Lectures

Week 1
+ Week 2

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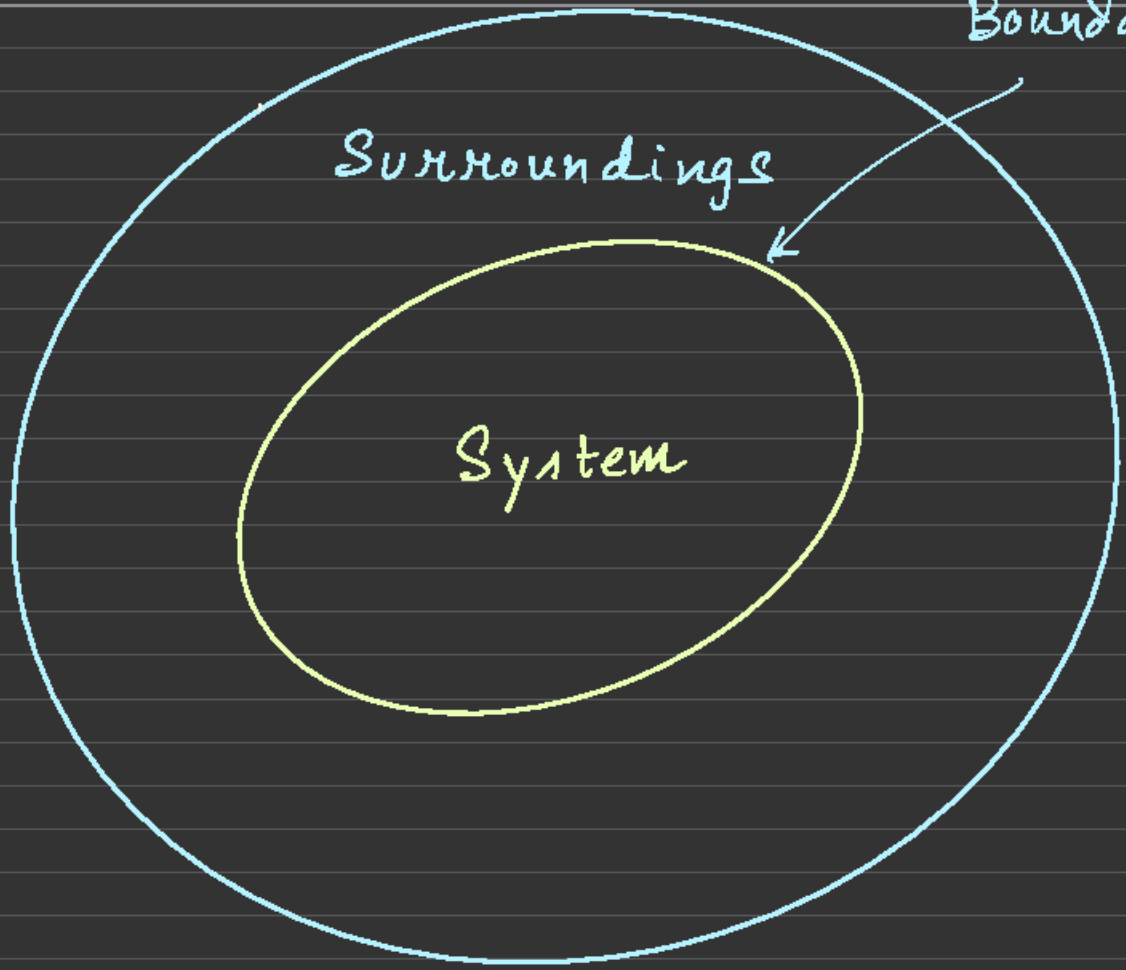
Thermodynamics of Materials is a study of how heat and various forms of work relate to the physical properties of materials

Equilibrium thermodynamics

Rate-independent

Thermal equilibrium
Mechanical equilibrium
Chemical equilibrium

Universe in thermodynamics



Boundary or wall

Universe

= System + Surroundings

System
– A body of matter that is our focus of study

Surrounding – Everything else excluding the system that is influenced by changes happening in the system

Laws of Thermodynamics

1. There exists a property of the universe, called energy, that remains conserved regardless of the processes that take place
2. There exists a property of the universe, called entropy, that always changes in the same direction regardless of the processes that take place.
3. There exists an absolute zero of temperature (lower limit to temperature) at which all substances have the same entropy

What is energy? It is the capacity or ability of a physical system to do work

Categories of Energy in a body or a System

1. Potential Energy - Energy associated with the position or configuration of a body in a potential field

$E_p = mgh$ } h

2. Kinetic Energy - Energy associated with the motion of a body



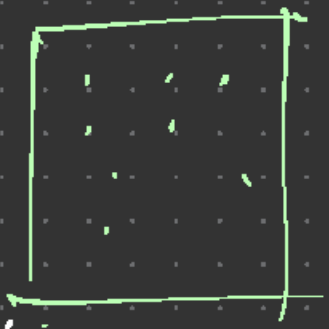
$E_k = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2$

3. Internal Energy - Energy associated with the internal condition or state of a body that does not depend on its motion or position in space

Internal Energy U

Internal State of a System macroscopically

Energy of a body associated with the microscopic motion and interactions of its constituent particles.



Microscopically



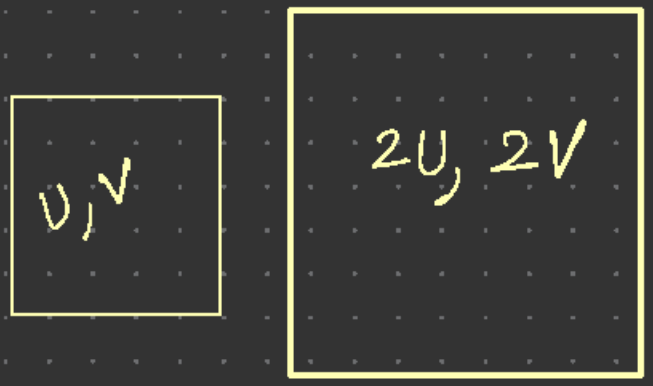
Molecules or atoms that constitutes the system

Macroscopic

U = Kinetic energy of molecules (E_k) + Potential energy of molecules (E_p)

U is total internal energy of the system

U is an extensive property

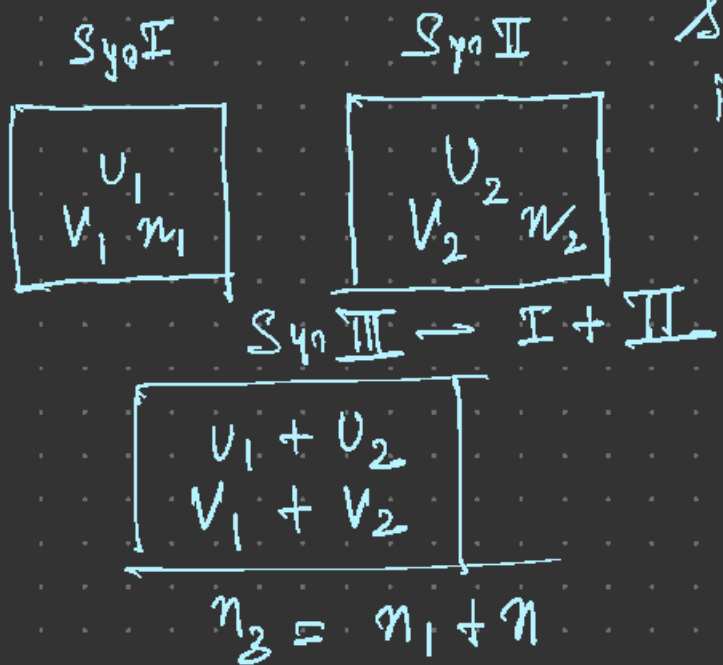


Depends on the extent or size of the system

Intensive property

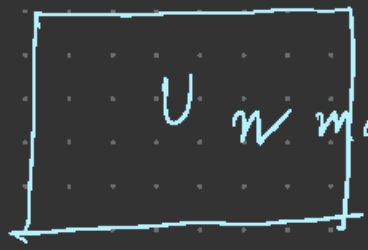
$$\bar{U} = \frac{U}{n}$$

Specific internal energy

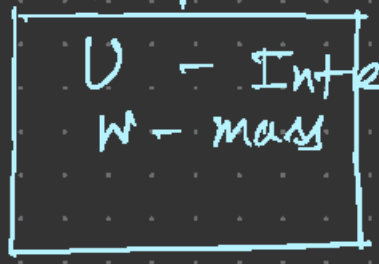


Unary System

A system containing one chemical species

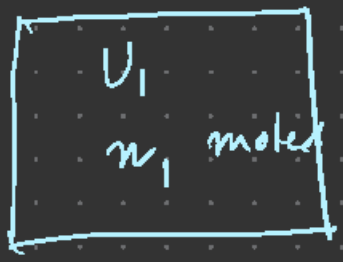


System A

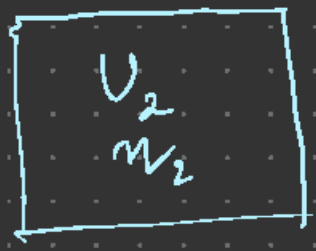


$\bar{U} = \frac{U}{W}$ = Energy per unit mass

Sys I



Sys II



Sys I
molar internal energy

$\bar{U}_1 = \frac{U_1}{n_1}$

Sys II
molar internal energy

$\bar{U}_2 = \frac{U_2}{n_2}$

Syo I	Syo II
U_1	U_2
n_1	n_2
$\bar{U}_1 = \frac{U_1}{n_1}$	$\bar{U}_2 = \frac{U_2}{n_2}$

Syo III — Syo I + Syo II

$U_3 = U_1 + U_2$

$n_3 = n_1 + n_2$

$\bar{U}_3 = \frac{U_3}{n_3}$

molar internal energy

$$\bar{U}_3 \neq \bar{U}_1 + \bar{U}_2$$

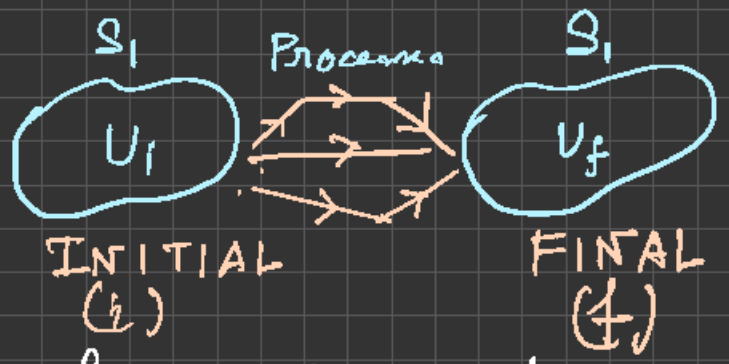
$$\Rightarrow \frac{U_3}{n_3} \neq \frac{U_1}{n_1} + \frac{U_2}{n_2}$$

$$\Rightarrow \frac{U_1 + U_2}{n_1 + n_2} \neq \frac{U_1}{n_1} + \frac{U_2}{n_2}$$

$\therefore \frac{U_1 + U_2}{n_1 + n_2} \neq \frac{U_1}{n_1} + \frac{U_2}{n_2}$

$\bar{U}$ - molar internal energy is an intensive property

Change In U: ΔU



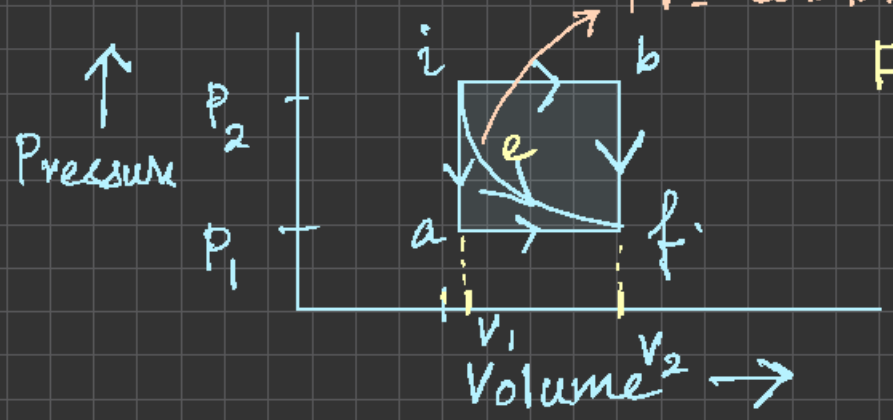
$$\Delta U = U_f - U_i$$

U_f: Internal energy of the final state of the system

U_i: Internal energy of the initial state of a system

U is a state function

A thermodynamic process can change a system from i to f along several possible paths



Few possible paths from i to f

1. $i \rightarrow a \rightarrow f$
2. $i \rightarrow b \rightarrow f$
3. $i \rightarrow e \rightarrow f$

ΔU does not depend on the path taken

U is a state function

Functions which depend only on the State of the system (e.g., initial and final states) and does not depend on the path that the system takes is a State function

$$\Delta U = U_f - U_i$$

Consider infinitesimal change dU of the system

$$\int_i^f dU = U_f - U_i = \Delta U$$

$$\int_i^f dU = U_f - U_i$$

$$\Delta U = U_f - U_i$$

Change in internal energy from State i to State f

Infinitesimal change or differential change in internal energy $\rightarrow dU$

$$\int_i^f dU = U_f - U_i$$

dU is called a total differential or an exact differential

SI unit of internal energy U is Joule

$$1 \text{ Joule} = 1 \text{ Newton} \cdot m$$

$$= 1 \text{ kg } m^2 s^{-2}$$

Heat and work also have the same units as U

Internal energy per mole U_m (kJ/mole)

1 calorie is the heat input to raise the temperature of 1g of water by 1°C

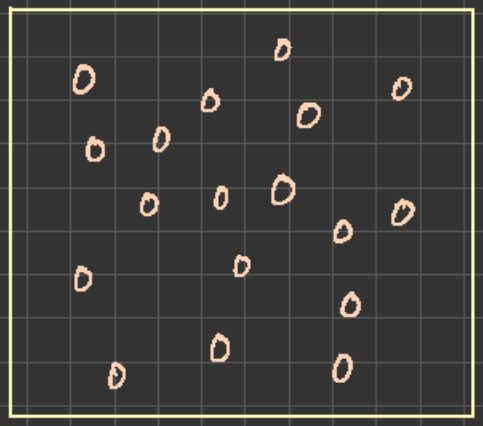
$$1 \text{ calorie} = 4.184 \text{ J} \quad \text{(exact conversion)}$$

Electron-volt (eV) is the kinetic energy acquired by an electron when it is accelerated from rest through a potential difference of 1 V.

$$1 \text{ eV} = 0.16 \times 10^{-18} \text{ J}$$

Microscopic or molecular level interpretation

Example: Helium

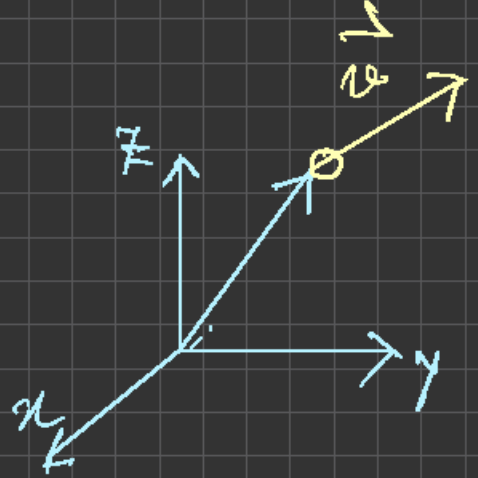


Monoatomic Gas enclosed in a container

How to describe one He atom in the 3D space –

Position x, y, z

Momentum v_x, v_y, v_z per unit mass



1 mole He = N_A atoms of He

Avogadro Number

$N_A = 6.023 \times 10^{23}$

$6N_A$ variables to describe 1 mole of He at some temperature T

Microscopic or molecular level understanding of U

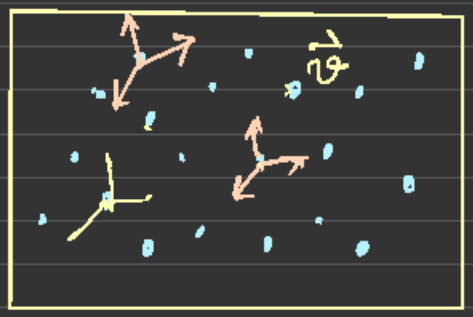
Degrees OF FREEDOM

1. Translational kinetic energy

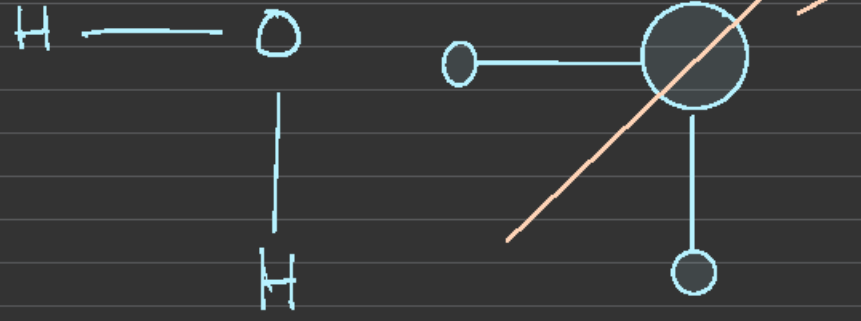
$$E_k = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2$$

2. Rotational kinetic energy

$\vec{v}$
(v_x, v_y, v_z)
(x, y, z)

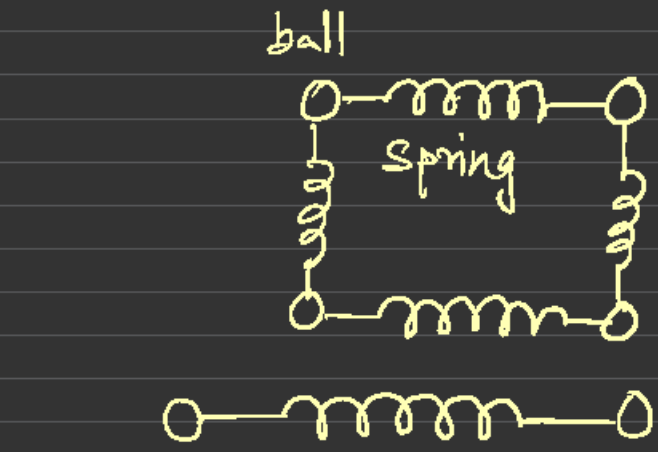


Each atom in the box has six degrees



ω – angular velocity
I – moment of inertia
$\frac{1}{2} I \omega^2$

3. Vibrational kinetic energy

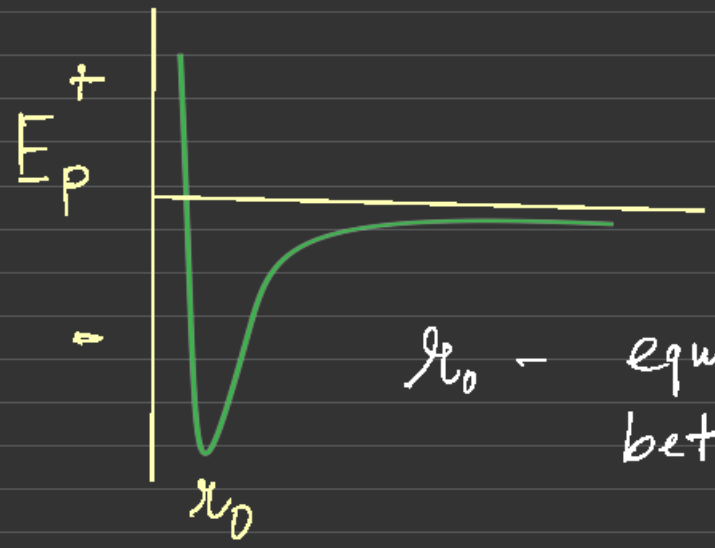


balls are atoms

springs are bonds

$= \frac{1}{2} k x^2$

k is the spring constant



r_0 – equilibrium distance between any two atoms

$r_0 \pm x$

Potential Energy at the molecular level

- Interactions between atoms or molecules

Example:

Ionic Solids: Coulombic interactions between charged ions

eg. NaCl

Na^+ Cl^- ↔

Bond energy: Ionic bond

Covalent bond

Metallic bond

Equipartition theorem (from classical mechanics)

For an assembly of particles in equilibrium at temperature T, the average or mean value of each quadratic contribution to the energy is the same and equal to $\frac{1}{2} k_B T$.

$k_B = 1.381 \times 10^{-23}$ J K^{-1} (Boltzmann's constant) per atom

Universal Gas Constant $R = 8.314$ J/mol·K

$k_B = R / N_A$

$k_B T \rightarrow \frac{\text{Joules}}{\text{atom}}$

$N_A = 6.023 \times 10^{23}$ (Avogadro number)

1 mole of a substance contains N_A atoms/molecules

$k_B = R N_A = 1.381 \times 10^{-23}$ J/atom-K $\quad \frac{J}{\text{mole-K}} \rightarrow \frac{J}{\text{atom-K}}$

Three quadratic terms per atom in a monoatomic gas

Mean internal energy per atom $= 3/2\ k_B T$

There are N_A atoms per mole

$\therefore U_M = U_M(0) + \frac{3}{2} N_A k_B T = U_M(0) + 3/2\ RT$

$U_M(0)$: molar internal energy at $T = 0$ K

For condensed phases (solids, liquids)

Interacting atoms also has contribution from the potential energy

Example: Ionic solids/liquids have Coulombic/electrostatic interactions between the ions

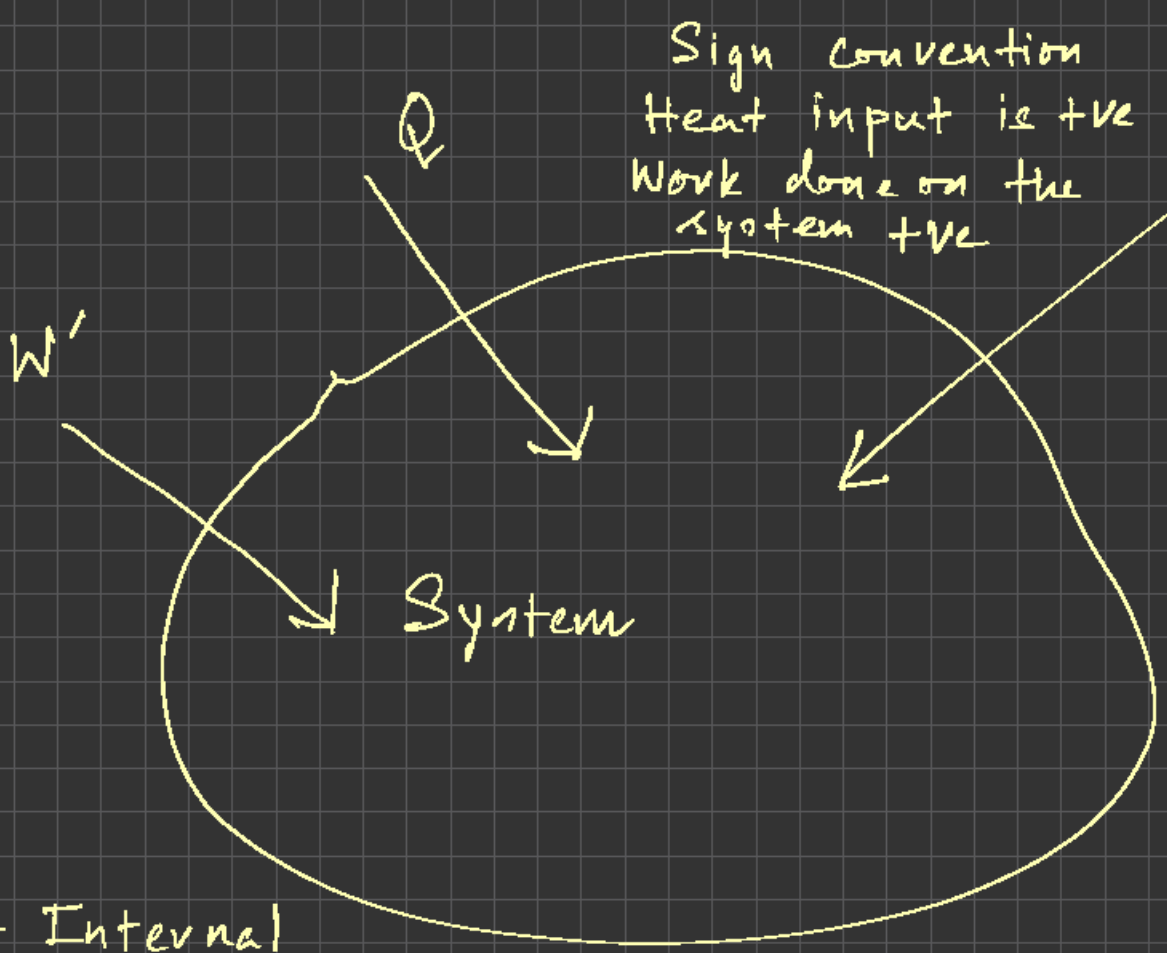
Interactions at the molecular level are complex in condensed phases

First Law of Thermodynamics

- Principle of Conservation of Energy

Statement :

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



Q : Heat input to a closed System

W : Mechanical work done on the closed system

W' : Chemical work done on the closed System

U_i - Internal energy before any heat or work is added

U_f - After addition of heat and work

ΔU : Change in internal energy

$$U_f - U_i$$

$$\Delta U = Q + W$$

— principle of Conservation of energy

Infinitesimal or differential form of the first law

$$dU = \underline{\delta q} + \underline{\delta w}$$

dU – exact differential

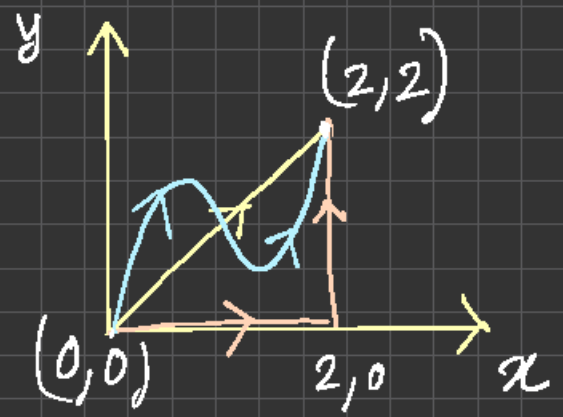
d denotes exact differential
Integral is path-independent $\int_i^f dU = U_f - U_i$

δ denotes inexact differential
Integral depends on the path taken

Examples

$z(x,y) = xy$ $\quad z(x,y)$ $\quad dz$ is an exact differential

$$dz = d(xy) = y\,dx + x\,dy$$



$$\Delta z = \int_{0,0}^{2,2} dz = \int_{0,0}^{2,2} d(xy) = \Big[xy\Big]_{0,0}^{2,2}$$

$$= (2\cdot 2) - (0\cdot 0)$$

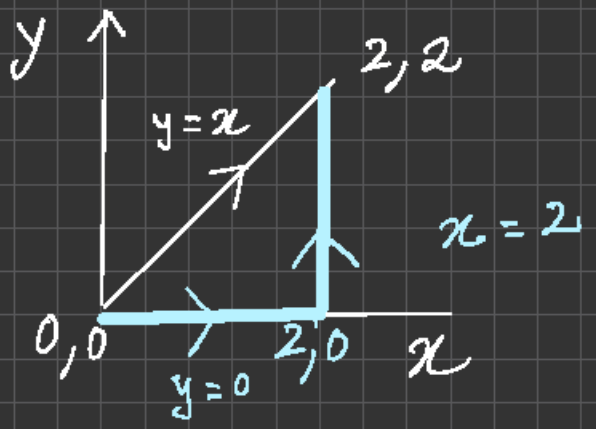
$$= 4$$

dz is a total or exact differential

Consider inexact differential

$$\delta W = y\,dx$$

$$\Delta W = \int_{0,0}^{2,2} \delta W$$



$$\Delta W = \int_{0,0}^{2,2} y\,dx = \int_0^2 x\,dx = \left[\frac{x^2}{2}\right]_0^2$$

$$= 2$$

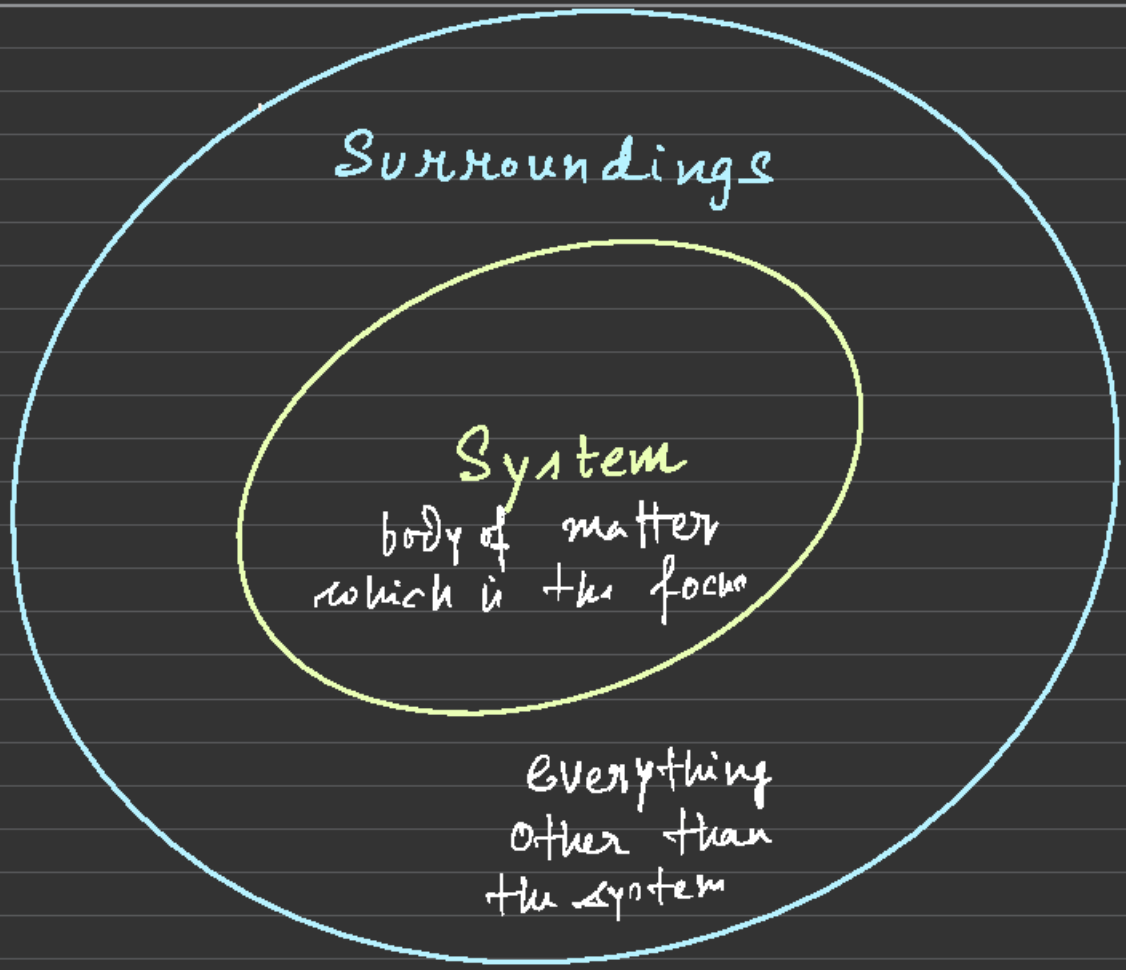
Along the blue path

$$0,0 \rightarrow 2,0 \rightarrow 2,2$$

$$\Delta W = \int_{0,0}^{2,0} y\,dx + \int_{2,0}^{2,2} y\,dx$$

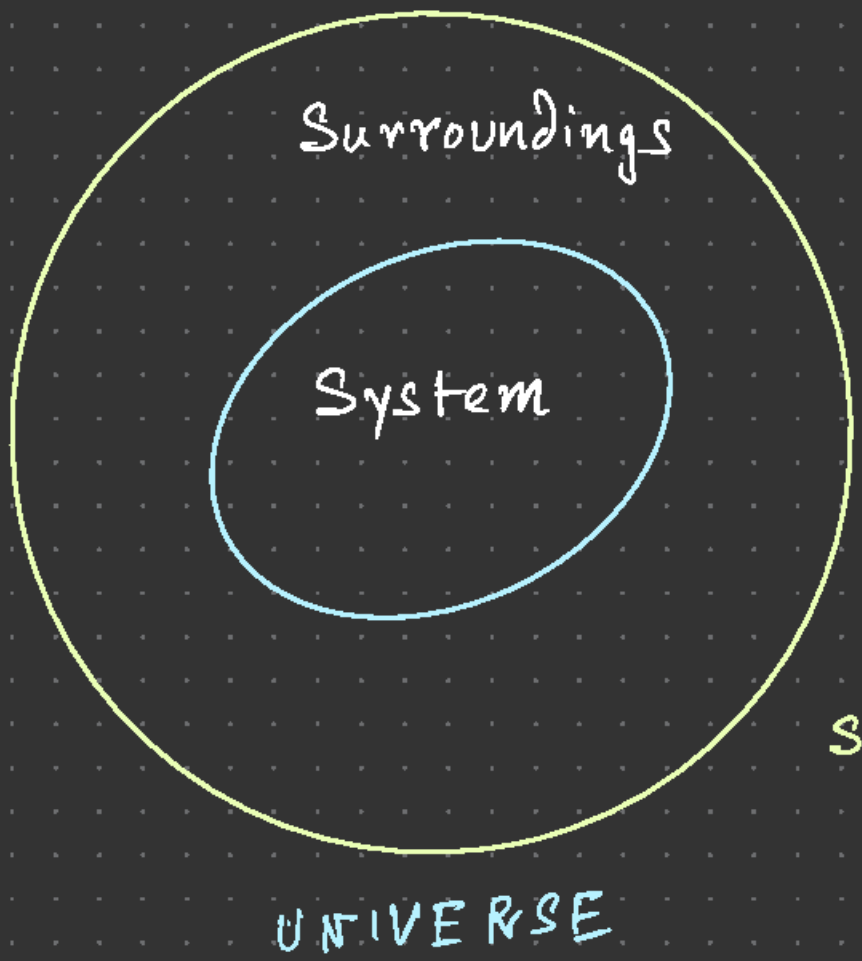
$$= 0 + 0 = 0$$

Universe in thermodynamics



Universe

= System + Surroundings



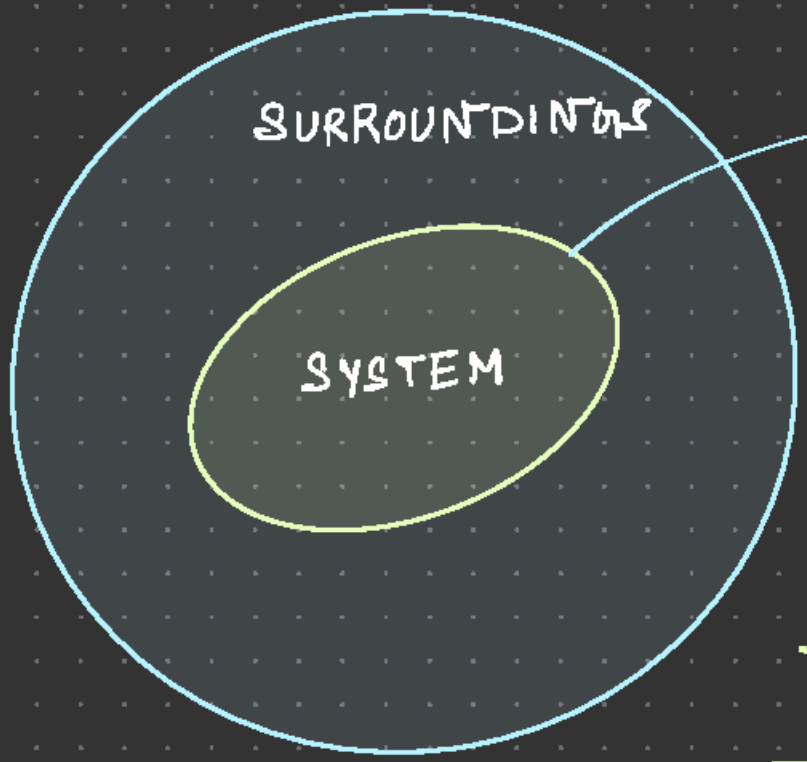
Universe = System + Surroundings

System: A body of matter that is studied

– a portion or subset of the universe that is studied

Surroundings – Everything else in the universe that is outside the system

The region outside the system that is influenced/affected by thermodynamic changes occuring inside the system is called "the surroundings"



→ BOUNDARY OR WALL

Wall or boundary separates the system from the surroundings

STATE of a system

- Condition of a thermodynamic system at the time of observation is described using a set of thermodynamic properties

U, V, N_a, N_b, N_c

a, b, c

- extensive properties

Thermodynamic properties –

Temperature T } Intensive properties
Pressure P }
Volume V

Chemical composition $c_A, c_B, c_C, \cdots$

When a system passes through a thermodynamic process, its properties change.

Thermodynamic processes involve

1. Transfer of heat to or from the system
2. Transfer of mechanical work to or from the system
3. Transfer of chemical work to or from the system

Let us take the example of a glass container containing water at room temperature and pressure. Container is covered with a green lid.



SYSTEM – Liquid water + Air within the container

SURROUNDINGS – Region in the vicinity of the system affected by the glass of water

Note: Air column in the container contains water vapour in equilibrium with water in the container

The system is closed. It can only exchange energy with the surroundings (only flow of heat is allowed through the walls of the container)

Properties of the system within the container

$T = 25^\circ C$ or $298\ K$

$P = 1$ atmosphere

$V = 1$ litre

Chemical component – 0.8 litre water
0.2 litre air

Remove the lid of the container

Open system: allows exchange of matter and energy with surroundings

$T = 25^\circ C$, $P = 1$ atm. $V = 1$ litre

Chemical Component - 0.8 litre water
0.2 litre of air

The container is placed on a hot plate and the hot plate temperature is kept at 60 C.

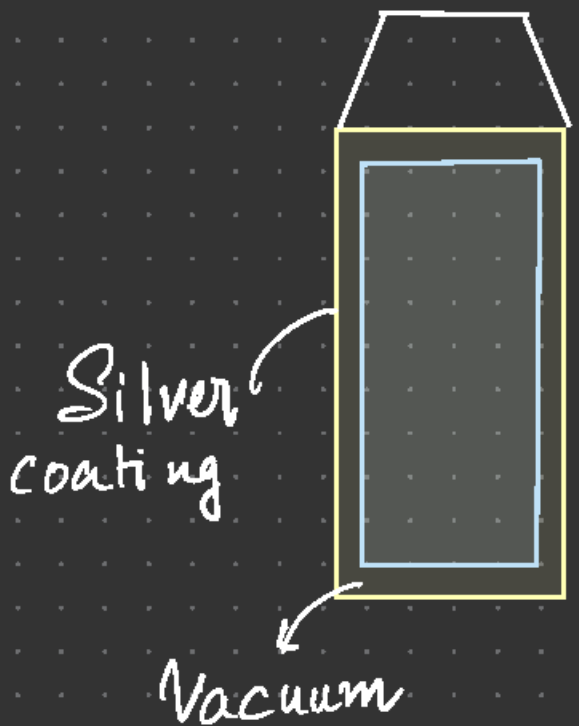
What happens to the open system?

Temperature inside the container increases to 60°C. Water starts evaporating.

Temperature of Surroundings increases to 60°C. P = 1 atm. V = 1 litre

Chemical composition: 0.5 L of water, 0.5 L of air

Let us consider a thermos flask containing cold water at 15°C and 1 atm. pressure



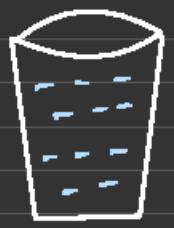
ISOLATED

SYSTEM: Water inside sealed thermos flask at 15°C and 1 atm. pressure.
Volume of water
= Volume inside the flask
= 1 litre

SURROUNDINGS:
Region outsid the wall of the flask

WALL: Vacuum sealed with Silver lining
- does not allow exchange of heat energy and matter with the surrounding.

Classification of thermodynamic systems



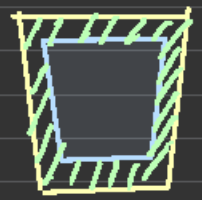
OPEN System

Allows exchange of energy and matter with the surroundings



CLOSED System

Allows exchange of energy with the surroundings



ISOLATED System

Does not allow exchange of matter and energy with the surroundings

Types of Wall

WALL

- Adiabatic - Does not allow exchange of heat energy between system and surroundings
- Diathermal - Allows heat transfer between system and surroundings
- Impermeable - Does not allow flow of matter between the system and surroundings
- Permeable - Allows flow of matter between the system and surroundings
- Rigid - Does not allow flow of mechanical work between the system and surroundings
- Flexible - Movable, opposite of Rigid

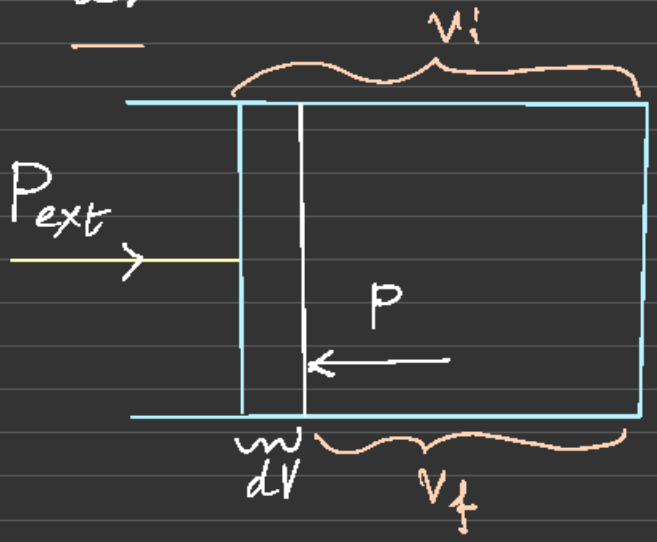
$dU = \delta Q - \delta W$

$\delta W = P\,dV$

Mechanical work

Work = Force times Displacement

$\delta W = \vec{F} \cdot \vec{dx}$



$P = -P_{ext}$

$\Delta V = V_f - V_i$

< 0

$= -P\,dV$

Why the −ve sign?

Sign convention

Work done by the surroundings on the system is +ve.

Heat flow from the surroundings into the system is +ve

$dU = \delta Q + \delta W = \delta Q - P\,dV$

$W = -P_{ext}\,\Delta V$ (positive)

$$\Delta U = Q + W + W'$$

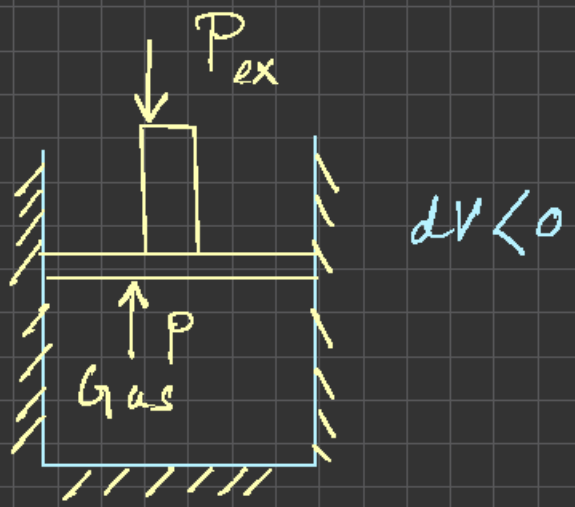
In the differential form:

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

$$\delta W = \vec{F} \cdot d\vec{x} = \frac{F}{A} A\, dx$$

Mechanical work

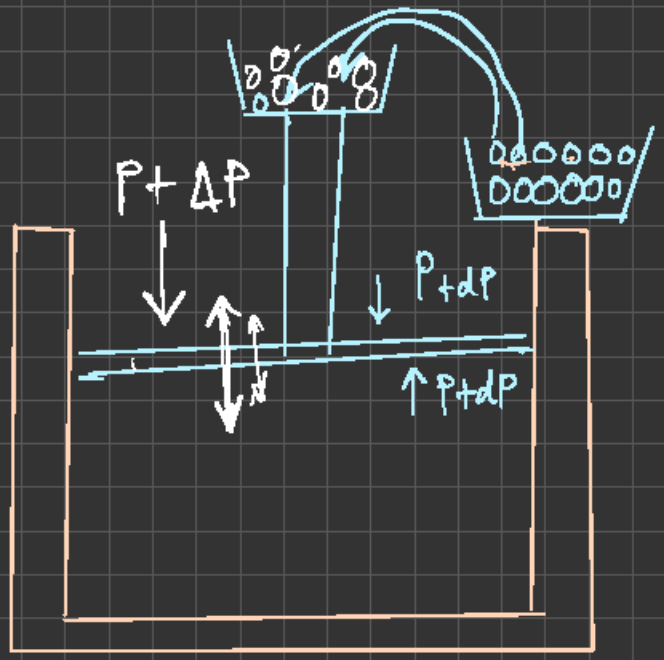
$$= -P\, dV \quad (+ve)$$



Work done on the system is +ve

If the external pressure is adjusted such that it remains the same as internal pressure, the work done is reversible

Reversible processes is infinitesimally slow or quasistatic - system boundaries or walls do not accelerate



Pebbles

Put one by one

quasistatic/

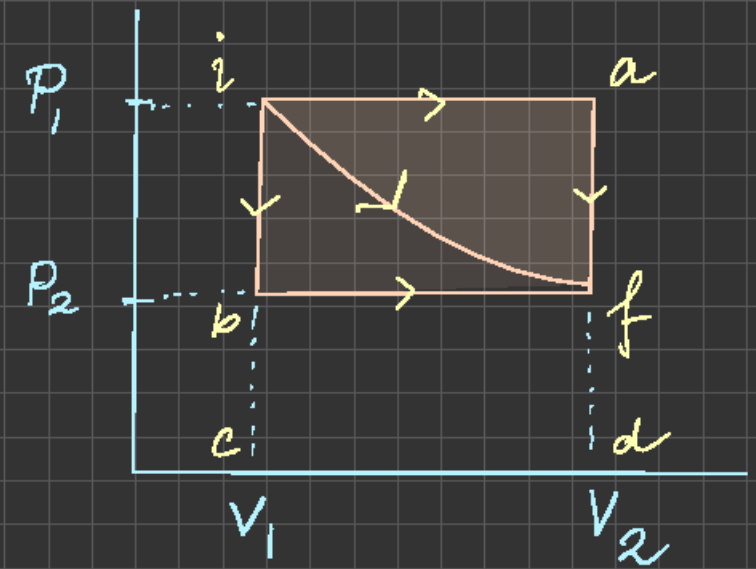
Reversible

Thermodynamic equilibrium

- Net force is zero ?

Reversible process - Infinitesimally slow

At each small increment of external pressure $P_{ext} + dP$, the system is allowed to come to thermodynamic equilibrium such that the internal pressure is equal to the external pressure



$\delta W = -\oint dV$

Path $i \to b \to f$

$i \to b$ isochoric process
Volume remains V_1
Pressure changes from P_1 to P_2

$b \to f$
volume expands from V_1 to V_2 at constant pressure P_2

Work done =

$$W = -\int_{V_1}^{V_2} p \, dV$$

$b \to f$ is an isobaric path

P_2 is constant

$$\therefore W = -P_2 \int_{V_1}^{V_2} dV = -P_2 (V_2 - V_1)$$

Work in a isochoric process

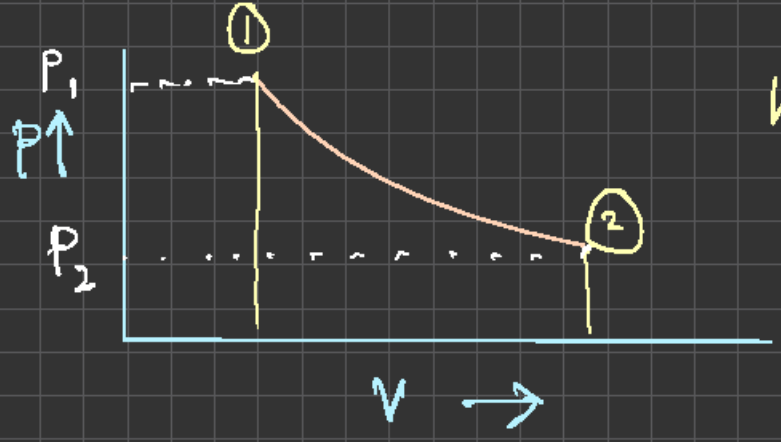
$$W = -\int p\,dV$$

But $dV = 0$ $\therefore$ $W = 0$

Work done in a process where $PV = k$

For 1 mole ideal gas $PV = RT$

when T is constant (isothermal) $PV = k$



$$W = -\int_1^2 p\,dV$$

$$= -k\int_1^2 \frac{dV}{V}$$

$$= -k\,\ln\left(\frac{V_2}{V_1}\right) = -P_1V_1\ln\left(\frac{V_2}{V_1}\right)$$

For a polytropic process

$$PV^n = C$$

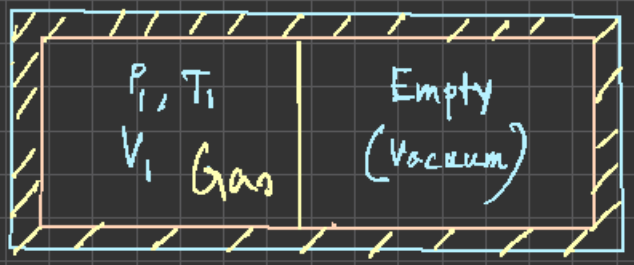
$$-\int p\,dV$$

where C is a constant

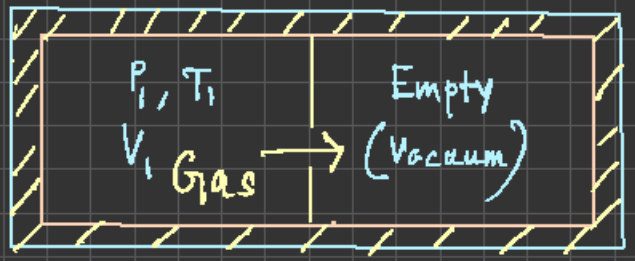
Let us consider free expansion of an ideal gas

V_c – volume of the entire system

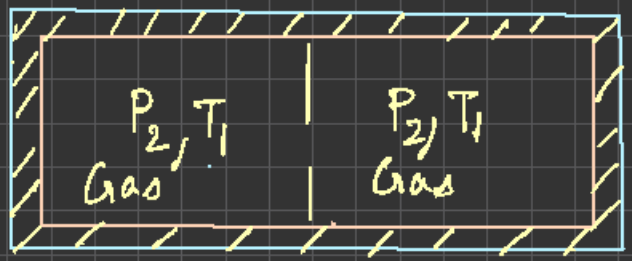
State 1



Intermediate state



State 2



State 1

$V = V_1$, $T = T_1$

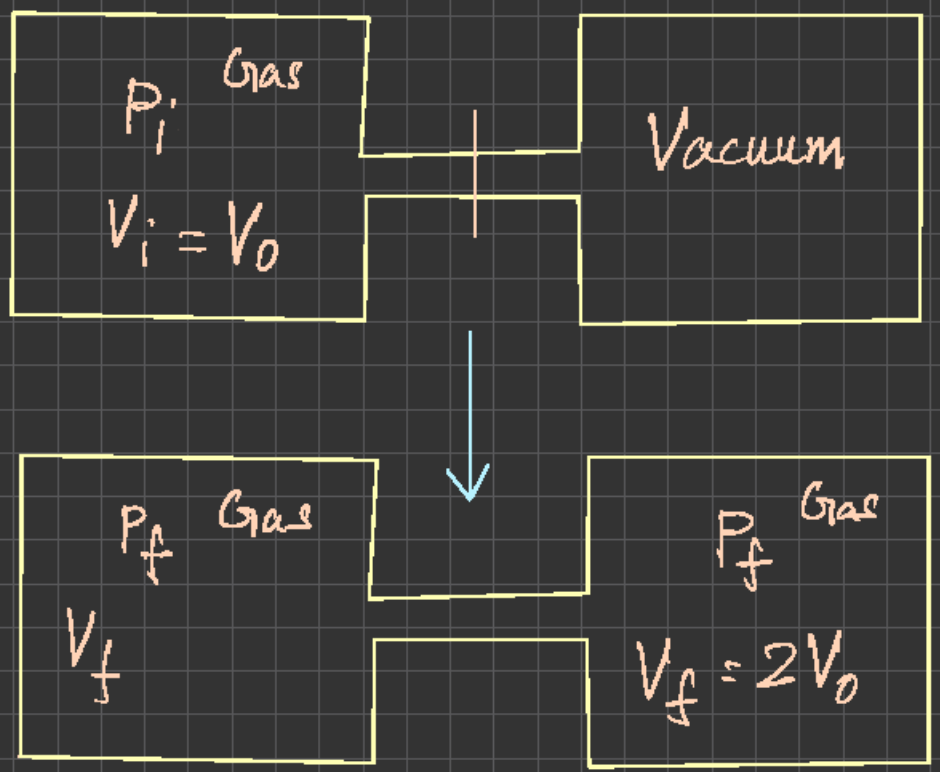
State 2

$V = V_c$, $T = T_1$

What is the work done?

What is ΔU?

Free expansion - Joule expansion



Volume of each chamber is V_0

There is no restriction to expansion

Different types of work

Expansion: $-p_{ex}\, dV$

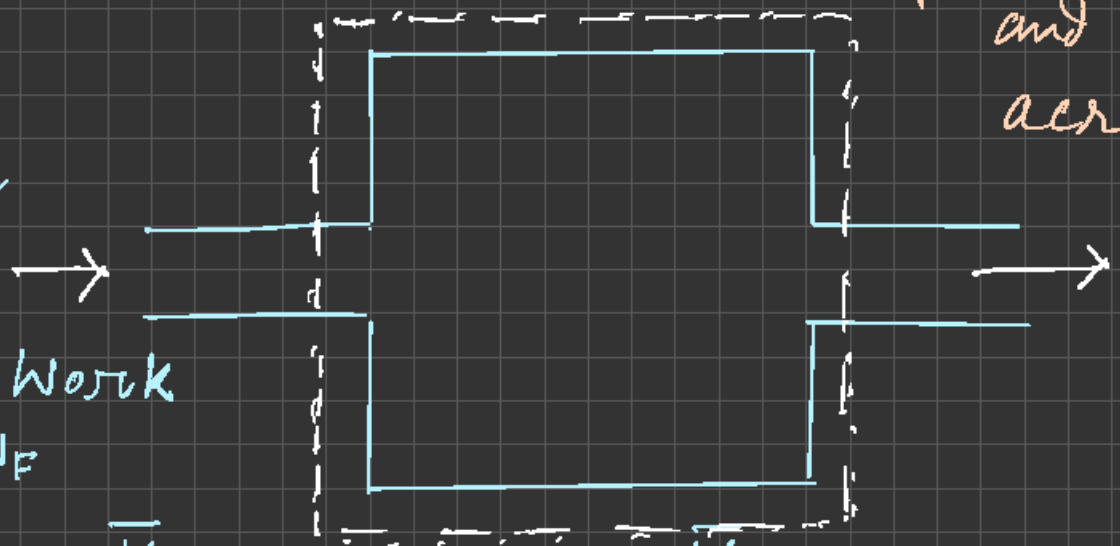
Surface expansion: $\gamma\, d\Gamma$

Γ is surface area
γ is surface tension

$-F\, dz$

F: Generalized force
dz: Generalized displacement

Open System – Transfer of matter and energy across wall



$V_{in} = \bar{V}_{in}\, m_{in}$ — $\bar{V}$ – Volume per unit mass (specific volume)

$V_{out} = \bar{V}_{out}\, m_{out}$

$$(W_F)_{in} = \int_0^m P\, dV_{in}$$

$$= \int_0^{m_i} P\, \bar{V}_{in}\, dm_{in}$$

$$= P \bar{V}_{in} m_i$$

Differential form

$$\delta (W_F)_{in} = + P_{in} \bar{V}_{in} \delta m_{in}$$

$$\delta (W_F)_{out} = - P_{out} \bar{V}_{out} \delta m_{out}$$

$$(\delta Q)_{in} = + \bar{U}_{in} \delta m_{in} \rightarrow \text{Internal energy entering the system}$$

$$(\delta Q)_{out} = - \bar{U}_{out} \delta m_{out} \rightarrow \text{Internal energy leaving the system}$$

For a closed System

First Law $\quad dU = \delta Q + \delta W$

Or, $\delta Q + \delta W = dU$ { First Law for a closed System }

Open System

$$(\delta Q)_{in} - (\delta Q)_{out} + (\delta W_F)_{in} - (\delta W_F)_{out} + \delta Q + \delta W = dU$$

What is the form of First Law if we include kinetic energy and potential energy of the system?

Closed System:

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

K_E : Kinetic energy of the system

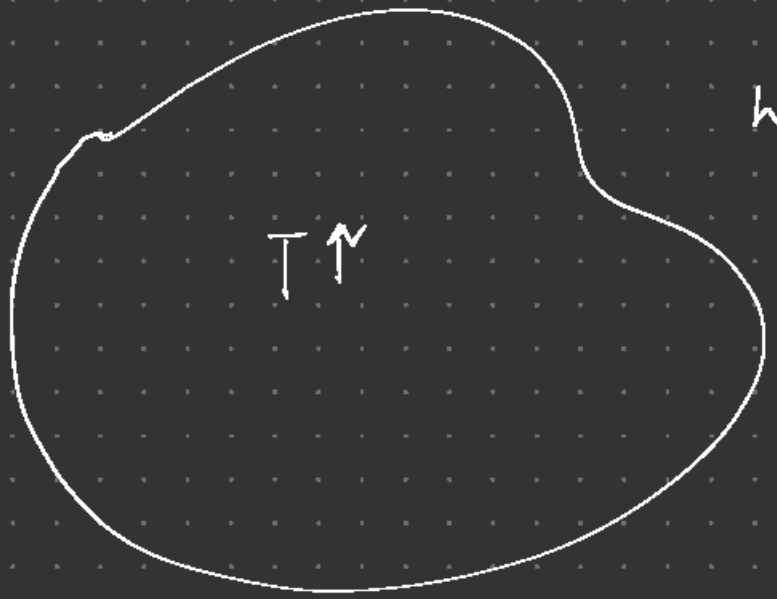
P_E : Potential energy of the system

What about Open System?

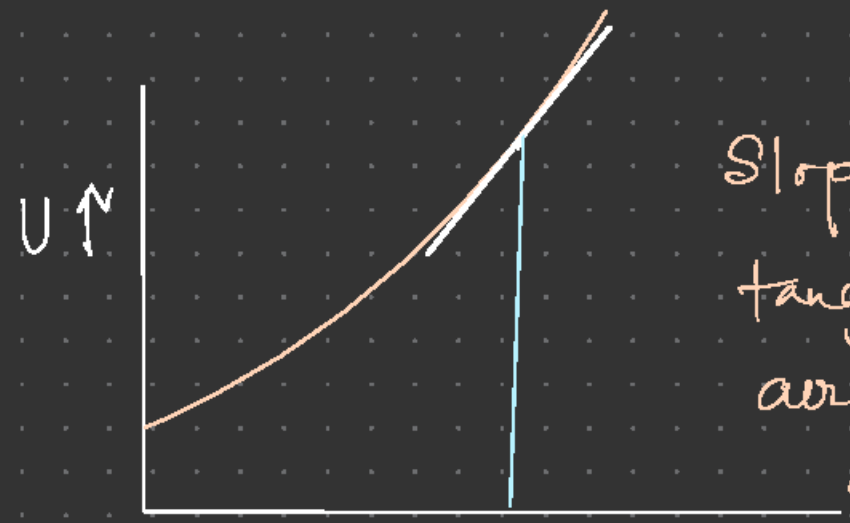
Week 2

Heat capacity C

- Amount of heat or thermal energy required to raise the temperature of a material



When temperature of a system is raised, does U increase or decrease?



Slope of the tangent to the curve is heat capacity of the system

What happens to the internal energy of a system when volume increases?

U is a state function

$$U = U(T, V)$$

dU is an exact differential

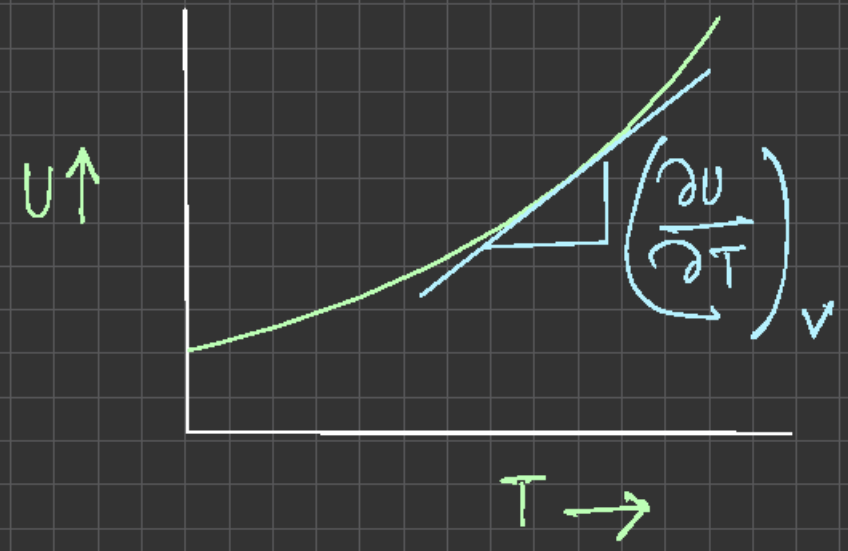
$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$Z(X, Y)$$

$$dZ = M\,dX + N\,dY$$

$$M = \left(\frac{\partial Z}{\partial X}\right)_Y \qquad N = \left(\frac{\partial Z}{\partial Y}\right)_X$$

$$\frac{\partial M}{\partial Y} = \frac{\partial^2 Z}{\partial X \partial Y} = \frac{\partial^2 Z}{\partial Y \partial X} = \frac{\partial N}{\partial X}$$

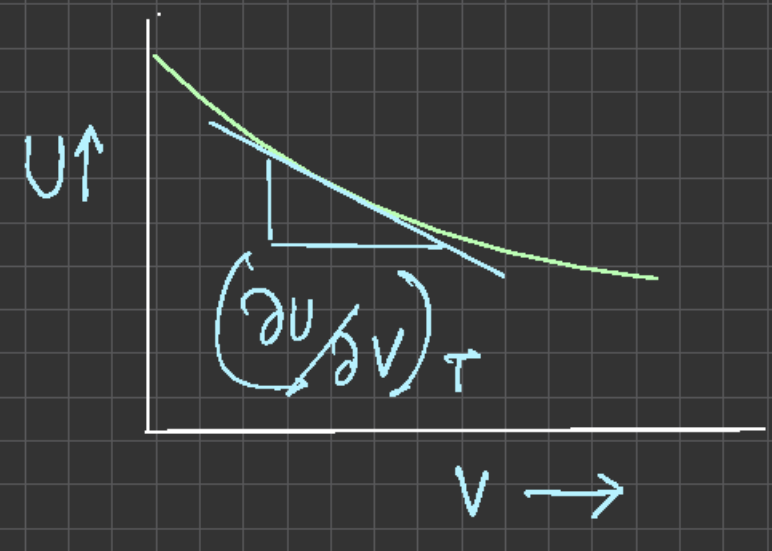


Heat input to system is positive

$$dU = \delta q - p\,dV$$

$$dU = \delta q = C_V\,dT$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$



For systems with interacting molecules or atoms:

Interactions increase when the interaction distance is less

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$$

FOR IDEAL GAS

Gas molecules do not interact

$$\therefore \quad \pi_T = \left(\frac{\partial U}{\partial V}\right)_T = 0$$

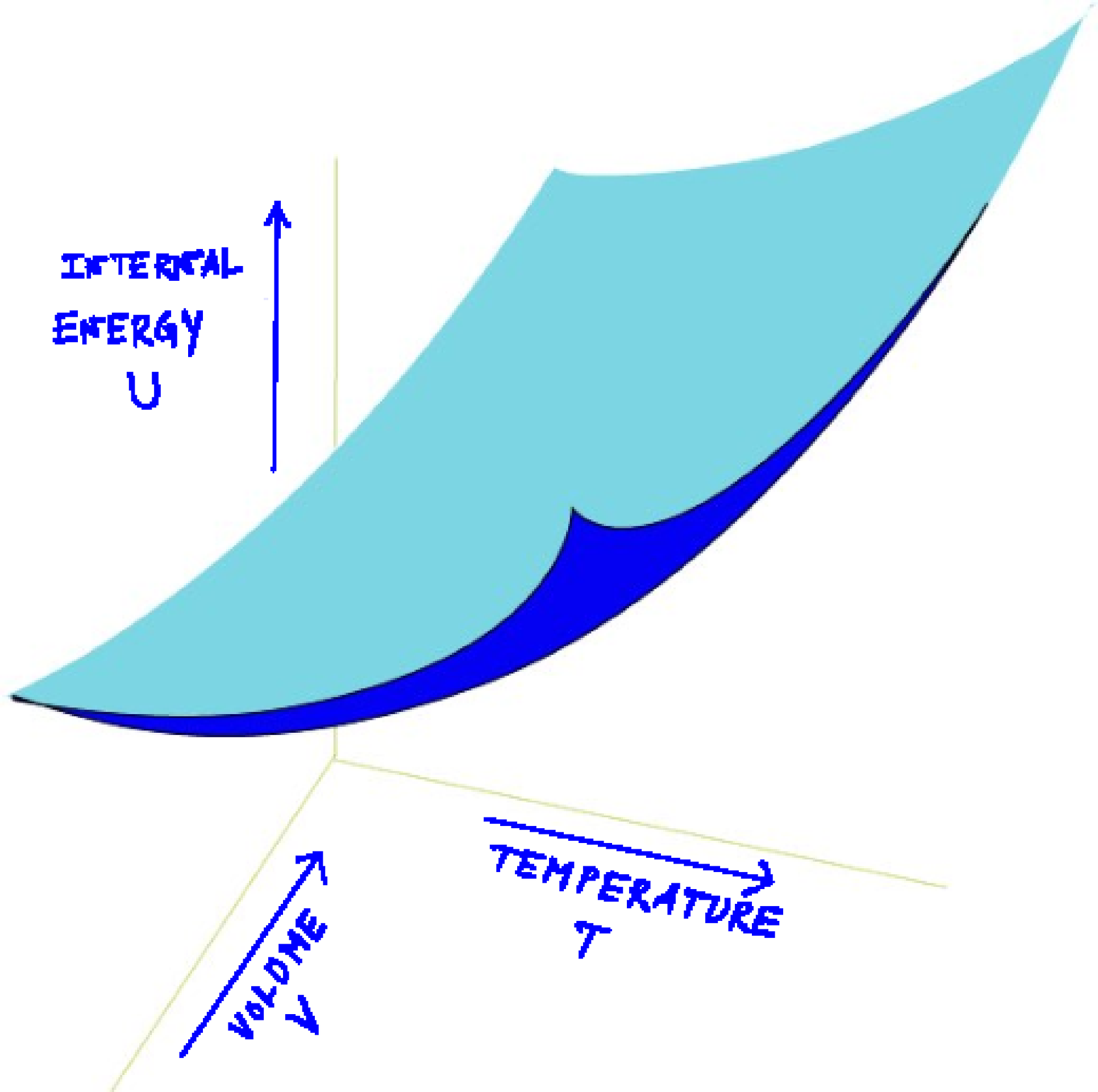
$$dU = \delta q - p\,dV$$

$$= C_V\,dT - p\,dV \quad \text{— (1)}$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad \text{— (2)}$$

COMPARE (1) and (2)

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad \pi_T = -p = \left(\frac{\partial U}{\partial V}\right)_T$$


INTERNAL
ENERGY
U
TEMPERATURE
T
VOLUME
V

If the energy of an ideal gas is $\frac{3}{2}RT$, what is its C_V?

What is molar heat capacity at constant volume?

$$C_{V,m} = \frac{C_V}{n}$$ where n is the no. of moles of the material

$C_{V,m}$ (polyatomic gases) ~ 25 J/mole-K $25\ J\ K^{-1}\ mol^{-1}$

Specific heat : Heat capacity per unit mass

Specific heat of water at room temperature

$\sim 4\ J\ K^{-1}\ g^{-1}$

What is its molar heat capacity?

Atomic mass of hydrogen = 1 u

Atomic mass of oxygen = 16 u

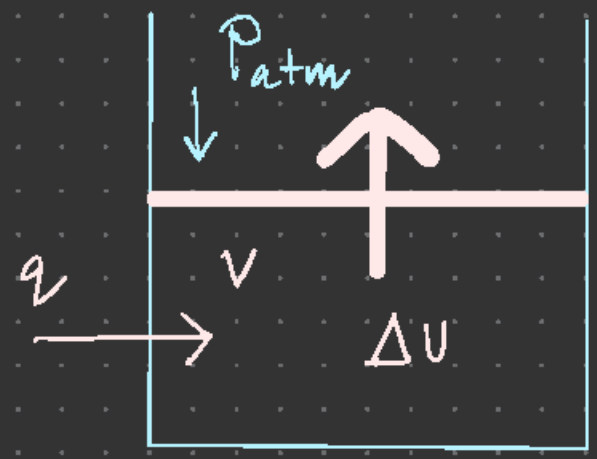
At CONSTANT VOLUME

$$dU = C_V \, dT$$

or,

$$\Delta U = C_V \, \Delta T$$

$$Q_V = \Delta U = C_V \, \Delta T$$



$\Delta V > 0$

work done by the system

$= - p_{atm} \, \Delta V$

The MEMBRANE is FLEXIBLE

Volume can change

$$\Delta U = q - p\Delta V$$

$$q = \Delta U + p\Delta V$$

Is $q > \Delta U$?

Define Enthalpy H

$$H = U + pV$$

Enthalpy is a State function

At constant pressure

$$dH = \delta q$$ (differential change)

or, for a macroscopically measurable change

$$\Delta H = q_p$$ (heat input at constant pressure)

Starting from the definition of H, prove that

$$dH = \delta q$$

Heat capacity C

$$\delta q = C\,dT$$

$$dU = \delta q - p\,dV$$

$$= C\,dT - p\,dV$$

At constant volume $C = C_V$

$$dV = 0$$

$$\therefore \quad dU = C_V\,dT$$

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V$$

$$dU = \delta q - p\,dV$$

$$dH = dU + p\,dV + V\,dp$$

$$= \delta q + V\,dp$$

At constant pressure

$$dp = 0$$

$$dH = \delta q_p = C_p\,dT$$

$$\therefore \quad C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

C_p – Heat capacity at constant pressure

ASIDE:

Phonons or lattice vibrations in solids - lattice heat capacity

- Peter Debye in 1912 estimated the phonon contribution to heat capacity

https://www.nist.gov/si-redefinition/kelvin/kelvin-thermodynamic-temperature

Phonons - standing wave modes in a crystal

Maximum allowed phonon frequency (Debye frequency) ν_D

$$T_D = \frac{h\nu_D}{k_B}$$

$$C_V = 9Nk_B\left[\frac{T}{T_D}\right]^3 \int_0^{T_D/T} \frac{x^4 e^x}{(e^x-1)^2}\,dx$$

$T \ll T_D$

As $x \to \infty$

$$C_V = \frac{12\pi^4}{5} Nk_B \left(\frac{T}{T_D}\right)^3$$

ASIDE:

When $T \gg T_D$ Here $e^x - 1 \approx x \quad |x| \ll 1$

Atomic mass (u)

Pb 207

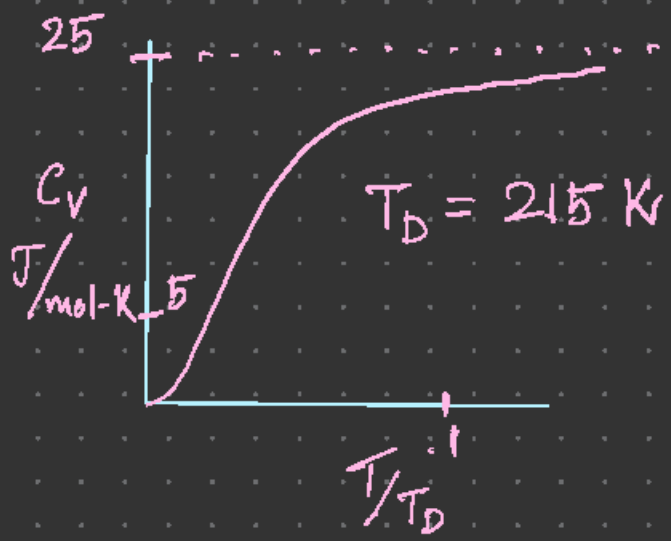
Cu 63·6

$$\frac{C_v}{N k_B} \approx 9 \left(\frac{T}{T_D}\right)^3 \int_0^{T_D/T} \frac{x^4}{x^2}\, dx$$

$$\approx 3 \quad \text{(Dulong and Petit law)}$$

or, $C_v = 3 N k_B$

If $N = N_A$, $C_v = 3R$



Note that specific heat in J/gm-K will be different

Say Pb and Cu

Convert $J/mol-K$

to $J/gm-K$

$$y \frac{J}{mol-K} = \frac{y}{A} \frac{J}{gm-K}$$

$\therefore$ Pb has less Specific heat than Cu

What is the difference between ΔH and ΔU ?

$$dH = dU + pdV + Vdp$$

At constant pressure, $dp = 0$

$$\therefore \quad dH = dU + pdV$$

or,
$$\Delta H = \Delta U + p\Delta V$$

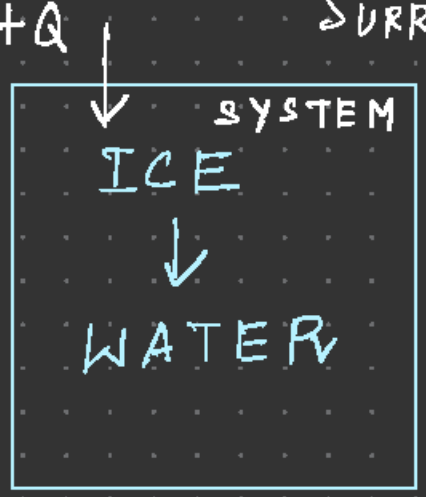
Enthalpy of fusion (melting) of ice at 0°c and 1atm pressure is 6 kJ/mol. The molar volume of ice at 0°C is 0.0196 l. Molar volume of water at 0°C is 0.018 l. Find ΔH and ΔU of fusion of ice at 1 atm. pressure.

$$\text{Ice} \xrightarrow{\text{melting}} \text{Water}$$

Endothermic process
- Heat is absorbed by the system from the surroundings

Exothermic process
- Heat is released by the system to the surroundings

Ice $\xrightarrow{\text{Melting}}$ Water



ICE (System) absorbs heat from surroundings during melting.

$\Rightarrow$ Heat input to the system

Q is +ve

At constant 1 atm pressure, 1 mole ice needs 6 kJ heat input

$1\ L = 1\ dm^3$

$= 0.001\ m^3$

1 atm.

$= 101325\ Pa$

$= 101325\ N/m^2$

1 L-atm.

$= 0.001\ m^3 \times 101325\ N/m^2$

$= 101.325\ N\ m$

$= 101.325\ J$

$Q = Q_p = \Delta H = 6\ kJ$

(Constant P)

$\Delta H = \Delta U + P\Delta V$ (constant pressure)

$P = 1$ atm.

Volume of 1 mole ice $= 0.0196$ L

Volume of 1 mole water $= 0.018$ L

$\therefore \Delta V = V_{water} - V_{ice}$

$= (0.018 - 0.0196)$ L

$= -0.0016$ L

$= -1.6 \times 10^{-3}$ L

$\therefore P\Delta V$

$= 1$ atm $\times (-1.6 \times 10^{-3})$ L

$= -1.6 \times 10^{-3} \times 101.325$ J

$= -0.16212$ J

$$\Delta H = 6 \text{ kJ}$$

$$= 6000 \text{ J}$$

$$\therefore \quad 6000 = \Delta U + (-0.16212)$$

$$\therefore \quad \Delta U = 6000.16212 \text{ J}$$

$$\approx 6000 \text{ J}$$

Thus $P\Delta V$ is negligible for a phase change process that involves condensed phases - ice and water.

Combustion reaction that involves gases

Graphite + Oxygen $\longrightarrow$ Carbon dioxide

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

Is combustion reaction an exothermic process?

Combustion produces heat and releases heat to the surroundings. It is an exothermic process

At 298 K and 1 atm pressure, $\Delta H^{\circ}_{r} = -394\ kJ/mol$

Molar volume of graphite = $0.0053\ L$

Find ΔU°_{r}

$$C(s) + O_2(g) \xrightarrow[1\ atm.]{298K} CO_2(g) \qquad \Delta H^{\circ}_r = -394\ kJ/mole$$

1 mol 1 mol 1 mol

1 mole of oxygen is consumed and 1 mole of CO_2 is produced

Assume that O_2 and CO_2 are ideal gases following the equation of state

$$PV = nRT$$

n is the no. of moles of gas

For O_2, $n = 1$

For CO_2, $n = 1$

$$H = U + PV$$

$$PV = nRT$$

$$H = U + nRT$$

or, $$dH = dU + d(nRT)$$

$$= dU + RT\,dn + nR\,dT$$

If T is constant, $dT = 0$

$$\therefore \quad dH = dU + RT\,dn$$

or, $$\Delta H = \Delta U + RT\,\Delta n$$

n (before reaction) $= 1$

n (after reaction) $= 1$

$\therefore \quad \Delta n = n_{product} - n_{reactant}$

$= 1 - 1$

$= 0$

n denotes no. of moles of gas

$$\Delta U = \Delta H - RT\Delta n$$

$$= \Delta H = -394 \text{ kJ/mol}$$

Note that moles of $C(s)$ are not taken into account.

Think of the difference in molar volume

Note:

Heat Capacity of materials can change with temperature

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$ is an extensive property as H is extensive

Replace H by $\bar{H}$ or H_m

Then $$C_{p,\text{molar}} = \left(\frac{\partial \bar{H}}{\partial T}\right)_p$$ is an intensive property

We will use C_p to denote molar heat capacity

c_p to denote specific heat or heat capacity per unit mass

Empirical Relation between C_p and T

$$C_p(T) = a + bT + \frac{c}{T^2} \qquad \left(\frac{J}{mol\text{-}K}\right)$$

Determine a, b, c from calorimetry

	a	$b \times 10^3$ (1/K)	$c \times 10^{-5}$ (K^2)	Range of temperature
Ag(s)	21.30	8.54	1.51	298 - 1234 K
C(s, graphite)	17.15	4.27	-8.79	298 - 2300 K
Ni (l)	38.49	-	-	1728 - 1900 K
N_2(g)	28.58	3.77	-0.5	298 - 500 K

How does the molar enthalpy of N_2 change when heated from 30°C to 100°C?

$$dH_m = C_p\, dT$$

$$C_p = a + bT + \frac{c}{T^2}$$

$$\int_{H(303K)}^{H(373K)} dH_m = \int_{303\,K}^{373\,K} \left(a + bT + \frac{c}{T^2}\right) dT$$

$$= a\left[T\right]_{303}^{373} + b\left[\frac{T^2}{2}\right]$$