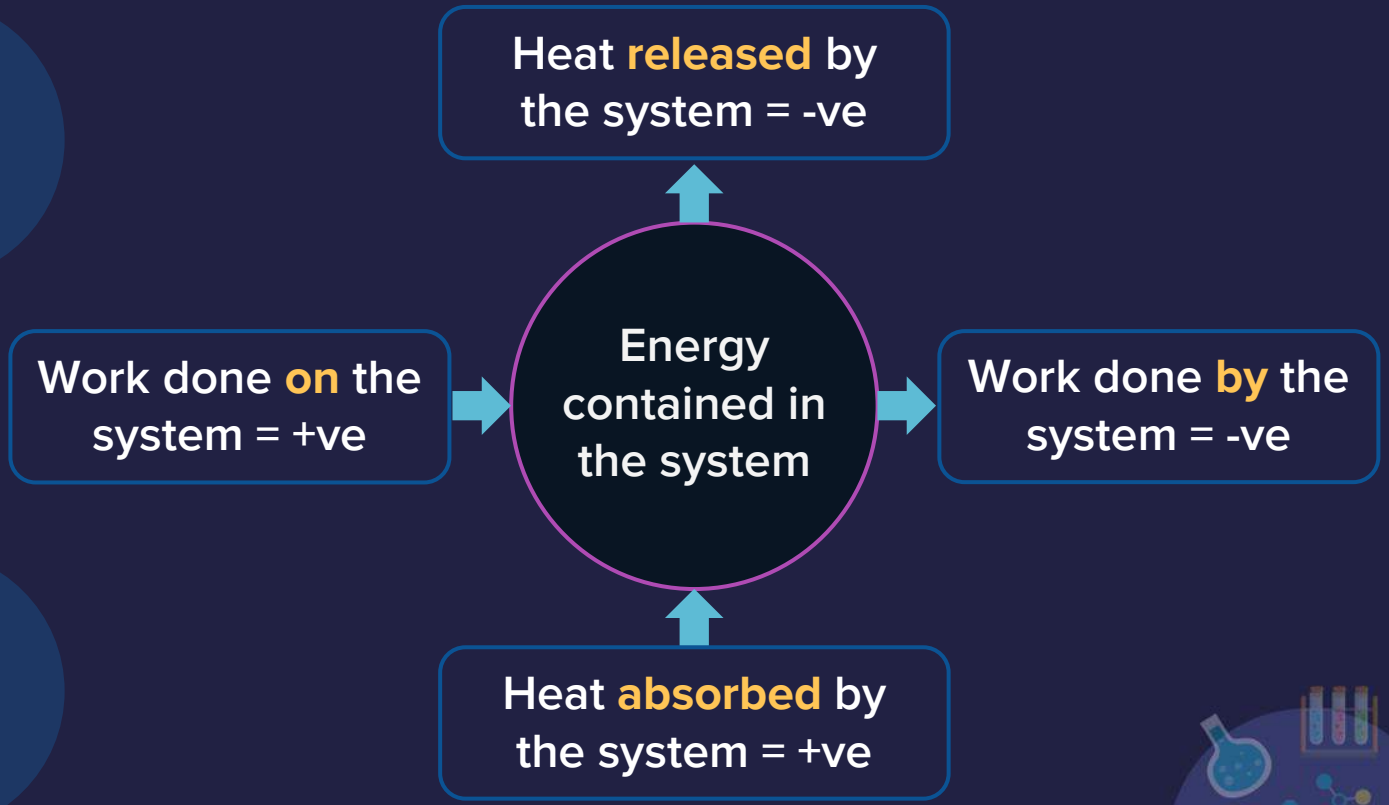
$$\Delta U = q + W$$

Change in internal energy	=	Heat given to the system	+	Work done on the system

Sign Convention of Heat and Work

Positive
Anything which **increases energy** of the system

Negative
Anything which **decreases energy** of the system



Heat Capacity

Water has high Heat Capacity

Lots of energy is needed to raise its temperature

Total Heat Capacity (C_T)

Heat required to **raise the temperature** of the system by **1 °C** under the given process

$$C_T = \frac{dq}{dT} \text{ J °C}^{-1}$$

Total Heat Capacity (C_T)

C_T — **Extensive property** & **path function**

$$C_T = \frac{dq}{dT}$$

$$dq = C_T\, dT$$

On integrating,

$$\int dq = \int C_T\, dT$$

If C_T is **independent** of temperature,

$$q = C_T\, \Delta T$$

Molar Heat Capacity (C_m)

Heat required to **raise the temperature** of **1 mol** of a substance by **1 °C**

$$C_m = \frac{dq}{ndT} \text{ J/mol °C}$$

$$C_m = \frac{C_T}{n}$$

Molar Heat Capacity (C_m)

C_m — **Intensive property & path function**

$$C_m = \frac{dq}{ndT}$$

$$dq = nC_m dT$$

On integrating,

$$\int dq = \int nC_m\, dT$$

If C_m is **independent** of temperature,

$$q = nC_m \Delta T$$

$$C_m = \frac{dq}{ndT}$$

- Molar Heat Capacity at **constant V** ($C_{v,\,m}$)
- Molar Heat Capacity at **constant P** ($C_{p,\,m}$)

Specific Heat Capacity (s)

Heat required to **raise the temperature** of **1 g** of a substance by **1 °C**

$$s = \frac{dq}{mdT} \text{ J/ g °C}$$

Specific Heat Capacity (s)

s	Intensive property & path function

$$s = \frac{dq}{m\,dT}$$

$$dq = m\,s\,dT$$

On integrating,

$$\int dq = \int m\,s\,dT$$

If s is independent of temperature,

$$q = m\,s\,\Delta T$$

Molar Heat Capacity (C_m)

Isothermal process	C_m	=	$\pm \infty$
Isobaric process	C_m	=	$C_{p,\,m}$
Isochoric process	C_m	=	$C_{v,\,m}$
Adiabatic process	C_m	=	0

Expression for P-V Work

$$P = \frac{F}{A}$$

$$F = P \times A$$

P	External Pressure
A	Piston area
F	Force on piston

Expression for P-V Work

Work required to move piston a distance **d/** against an opposing force of magnitude **F** is,

$W = -F \times d/$

$dW = -P_{ext} \times A \times d/$

$dW = -P_{ext} \times dV$

$dW = -P_{ext}\, dV$

Remember!!

P × V = L atm (Unit of energy)

1 J = 10^7 ergs = 1 N m = 1 kg m^2/s^2

1 L atm = 101.3 J = 24.206 cal

Mathematical Expression for the Ist Law

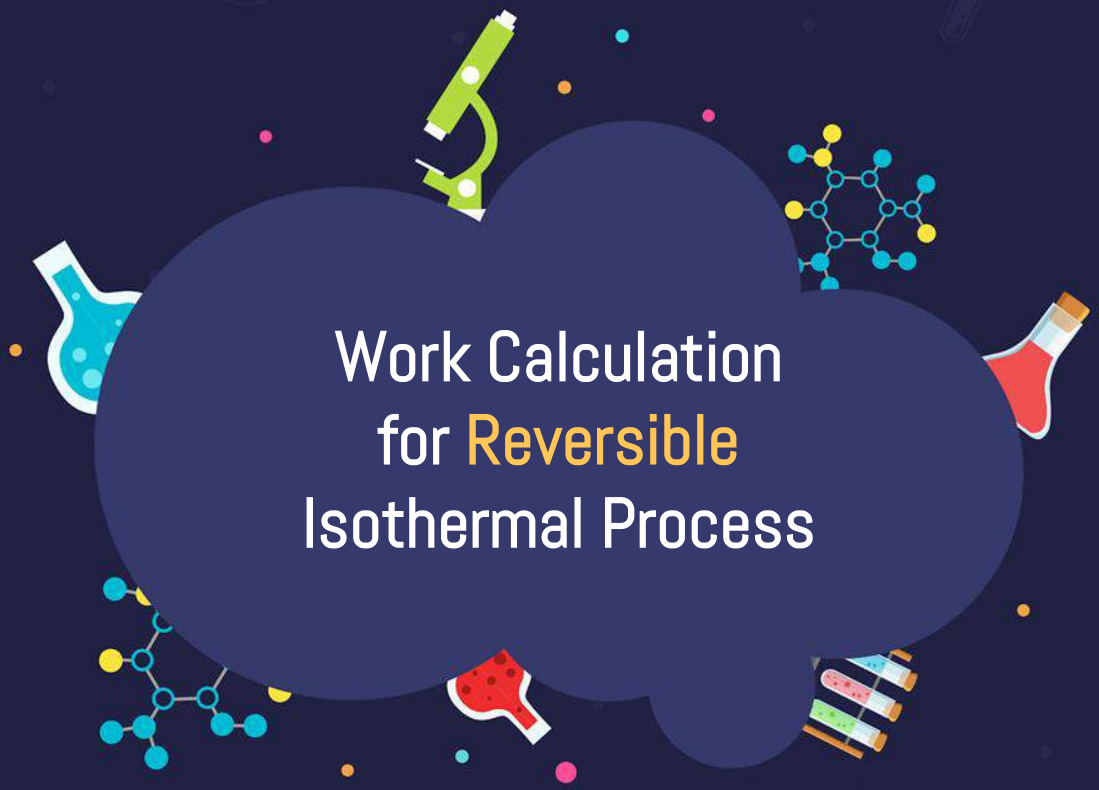
$$dU = dq + dW$$

At constant volume

$$dW = 0$$

$$\Rightarrow \quad dU = dq_v$$

$$dU = nC_{v.\,m}\,dT$$


Work Calculation
for Reversible
Isothermal Process

Isothermal Reversible Process

$$W_{rev} = -\int_{V_i}^{V_f} P_{ext}\, dV$$

$$W_{rev} = -\int_{V_i}^{V_f} (P_{gas} \pm dP)\, dV$$

dP x dV ----→ very small, so can be neglected

Isothermal Reversible Process

$$W_{rev} = -\int_{V_i}^{V_f} P_{gas}\, dV$$

$$P_{gas} = \frac{nRT}{V}$$

$$W_{rev} = -\int_{V_i}^{V_f} \frac{nRT}{V}\, dV$$

$$W_{rev} = -nRT\int_{V_i}^{V_f} \frac{dV}{V}$$

Isothermal Reversible Process

$$W_{rev} = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT [\ln V]_{V_i}^{V_f}$$

Since, $\int \frac{dx}{x} = \ln x$

$$= -nRT [\ln V_f - V_i]$$

$$= -nRT \ln \frac{V_f}{V_i}$$

Since, $\ln x_2 - \ln x_1 = \ln \frac{x_2}{x_1}$

Isothermal Reversible Process

$$W_{rev} = -2.303\ nRT \log \frac{V_f}{V_i}$$

$$W_{rev} = -2.303\ nRT \log \frac{P_i}{P_f}$$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

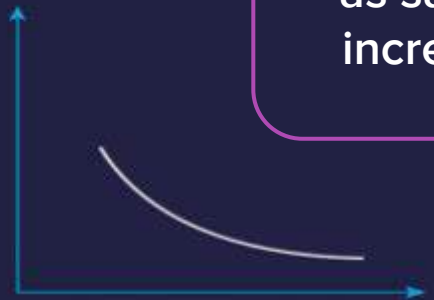
At the same temperature
Boyle's law

Isothermal Reversible Compression

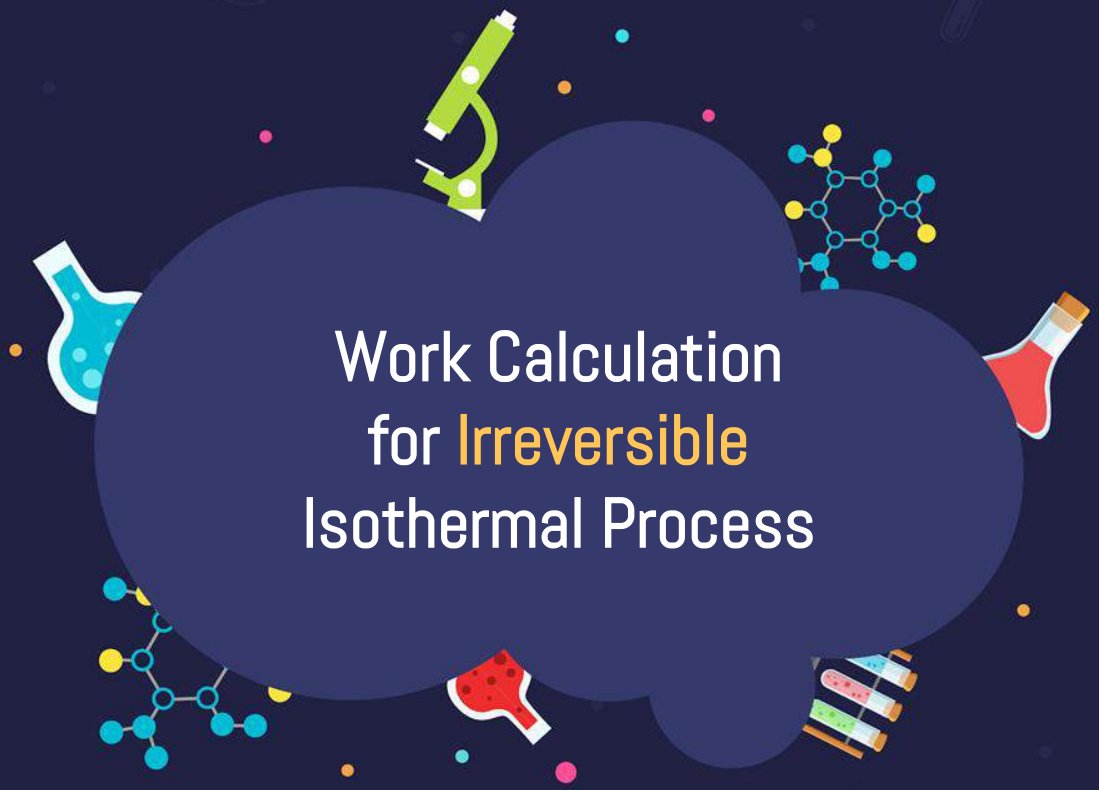
P_{ext} changes such that it is always infinitesimally higher than P_{gas}

Reversible compression occurs

Suppose we keep sand particles slowly on movable piston so that in each step one particle falling on piston compresses infinitesimely the volume



P_{ext} is not constant, it increases very slowly as sand particles increases on the piston.


Work Calculation
for Irreversible
Isothermal Process

Isothermal Irreversible Expansion

Single step expansion

On removing the brick, expansion of the gas will take place against a **constant external pressure.**

$$P_{ext} = P_{atm}$$

Isothermal Irreversible Expansion

Two step expansion

A brick of mass M was divided into two fragments of equal masses i.e. $\frac{M}{2}$

Removing one fragment,

$$P_{ext} = P_{atm} + \frac{Mg}{A} - \frac{Mg}{2A}$$

$$P_{ext} = P_{atm} + \frac{Mg}{2A}$$

Isothermal Irreversible Expansion

$$dW_1 = -P_{ext}\,dV$$

P_{ext} is constant

$$\int dW_1 = \int_{V_i}^{V_1} -P_{ext}\,dV = -P_{ext}\int_{V_i}^{V_1} dV$$

$$W_1 = -P_{ext}\,(V_1 - V_i)$$

$$W_1 = -\left[P_{atm} + \frac{Mg}{2A}\right](V_1 - V_i)$$

Isothermal Irreversible Expansion

Removing the second fragment,

$$P_{ext} = P_{atm} + \frac{Mg}{2A} - \frac{Mg}{2A}$$

$$P_{ext} = P_{atm}$$

Isothermal Irreversible Expansion

$$dW_2 = -P_{ext}\,dV$$

P_{ext} is constant

$$\int dW_2 = \int_{V_1}^{V_f} -P_{ext}\,dV = -P_{ext}\int_{V_1}^{V_f} dV$$

$$W_2 = -P_{ext}\,(V_f - V_1)$$

$$W_2 = -P_{atm}\,(V_f - V_1)$$

Isothermal Irreversible Expansion

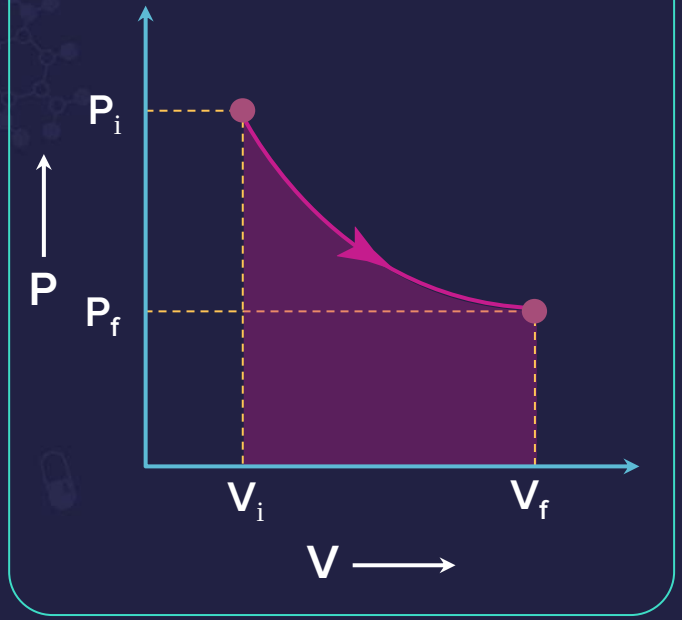
$$W_{total} = W_1 + W_2$$

$$W_{total} = -\left[P_{atm} + \frac{Mg}{2A}\right](V_1 - V_i) + -P_{atm}(V_f - V_1)$$

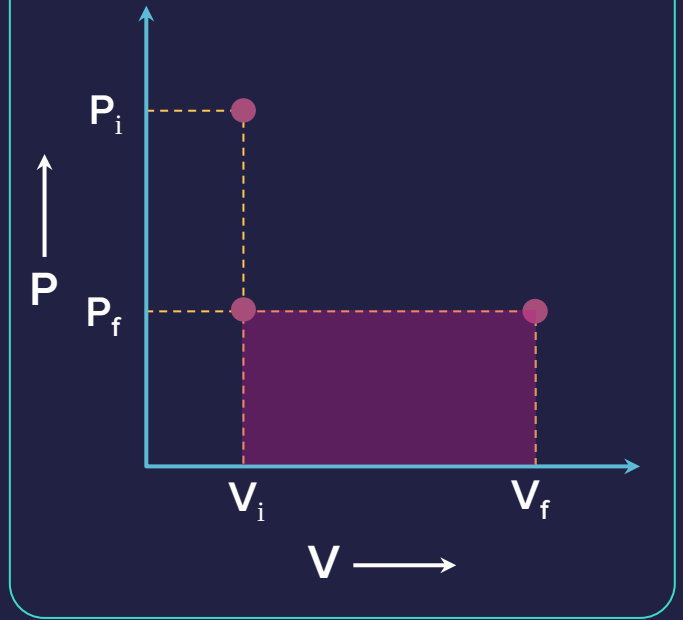
If the irreversible process consists of n-steps, where $n \to \infty$, the process becomes reversible.

Work Comparison for Isothermal Process

Reversible Expansion



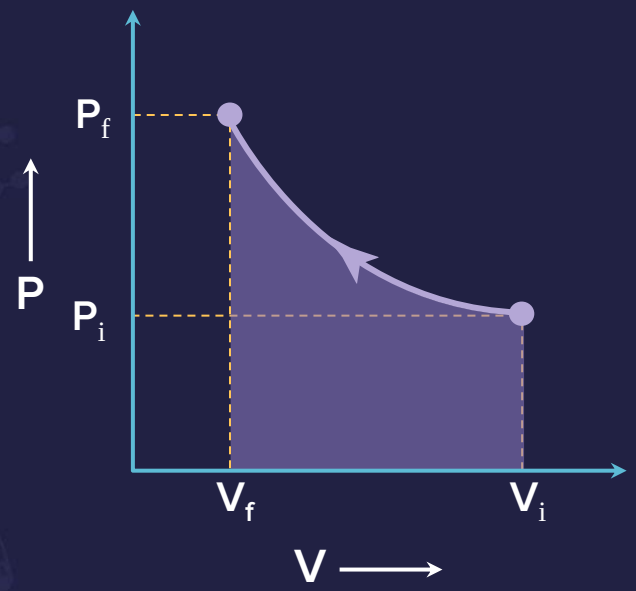
Irreversible Expansion



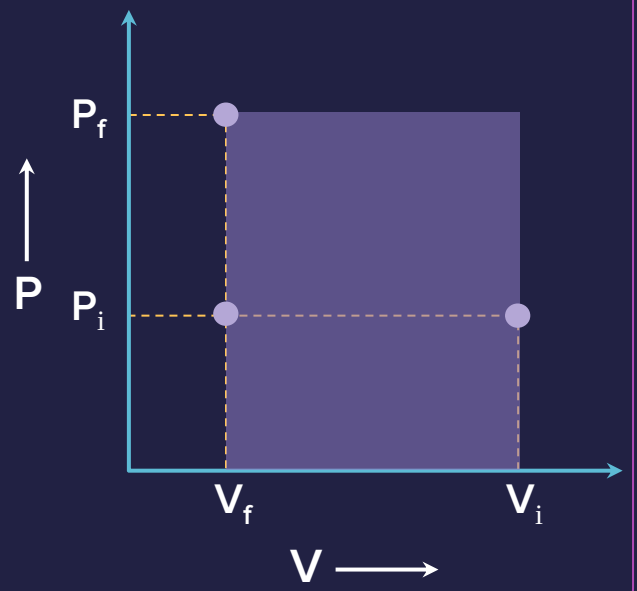
$$|W_{rev}| > |W_{irrev}|$$

Work Comparison for Isothermal Process

Reversible Compression



Irreversible Compression



$$W_{irrev} > W_{rev}$$

Conclusion

Output	Work done **by** the system
Input	Work done **on** the system
Work done on the gas	**Minimum** in reversible process
Work done by the gas	**Maximum** in reversible process

Remember!!

Process is **irreversible** when

- Expansion/ compression against a constant external pressure
- Change is sudden

Isochoric and Isobaric process

Isochoric Process

Since, $dV = 0$

So, $W = 0$

for both **reversible** and **irreversible** processes

Isobaric Process

Since, $P = \text{constant}$

So, $W = -P_{ext}(V_f - V_i)$

for a **reversible** process

Adiabatic Process

$$q = 0$$

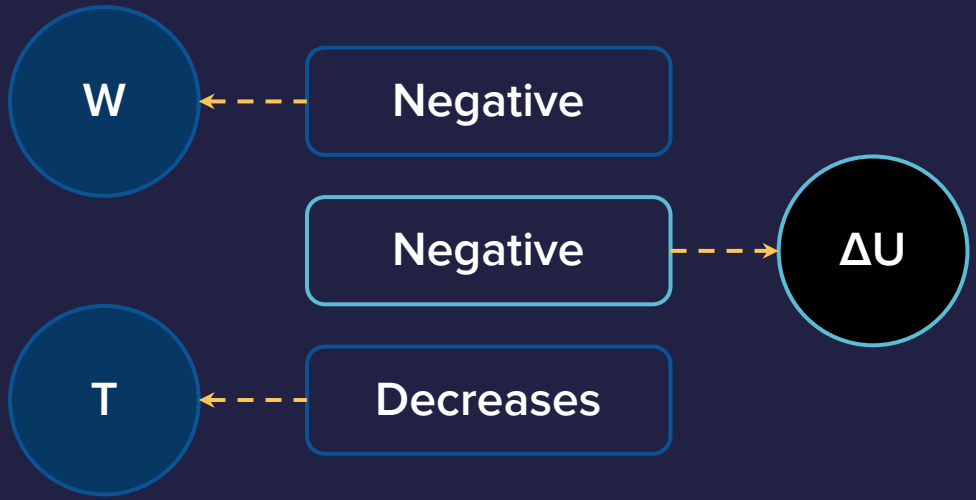
Heat can neither enter nor leave the system

From the First law of thermodynamics,

$$\Delta U = q + W$$

$$\Delta U = W$$

Adiabatic Expansion



Work is done by the system at the expense of internal energy → Cooling

Adiabatic Compression

Work is done on the system, which is stored as the internal energy → Heating

Adiabatic Process

No heat exchange between the system and the surrounding

$$dq = 0$$

$$dU = n C_{v,m} dT$$

$$dW = - P_{ext} dV$$

$$dU = dq + dW$$

$$n C_{v,m} dT = - P_{ext} dV$$

Remember!!

Since, $C_{p,m} - C_{v,m} = R$

Dividing by $C_{v,m}$

$$\frac{C_{p,m}}{C_{v,m}} - 1 = \frac{R}{C_{v,m}}$$

$$\gamma - 1 = \frac{R}{C_{v,m}}$$

$$C_{v,m} = \frac{R}{\gamma - 1}$$

Poisson's Ratio

$$\gamma = \frac{C_{p,m}}{C_{v,m}}$$

Reversible Adiabatic Process

$$n\,C_{v,m}\,dT = -P_{ext}\,dV$$

For a reversible process

$$P_{ext} = P_{gas} = \frac{nRT}{V}$$

$$n\,C_{v,m}\,dT = -\frac{nRT}{V}\,dV$$

$$\int n\,C_{v,m}\,dT = \int -\frac{nRT}{V}\,dV$$

Reversible Adiabatic Process

$$\int_{T_1}^{T_2} \frac{C_{v,m}}{T}\,dT = -\int_{V_1}^{V_2} \frac{R}{V}\,dV$$

$$C_{v,m} \ln\frac{T_2}{T_1} = -R \ln\frac{V_2}{V_1}$$

T_1	Initial temperature
T_2	Final temperature
V_1	Initial volume
V_2	Final volume

Reversible Adiabatic Process

$$\ln\left(\frac{T_2}{T_1}\right) = -\frac{R}{C_{v,m}} \ln\left(\frac{V_2}{V_1}\right)$$

$$a \ln x = \ln x^a$$

$$\ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_2}{V_1}\right)^{-\frac{R}{C_{v,m}}}$$

Reversible Adiabatic Process

$$\ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_2}{V_1}\right)^{1-\gamma}$$

$$\frac{R}{C_{v,m}} = \gamma - 1$$

$$\ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

Reversible Adiabatic Process

$PV = nRT,\ T = \frac{PV}{nR}$

$T_2 V_2^{\gamma - 1} = T_1 V_1^{\gamma - 1}$

$T V^{\gamma - 1} = \text{Constant}$

$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$

$P V^{\gamma} = \text{Constant}$

$P V^{\gamma} = \text{Constant}$

Valid only for a **reversible adiabatic** process

Similarly, using ideal gas equation, we can have relation with P and T.

At normal temperature degree of freedom (f) includes translational and rotational freedom only

Gas	f	$C_{v,m}\left[\frac{f}{2}R\right]$	$C_{p,m}\left[\frac{f+2}{2}R\right]$	$\gamma = \left[\frac{f+2}{f}\right]$
Monoatomic	3	$\frac{3R}{2}$	$\frac{5R}{2}$	$\frac{5}{3}$
Diatomic	5	$\frac{5R}{2}$	$\frac{7R}{2}$	$\frac{7}{5}$
Linear polyatomic	5	$\frac{5R}{2}$	$\frac{7R}{2}$	$\frac{7}{5}$
Non-Linear polyatomic	6	$\frac{6R}{2}$	$\frac{8R}{2}$	$\frac{8}{6}$

Generally, we ignore vibrational degree of freedom and consider only translational and rotational degree of freedom(f) but at high temperature vibrational degree of freedom are also present.

Work Done in Reversible Adiabatic Process

$$W = -\int P_{ext}\, dV \qquad P_{gas} = P_{ext}$$

$$PV^{\gamma} = K \qquad W = -\int \frac{K}{V^{\gamma}}\, dV$$

$$W = -K\,\frac{[V_2^{-\gamma+1} - V_1^{-\gamma+1}]}{1-\gamma} \qquad W = \frac{[P_2V_2^{\gamma}V_2^{1-\gamma} - P_1V_1^{\gamma}V_1^{1-\gamma}]}{\gamma - 1}$$

As, $K = P_2V_2^{\gamma} = P_1V_1^{\gamma}$

Work Done in Reversible Adiabatic Process

For an ideal gas,

Total Work Done in a **Reversible Adiabatic Process**

$$W = \frac{[P_2V_2 - P_1V_1]}{\gamma - 1}$$

Irreversible Adiabatic Process

$$W = -\int P_{ext}\, dV \dashrightarrow W = -P_{ext}(V_2 - V_1)$$

$$dq = 0$$

$$dU = dq + dW$$

$$\int dU = \int dW$$

$$W = \Delta U$$

Irreversible Adiabatic Process

$$W = nC_{v,m}(T_2 - T_1)$$

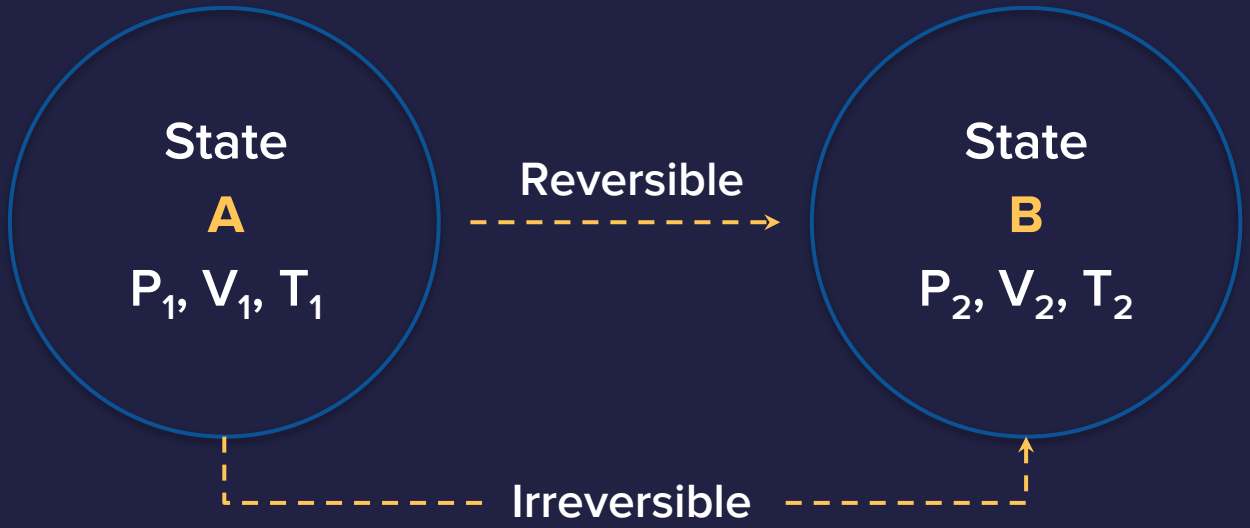
$$C_{v,m} = \frac{R}{\gamma - 1}$$

$$W = \frac{nR(T_2 - T_1)}{\gamma - 1}$$

For an ideal gas

$$W = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$$

Reversible and Irreversible Adiabatic Processes



Reversible and Irreversible Adiabatic Processes

If the two states are linked by an **adiabatic reversible** and **irreversible path** then

$$W_{irrev} = \Delta U_{irrev}$$

$$W_{rev} = \Delta U_{rev}$$

Contradictions

As U is a state function;

$\Delta U_{rev} = \Delta U_{irrev}$

$W_{rev} = W_{irrev}$

Which is a contradiction as **W** is a path function

If we assume $W_{rev} \neq W_{irrev}$

It implies that $\Delta U_{rev} \neq \Delta U_{irrev}$

Which again is a contradiction as **U** is a **state function**

Conclusions

Two states **A** and **B** can never lie both on a reversible as well as irreversible adiabatic path

Graphical Comparison of Different Thermodynamic Processes

For a reversible isothermal process,

$$PV = \text{Constant}$$

On differentiating,

$$PdV + VdP = 0$$

$$\frac{dP}{dV} \Rightarrow -\frac{P}{V}$$

Graphical Comparison of Different Thermodynamic Processes

For an reversible adiabatic process,

$$PV^{\gamma} = \text{Constant}$$

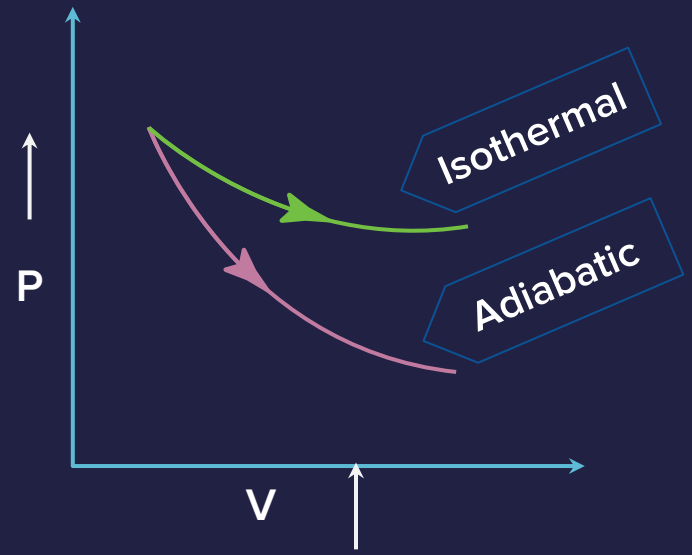
On differentiating,

$$P\gamma V^{\gamma-1}\,dV + V^{\gamma}\,dP = 0$$

$$\frac{dP}{dV} \Rightarrow -\gamma\frac{P}{V}$$

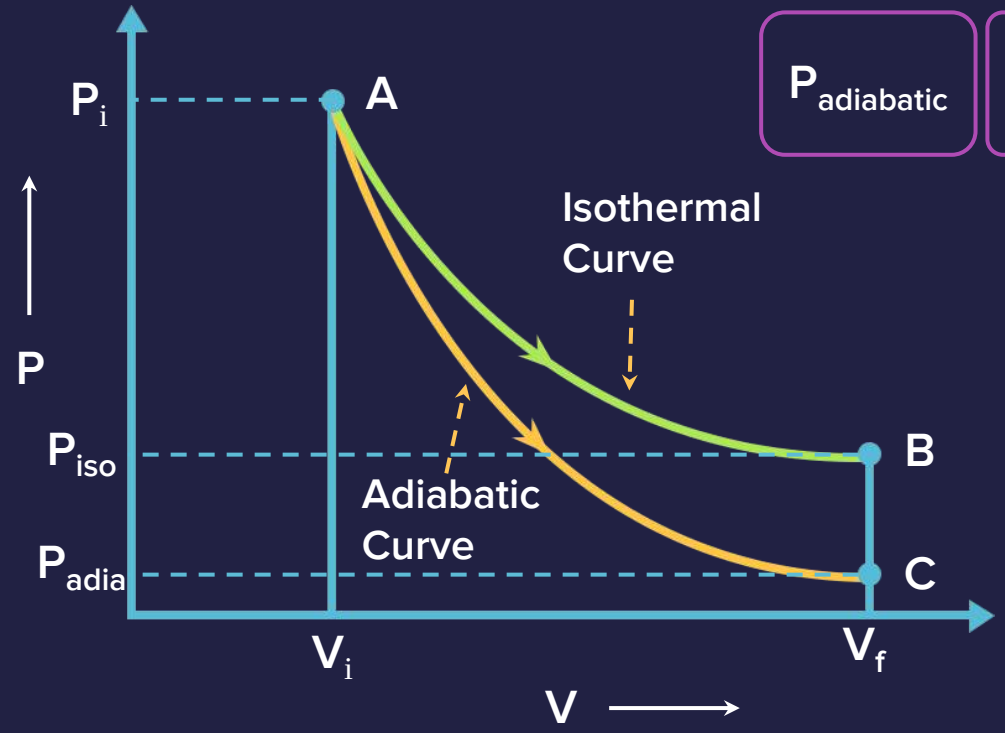
For an ideal gas ----> $\gamma > 1$

Graphical Comparison of Different Thermodynamic Processes



Slope of **P-V curve is more negative** in case of an **adiabatic process**

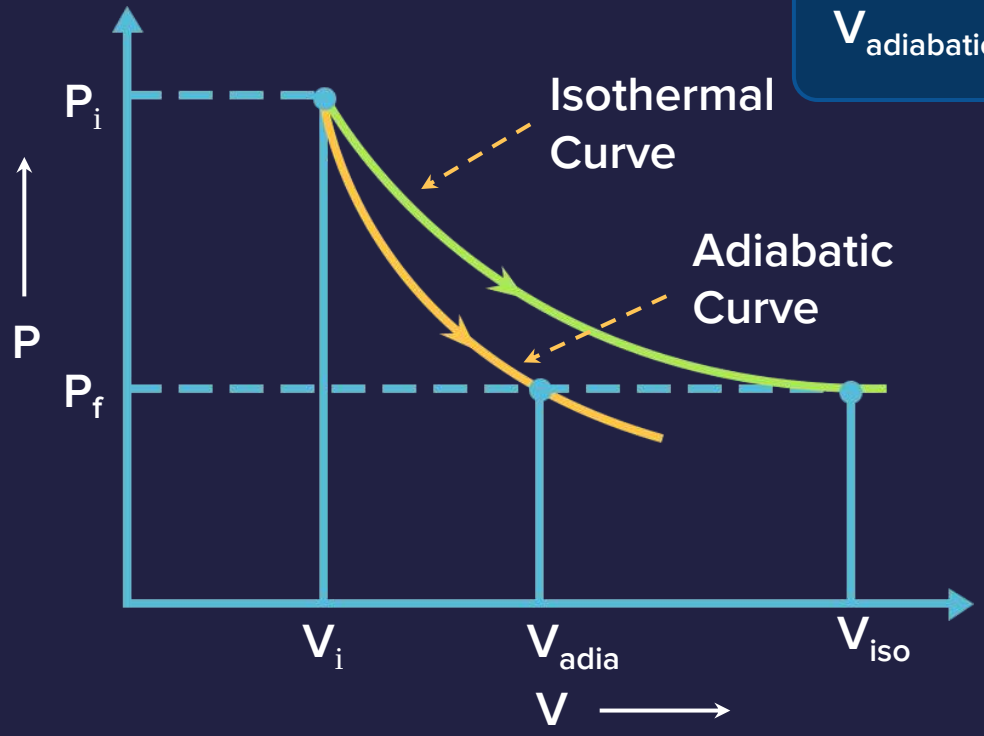
Expanded Till the Same Final Volume



$P_{adiabatic} < P_{isothermal}$

Expanded Till the Same Final Pressure

$V_{adiabatic} < V_{isothermal}$



Most chemical reactions are carried out at **constant atmospheric pressure** & not at constant volume

Need to define **another state function** suitable under these conditions

Mathematical Expression

$$q_p = U_2 + PV_2 - U_1 + PV_1$$

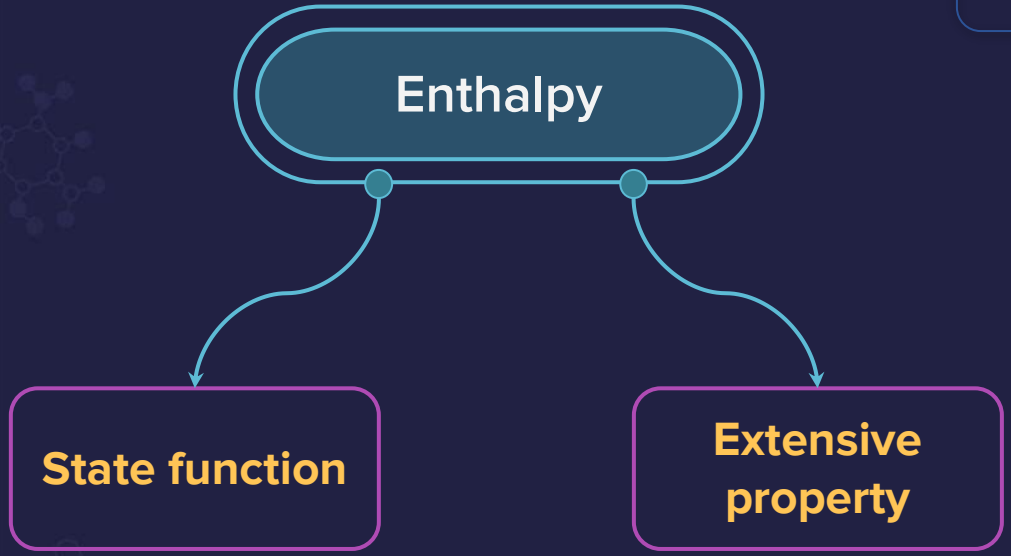
Defining, $H = U + PV$

$$q_p = H_2 - H_1 = \Delta H$$

Enthalpy (H)

Sum of **Internal energy** and **PV energy** of a system under a given set of conditions

Important Features of Enthalpy



$$H = U + PV$$

H	Enthalpy of the system
U	Internal energy of the system
P	Pressure of the system
V	Volume of the system

Enthalpy Change (ΔH)

Measure of heat change (evolved or absorbed) taking place during a process at **constant P**

ΔH = +ve — **Endothermic Process**

Exothermic Process — **ΔH = -ve**

Enthalpy Change (ΔH)

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = \Delta U + P_f V_f - P_i V_i$$

At constant pressure,

For solids & liquids	For gases
$\Delta V \simeq 0$	ΔV is significant
$P\Delta V$ is insignificant	$P\Delta V$ is significant
$\Delta H \simeq \Delta U$	$\Delta H \neq \Delta U$

Relationship Between ΔH & ΔU

At constant P

$$\Delta H = \Delta U + P\Delta V$$

For ideal gas

$$P\Delta V = \Delta n_g RT$$

At constant T

Relationship Between ΔH & ΔU

Δn_g = $\Sigma n_{g\ (products)}$ - $\Sigma n_{g\ (reactants)}$

Δn_g Change in the number of gaseous moles

Example: $N_2\ (g) + 3H_2\ (g) \longrightarrow 2NH_3\ (g)$

$\Delta n_g = 2 - (1 + 3) = -2$

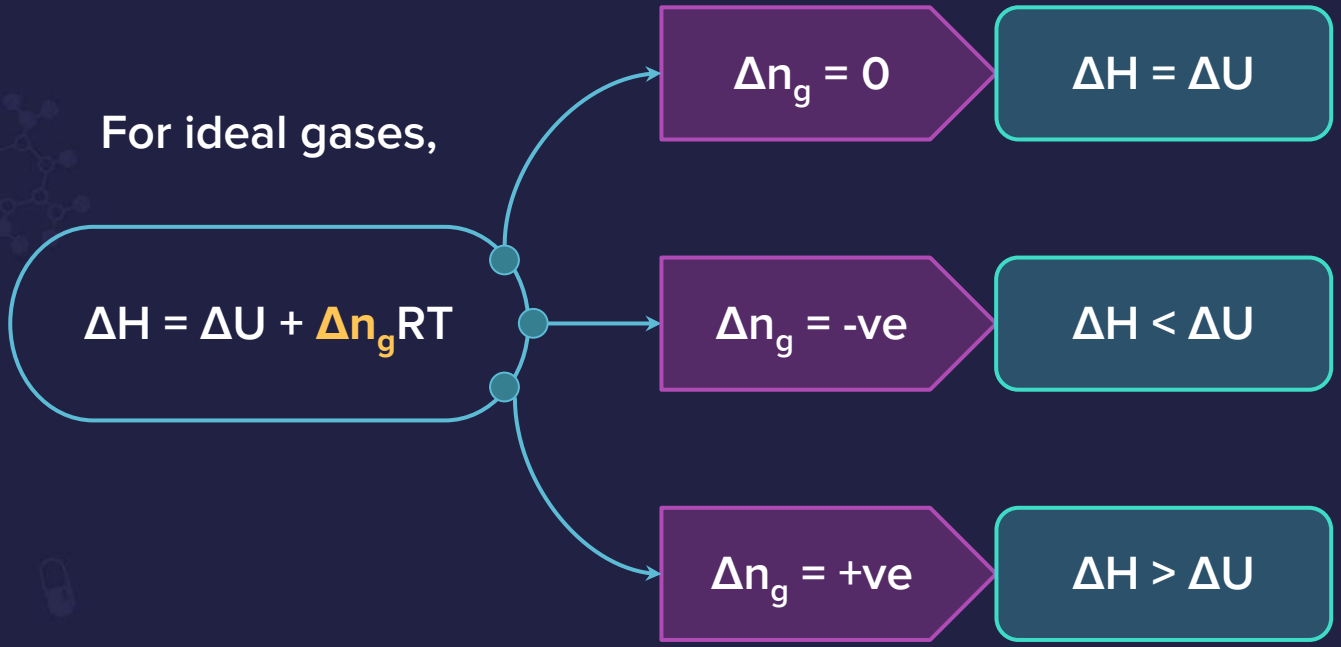
Relationship Between ΔH & ΔU

$$\Delta H = \Delta U + \Delta n_g RT$$

ΔH	Heat change at constant P
ΔU	Heat change at constant V

Moral of the Equation

For ideal gases,



Relation Between ΔH and $C_{p,m}$

$$\Delta H = \Delta U + \Delta(PV)$$

Since $PV = nRT$

$$\Delta H = nC_{v,m}(T_2 - T_1) + nR(T_2 - T_1)$$

$$\Delta H = n(C_{v,m} + R)(T_2 - T_1)$$

$$\Delta H = nC_{p,m}(T_2 - T_1)$$

dU & dH can be Related to the Degrees of Freedom!

For an **ideal gas** undergoing a process,

$$dU = nC_{v,m}dT = \frac{f}{2}nRdT$$

$$dH = nC_{p,m}dT = \left(\frac{f}{2}+1\right)nRdT$$

dU & dH can be Related to the Degrees of Freedom!

For **solid & liquid** systems

$$dU = nC_{v,m}dT \neq \frac{f}{2}nRdT$$

$$dH = nC_{p,m}dT \neq \left(\frac{f}{2}+1\right)nRdT$$

Melting of Ice/Freezing of Water

During these processes the **temperature doesn't change**, but **U does change**

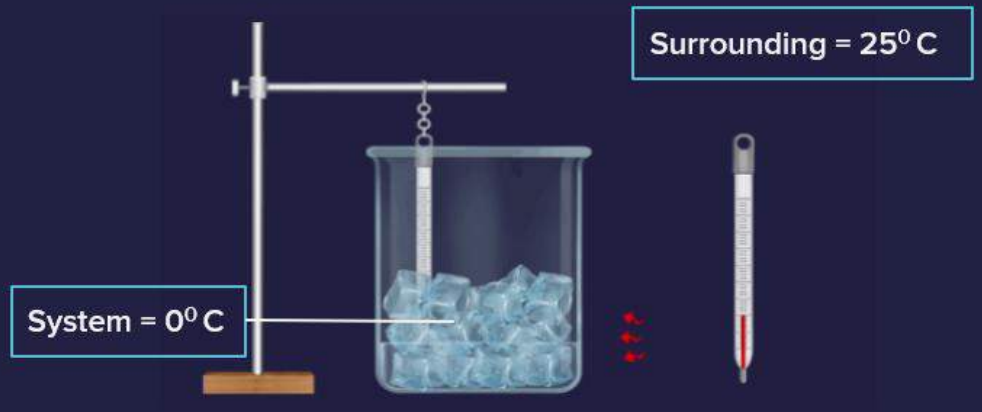
Remains the same

- **K.E.** of the molecule
- **P.E.** of the molecule

Changes

Melting of Ice/Freezing of Water

P.E. change because of the interparticle interactions



Limitations of the 1st Law

No information about the **extent of the reaction** under given conditions

Unable to predict the **direction or the spontaneity** of a process

Spontaneous Process

Spontaneous Process: A process which has the natural tendency to **occur either on its own or after proper initiation** under a given set of conditions

Non-Spontaneous Process: Process that **cannot occur on its own** rather they continue till they receive **outside assistance**

Can we Identify Spontaneity using ΔH?

Process is spontaneous in a given direction when

Energy ↓

ΔH < 0

Spontaneous process

Before the partition is removed

Pick a gas molecule from the left container	The molecule will be of gas A
Pick a gas molecule from the right container	The molecule will be of gas B

After the partition is removed

Pick a molecule from the container

The molecule can be of either gas A or gas B

System has become less predictable or **more disordered**

Observations

a

	ΔH	Process
Melting of ice (T > 0 °C, P = 1 bar)	+ve	Spontaneous

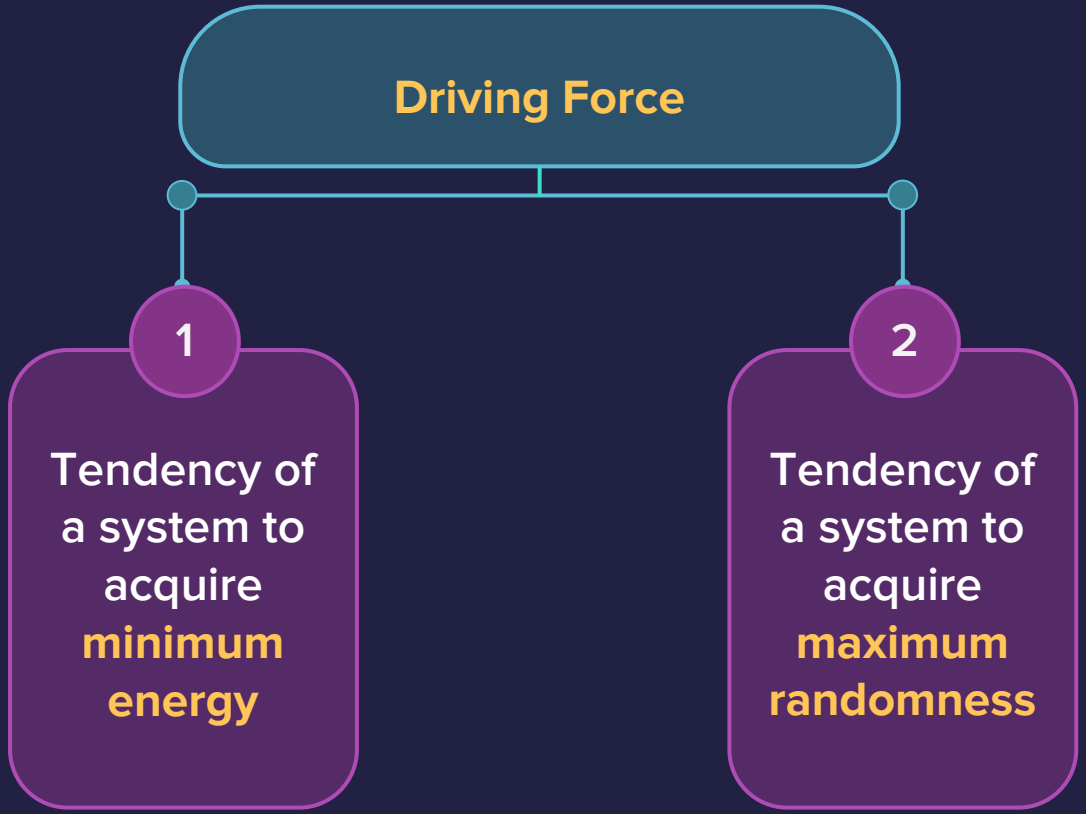
b

	ΔH	Process
Evaporation	+ve	Spontaneous

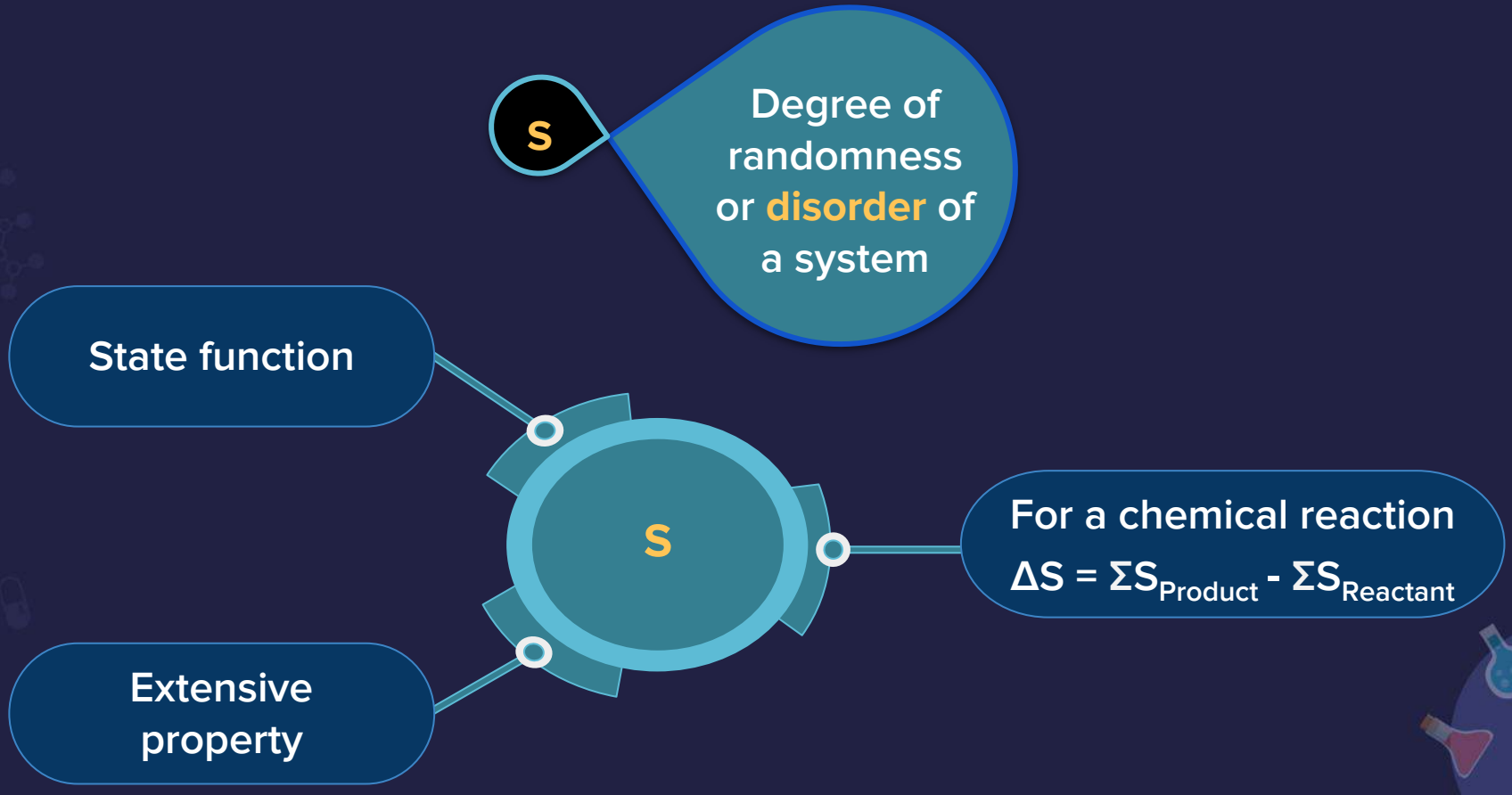
Melting	Solid ----→ Liquid	**Disorderness** ↑
Evaporation	Liquid ----→ Gas	**Disorderness** ↑

In an **isolated system**, there is always a tendency to become **more disordered**

Criteria for **spontaneous change**


Driving Force
1
Tendency of a system to acquire minimum energy
2
Tendency of a system to acquire maximum randomness

Properties of Entropy



Entropy Change

Regularity in structure ↓

Entropy ↑

For a given substance,

Lowest entropy

Crystalline solid state

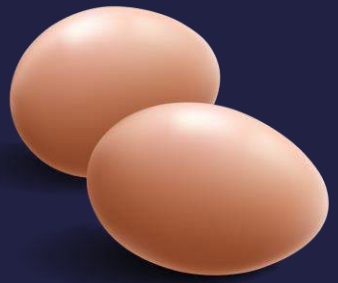
Gaseous state

Highest entropy

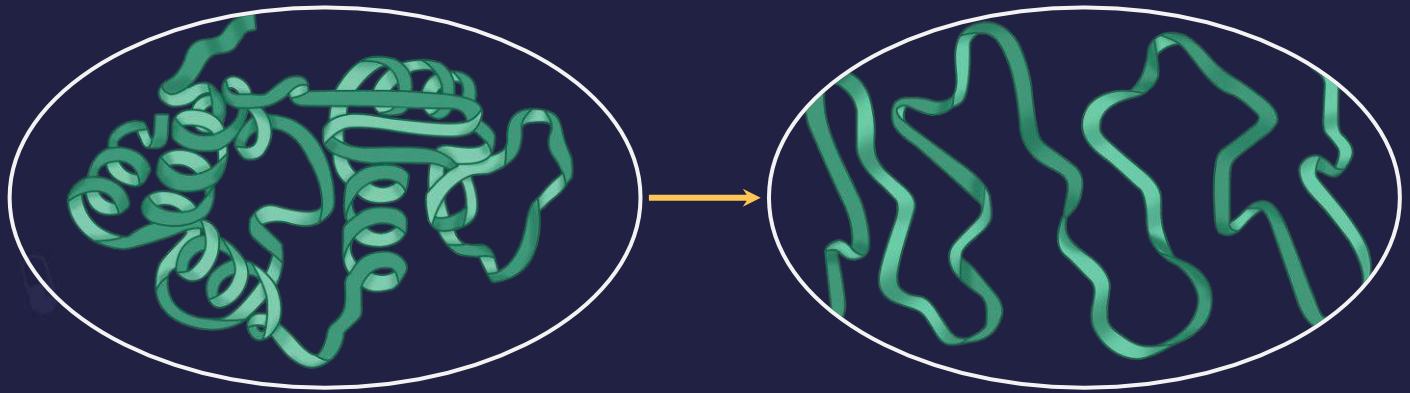
Entropy

In a physical or a chemical process as the system moves from a less random state to a more random state, **entropy increases.**

Boiling of an Egg



On boiling an egg, denaturation of protein happens, so entropy increases.



Entropy Change

Heat is added to the system

Molecular **motions** ↑

Randomness ↑

$dS_{sys} \propto q_{rev,\ sys}$

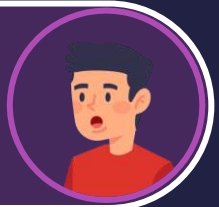
Entropy Change

Temperature ↑

Randomness ↑

But $dS_{sys} \propto \frac{1}{T}$ (For same $q_{rev, sys}$)

Confused???



Entropy Change

$dS_{sys} \propto q_{rev,\,sys}$

$dS_{sys} \propto \frac{1}{T}$

At higher T, entropy is already high

Heat addition will not change the entropy much

$dS = \frac{dq_{rev}}{T}$

$\int dS = \int \frac{dq_{rev}}{T}$

$\Delta S = \frac{q_{rev}}{T}$

SI unit = $J\ K^{-1}$

ΔS_{system}

Since **S** is a **state function,**

$$\Delta S_{reversible} = \Delta S_{irreversible}$$

$$\Delta S_{irreversible} = \int_{A}^{B} \frac{q_{rev}}{T}$$

Entropy Change for an Ideal Gas

$$dS_{sys} = \frac{dq_{rev}}{T}$$

$$TdS_{sys} = dq_{rev}$$

$dU = dq + dW$

$$TdS_{sys} = dU - dW$$

$$TdS_{sys} = nC_{V,m}dT + P_{gas}dV$$

$P_{gas} = P_{ext}$

Entropy Change for an Ideal Gas

$$TdS_{sys} = nC_{V,m}dT + \frac{nRT}{V}dV$$

$$dS_{sys} = \frac{nC_{V,m}dT}{T} + \frac{nR}{V}dV$$

On **integrating the above equation,**

$$\int_{S_1}^{S_2} dS_{sys} = \int_{T_1}^{T_2} \frac{nC_{V,m}dT}{T} + \int_{V_1}^{V_2} \frac{nR}{V}dV$$

Entropy Change for an Ideal Gas

$$\Delta S_{sys} = nC_{V,m} \ln\frac{T_2}{T_1} + nR \ln\frac{V_2}{V_1}$$

Derived for a **reversible process** but it is also valid for **irreversible processes as S is a state function.**

Entropy Change for an Ideal Gas

Since,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{V_2}{V_1} = \frac{P_1T_2}{P_2T_1}$$

$$\Delta S_{sys} = nC_{V,m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} + nR \ln \frac{T_2}{T_1}$$

Entropy Change for an Ideal Gas

$$\Delta S_{sys} = n\,(C_{V,m} + R)\,\ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2}$$

Since, $C_{P,m} - C_{V,m} = R$

$$\Delta S_{sys} = n\,C_{P,m}\,\ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2}$$

Calculation of ΔS_{surr}

All heat exchanges with surroundings are considered to be **reversible.**

$$\Delta S_{surr} = \int \frac{dq_{surr}}{T}$$

For surrounding, **T is constant**

$$\Delta S_{surr} = \frac{1}{T} \int dq_{surr} = \frac{q_{surr}}{T}$$

Calculation of ΔS_{surr}

According to the **Law of conservation of energy,**

$$q_{surr} = -q_{sys}$$

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

Entropy Change for Solids and Liquids

$$\Delta S_{sys} = \int_A^B \frac{dq_{rev}}{T} = \int_A^B \frac{dU - dW}{T}$$

$$\Delta S_{sys} = \int_A^B \frac{nC_m dT + P_{ext}\, dV}{T}$$

For solids & liquids

$C_{p,m} \simeq C_{v,m} \simeq C_m$

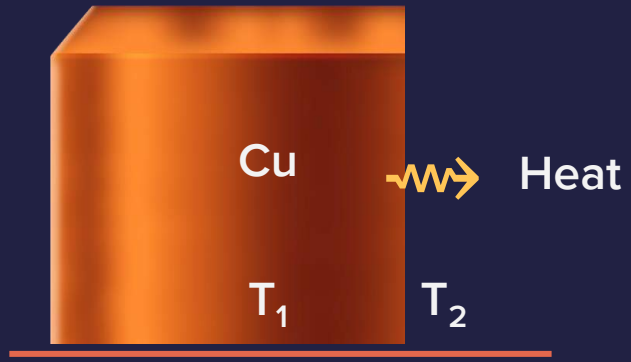
Entropy Change for Solids and Liquids

Solid & liquids are **incompressible** phases of a substance, $dV \approx 0$

$$\Delta S_{sys} = nC_m \ln \frac{T_2}{T_1}$$

Entropy Calculation for Solid Systems

A copper block kept in an open atmosphere



$$T_1 > T_2$$

Entropy Calculation for Solid Systems

$$\Delta S_{sys} = \int_{T_1}^{T_2} \frac{dq_{rev}}{T}$$

$$\Delta S_{sys} = \int_{T_1}^{T_2} \frac{msdT}{T} = ms \ln \frac{T_2}{T_1}$$

s	Specific heat of Cu

Entropy Calculation for Solid Systems

$$\Delta S_{surr} = \frac{q_{surr}}{T_2}$$

$$q_{surr} = - q_{sys} = - ms\,(T_2 - T_1)$$

$$\Delta S_{surr} = \frac{ms\,(T_1 - T_2)}{T_2}$$

Entropy Calculation for Solid Systems

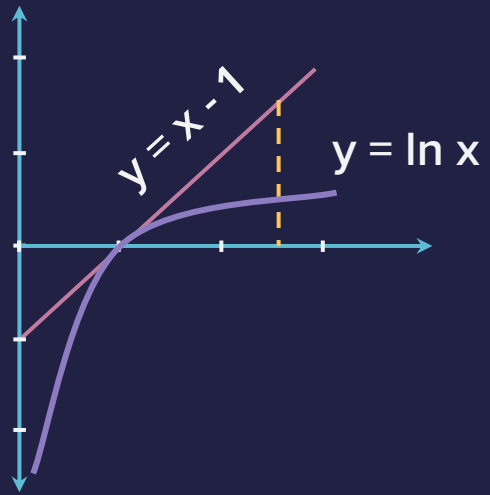
$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{univ} = ms \ln \frac{T_2}{T_1} + \frac{ms\,(T_1 - T_2)}{T_2}$$

Entropy Calculation for Solid Systems

$$\Delta S_{univ} = ms\left(\frac{T_1}{T_2} - 1\right) - ms \ln \frac{T_1}{T_2} > 0$$

$y = x - 1$ $\qquad$ $y = \ln x$



Calculation of ΔS_{univ} for an Isothermal Process

For a **Reversible process**

State A (P_1, V_1, T_1) $\xrightarrow{\Delta S_{reversible}}$ State B (P_2, V_2, T_1)

$$\Delta S_{sys} = nC_{V,m} \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}$$

For an ideal gas

As $T_i = T_f$

$$\Delta S_{sys} = nR \ln \frac{V_2}{V_1}$$

Calculation of ΔS_{univ} for an Isothermal Process

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

$$dU = dq + dW \dashrightarrow \because T_1 = T_2 \Rightarrow dU = 0$$

For system,

$$dq = -dW$$

$$q_{sys} = -W$$

Calculation of ΔS_{univ} for an Isothermal Process

$$W = -nRT \ln \frac{V_2}{V_1}$$

$$q_{sys} = nRT \ln \frac{V_2}{V_1}$$

$$\therefore \Delta S_{surr} = \frac{-nRT \ln \left[\frac{V_2}{V_1}\right]}{T}$$

$$\Delta S_{surr} = -nR \ln \frac{V_2}{V_1}$$

Calculation of ΔS_{univ} for an Isothermal Process

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{univ} = nR \ln \frac{V_2}{V_1} - nR \ln \frac{V_2}{V_1} = 0$$

Calculation of ΔS_{univ} for an Isothermal Process

For an **irreversible process**

State A (P_1, V_1, T_1) $\xrightarrow{\Delta S_{irreversible}}$ State B (P_2, V_2, T_1)

$$\Delta S_{sys} = nR \ln \frac{V_2}{V_1}$$

For an ideal gas

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

Calculation of ΔS_{univ} for an Isothermal Process

As $q_{sys} = -W$ for an isothermal process

$$q_{sys} = P_{ext}(V_2 - V_1)$$

$$\Delta S_{surr} = \frac{-P_{ext}(V_2 - V_1)}{T}$$

Calculation of ΔS_{univ} for an Isothermal Process

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{univ} = nR \ln \frac{V_2}{V_1} + \frac{-P_{ext}(V_2 - V_1)}{T}$$

$$\Delta S_{univ} = \frac{1}{T}\left(nRT \ln \frac{V_2}{V_1} - P_{ext}(V_2 - V_1)\right)$$

Calculation of ΔS_{univ} for an Isothermal Process

For Isothermal compression

$$\Delta S_{univ} = \frac{1}{T}\left[- P_{ext}(V_2 - V_1) - \left[- nRT \ln \frac{V_2}{V_1} \right] \right] > 0$$

W_{irrev} W_{rev}

Calculation of ΔS_{univ} for an Isothermal Process

For Isothermal expansion

$$\Delta S_{univ} = \frac{1}{T}\left(nRT \ln \frac{V_2}{V_1} - P_{ext}(V_2 - V_1)\right) > 0$$

$|W_{rev}|$ $|W_{irrev}|$

Calculation of ΔS_{univ} for an Adiabatic Process

$$\Delta S_{sys} = nC_{V,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

Entropy Change in a Reversible Adiabatic Process

For a **reversible adiabatic process**

$$TV^{(\gamma - 1)} = \text{Constant}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{(\gamma - 1)}$$

$$\Delta S_{sys} = nC_{v,m} \ln \left(\frac{V_1}{V_2}\right)^{(\gamma - 1)} + nR \ln \frac{V_2}{V_1}$$

Entropy Change in a Reversible Adiabatic Process

We know that, $(\gamma - 1) = \frac{C_{P.m}}{C_{v.m}} - 1$

$C_{v.m}(\gamma - 1) = R$ For an ideal gas

$$\Delta S_{sys} = nR \ln \left[\frac{V_1}{V_2}\right] + nR \ln \left[\frac{V_2}{V_1}\right]$$

Entropy Change in a Reversible Adiabatic Process

$$\Delta S_{sys} = 0$$

Since, $q_{sys} = 0$,

$$\Delta S_{surr} = \frac{-q_{sys}}{T} = 0$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$$

Entropy Change in a Reversible Adiabatic Process

Since for a reversible adiabatic process,

$$\Delta S_{sys} = nC_{v,m} \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i} = 0$$

$$nC_{v,m} \ln \frac{T_f}{T_i} = -nR \ln \frac{V_f}{V_i}$$

Entropy Change in an Irreversible Adiabatic Process

$$\Delta S_{sys} = nC_{V,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

Entropy Change in an Irreversible Adiabatic Process

For an irreversible adiabatic **expansion: $V_2 > V_1$**

Assuming $(V_2)_{irrev} = (V_2)_{rev}$

Magnitude wise: $nC_{v,m} \ln \frac{T_2}{T_1} < nR \ln \frac{V_2}{V_1}$

$(T_2)_{irrev} > (T_2)_{rev}$

Entropy Change in an Irreversible Adiabatic Process

$$\Delta S_{sys} = nC_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} > 0$$

$$\Delta S_{surr} = 0 \qquad \Delta S_{univ} > 0$$

Entropy Change in an Irreversible Adiabatic Process

For an irreversible adiabatic **compression: $V_1 > V_2$**

Assuming $(V_2)_{irrev} = (V_2)_{rev}$

Magnitude wise: $nC_{v,m} \ln \frac{T_2}{T_1} > nR \ln \frac{V_2}{V_1}$ ← $(T_2)_{irrev} > (T_2)_{rev}$

$$\Delta S_{sys} = nC_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} > 0$$

$$\Delta S_{surr} = 0 \qquad \Delta S_{univ} > 0$$

Phase Transformation

Phase change occurs at **constant P & T** and is considered to be **reversible** if it occurs at its **transition temperature** at a given pressure.

Entropy Change for Fusion

$H_2O\ (s) \longrightarrow H_2O\ (l)$ ⇢ $\Delta_r H = \Delta_{fus} H$

At constant pressure, $q = q_P = \Delta H$

$$\Delta_{fus} S = \frac{q_{rev}}{T} = \frac{\Delta_{fus} H}{T_m}$$

T_m: Melting point (K) of a substance

Entropy Change for Vaporization

$H_2O\ (l) \longrightarrow H_2O\ (g)$ --- $\Delta_r H = \Delta_{vap} H$

At constant pressure, $q = q_P = \Delta H$

$$\Delta_{vap} S = \frac{q_{rev}}{T} = \frac{\Delta_{vap} H}{T_b}$$

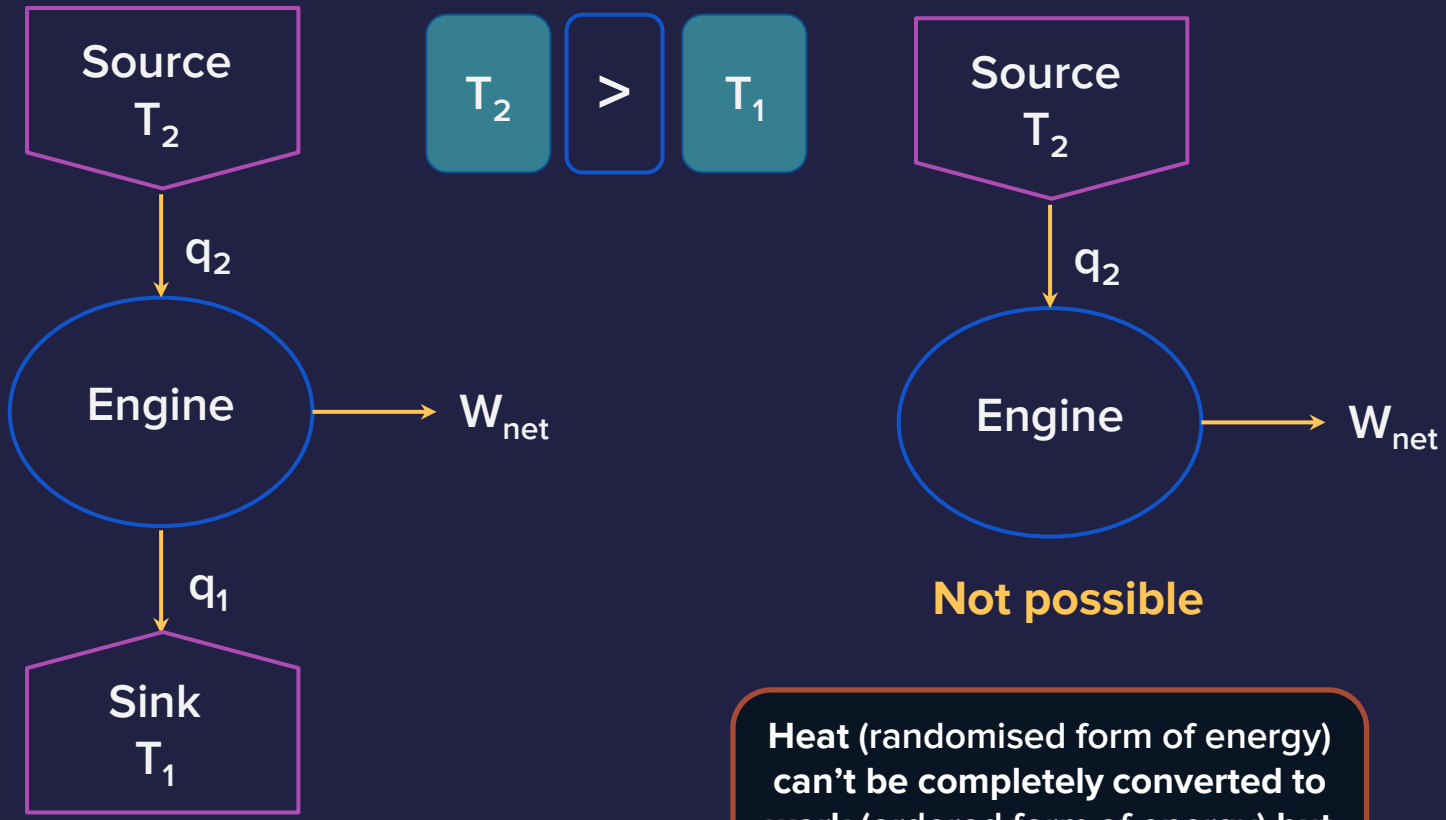
T_b: Boiling point (in K) of a substance


Second Law of Thermodynamics

Second Law of Thermodynamics

Kelvin - Planck Statement

It is **impossible** for a system to undergo a **cyclic process** whose sole effects are the **flow of heat into the system** from a heat reservoir and the performance of an equivalent **amount of work by the system** on the surroundings.


Source
T_2
q_2
Engine
W_{net}
q_1
Sink
T_1
Feasible arrangement
T_2 > T_1
Source
T_2
q_2
Engine
W_{net}
Not possible
Heat (randomised form of energy) can't be completely converted to work (ordered form of energy) but reverse is possible.

Second Law of Thermodynamics

Whenever a **spontaneous process** takes place in the universe, the total **entropy** of the universe **increases.**

Second Law of Thermodynamics

For a **spontaneous process,**

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$$

ΔS_{univ}	Entropy change of the universe
ΔS_{sys}	Entropy change of the system
ΔS_{surr}	Entropy change of the surrounding

Entropy Change

Reversible process

$$\Delta S_{univ} = 0$$

$$\Rightarrow \quad \Delta S_{sys} = -\Delta S_{surr}$$

Irreversible process

$$\Delta S_{univ} > 0$$

Entropy Change

Entropy of an isolated system is a **maximum** when the system is in **equilibrium**

$$\Delta S = 0$$

Gibbs Free Energy (G)

A **system parameter** to predict the **spontaneity** of a chemical reaction

kJ/mol or J/mol

State function

G

Extensive property

For a spontaneous process, $\Delta S_{universe} > 0$. $\Delta S_{universe}$ includes $\Delta S_{surrounding}$. To avoid calculation of surrounding, we define a new state function which can tell about spontaneity

Spontaneous Process

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$$

If system is in **thermal equilibrium** with the surrounding

$$T_{sys} = T_{surr} = T$$

$$\Delta H_{surr} = - \Delta H_{sys}$$

Spontaneous Process

$$\Delta S_{surr} = \frac{q_{surr}}{T} = \frac{\Delta H_{surr}}{T} = -\frac{\Delta H_{sys}}{T}$$

At constant P

$$\Delta S_{univ} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T}$$

$$T\Delta S_{univ} = T\Delta S_{sys} - \Delta H_{sys}$$

Spontaneous Process

For spontaneous process

$$\Delta S_{univ} > 0$$

$$T\Delta S_{sys} - \Delta H_{sys} > 0$$

$$\Rightarrow -(\Delta H_{sys} - T\Delta S_{sys}) > 0$$

$$\Rightarrow \Delta H_{sys} - T\Delta S_{sys} < 0$$

Gibbs Free Energy

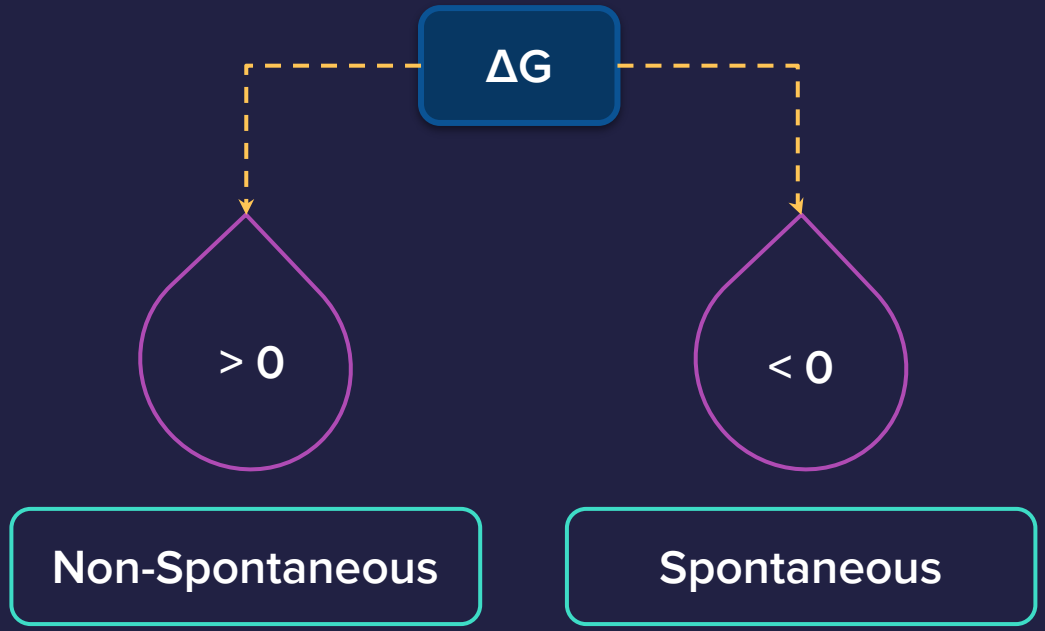
Defining $G = H - TS$

At **constant T**, the change in Gibbs free energy between two states will be,

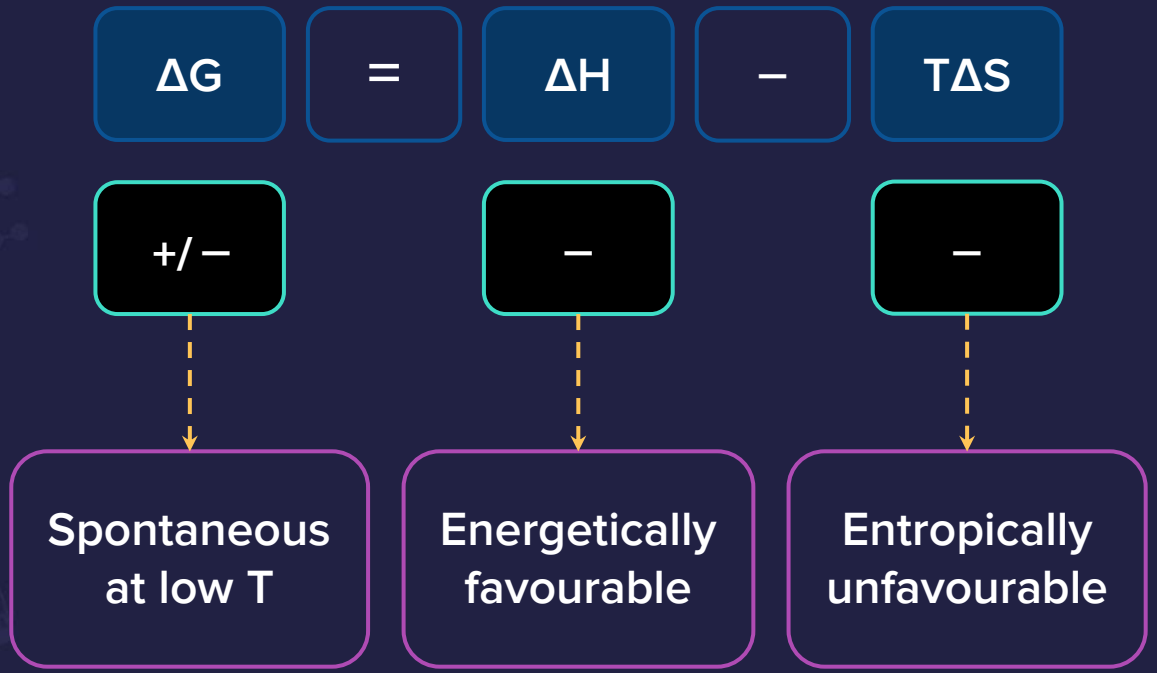
$$\Delta G = \Delta H - T\Delta S$$

Spontaneity of a Process

For a process taking place at constant T & P

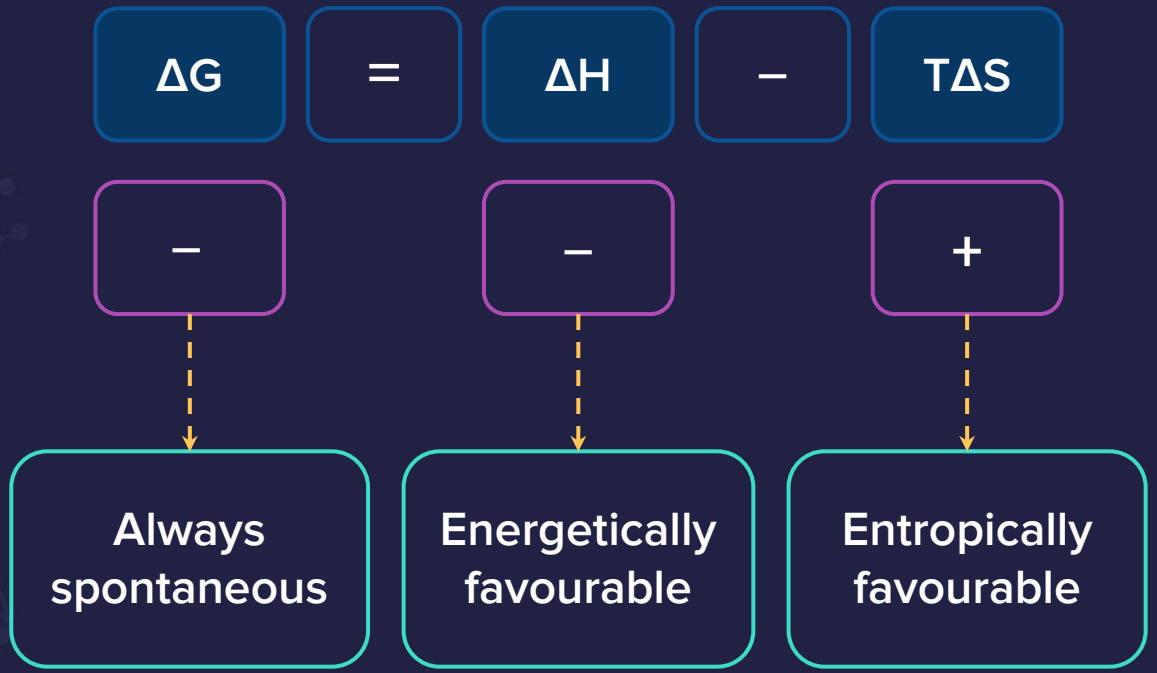


Spontaneity of a Process



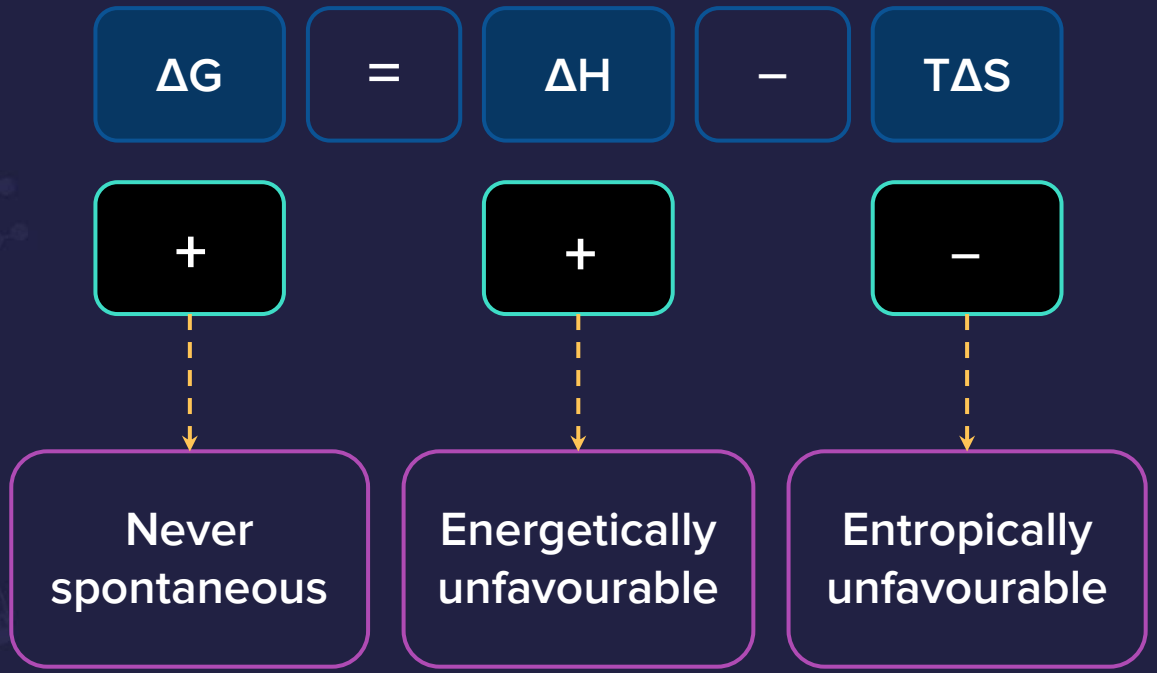
In this case, ΔG will be negative only when |ΔH| > |TΔS|.
If a reaction is favourable for enthalpy (i.e., enthalpy decreases) and unfavourable for entropy (i.e., entropy decreases), the reaction will be spontaneous only at lower temperatures (becomes less spontaneous as the temperature increases).

Spontaneity of a Process



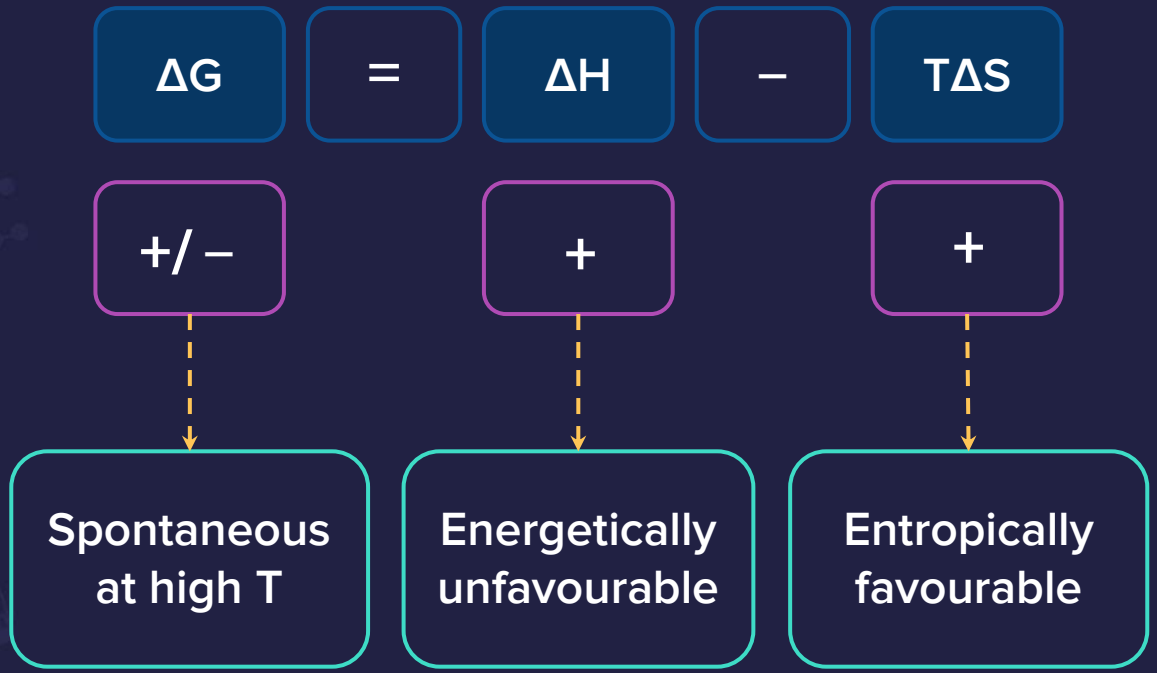
In this case, ΔG will be negative always (Subtracting a positive value from a negative value will always result in a negative value).
If a reaction is favourable for enthalpy (i.e., enthalpy decreases) and favourable for entropy (i.e., entropy increases), the reaction will always be spontaneous.

Spontaneity of a Process



In this case, ΔG will be positive always (Subtracting a negative value from a positive value will always result in a +ve value).
If a reaction is unfavourable for enthalpy (i.e., enthalpy increases) and unfavourable for entropy (i.e., entropy decreases), the reaction will always be non - spontaneous.

Spontaneity of a Process



In this case, ΔG will be negative only when |ΔH| < |TΔS|.
If a reaction is unfavourable for enthalpy (i.e., enthalpy increases) and favourable for entropy (i.e., entropy increases), the reaction will be spontaneous only at higher temperatures (Becomes less spontaneous as the temperature decreases).

Gibbs Free Energy

$$G = H - TS$$

$$dG = dH - d(TS)$$

Since, $dH = dU + d(PV)$

$$dU = dq + dW$$

Gibbs Free Energy

$$dG = dq + dW + PdV + VdP - TdS + SdT$$

$$dG = dq + dW_{PV} + dW_{non\text{-}PV} + PdV + VdP - TdS + SdT$$

$$dW_{PV} = -PdV$$

$$dq = TdS$$

$$dG = VdP - SdT + dW_{non\text{-}PV}$$

Case - I

If $dW_{non\text{-}PV} = 0$

At constant T: $dG = VdP$

For an ideal gas: $V = \frac{nRT}{P}$

$$dG = \frac{nRT}{P} dP$$

Case - I

$$dG = \frac{nRT}{P} dP$$

$$\int dG = \int \frac{nRT}{P} dP$$

$$\Delta G = nRT \ln \left(\frac{P_f}{P_i} \right)$$

Case - II

If $dW_{non\text{-}PV} = 0$

At constant T: $dG = VdP$

For solids & iquids: $\int_{G_i}^{G_f} dG = \int_{P_i}^{P_f} VdP$

$\Delta G = V(P_f - P_i)$

Case - III

If $dW_{non\text{-}PV} = 0$

At constant P

$dG = -SdT$

$$S = \left(-\frac{dG}{dT}\right)_P$$

Case - IV

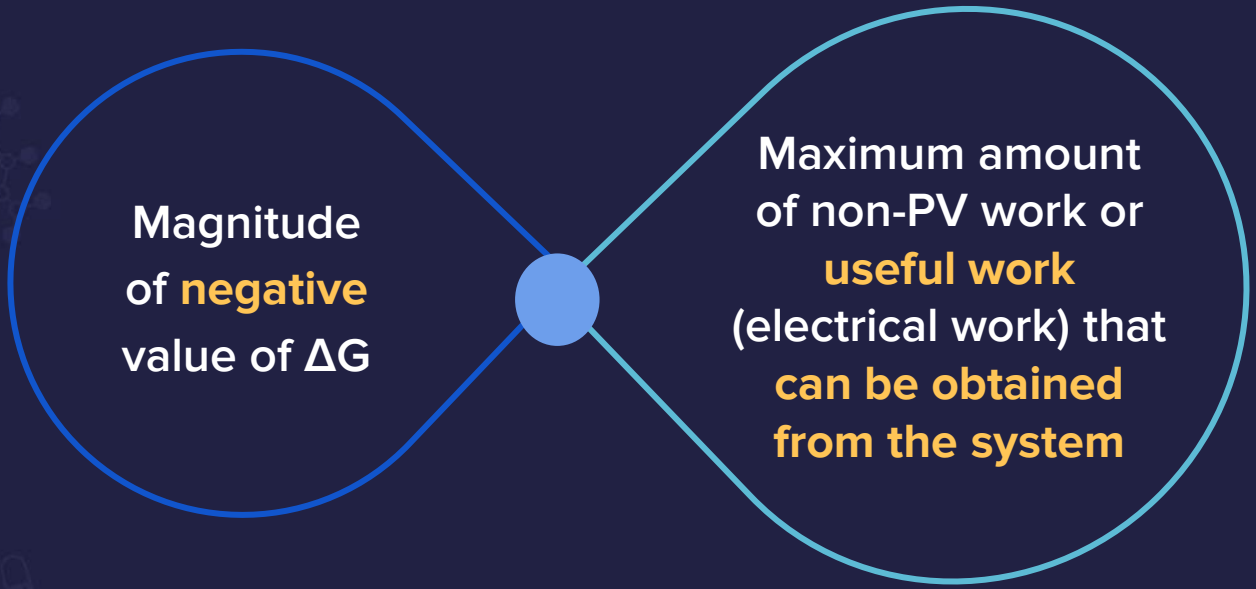
At constant T & P

$$dG = dW_{non\text{-}PV}$$

$$\int dG = \int dW_{non\text{-}PV}$$

$$\Delta G = W_{non\text{-}PV}$$

Physical Interpretation of ΔG



Physical Interpretation of ΔG

Third Law of Thermodynamics

Entropy of **perfect crystals** of all **pure** elements & compounds is **zero at 0 K**

$$\Delta S = S_{T\,(K)} - S_{0\,(K)}$$

Absolute Entropy of a Pure Substance

Absolute value of entropy unlike the absolute value of **enthalpy for any pure substance** can be calculated at **any given temperature**

Absolute Entropy of a Pure Substance

$$\Delta S = S_{T\,(K)} - S_{0\,(K)} = \int_0^T \frac{nC_m dT}{T}$$

$$S_{T\,(K)} = S_{0\,(K)} + \int_0^T \frac{nC_m dT}{T}$$

If phase changes between 0 K & T K:
Entropy of phase change will also add

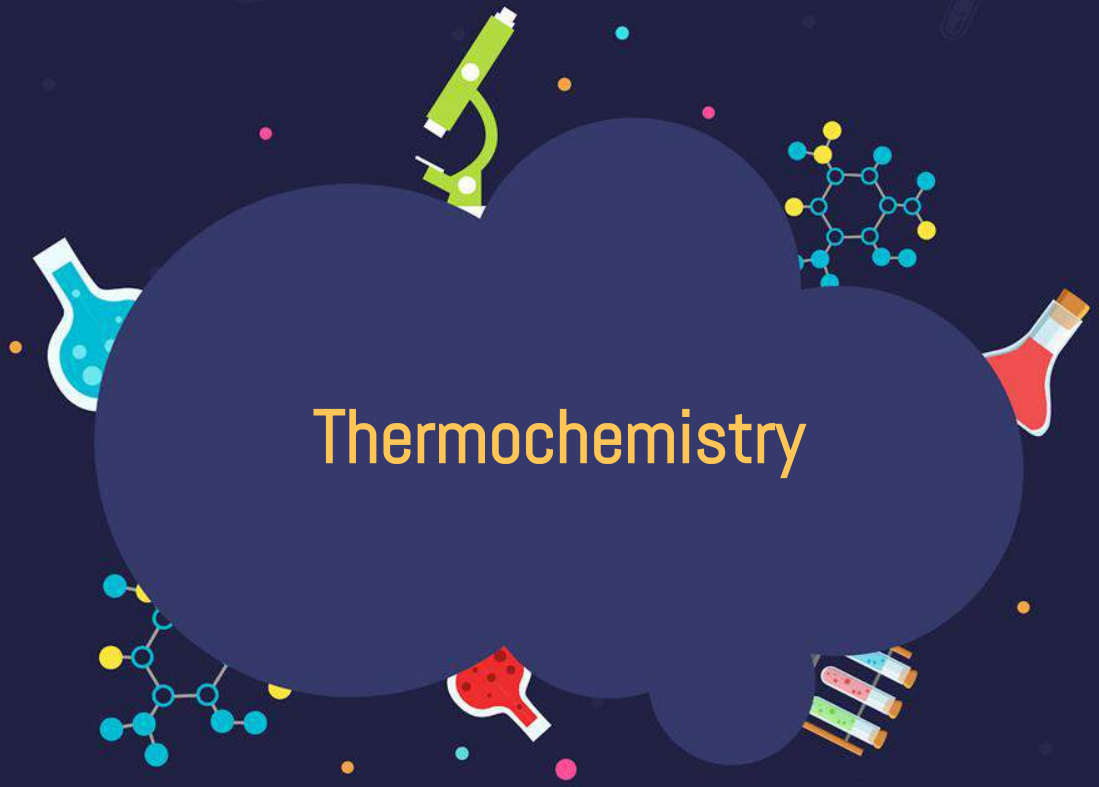
Standard Entropy Changes in Chemical Reactions

$$aA\,(g) + bB\,(g) \longrightarrow cC\,(g) + dD\,(g)$$

$$\Delta_r S^\circ = \Sigma\, S^\circ\,(\text{Products}) - \Sigma\, S^\circ\,(\text{Reactants})$$

$$\Delta_r S^\circ = cS^\circ_{m,C} + dS^\circ_{m,D} - aS^\circ_{m,A} + bS^\circ_{m,B}$$

S°_m Standard molar entropy


Thermochemistry

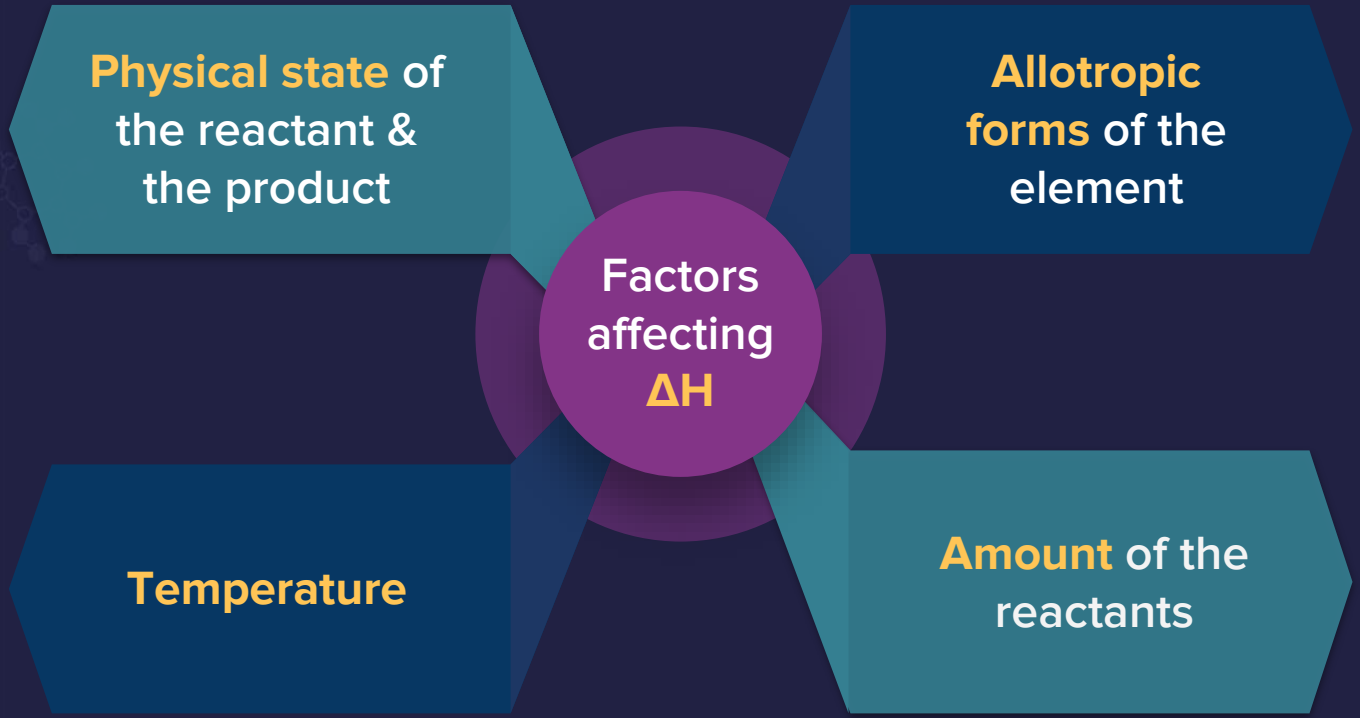
Need for Thermochemistry

Provides a **theoretical approach** for **calculating** the **Heat change** in a reaction

Performing an **experiment** for calculating the heat change for every reaction can be avoided

Study of the **energy transferred as heat** during the course of a chemical reaction or a physical change

Factors Affecting Enthalpy Change



Enthalpy of Reaction ($\Delta_r H$)

Enthalpy change when the amounts of reactants consumed & products formed will be equal to **corresponding stoichiometric numbers expressed in mole.**

Enthalpy of Reaction ($\Delta_r H$)

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ $\quad \Delta_r H = -890\ kJ/mol$

'Per mole' in $\Delta_r H$ means 'per mole $CH_4(g)$', 'per 2 mole $O_2(g)$', 'per mol $CO_2(g)$', or 'per 2 mol $H_2O(l)$'

Enthalpy of reaction refers to the entire chemical equation and **not to any particular reactant or product.**

Enthalpy of Reaction

$$\Delta_r H = \Sigma a_i H_{m,P} - \Sigma b_i H_{m,R}$$

a_i	Stoichiometric coefficients of the products
b_i	Stoichiometric coefficients of the reactants
H_m	Molar enthalpy

Enthalpy of Reaction

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta_r H = \Sigma a_i H_{m,P} - \Sigma b_i H_{m,R}$$

$$\Delta_r H = H_m(CO_2, g) + 2H_m(H_2O, l) - H_m(CH_4, g) + 2H_m(O_2, g)$$

Standard Enthalpy of Reaction ($\Delta_r H^o$)

Enthalpy change for a reaction when all the participating substances are in their **standard states**

Standard State

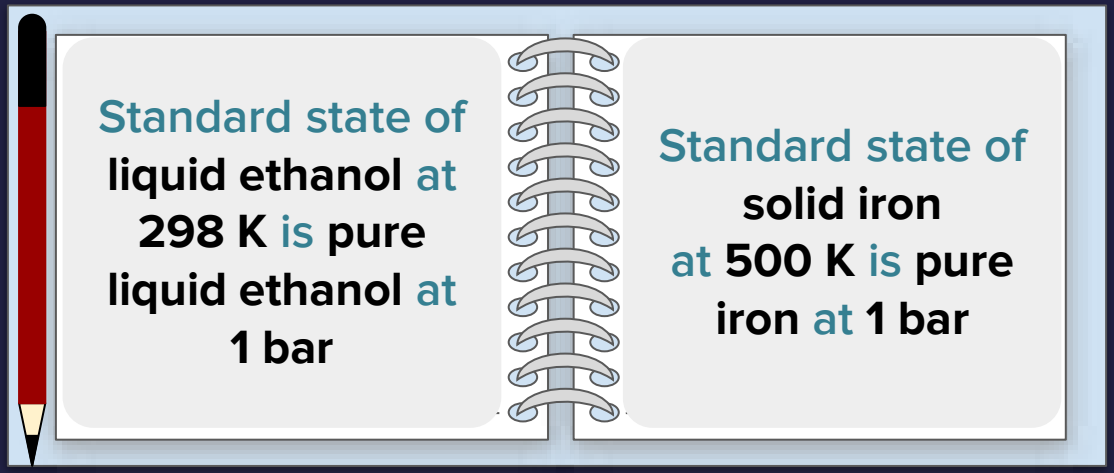
Standard state of a substance at a **specified temperature** is its **pure form** at **1 bar**

° represents standard conditions

Standard State

For Pure Crystalline Solid	Pure crystalline solid at **1 bar pressure** at a specified temperature
For Substance or Ion in Solution	Species at **1 M concentration, 1 bar pressure** at a specified temperature
For Liquids	Pure liquid at **1 bar pressure** at a specified temperature
For Gases	**Ideal gas** at **1 bar partial pressure** at a specified temperature

Standard States



Thermochemical Equation

Balanced chemical equation with the value of its **enthalpy change**.

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; $\Delta_r H = -91.8$ kJ/mol

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; $\Delta_r H = -91.8$ kJ/mol

On reversing the equation

$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$; $\Delta_r H = +91.8$ kJ/mol

Thermochemical Equation

Similarly,

On Multiplying by $\frac{1}{2}$

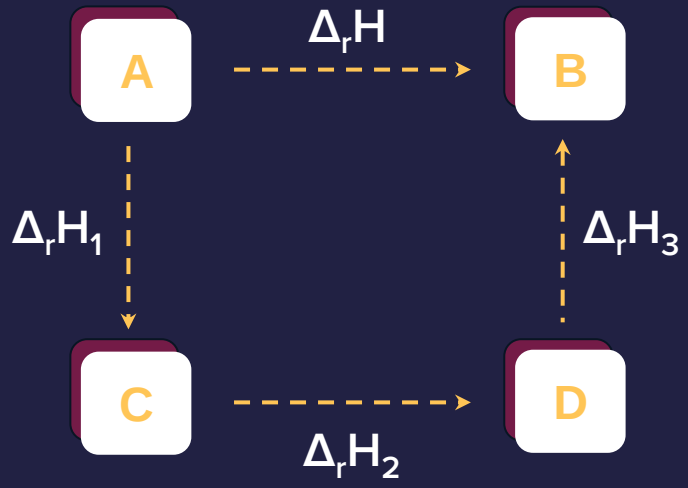
$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g);\ \Delta_rH = -45.9\ kJ/mol$$

Multiplying by 2,

$$2N_2(g) + 6H_2(g) \longrightarrow 4NH_3(g);\ \Delta_rH = -183.6\ kJ/mol$$

Hess's Law of Constant Heat Summation

Heat absorbed or evolved in a given chemical equation is the **same** whether the process occurs in **one step or several steps.**



$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3$$

Hess's Law of Constant Heat Summation

$2NaHCO_3\,(s) \longrightarrow Na_2CO_3\,(s) + CO_2\,(g) + H_2O\,(g)$ $\quad \Delta_rH^\circ = ?$

$NaHCO_3\,(s) + HCl\,(aq) \longrightarrow NaCl\,(aq) + CO_2\,(g) + H_2O\,(g) \dashrightarrow \Delta_rH^\circ_1$ ..... (i)

$Na_2CO_3\,(s) + 2HCl\,(aq) \longrightarrow 2NaCl\,(aq) + CO_2\,(g) + H_2O\,(g) \dashrightarrow \Delta_rH^\circ_2$ ..... (ii)

Hess's Law of Constant Heat Summation

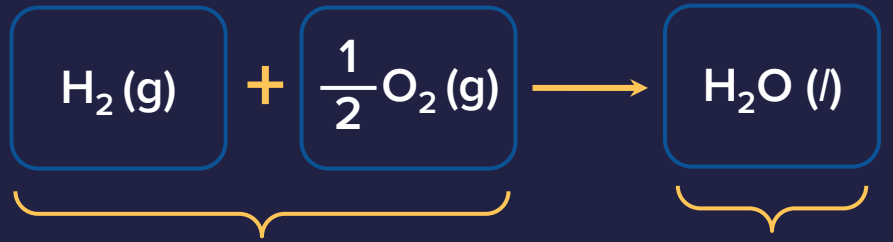
Multiplying equation (i) by 2 and
subtracting the equation (ii) from (i) we get,

$$2NaHCO_3\,(s) \longrightarrow Na_2CO_3\,(s) + CO_2\,(g) + H_2O\,(g) \dashrightarrow \Delta_rH^o$$

$$\Delta_rH^o = 2\Delta_rH^o_1 - \Delta_rH^o_2$$

Standard Enthalpy of Formation ($\Delta_f H^o$)

Enthalpy change for the formation of **one mole of a compound** from **its constituent elements in their standard states**



$\Delta_f H^o$ = - 285.8 kJ/mol

Standard Enthalpy of Formation ($\Delta_f H^o$)

$$H_2\,(g) + Br_2\,(l) \longrightarrow 2\,HBr\,(g)$$

$\Delta_r H^o$ = -72.8 kJ/mol

$\Delta_r H^o = 2\Delta_f H^o$

Species	$\Delta_f H°$
I_2 (s)	0
Br_2 (l)	0
H_2 (g)	0
H^+ (aq)	0
F_2 (g)	0
Cl_2 (g)	0

Remember!!

Standard enthalpy of formation of elements in pure state at 298 K and 1 bar is **Zero.**

I_2 (s)

Hg (/)

F_2 (g)

Standard Enthalpy of Formation

Species	$\Delta_f H°$	
O_2 (g)	=	0
O_3 (g)	>	0
S, rhombic (s)	=	0
S, monoclinic (s)	>	0
C, graphite (s)	=	0
C, diamond (s)	>	0

Generally, the value of **standard enthalpy of formation of the most stable allotrope** is zero.

Exception

Order of Stability

White P < Red P < Black P

Though white phosphorous is taken as standard but it is the most reactive form of phosphorous.

$\Delta_f H°$ (P, white) = 0

Enthalpy of Reaction from Enthalpies of Formation

$$\Delta_r H = \Sigma a_i \Delta_f H_P - \Sigma b_i \Delta_f H_R$$

a_i	Stoichiometric coefficients of the products
b_i	Stoichiometric coefficients of the reactants

Enthalpy of Combustion ($\Delta_c H$)

Enthalpy change when one mole of a **compound combines with the requisite amount of oxygen** to give products in their stable form

Enthalpy of Combustion

$C_6H_{12}O_6\,(g) + 6O_2\,(g) \longrightarrow 6CO_2\,(g) + 6H_2O\,(l)$	$\Delta_C H^o$	=	- 2802 kJ/mol
$C\,(graphite, s) + O_2\,(g) \longrightarrow CO_2\,(g)$	$\Delta_C H^o$	=	- 393.5 kJ/mol

Enthalpy of Combustion

Application of **Enthalpy of Combustion**

- Calorific value
- To determine enthalpy of reaction

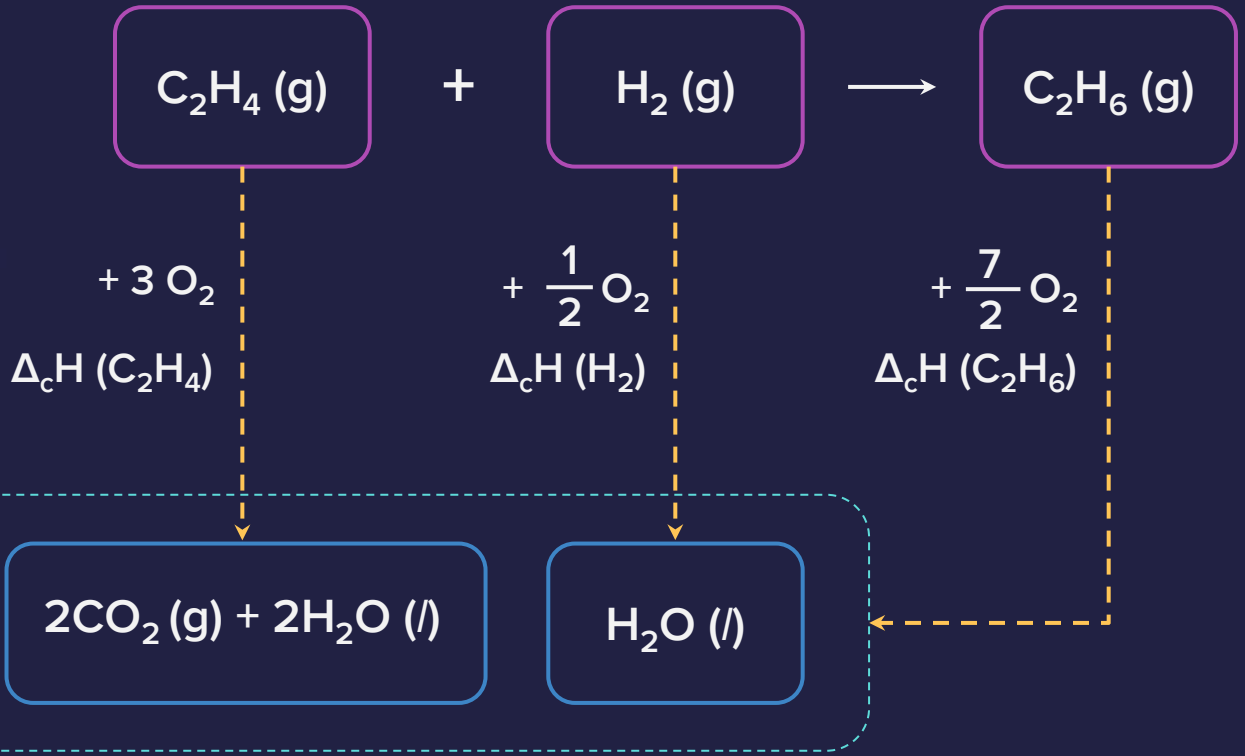
Calorific Value

Amount of **heat released** during the **complete combustion** of a **unit mass** of a substance

$$\text{Calorific Value} = \frac{\Delta_c H}{\text{Molar Mass}}$$

Units	J/g or Cal/g

Determine Enthalpy of Reaction



Determine Enthalpy of Reaction

Using Hess's law,

$\Delta_c H [C_2H_4 (g)] + \Delta_c H [H_2 (g)] = \Delta_r H + \Delta_c H [C_2H_6 (g)]$

$\Delta_r H = \Delta_c H [C_2H_4 (g)] + \Delta_c H [H_2 (g)] - \Delta_c H [C_2H_6 (g)]$

$\Delta_r H = \Sigma (\Delta_c H)_{Reactants} - \Sigma (\Delta_c H)_{Products}$

Calorimetry

Calorimetry

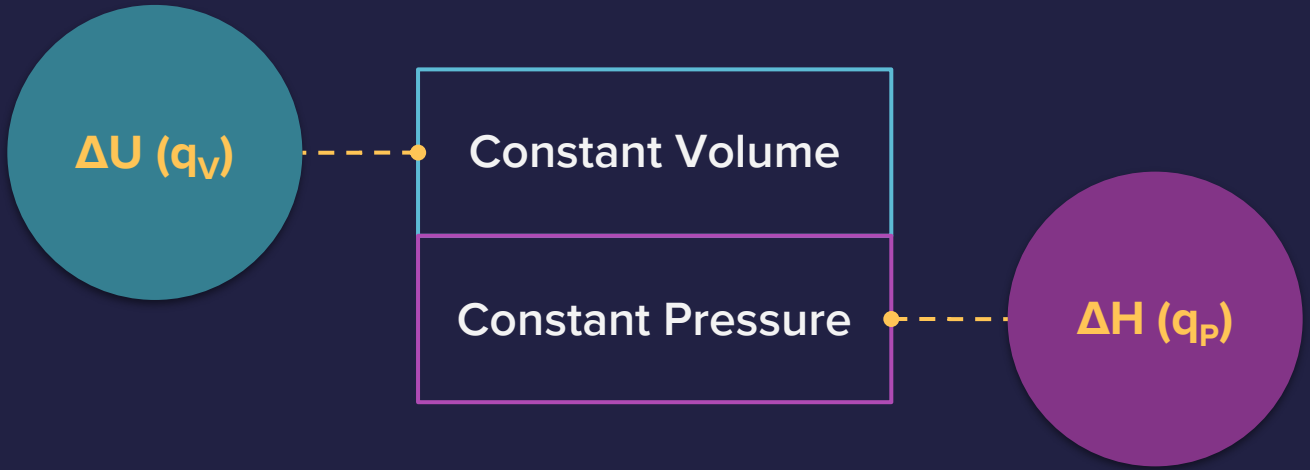
Study of **heat transfer** during physical & chemical processes

Device for measuring the **energy transferred as heat**

Calorimeter

Calorimetry

Measurements are made under **two different conditions**

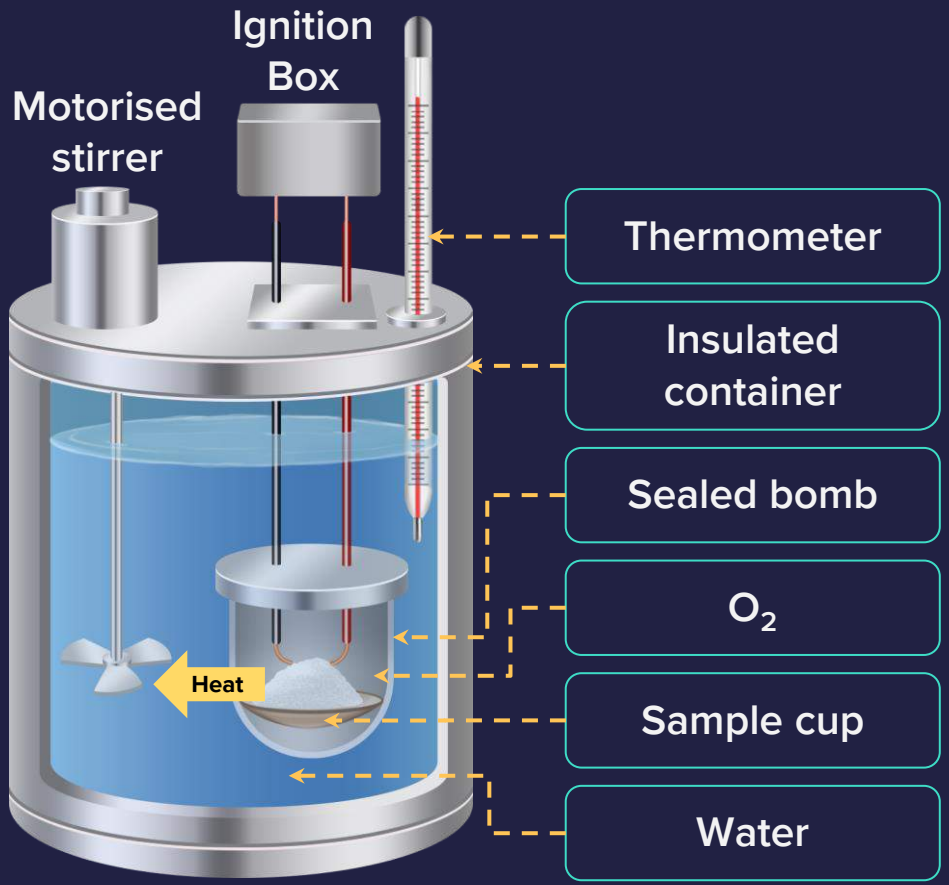


ΔU Measurements

A combustible substance is burnt in the presence of **pure O_2** in the steel bomb

Steel bomb is immersed in **water bath**

Bomb Calorimeter



Heat evolved during the reaction is **transferred to the water** around the bomb

Temperature of the water is monitored

Sample is ignited by the electric shock provided by the ignition box, heat is being radiated by the combustion of the sample and got transferred to the liquid where it gets uniformly distributed by the stirrer, consequently the thermometer shows rise in the temperature.

ΔU Measurements

$$q_v = \Delta U = m_{water}\, s_{water}\, \Delta T + C\, \Delta T$$

m	Mass
C	Heat capacity of calorimeter system
s	Specific heat
ΔT	Change in temperature

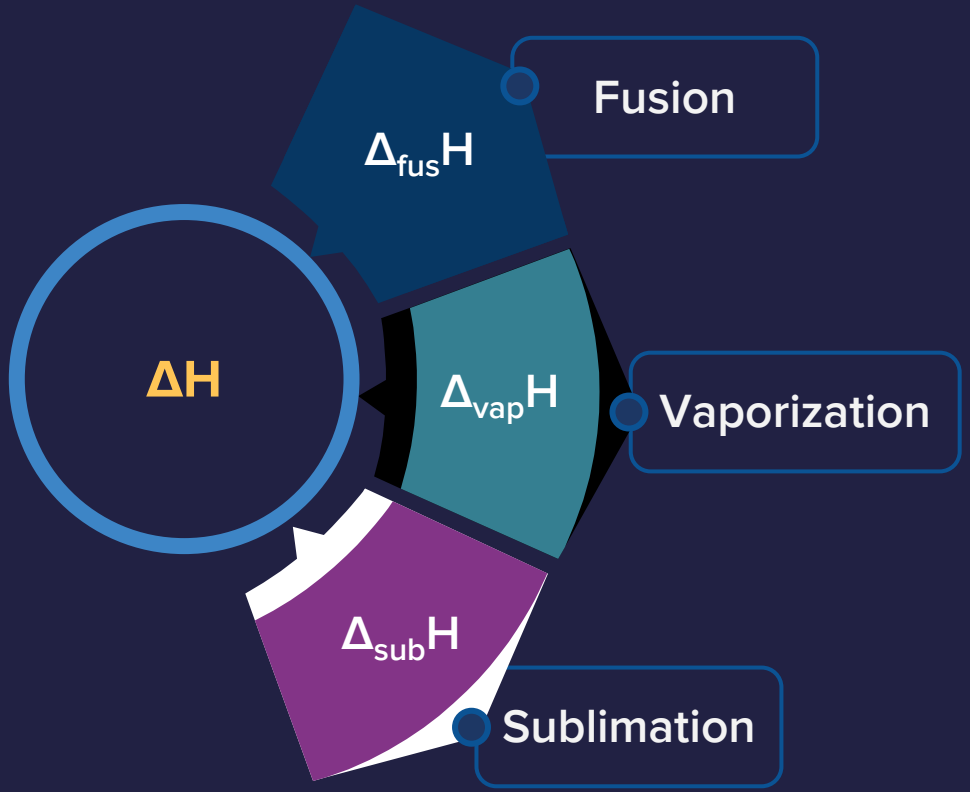
ΔU Measurements

$$q_v = \Delta U = (m_{water} + W.E.)\, s_{water}\, \Delta T$$

Water equivalent (W.E.)

Mass of water that would **absorb** the same amount of **heat** as absorbed by stirrer, thermometer, bomb etc.

Enthalpy Changes during Phase Transformations



Enthalpy of Fusion ($\Delta_{fus}H$)

Enthalpy change when **1 mole of a solid** is completely converted into **liquid state** at its **melting point**

$H_2O\ (s) \longrightarrow H_2O\ (l)$

$\Delta_{fus}H^{o} = 6$ kJ/mol

Always +ve

Endothermic

Enthalpy of Vaporization ($\Delta_{vap}H$)

Enthalpy change when **1 mole of a liquid** is completely converted into its **vapors** at its **boiling point**

$H_2O\ (l) \longrightarrow H_2O\ (g)$

$\Delta_{vap}H^o = 40.79$ kJ/mol

Always +ve

Endothermic

Enthalpy of Sublimation ($\Delta_{sub}H$)

Enthalpy change when **1 mole of a solid** is directly converted into **vapors** at **sublimation temperature**

$CO_2\ (s) \longrightarrow CO_2\ (g)$

$\Delta_{sub}H^{o} = 25.2$ kJ/mol

Enthalpy of Transition ($\Delta_{trans}H$)

Enthalpy change when **one mole of an allotropic form** changes to another allotropic form

$\Delta_{trans}H^{o}$ = 1.90 kJ/mol

C (s) **Graphite** ⟶ C (s) **Diamond**

Enthalpy of Atomization ($\Delta_a H$)

Enthalpy **change** when one mole of substance converts into gaseous atoms

$$H_2\,(g) \longrightarrow 2H\,(g)$$

Bond enthalpy

- Bond dissociation enthalpy
- Mean bond enthalpy

Bond Enthalpy for Diatomic Molecules

Bond Dissociation Enthalpy ($\Delta_{BDE}H$)

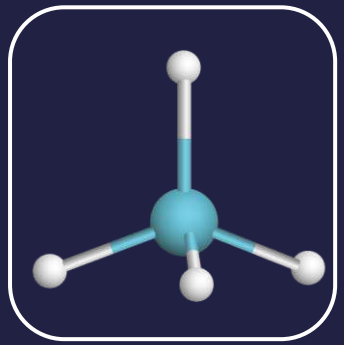
Enthalpy required to **dissociate** a given **bond** of some specific compound.

$$H_2\,(g) \longrightarrow 2H\,(g)$$

Bond Enthalpy of Polyatomic Molecules

In methane, all the four **C – H bonds** are identical in **bond length** & **energy**

But the energy required to **break** the individual **C – H bonds** in each successive step differs



Bond Enthalpy of Polyatomic Molecules

$CH_4(g) \longrightarrow CH_3(g) + H(g)$	$\Delta_{C-H}H^\circ$	=	+427 kJ/mol
$CH_3(g) \longrightarrow CH_2(g) + H(g)$	$\Delta_{C-H}H^\circ$	=	+439 kJ/mol
$CH_2(g) \longrightarrow CH(g) + H(g)$	$\Delta_{C-H}H^\circ$	=	+452 kJ/mol
$CH(g) \longrightarrow C(g) + H(g)$	$\Delta_{C-H}H^\circ$	=	+347 kJ/mol

Bond Enthalpy of Polyatomic Molecules

$$CH_4\,(g) \longrightarrow C\,(g) + 4H\,(g)$$

$\Delta_a H^\circ$	=	427 + 439 + 452 + 347	=	+1665 kJ/mol

Mean Bond Enthalpy

$\Delta_a H^\circ = +1665 \text{ kJ/mol}$

$\Delta_{C\text{-}H} H^\circ = \frac{1}{4} (\Delta_a H^\circ)$

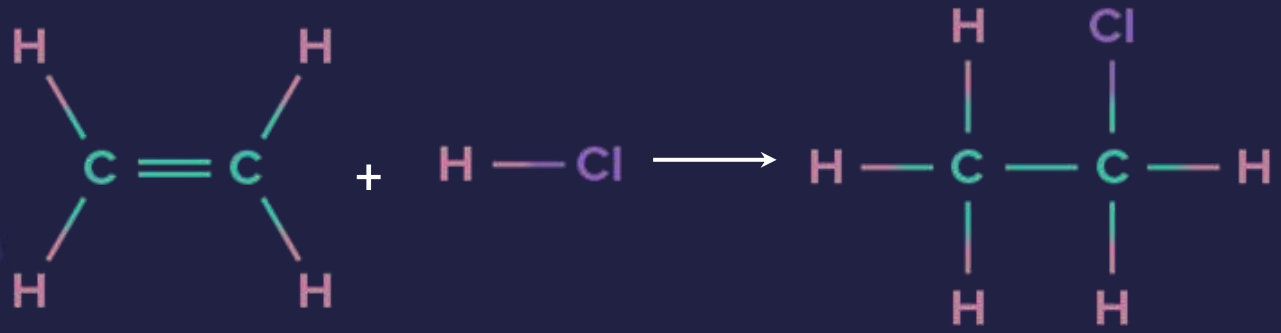
$\frac{1}{4} (\Delta_a H^\circ) = \frac{1}{4} (1665 \text{ kJ/mol})$

$\Delta_{C\text{-}H} H^\circ = 416 \text{ kJ/mol}$

Applications of Bond Enthalpy

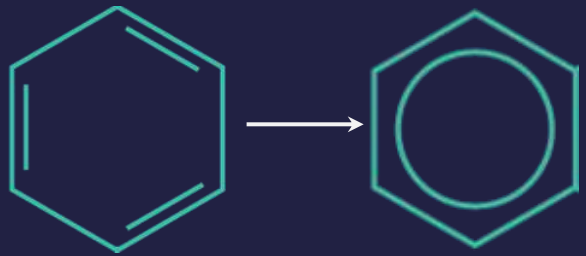
Determination of **enthalpy of reaction**

$$C_2H_4\,(g) + HCl\,(g) \longrightarrow C_2H_5Cl\,(g)$$



Resonance Energy ($\Delta_{RE}H$)

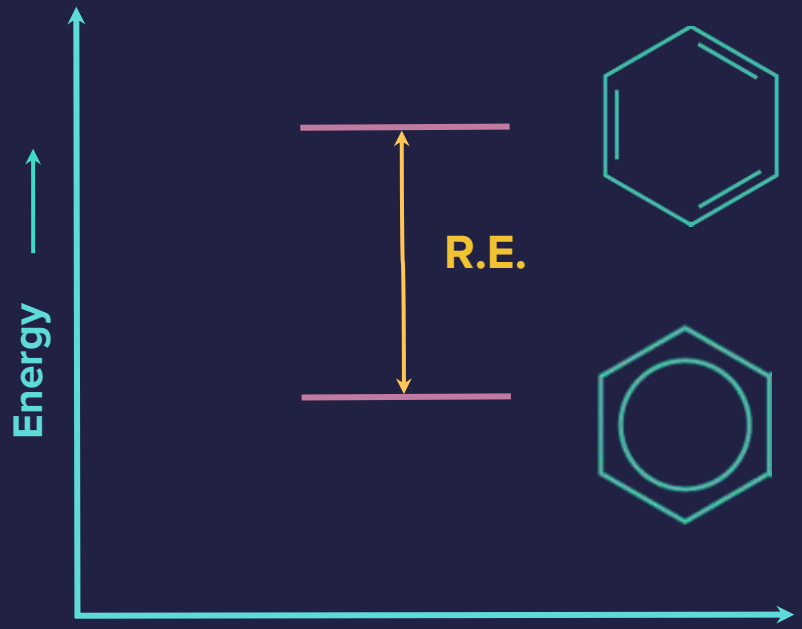
Difference in energy of the **most stable** resonating structure and the energy of the **actual molecule**



$\Delta_r H = \Delta_{RE} H$

Resonance energy can't be determined from the reaction because resonating structures do not exist. So, resonance energy is determined indirectly using bond enthalpy.

Resonance Energy



Determination of Resonance Energy

$\Delta_{RE}H$ = $\Delta_f H_{experimental}$ − $\Delta_f H_{theoritical}$

Always negative

Calculated from B.E.

Determination of Resonance Energy

$$\Delta_{RE}H = \Delta_c H_{calculated} - \Delta_c H_{experimental}$$

$$\Delta_{RE}H = \Delta_H H_{theoritical} - \Delta_H H_{experimental}$$

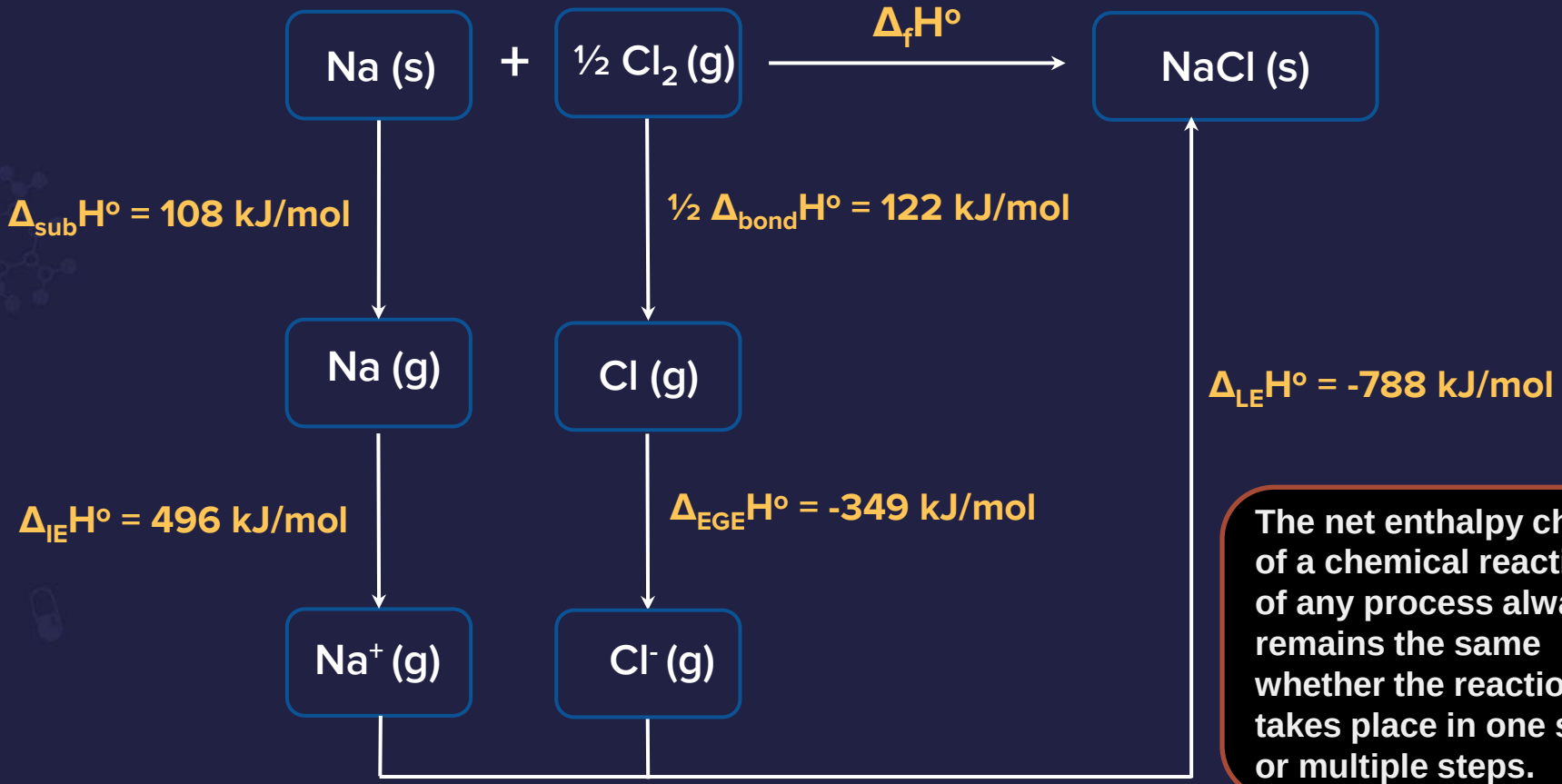
$\Delta_c H$	Enthalpy of Combustion
$\Delta_H H$	Enthalpy of Hydrogenation

Lattice Enthalpy

Energy released when one mole of a **solid ionic compound** is formed from its **gaseous constituent ions**

Lattice enthalpy of an ionic compound can be determined using the **Born-Haber cycle**

Born Haber Cycle of NaCl



The net enthalpy change of a chemical reaction or of any process always remains the same whether the reaction takes place in one step or multiple steps.

Born Haber Cycle of NaCl

$\Delta_f H^\circ$ = 108 kJ/mol + 122 kJ/mol + 496 kJ/mol + -349 kJ/mol + -788 kJ/mol

$\Delta_f H^\circ$ = -411 kJ/mol

Enthalpy of Hydration

$\Delta_{hyd}H$

For **gaseous ions**

For **anhydrous** or **partially hydrated** salts

Enthalpy change when **1 mole of a gaseous ion** is hydrated in large amount of water to form an **aqueous ion**

$$Cl^-(g) + aq \longrightarrow Cl^-(aq)$$

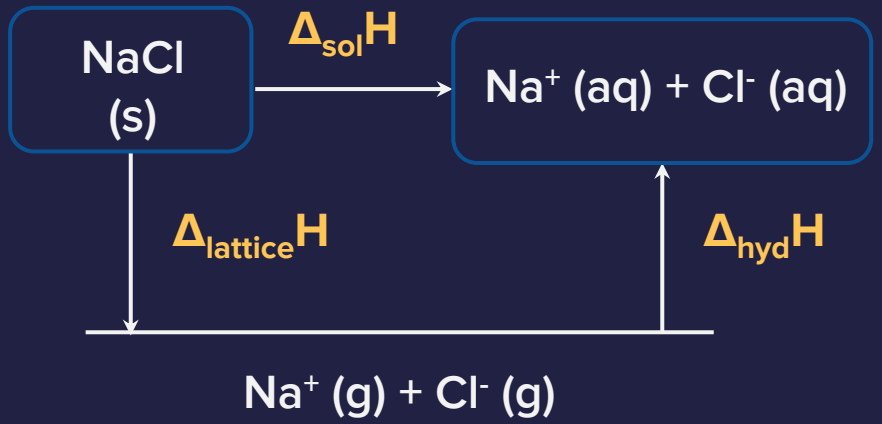
Enthalpy of Hydration of Anhydrous or Partially Hydrated Salts

Enthalpy change when anhydrous or partially hydrated salt **combines with the requisite amount of water** to form a **new hydrated stable salt**

$$CuSO_4\,(s) + 5H_2O\,(l) \longrightarrow CuSO_4.5H_2O\,(s)$$

Enthalpy of Solution ($\Delta_{sol}H$)

Enthalpy change when **one mole of a solute is** dissolved in **excess of solvent** so that further dilution does not involve any heat change



For Ionic Compounds

$$\Delta_{sol}H = \Delta_{lattice}H + \Delta_{hyd}H$$

Integral Enthalpy of Solution

Enthalpy change when one mole of the **solute** is dissolved in a **definite quantity of solvent** to produce a solution of a desired concentration

$HCl\ (g) + 10H_2O\ (l) \longrightarrow HCl\ (10H_2O)$

$\Delta H = -69.5$ kJ/mol

$HCl\ (g) + 25H_2O\ (l) \longrightarrow HCl\ (25H_2O)$

$\Delta H = -72.3$ kJ/mol

Integral Enthalpy of Solution

$HCl\ (g) + 25\ H_2O\ (l) \longrightarrow HCl\ (25\ H_2O)$

$\Delta H = -72.3$ kJ/mol

$HCl\ (g) + 40\ H_2O\ (l) \longrightarrow HCl\ (40\ H_2O)$

$\Delta H = -73.0$ kJ/mol

Enthalpy of Dilution

Enthalpy change when a solution of 1 mole of a **solute is diluted from a higher concentration to a lower concentration**

Dissolving gaseous HCl in water

$$HCl\ (25\ H_2O) + 15\ H_2O \longrightarrow HCl\ (40\ H_2O)$$

ΔH = - 73 kJ/mol - - 72.3 kJ/mol

ΔH = - 0.7 kJ/mol ← **Enthalpy of dilution**

Kirchhoff's Equation

Relates enthalpies of a reaction
at **two different temperatures**

$$aA + bB \longrightarrow cC + dD$$

Let the standard enthalpy
of reaction at temperature T_1 be ΔH°_1

$$\Delta H^\circ_1 = cH_m^\circ(C, T_1) + dH_m^\circ(D, T_1) - aH_m^\circ(A, T_1) - bH_m^\circ(B, T_1)$$

Kirchhoff's Equation

If same reaction is carried out at temperature T_2

$$\Delta H^\circ_2 = cH_m^\circ(C, T_2) + dH_m^\circ(D, T_2) - aH_m^\circ(A, T_2) - bH_m^\circ(B, T_2)$$

$$\Delta H^\circ = \Delta H^\circ_2 - \Delta H^\circ_1$$

$$= c\{H_m^\circ(C, T_2) - H_m^\circ(C, T_1)\} + d\{H_m^\circ(D, T_2) - H_m^\circ(D, T_1)\} - a\{H_m^\circ(A, T_2) - H_m^\circ(A, T_1)\} - b\{H_m^\circ(B, T_2) - H_m^\circ(B, T_1)\}$$

Kirchhoff's Equation

$$H_m^\circ(A, T_2) - H_m^\circ(A, T_1) = C_{P,m,A}(T_2 - T_1)$$

Heat required at **constant pressure** to increase temperature of one mole of A from **T_1 to T_2.**

Kirchhoff's Equation

Similarly,

$$H_m^\circ(B, T_2) - H_m^\circ(B, T_1) = C_{P,m,B}\,(T_2 - T_1)$$

$$H_m^\circ(C, T_2) - H_m^\circ(C, T_1) = C_{P,m,C}\,(T_2 - T_1)$$

$$H_m^\circ(D, T_2) - H_m^\circ(D, T_1) = C_{P,m,D}\,(T_2 - T_1)$$

Kirchhoff's Equation

$$\Delta H^\circ = \Delta H^\circ_2 - \Delta H^\circ_1$$

$$\Delta H^\circ = cC_{P,m,C}\,(T_2 - T_1) + dC_{P,m,D}\,(T_2 - T_1) - [aC_{P,m,A}\,(T_2 - T_1) - bC_{P,m,B}\,(T_2 - T_1)]$$

$$\Delta H^\circ = [cC_{P,m,C} + dC_{P,m,D} - aC_{P,m,A} - bC_{P,m,B}]\,(T_2 - T_1)$$

Kirchhoff's Equation

$$\Delta H^{\circ} = \Delta H^{\circ}_2 - \Delta H^{\circ}_1 = \Delta_r C_{p,m} (T_2 - T_1)$$

Where,

$$\Delta_r C_{p,m} = (d \times C_{p,m,D}) + (c \times C_{p,m,C}) - (a \times C_{p,m,A}) - (b \times C_{p,m,B})$$

Kirchhoff's Equation

If $\Delta_r C_{p,m}$ is a function of temperature

$$\Delta H^\circ_2 = \Delta H^\circ_1 + \int_{T_1}^{T_2} (\Delta_r C_{p,m})\, dT$$