THERMODYNAMICS AND STATISTICAL MECHANICS

CHAPTER 2 –FIRST LAW OF THERMODYNAMICS

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Introduction (Laws of Classical Thermodynamics)

Zeroth Law: If two systems are independently in equilibrium with a third one, then they are in thermal equilibrium with each other. This law establishes the concept of temperature.

A is equilibrium with B and B is in equilibrium with C. So, A and C are in thermal equilibrium.
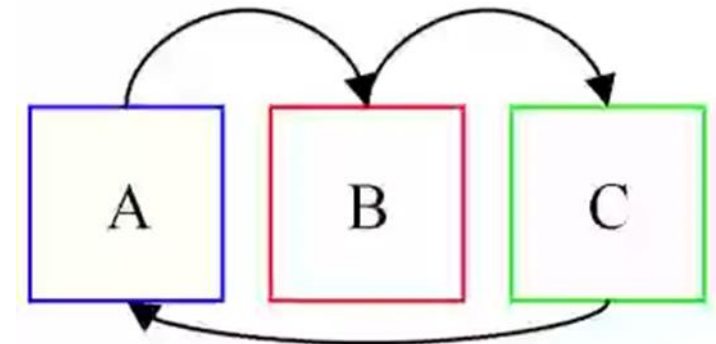
Introduction (Laws of Classical Thermodynamics)

First Law: Energy is conserved in any process if heat is taken into account.
$$dU \ = \ dQ \ + \ dW$$

Here we consider the work done on the system as positive.

Otherwise

The change in internal energy of a system equals the heat added to the system minus the work done by the system
$$dU \ = \ dQ \ - \ dW$$

Introduction (Laws of Classical Thermodynamics)

Second Law: The entropy of a closed system either remains constant or increases (in any irreversible process). It is unaltered in any reversible process.

- For a reversible process: $\Delta S = 0$

- An irreversible process: $\Delta S > 0$

Consequences:

- No heat engine can be 100% efficient.

- No refrigerator can transfer heat from a colder to a hotter reservoir without external work. $\Delta S \geq 0$

Introduction (Laws of Classical Thermodynamics)

Third Law: **The Quest for Absolute Zero**. At absolute zero (0 K), a perfect crystal reaches zero entropy (S = 0), representing a state of perfect molecular order.

- **Key Constraint**: Absolute zero is a limit that can be approached but never actually reached (T→ 0, but T ≠ 0).

- **The Cooling Paradox**: Each cooling cycle removes less heat than the one before, making the final approach to 0 K infinitely long.

- **Motion vs. Order**: While thermal disorder vanishes, zero-point motion prevents atoms from becoming truly stationary, as dictated by quantum mechanics.

Fundamental of Thermodynamics

**Thermodynamics** is the study of the relationships between energy, heat, temperature, and work.

- **Temperature (T):** A measure of an object's tendency to spontaneously give up energy to its surroundings.

- **Heat (Q):** The spontaneous flow of energy from one object to another driven solely by a temperature difference.

- **Work (W):** Any non-spontaneous energy transfer into or out of a system (e.g., mechanical displacement or electrical flow).

- **The Law of Conservation (First Law).** Energy is never created or destroyed; it is only transformed. The total energy of the universe remains constant.

Forms of Energy: Kinetic, Electrostatic, Gravitational, Chemical, and Nuclear.

Systems, Surroundings, and Boundaries

In thermodynamics, we define our universe in three parts:

- **System**: The specific matter or region being studied.

- **Surroundings**: Everything external to the system.

- **Boundary**: The real or imaginary surface that separates the system from its surroundings.

Surroundings

System
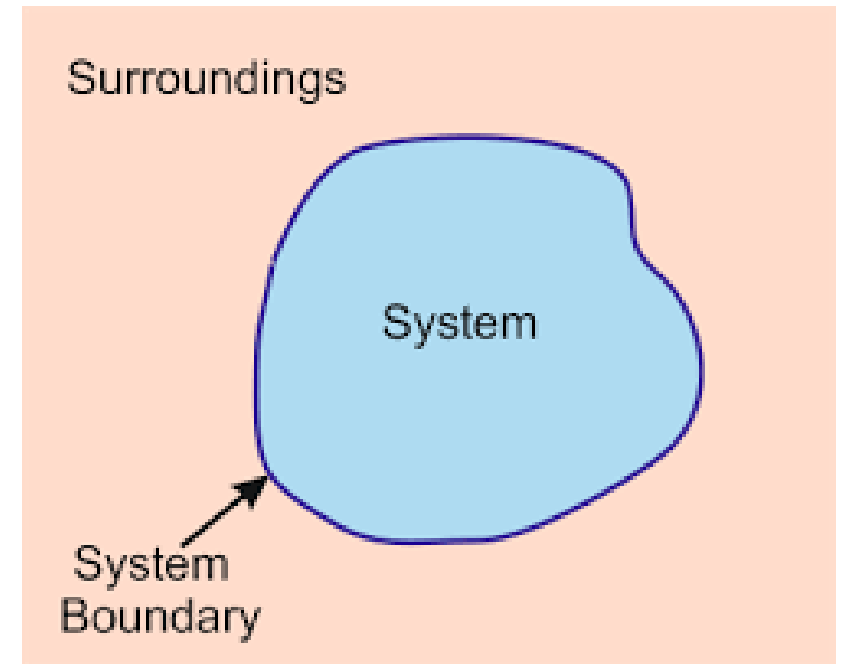
System Boundary

Types of Boundaries

Boundaries dictate how the system interacts with the world (closed or open):

Fixed vs. Movable: A boundary can be rigid (like a steel tank) or flexible (like a piston or a balloon).

Permeability: Boundaries are classified by what they allow to pass—mass, heat, or work.
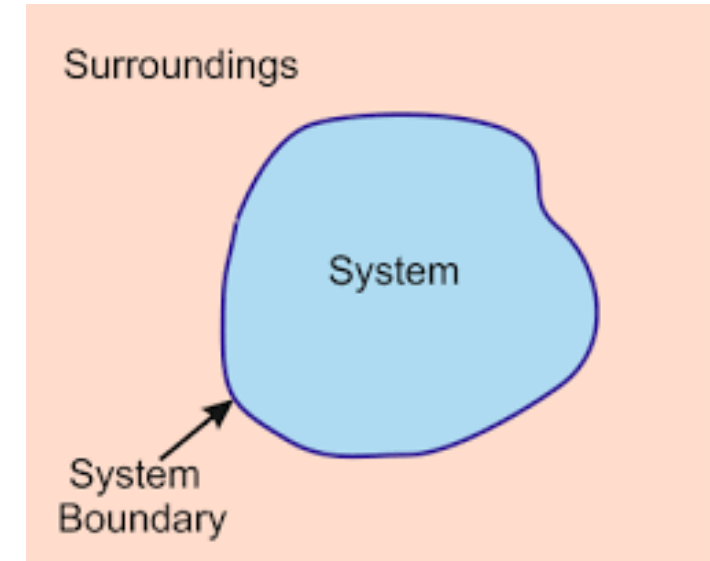

System Type	Mass Transfer?	Energy Transfer?	Example
Closed System	No	Yes (Heat/Work)	A sealed balloon or a piston-cylinder.
Open System	Yes	Yes	A turbine, nozzle, or a water heater.
Isolated System	No	No	An ideal thermos (no heat or mass exchange).

Types of Thermodynamics Walls

The nature of the boundary (the "wall") determines how a system interacts with its surroundings..

➢ **Adiabatic Walls**: An adiabatic wall is a perfect insulator. It prevents the transfer of heat (Q = 0) between the system and the surroundings.

  • Note: While heat cannot pass, energy can still be transferred as work if the wall is movable (like a piston).

➢ **Diathermal walls: I**t is a thermal conductor (e.g., a thin sheet of metal). It allows the transfer of energy as heat, enabling the system to reach thermal equilibrium with its surroundings.

It prevents the transfer of matter but allows temperatures to equalize.
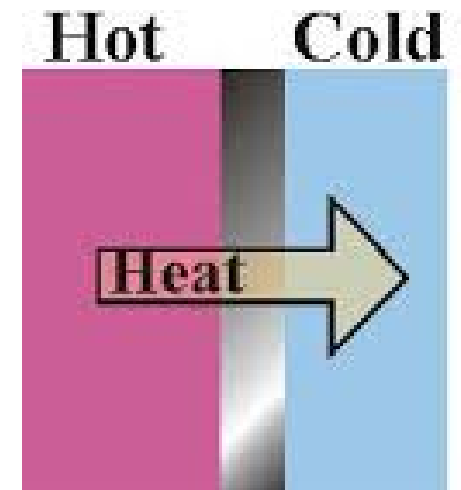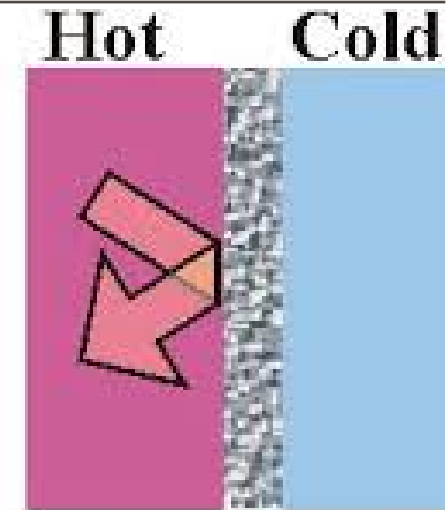
The Isolated System & Equilibrium

The Isolated System: A system is isolated only if it is contained by walls that are:

- Adiabatic (no heat transfer).

- Rigid (no work/mechanical transfer).

- Impermeable (no mass transfer).

Thermodynamic Equilibrium: If an isolated system is left undisturbed for a long enough period, it reaches a state where its macroscopic properties (like pressure, temperature, and density) no longer change over time. This state is known as Thermodynamic Equilibrium.

The Postulate of Equilibrium: All isolated systems will eventually "relax" into this stable, uniform state.

Equilibrium and Processes

Thermodynamic Equilibrium. A system is in equilibrium when its macroscopic properties are uniform throughout and do not change over time (provided the system is isolated). To reach full thermodynamic equilibrium, several conditions must be met:

- Thermal Equilibrium: The temperature is the same throughout the system.

- Mechanical Equilibrium: There are no unbalanced forces or pressure gradients.

- Phase Equilibrium: The mass of each phase (solid, liquid, gas) remains constant.

- Chemical Equilibrium: The chemical composition does not change over time.

Equilibrium and Processes

Processes and Paths. When a system moves from one equilibrium state to another, it undergoes a Thermodynamic Process.

- **Path**: The specific sequence of intermediate states the system passes through during a process.

- **Quasi-static Process**: A process that happens slowly enough that the system remains infinitesimally close to an equilibrium state at every point.

Type	Definition	Examples
State Variable (Function)	Depends only on the **current state** of the system, not how it got there. They are **path-independent**.	Pressure (P), Volume (V), Temp (T), Internal Energy (U)
Path Function	Values depend on the specific **route taken** between two states.	Heat (Q) and Work (W)

Quasi-Static vs Reversible Process

***Q**uasi-static Process (The "slow" Process):* A process that happens so slowly that the system remains in internal equilibrium at every instant.

Uniformity: Temperature (T) and Pressure (P) remain uniform throughout the system at all times.

Path: The process can be drawn as a continuous line on a P-V diagram because every intermediate point is a defined equilibrium state.


Gas

Insulation
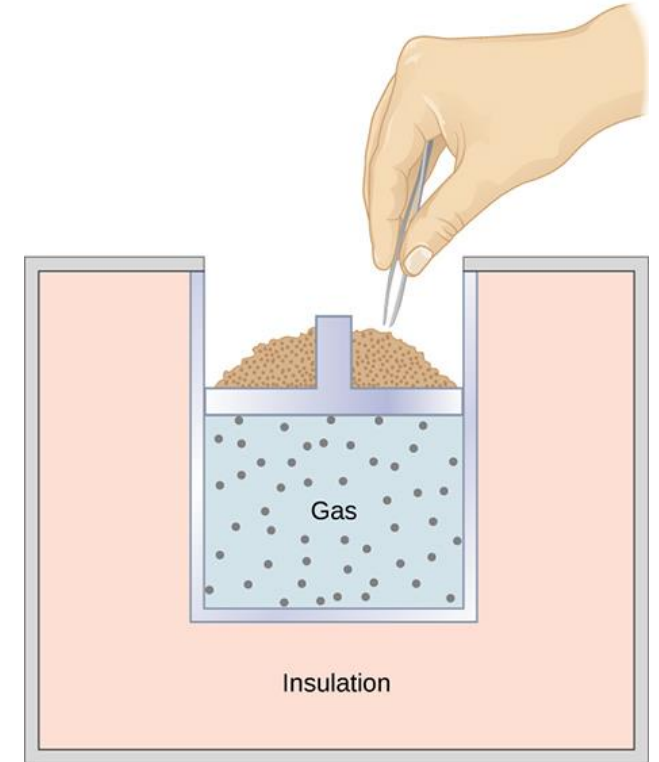
Quasi-Static vs Reversible Process

Reversible Process (The "Ideal" Process). A process is reversible if both the system and its surroundings can be returned to their exact initial states without leaving any change in the universe.

The Two Requirements for Reversibility:

1. It must be Quasi-static: The system must stay in equilibrium along the path.

2. It must be Non-Dissipative: There are no "losses" due to friction, viscosity, electrical resistance, or turbulence.

Key Distinction: All reversible processes are quasi-static, but not all quasi-static processes are reversible.


Gas

Insulation
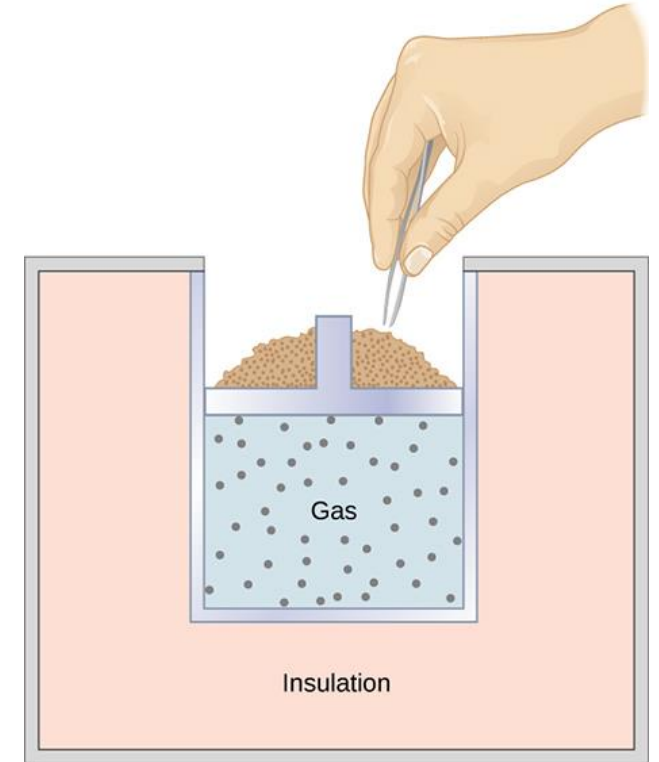
Quasi-Static vs Reversible Process

Feature	Quasi-Static Process	Reversible Process
Speed	Infinitely slow.	Infinitely slow.
Equilibrium	Maintained throughout.	Maintained throughout.
Dissipation	Can have friction (e.g., a piston moving slowly against high friction).	Zero friction or energy "loss."
Restoration	System might return, but surroundings are changed.	System and Surroundings both return to original states.

Common Thermodynamics Processes

The **prefix "ISO-"** comes from the Greek isos, meaning "equal." It designates a process where a specific property remains constant.
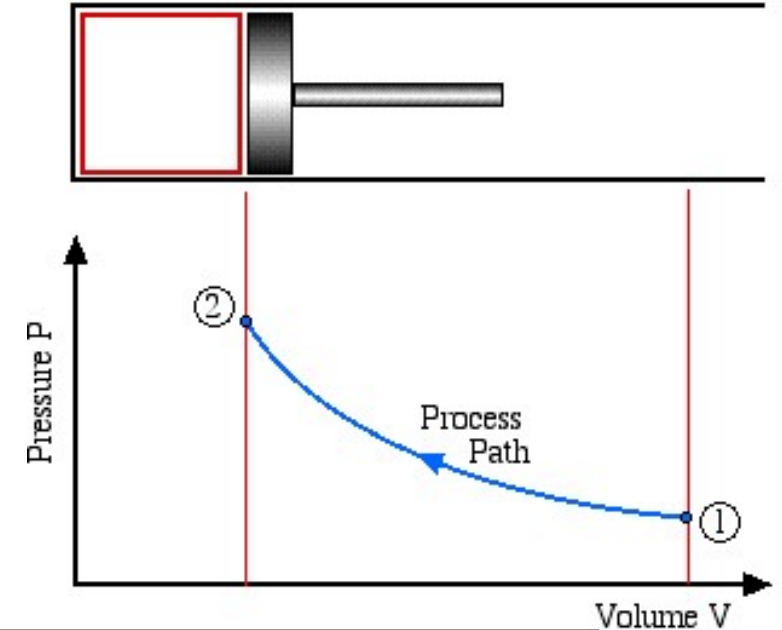

Process	Constant Property	Mathematical Condition
Isothermal	Temperature	$\Delta T = 0$ (T = constant)
Isobaric	Pressure	$\Delta P = 0$ (P = constant)
Isochoric (isometric or isovolumetric)	Volume	$\Delta V = 0$ (V = constant)

Thermodynamics Cycles

A Cycle is a sequence of processes where the system eventually returns to its initial state.

- Condition: Since the start and end points are the same, the net change in any state function (like internal energy or temperature) is zero: $\Delta U_{cycle} = 0$.

- Work & Heat: While the state doesn't change, the system can still perform net Work (W) or exchange net Heat (Q) over the course of the cycle. This is the basis for engines and refrigerators.
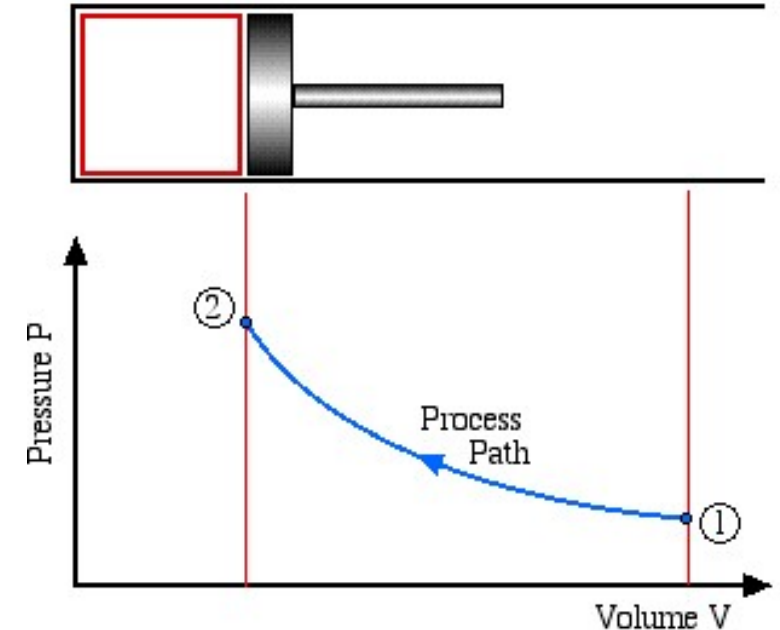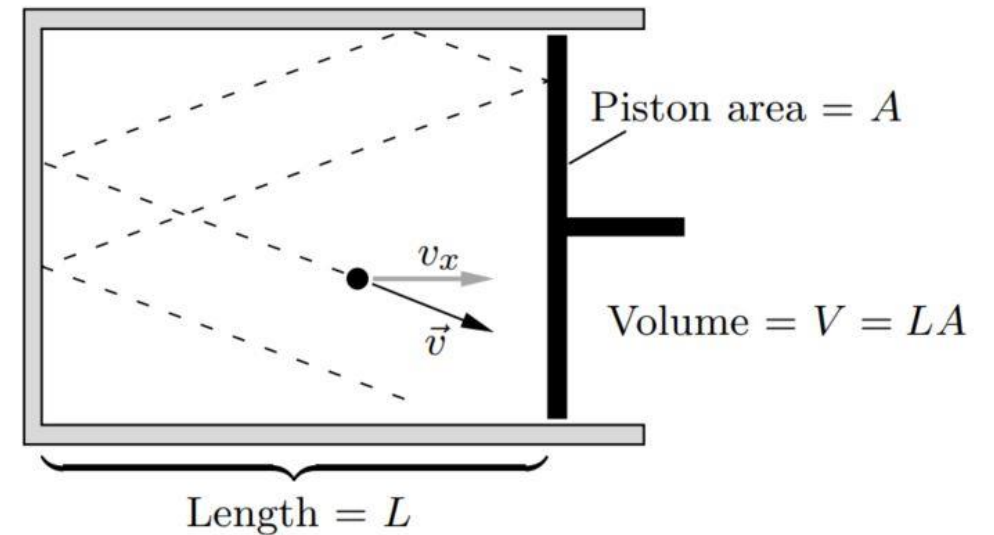
Ideal Gas

Low density gas follows the ideal gas law:
$$PV = nRT$$

Where $N = n \times N_A$

$$PV = \frac{N}{N_A} RT \Rightarrow PV = N k_B T$$

- Universal constant, R, in SI units is 8.31 J /mol.K,
- Boltzmann constant: $k_B = 1.38 \times 10^{-23} \, J/K$
- Avogadro's number: $N_A = 6.02 \times 10^{23} \, mol^{-1}$
- SI unit of pressure: $1 \, Pa = 1 \, N/m^2$
- $1 \, atm = 1.013 \times 10^5 \, Pa$
- $1 \, bar = 1 \times 10^5 \, Pa$

Piston area $= A$

Volume $= V = LA$

Length $= L$

Pressure: Microscopic Model of an Ideal Gas

Consider an **ideal gas** confined in a chamber of length L along the x-direction, with a piston (or wall) of area A. The pressure on the wall arises from **molecular collisions**. The average pressure on the piston is defined as :

Piston area $= A$

Volume $= V = LA$

Length $= L$

$$\vec{P} = \frac{F_x}{A}$$

By Newton's third law,
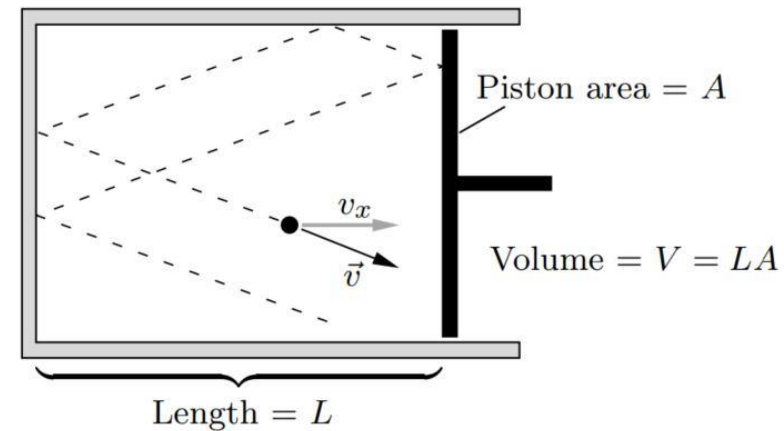
$$F_{x,on\ piston} = -F_{x,on\ molecule}$$

For a gas molecule of mass m with velocity component v_x

- Time between successive collisions with the same wall:

$$\Delta t = \frac{2L}{v_x}$$

Change in momentum during an elastic collision:

$$\Delta v_x = v_{x,final} - v_{x,initial} = (-v_x) - (v_x) = -2\,v_x$$

Pressure: Microscopic Model of an Ideal Gas

The average force on molecule is:

$$\vec{F}_{x,\,gas} = m\left(\frac{\Delta v_x}{\Delta t}\right) = m\left(-\frac{2v_x}{2L/v_x}\right) = -\frac{mv_x^2}{L}$$

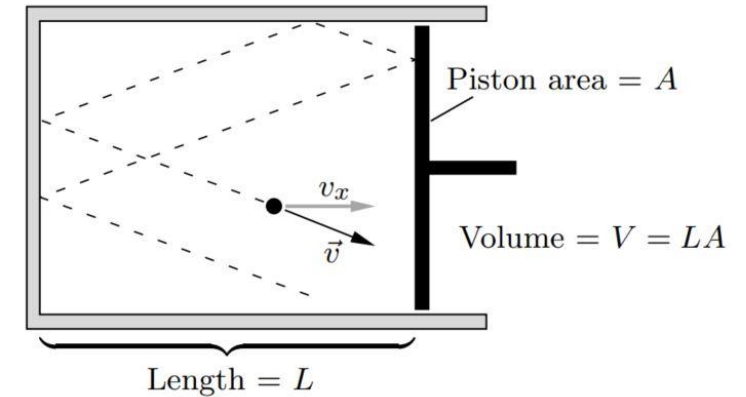The negative sign indicated the force direction; the pressure depends on the magnitude.

The pressure becomes on the wall

$$P = -\frac{F_{x,gas}}{A} = -\left(\frac{mv_x^2}{L\,A}\right) = \frac{mv_x^2}{V}$$

Where the volume $V = AL$

For a gas with many molecules and isotropic motion, this result is averaged over all molecules, leading to:

$$P = \frac{1}{3}\frac{Nm\langle v^2\rangle}{V}$$

Piston area $= A$

v_x

Volume $= V = LA$

Length $= L$

Average Pressure and Molecular Kinetic Energy

From the kinetic-theory derivation, the average pressure satisfies

$$PV = mv_{1x}^2 + mv_{2x}^2 + m\,v_{3x}^2 + \cdots$$

For a gas containing a large number NN of molecules, this becomes

$$PV = Nm\,\overline{v_x^2} = Nm\langle v_x^2\rangle$$

where $\overline{v_x^2}$ is mean square x-component of the molecular velocity.

Relation to Temperature

$$kT = m\langle v_x^2\rangle \Rightarrow \frac{1}{2}m\langle v_x^2\rangle = \frac{1}{2}k_B T$$

The average translational kinetic energy is then

$$\langle K_{trans}\rangle = \frac{1}{2}m\left(\overline{v_x^2 + v_y^2 + v_z^2}\right) = \frac{3}{2}k_B T$$

Since molecular motion is isotropic $\langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_z^2\rangle$

Root-Mean-Square (RMS) Speed

The root-mean-square (rms) speed of molecules in an ideal gas is defined as

$$v_{rms} \equiv \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3 k_B T}{m}}$$

Thermal energy at room temperature:

In SI units

$$k_B T = \left(1. \times 10^{-23} \frac{J}{K} \right) (300 K) = 4.14 \times 10^{-21} J$$

In electron-volts

$$k_B T = \left(8.62 \times 10^{-5} \frac{eV}{K} \right) (300 K) = 0.026 \, eV \approx \frac{1}{40} \, eV$$

Equipartition Theorem

The Equipartition Theorem is not restricted to translational kinetic energy. Each independent quadratic term in the energy is called a degree of freedom.

Examples of quadratic degrees of freedom include:

- Translational kinetic energy:

$$\frac{1}{2}mv_x^2, \qquad \frac{1}{2}mv_y^2, \qquad \frac{1}{2}mv_z^2$$

- Rotational kinetic energy:

$$\frac{1}{2}I\omega_x^2, \qquad \frac{1}{2}I\omega_y^2,$$

- Vibrational (elastic) potential energy:

$$\frac{1}{2}k_s x^2$$

Equipartition Theorem

At temperature T, the average energy associated with each quadratic degree of freedom is
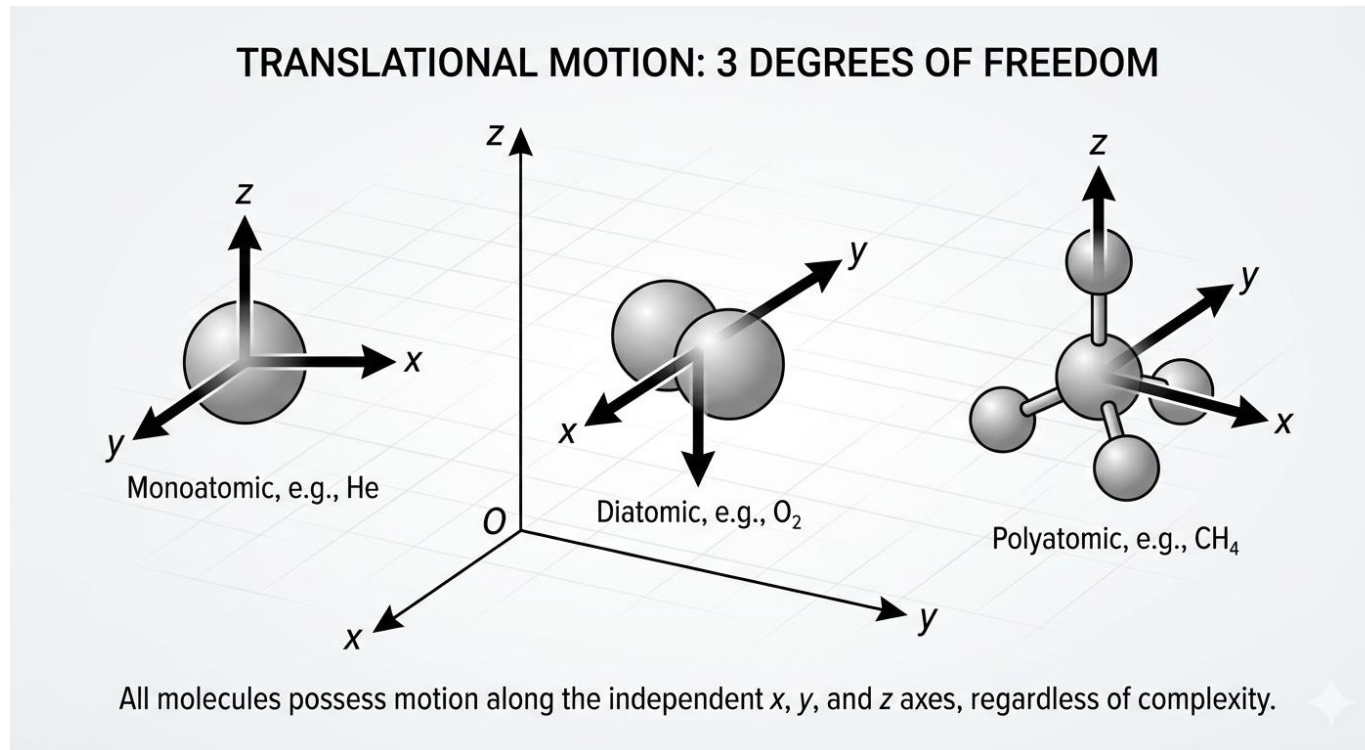
$$\frac{1}{2}kT$$

Total Thermal Energy

For a system of N molecules, each having f active quadratic degrees of freedom (with no other temperature-dependent energy contributions),

$$U = N.f.\frac{1}{2}\,kT$$

Translational Motion

All molecules (mono-, di-, and polyatomic) have 3 translational degrees of freedom

$\rightarrow$ motion along the x, y, and z directions; Transilational Energy $\frac{1}{2}mv_x^2$, $\frac{1}{2}mv_y^2$, and $\frac{1}{2}mv_z^2$

TRANSLATIONAL MOTION: 3 DEGREES OF FREEDOM

Monoatomic, e.g., He

Diatomic, e.g., O_2

Polyatomic, e.g., CH_4

All molecules possess motion along the independent x, y, and z axes, regardless of complexity.

Rotational Motion

- **Diatomic and linear molecules** (e.g., **CO, N₂, CO₂**):
  - Can rotate about two axes perpendicular to the molecular axis
  - Rotation about the bond axis contributes negligible moment of inertia
  - Rotational degrees of freedom = 2

- **Nonlinear polyatomic molecules** (e.g., **H₂O, CH₄**):
  - Can rotate about all three principal axes
  - Rotational degrees of freedom = 3

LINEAR MOLECULES
(2 Rotational DOF)

Rotation around x

Rotation around y

Negligible moment of inertia (z)

e.g., N₂

e.g., CO₂

Rotational Degrees of Freedom = 2

NONLINEAR POLYATOMIC MOLECULES
(3 Rotational DOF)

Rotation around x

Rotation around y

Rotation around x

e.g., H₂O

e.g., CH₄

Rotational Degrees of Freedom = 3
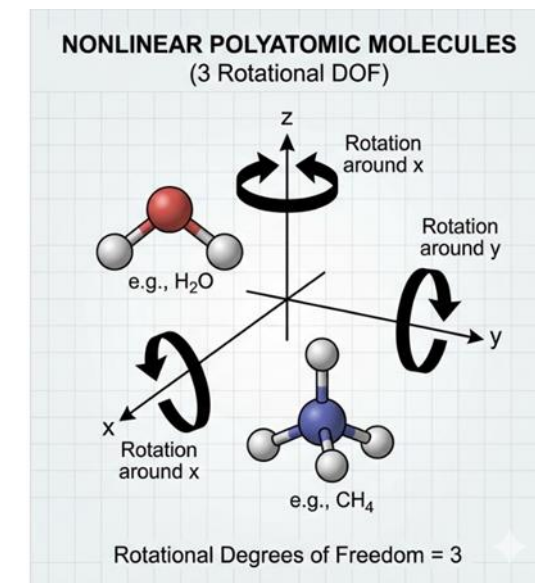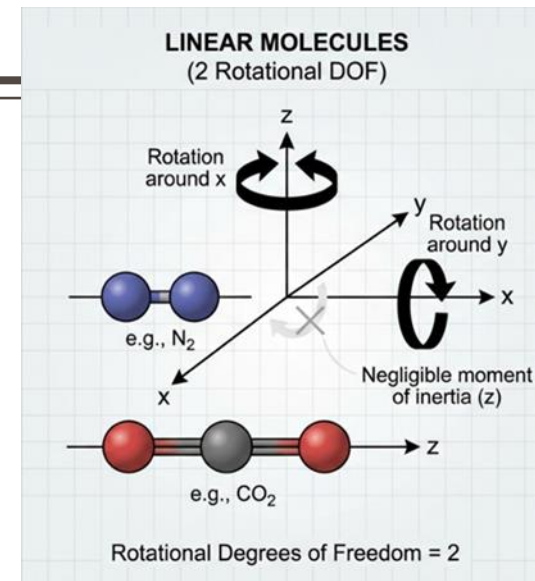
Vibrational Motion

- Molecules can vibrate through **stretching, bending, twisting**, etc.

- Each **normal mode of vibration contributes two degrees of freedom** (one kinetic + one potential).

- Number of vibrational modes depends on molecular geometry:
  - Linear *molecules:* $3N - 5$
  - Nonlinear *molecules:* $3N - 6$

Summary

Molecule Type	Translation	Rotation	Vibration	Total (3N)
Monatomic (e.g., He)	3	0	0	3
Linear (e.g., CO_2)	3	2	$3N - 5$	3N
Non-linear (e.g., H_2O)	3	3	3N - 6	3N

First Law of Thermodynamics (Conservation of Energy)

Energy can be neither created nor destroyed during a physical process; it can only be transferred or transformed from one form to another. This principle is known as the conservation of energy.

Mathematically, the First Law of Thermodynamics is written as
$$dU = dQ + dW$$

For a reversible process, work can be expressed as
$$dW = -P\, dV$$

which is equivalent to the familiar idea of $force \times distance$

- Compression, $dV < 0 \Rightarrow dW > 0$ where we are doing work on the system by squeezing

- Expansion $dV > 0 \Rightarrow dW < 0$ where work is done by the system

Generalized (Configuration) Work

Let X_i denote an extensive variable and y_i its corresponding intensive conjugate variable. For a reversible process, the differential configuration (generalized) work is given by

$$\partial W_{conf} = \sum_i y_i dX_i$$

System	Intensive	Extensive	Work
Gas, Liquid or Solid	Pressure, P	Volume, V	PdV
Film	Surface Tension, γ	Area, A	γdA
Magnetic Material	Magnetic Field, B	Magnetization, M	BdM
Dielectric Material	Electric Field, E	Polarization, P	EdP

First Law of Thermodynamics

Suppose now that we vary the state of a system through two different quasi-static paths. The change in energy is independent of the path taken: In contrast the work done
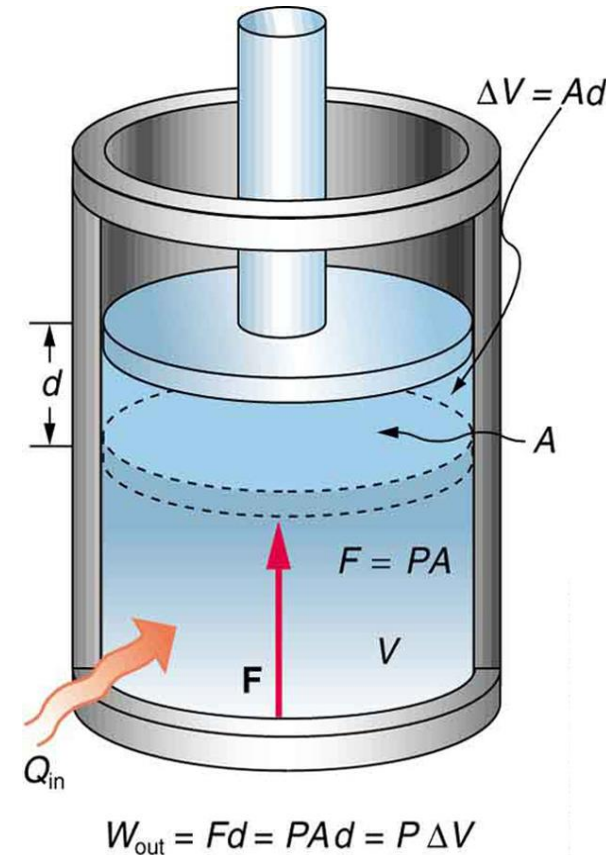
$$\oint dU = U(P_2, V_2) - U(P_1, V_1) = 0 \text{ (Internal energy is unchanged)}$$

Depends on the path taken:

$$\oint \partial W = \oint P\, dV = \oint \partial Q \neq 0$$

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

$$W_{gas} = \int_{V_i}^{V_f} \frac{N k_B T}{V}\, dV = N k_B T \, Log\left(\frac{V_f}{V_i}\right)$$

$\Delta V = Ad$

$F = PA$

$W_{out} = Fd = PAd = P\Delta V$

First Law of Thermodynamics

(a)
a. isochoric
b. isobaric

$$W = p_2(V_2 - V_1)$$

(b)
a. isobaric
b. isochoric

$$W = p_1(V_2 - V_1)$$

(c)
isothermal

$$W = \int_{V_i}^{V_f} p\, dV$$
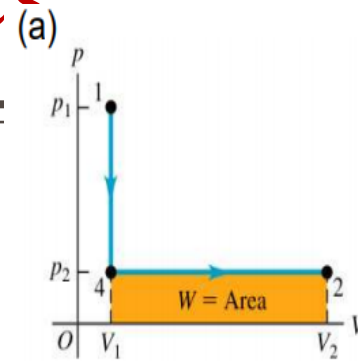
Let us consider a couple of other examples: Isobaric configuration work (constant pressure).

$$W_{gas} = \int_{V_{init}}^{V_{fin}} P_{gas}\, dV = P_{gas}(V_f - V_i)$$

Isochoric configuration work: isochoric means constant volume. So, $dV = 0$, which means that
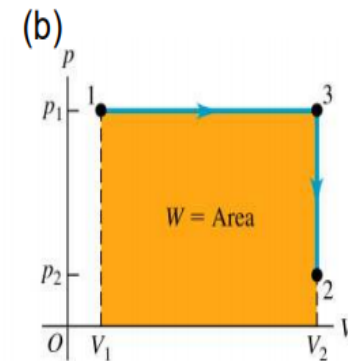
$$W_{gas} = \int_{V_{init}}^{V_{fin}} P_{gas}\, dV = 0$$

The work done equal to area under the curve. The work done in any is under the PV curve which yield to W_{net}.
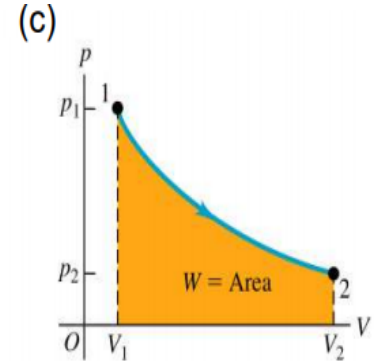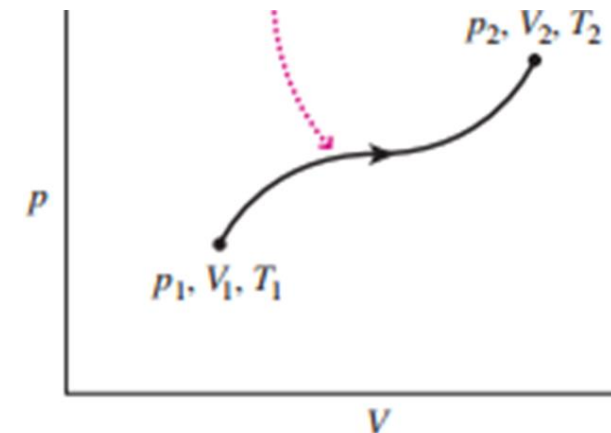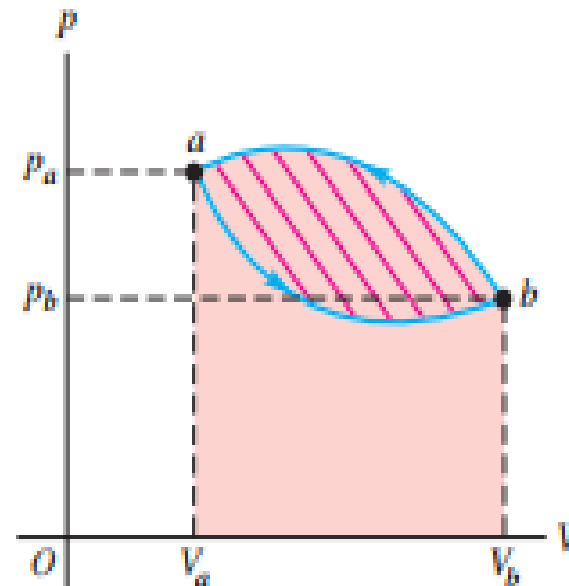
Example 2.1

Calculate what is the work done by a van der Waals gas when it expands isothermally from an initial volume v_i to a final volume v_f.

Hints: Van der Waals equation is $\left(P + \dfrac{a}{v^2} \right)(v - b) = k_B T$

Heat Capacity

Heat capacity is a property of a system that quantifies how much the system's temperature changes when energy is added as heat, along a specified thermodynamic path.

$$C_x = \frac{(energy\ input\ through\ heating\ along\ path\ x)}{(change\ in\ the\ temperature\ of\ the\ system)} = \left(\frac{\delta Q}{\delta T}\right)_x$$

Where,
- δQ= heat added to the system
- dT= resulting temperature change
- x specifies the thermodynamic constraint (path)

Heat Capacity

Common Heat Capacities
- **Constant volume:**

$$C_V = \left(\frac{\delta Q}{dT}\right)_V$$

- **Constant pressure:**

$$C_P = \left(\frac{\delta Q}{dT}\right)_P$$

Other examples (less common):
- Along saturation curve: C_{sat}
- Constant external field: C_H

Heat Capacity

Specific heat capacity refers to heat capacity **per unit mass**:

$$c = \frac{C}{m}$$

Heat transfer relation:

$$Q = mc\Delta T$$

Where,

- Q= heat added
- m= mass
- c= specific heat capacity
- ΔT= temperature change

Units
Heat capacity C: J·K^{-1}
Specific heat capacity c: J·kg^{-1}·K^{-1}

Heat Capacity at constant volume (Cv)

At constant volume for an ideal monoatomic gas:

$dU = dQ$ and $U = N\,\frac{3}{2}k_B T$, we get

$$C_V = \frac{\Delta Q_V}{\Delta T_V} = \frac{\Delta U}{\Delta T_V} = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial\,\frac{3Nk_B T}{2}}{\partial T}\right)_V$$

$$C_V = \frac{3Nk_B}{2} = \frac{3}{2}nR$$

Heat Capacity at constant volume (Cv)

We adopt the convention that dWdW is the work done on the system. The First Law is written as

$$dU = dQ + dW$$

Pressure-Volume work (Reversible Process): $dW = -PdV$

Heat Transfer Expressions, from the first law

$$dQ = dU - dW$$

- Work done on the system (compression):

$$dW > 0 \Rightarrow dQ = dU - dW = dU - |dW|$$

- Work done by the system (expansion):

$$dW < 0 \Rightarrow dQ = dU - dW = dU + |dW|$$

Heat Capacity at Constant Pressure (Cp)

The first law is

$$\mathrm{d}U = dQ + dW \text{ (by the system)}$$

The work done by the system is PdV,

$$dW = -PdV \Rightarrow dQ = dU + PdV$$

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

For an ideal monatomic gas, the internal energy depends only on temperature,

$$U = \frac{3}{2}Nk_BT \Rightarrow \left(\frac{\partial U}{\partial T}\right)_P = \frac{3}{2}Nk_BT = C_V$$

Heat Capacity at Constant Pressure (Cp)

Second term become using $PV = Nk_BT$

$$P\left(\frac{\partial V}{\partial T}\right)_P = P\frac{Nk_B}{P}\left(\frac{\partial T}{\partial T}\right)_P = Nk_B$$

So, for isobaric process:

$$C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P = C_V + Nk_B$$

Using $N = nN_A$ and $R = N_Ak_B$ is the universal gas constant

$$C_P = C_V + nR$$

Heat Capacity at Constant Pressure (Cp)

The physical meaning of $C_P > C_V$:

For a process at constant pressure, part of the energy transmitted to the system through heating goes into increasing the internal energy of the system, U, and part goes into performing work on the surroundings, doing expansion work, at constant pressure.

Example 2-2

You are told that the heat capacity at constant pressure, C_P, of a material varies as:

$C_P = N\left(a + bT - \dfrac{c}{T^2}\right)$ where a, b, and c are constants and N is the number of particles in the material.

Calculate the total energy transferred to the material through heating in an isobaric process in which the temperature is increased from T_o to $2T_o$.

Heat Capacity of Ideal gas

Heat capacity at constant volume, $C_V = \left(\dfrac{\partial U}{\partial T}\right)_V$

We don't want to confuse between specific heat capacity and heat capacity where specific heat capacity is $c = C/m$.

$$dQ = dU - dW = C_V dT + PdV$$

where $dW = -pdV$ and For adiabatic processes:

$$dQ = 0 \Rightarrow dT = -\frac{PdV}{C_V}$$

Recalling ideal gas equation, $PV = nRT$

$$T = \frac{PV}{nR} \quad \rightarrow \quad dT = \frac{PdV + VdP}{nR}$$

Heat Capacity of Ideal gas

We get

$$0 = PdV \left[\frac{nR + C_V}{C_V} \right] + VdP$$

Recalling $nR + C_V = C_P$

$$0 = PdV \left[\frac{C_P}{C_V} \right] + VdP = \gamma PdV + VdP$$

Where, $\gamma = C_P/C_V$

$$\gamma \frac{dV}{V} + \frac{dP}{P} = 0$$

Heat Capacity of Ideal gas

$$\gamma \frac{dV}{V} + \frac{dP}{P} = 0$$

By integrating

$$\gamma \ln(V) + \ln(P) = constant$$

$$\ln(V^\gamma) + \ln(P) = constant$$

$$PV^\gamma = constant$$

The above equation is for ideal gases, and recalling γ:

$$\gamma = \frac{C_p}{C_V} = \frac{(C_V + nR)}{C_V} = 1 + \frac{2}{f}$$

Where $U = n\,f\left(\frac{1}{2}RT\right) = C_V T \Rightarrow C_V = \frac{1}{2}n\,fR$, f is degrees of freedom.

Heat Capacity of Ideal gas

i. Monoatomic: $\gamma = 1 + \dfrac{2}{f} = 1 + \dfrac{2}{3} = 1.67$

ii. Diatomic: $\gamma = 1 + \dfrac{2}{f} = 1 + \dfrac{2}{5} = 1.40$

iii. Polyatomic: $\gamma = 1 + \dfrac{2}{f} = 1 + \dfrac{2}{6} = 1.33$

Now using the ideal gas equation $PV = nRT$, the above expression can rederived as

$$PV^{\gamma} = constant \rightarrow TV^{\gamma-1} = constant$$

And

$$\frac{T^{\gamma}}{P^{\gamma-1}} = constant$$

Degree of freedom for translation motion is 3 for atoms and molecules, but degree of freedom for rotation and frequency is depended on temperature.

Degrees of Freedom and Temperature Dependence

- Translational motion: 3 degree of freedom for all atoms and molecules and **is active at essentially all temperatures**.

Rotational and vibrational degrees of freedom **depend on temperature because their energy levels are quantized**.

- Rotational motion: linear molecule has 2 degree of freedom and polymolecule has 3 degree of freedom.

- Vibrational motion: linear molecule has $3N - 5$ of degree of freedom and polymolecule has $3N - 6$.

Degrees of Freedom and Temperature Dependence

For Example, Diatomic Molecule H_2

Low temperatures: Only translational motion is appreciably excited. Rotational and vibrational modes are "frozen out" due to large energy spacing between quantum levels.

Moderate temperatures ($\approx$ 100–300 K): Rotational degrees of freedom become active. Vibrational motion remains frozen out.

High temperatures ($\gtrsim$ **1000 K**): Vibrational degrees of freedom become active, contributing to the heat capacity
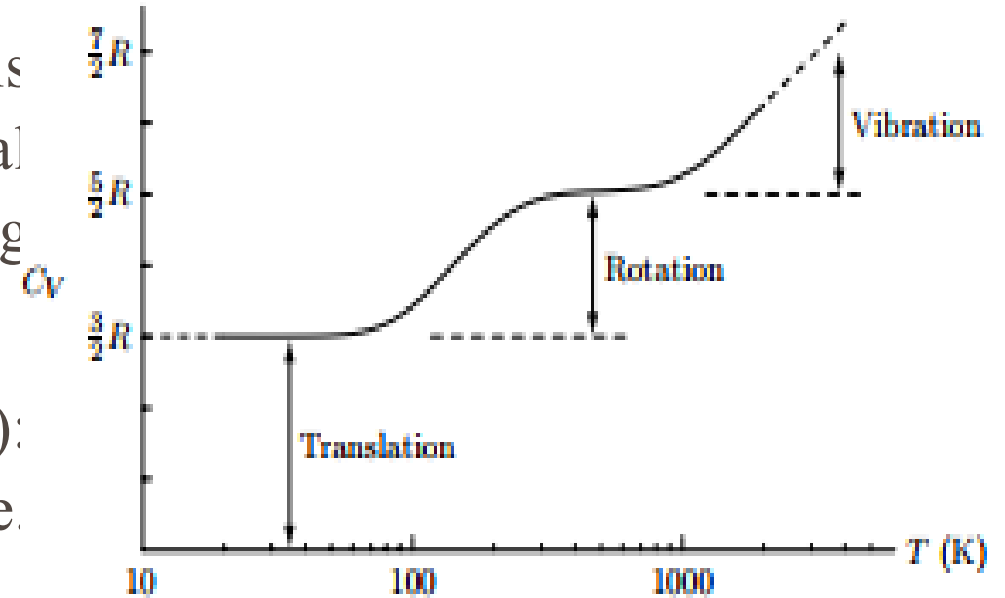
Heat capacity at constant volume of one mole of hydrogen (H2) gas as temperature.

Degrees of Freedom and Temperature Dependence

- The activation of degrees of freedom is determined by thermal energy relative to quantum level spacing, not by phase changes.

- H_2 becomes liquid only under specific pressure conditions; phase is not required for rotational or vibrational modes to freeze out.
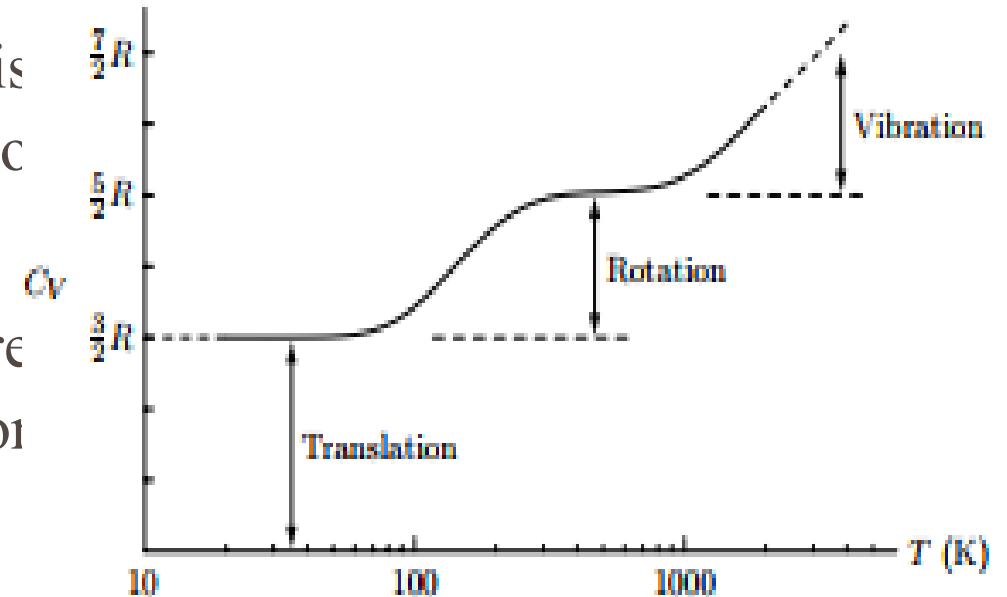
Heat capacity at constant volume of one mole of hydrogen (H2) gas as temperature.

Thermodynamic State

The state of a system is its condition at a specific moment, uniquely defined by its macroscopic properties (e.g., P, V, T, ρ, N).

The State Postulate: For a simple compressible system (one chemical species with a fixed number of particles), the state is uniquely determined by specifying two independent, intensive properties.

The Example of a Gas:

- If you define Pressure (P) and Volume (V), all other properties—such as Temperature (T), density (ρ), and even "secondary" properties like viscosity or thermal conductivity—are automatically fixed.

- These properties can be mapped on a state space (e.g., a PV diagram).

Thank you very much for your attention