THERMODYNAMICS

Is an empirical science. All the laws are experimentally founded.

Concerned with macroscopic variables — the gross measurable properties of a system — on human scale, and we feel the effect with our senses.
(long-standing observation)

Averages of variables pertaining to microscopic phenomena
(statistical attribute)

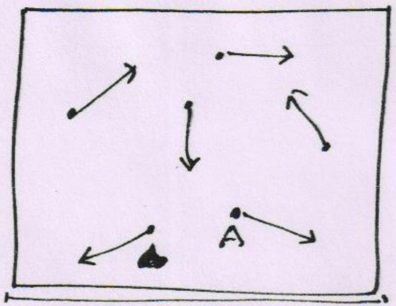
Examples:

1/. Pressure is a measure of the average force exerted by particles in a gas on the container walls.

2/. Temperature is a measure of the average kinetic energy possessed by the particles.

DIMENSIONAL TREATMENT

Cubic volume of edge l



Particles are moving freely with velocities $\vec{V}_1, \vec{V}_2, \vec{V}_3, \ldots \vec{V}_N$ (N number of particles).

x-components are: $\vec{V}_{1x}, \vec{V}_{2x}, \vec{V}_{3x}, \ldots, \vec{V}_{Nx}$

Change of momentum ~~of~~ due to a Single particle striking the Container wall elastically, is

$$\Delta p_1 = m v_{1x} - (-m v_{1x}) = 2 m v_{1x}$$

Time taken for this strike is, $\Delta t \sim \frac{2l}{v_{1x}}$

Time Rate of momentum change is

Force, $F_1 = \frac{2 m v_{1x}}{\Delta t} \sim \frac{2 m v_{1x}}{2l/v_{1x}}$

$\left(F_1 = \frac{\Delta p_1}{\Delta t} \right)$

$$\Rightarrow F_1 \sim \frac{m v_{1x}^2}{l}$$

Total force, $F = F_1 + F_2 + \dots + F_N$

$$F \sim \frac{m}{l}\left(V_{1x}^2 + V_{2x}^2 + \cdots + V_{Nx}^2\right)$$

(all particles have the same mass).

$$\Rightarrow \quad F \sim \frac{m}{l} N \frac{\left(V_{1x}^2 + V_{2x}^2 + \cdots + V_{Nx}^2\right)}{N}$$

$$\Rightarrow \quad F \sim \frac{m}{l} N \langle V_x^2 \rangle$$

$$\langle v^2 \rangle = \langle V_x^2 \rangle + \langle V_y^2 \rangle + \langle V_z^2 \rangle$$

And $\langle V_x^2 \rangle = \langle V_y^2 \rangle = \langle V_z^2 \rangle$

(By the Equipartition Theorem)

How?

$$\therefore \quad \langle v^2 \rangle = 3 \langle V_x^2 \rangle \Rightarrow \langle V_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle$$

$$\Rightarrow \quad F \sim \frac{m N}{l} \frac{1}{3} \langle v^2 \rangle$$

Pressure, $P = \dfrac{F}{\text{Area}}$ | $F \rightarrow$ Average force

$$\Rightarrow \quad P \approx \frac{F}{l^2} \sim \left[\frac{mN}{3l}\langle v^2\rangle\right]\frac{1}{l^2}$$

$$\Rightarrow \quad \boxed{P \sim \frac{1}{l^2}\left(\frac{mN}{3l}\langle v^2\rangle\right)}$$

Microscopic to macroscopic relation

Assumptions (Ideal gas):

1/. Non-interactive particles. Only interaction is collision.

2/. Point-like particles (particles occupy negligible volume compared to the volume of the gas). Valid assumption for a very dilute gas

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$$\text{Pressure} = \frac{\text{Energy}}{\text{Volume}}$$

Ideal Gas Equation of State.

$$PV = nRT \quad , \quad V = l^3 .$$

$$\therefore \; Pl^3 = nRT \sim \frac{mN}{3} \langle v^2 \rangle$$

$N = nN_A$ $\quad$ $n \rightarrow$ No. of moles

$N_A \rightarrow$ Avogadro's Number.

$$\therefore \; \cancel{n}RT \sim \frac{m \cancel{n} N_A}{3} \langle v^2 \rangle$$

$$\boxed{\sqrt{\langle v^2 \rangle} \propto \frac{1}{\sqrt{m}}}$$

$$\Rightarrow \; \frac{3}{2} \frac{RT}{N_A} \sim \frac{1}{2} m \langle v^2 \rangle$$

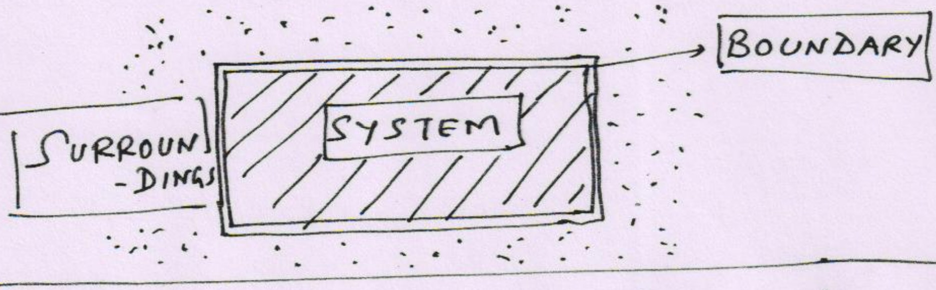
$$\Rightarrow \; \boxed{\frac{1}{2} m \langle v^2 \rangle \sim \frac{3}{2} k_B T}$$

1/. Temperature is an <u>average measure</u> of the kinetic energy.

2/. What is the temperature of a single-particle system?

Definitions :

A System is a restricted region in space with a finite portion of matter (or even radiation) separated from the surroundings by a boundary (a closed surface).



1/. Open Systems : Allows exchange of matter.

2/. Closed Systems : does not allow exchange of matter, but only exchange of energy.

3/. Isolated Systems : Does not allow exchange of either matter or energy.

Thermodynamic Coordinates:

In mechanics, to study a distributed system (eg. a rigid body), the chosen variables (coordinates) are position, velocity, time etc. All are mechanical coordinates, pertaining to physical properties EXTERNAL to the system

Thermodynamics looks into the INTERIOR of a distributed system, choosing an appropriate set? of THERMODYNAMIC COORDINATES, all to be determined under EQUILIBRIUM CONDITIONS. Eg. (P, V, T)

[FOR A SINGLE PARTICLE?] [Hydrostatic system]

EQUILIBRIUM : Exists between two systems, with respect to a chosen thermodynamic coordinate, if that coordinate does not change in time, and also remains statistically the same all throughout within a system

No.	Type of Equilibrium	Disrupting Cause	Restorative exchange
1/.	Mechanical	Pressure difference	Exchange of volume.
2/.	Chemical/ Diffusive	Density Difference	Exchange of matter (particles).
3/.	Thermal	Temperature difference	Energy exchange

(Hydrostatic System).

Equilibrium is restored on a relaxation time scale.

THERMODYNAMIC EQUILIBRIUM : When all three Conditions are met.

Intensive and Extensive Coordinates

Intensive Variables: Independent of the size of the system. All are local variables like pressure, density, temperature.

Extensive Variables: Proportional to the system size. All are global variables like ~~pressure,~~ mass, volume etc.

Thermodynamic Equilibrium is disrupted by changing intensive variables. Equilibrium is restored by changing extensive coordinates

Examples:

	Intensive (X)	Extensive (Y)
1/.	Force	Displacement
2/.	Surface tension	Area
3/.	Pressure (Hydrostatic System)	Volume
4/.	E. M. F.	Charge
5/.	Electric field, $\vec{E}$.	Total polarisation $\vec{P} \equiv \sum_i \vec{p}_i$
6/.	Magnetic field, $(\vec{H}\mu_0)$ $\downarrow$ $\vec{B}$	Total magnetisation $\vec{M} \equiv \sum_i \vec{m}_i$

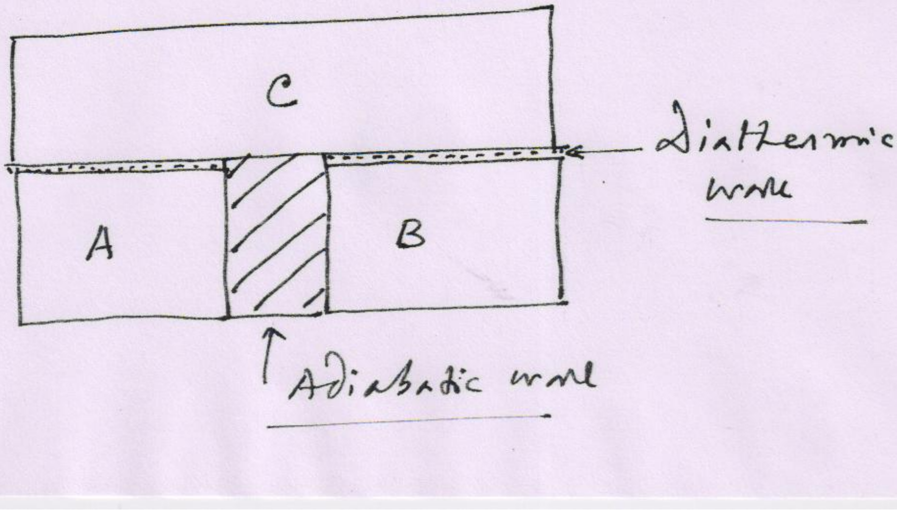
Product will always have the dimension of energy.

Thermodynamic Coordinates: (X, Y, T)

(Ralph Fowler)

Zeroth Law of Thermodynamics

Two systems separated from each other by an adiabatic wall (a wall is always a boundary), but separately in thermal equilibrium with a third system, which is separated by a diathermic wall, are also in thermal equilibrium with each other.



1/. Why "ZEROTH"?

Second Law
(Carnot)

First Law
(Kelvin + Helmholtz)

2/. Zeroth law and the concept of heat.

3/. Zeroth law and the concept of temperature.
Temperature is the equilibrium quantity.

4/. Makes NO reference to the nature of the system.

5/. Temperature is a scalar.

6/. What is the microscopic picture?

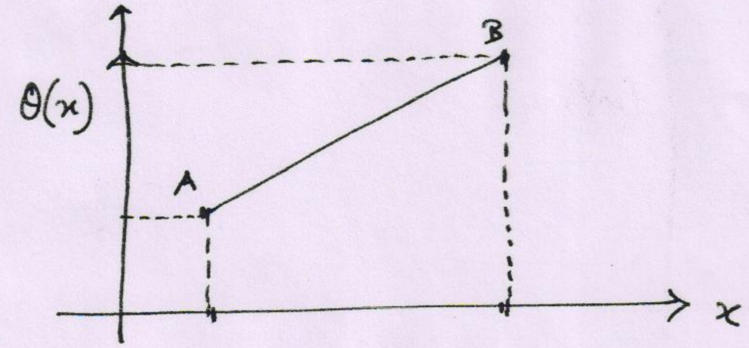
Thermometry : (Measuring Temperature)

$$\theta(x) = a + bx$$

$x \rightarrow$ Thermometric property,

E.g. Volume expansion (of Hg), resistance, etc.

Linear Scaling of temperature with a thermometric property.



1/ Centigrade Scale : Freezing and Boiling points of water. In between there are 100 steps.

Carolus Linnaeus

2/. <u>Celsius Scale</u>: Triple point of water (ice, liquid and gaseous phases in equilibrium). Step size as in centigrade scale. —— Anders Celsius

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3/. <u>Absolute Temperature scale</u>: (Kelvin)

$$p = \frac{AT}{V} = \frac{A}{V}(\theta + B) = \left(\frac{A}{V}\right)\theta + \frac{AB}{V}$$

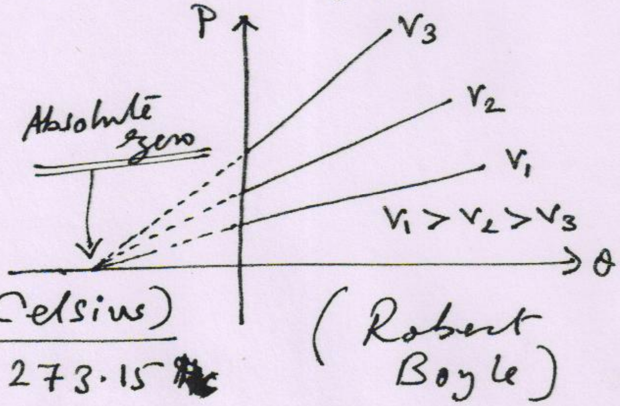
When $p = 0$,

$\theta = -B$

$B = 273.15\ ^\circ c$

(step size as in Celsius)

$T = \theta(^\circ c) + 273.15$ [illegible]



(Robert Boyle)

4/. <u>Fahrenheit</u>: Melting point of ice at 32°F.
Boiling point of water at 212°F
(180 steps in between)

5/. <u>Rankine</u>: Reference point is the <u>Absolute zero</u>, but step size is of <u>the</u> Fahrenheit scale.

Equation of State: (In a hydrostatic system)

A system is in thermodynamic equilibrium, when it is separately in mechanical, chemical and thermal equilibrium.

A hydrostatic system is governed by 3 coordinates, P, V, T. Under Equilibrium (when thermodynamic Coordinates refer to the system as a whole) Conditions, $f(P, V, T) = 0$

- An Equation of State

For Change of State?

1/. Experimentally determined.

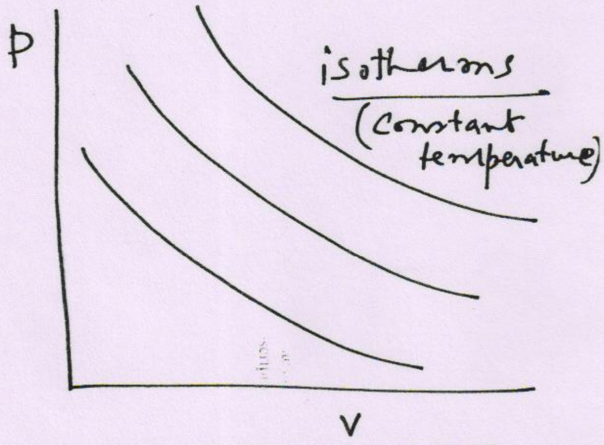
2/. Only two variables need to be specified independently.

The Ideal Gas Equation of State

$$pV = \alpha T$$

$$\alpha = nR$$

$$n = \frac{N}{N_A}$$



$$\boxed{pV = nRT = N\left(\frac{R}{N_A}\right)T = Nk_BT}$$

$$p = \frac{(Nm)}{V}\,\frac{k_BT}{m}$$

$m \rightarrow$ mass of a single particle.

$$\rho = \frac{Nm}{V}$$

$$\Rightarrow \boxed{p = \frac{\rho k_B T}{m}}$$

All in intensive variables.

Why? Needed for open systems.

Work : Force × displacement

Generalise to

i/. Intensive coordinate
× extensive coordinate

ii/. Always will have the dimension of energy.

iii/. $X\,dY$ in the (X, Y, T) form of thermodynamic coordinates

iv/. $X \longrightarrow$ Generalised "force"

$Y \longrightarrow$ Generalised "displacement".

Quasi-static Process:

Static ⇒ Equilibrium

In equilibrium, $V \equiv V(P, T)$
and/or $P \equiv P(V, T)$

$$dw = p\,dV \quad (\overset{dV\equiv}{\text{change}} \text{ in } V).$$

⇒ loss of equilibrium.

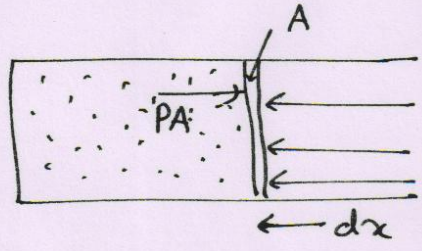
1/. Variations are infinitesimally small, and carried out very slowly.

2/. Small relaxation time scales.

3/. Infinitesimally small perturbation on an equilibrium (static) state.
⇒ $\boxed{\text{Quasi-Static}}$

Work in a Hydrostatic System

$$dw = (PA)\,dx$$
$$= P(A\,dx)$$



$\Rightarrow dW = P\,dV$ (External Work?)

(What is external work?)

Sign Convention:

$$\text{đ}W = -p\,dV$$ | Why the đ?

$dV < 0, \Rightarrow \text{đ}W > 0$

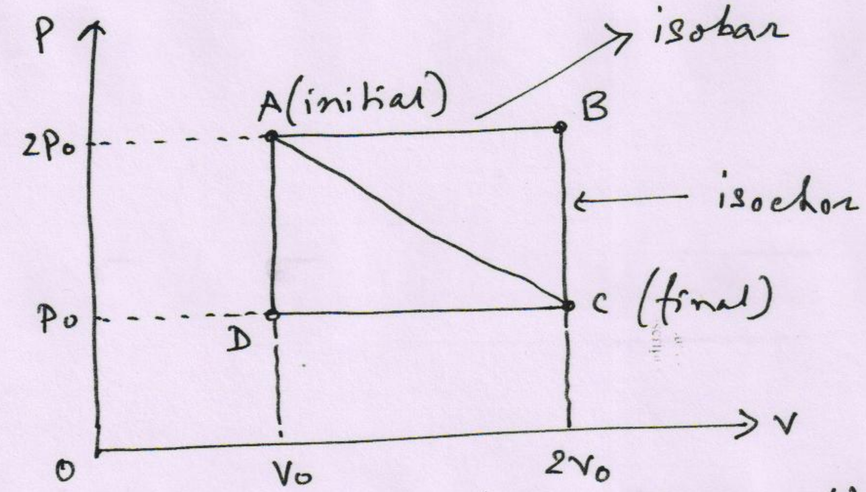
Work done on the system is positive.

$dV > 0, \Rightarrow \text{đ}W < 0$

Work done by the system is negative.

Valid for any expanding or contracting system under mechanical equilibrium.

Work depends on the path



Work done → Area in the PV graph

$$AD + DC \longrightarrow 0 - P_0(2V_0 - V_0)$$
$$= -P_0V_0$$

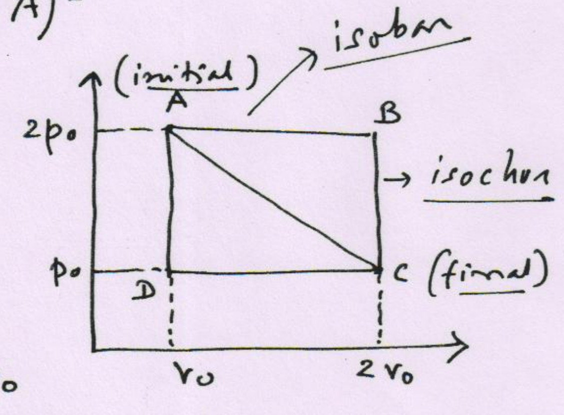
$$AC \longrightarrow -P_0(2V_0 - V_0) - \frac{1}{2}(2P_0 - P_0)(2V_0 - V_0)$$
$$= -P_0V_0 - \frac{1}{2}P_0V_0 = -\frac{3}{2}P_0V_0$$

$$AB + BC \longrightarrow -(2P_0 - P_0)(2V_0 - V_0)$$
$$-(P_0)(2V_0 - V_0)$$
$$= -P_0V_0 - P_0V_0 = -2P_0V_0$$

$$-2P_0(2V_0 - V_0)$$
$$-0$$
$$= -2P_0V_0$$

Path function, not a state function
(Process dependent)

Work, $\overset{W}{=} -\int p\,dv$



AD + DC:

$$W = 0 - p_0\int_{v_0}^{2v_0} dv$$

$$= 0 - p_0 v_0 = -p_0 v_0$$

AB + BC: $\Rightarrow W = -2p_0\int_{v_0}^{2v_0} dv - 0$

$$\Rightarrow W = -2p_0(2v_0 - v_0) = -2p_0 v_0$$

AC: A has $(V_0, 2P_0)$, C has $(2V_0, P_0)$

$$\frac{P - 2p_0}{2p_0 - p_0} = \frac{V - V_0}{V_0 - 2V_0}$$

$$\Rightarrow \frac{P - 2P_0}{P_0} = -\frac{V - V_0}{V_0} \Rightarrow P = -V\left(\frac{p_0}{v_0}\right) + 3P_0$$

$$\therefore W = -\int_{v_0}^{2v_0} p\,dV = -\left[\int_{v_0}^{2v_0} -\left(V\frac{p_0}{v_0}\right)dV + 3\int_{v_0}^{2v_0} P_0\,dV\right]$$

$$\Rightarrow W = -\left[-\frac{p_0}{v_0}\,\frac{V^2}{2}\Bigg|_{v_0}^{2v_0} + 3P_0\,V\Bigg|_{v_0}^{2v_0}\right]$$

$$\Rightarrow W = -\left[-\frac{p_0}{v_0}\cdot\frac{1}{2}\left(4v_0^2 - v_0^2\right) + 3P_0 v_0\right] = -\left[\frac{3}{2}P_0 v_0\right]$$

i.) Work is external to the system and depends on the process.

ii.) Energy in transit.

iii.) $đW$ is an inexact differential.
(Not a function of thermodynamic coordinates)

iv.) $đW = -p\,dV$ only when the process is quasi-static.

v.) $\int p\,dV$ cannot be integrated, unless we know how T varies.

Why? $p \equiv p(V,T)$.

What value of P where V changes?

$V \equiv V(P,T)$

$$\Rightarrow dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT$$

Taylor expansion:

$f = f(x)$ in equilibrium (x_0, f_0).

$f_0 = f(x_0)$.

$\Delta f = f'(x_0)\,\Delta x + \cdots$ | variation in a single variable.

Isothermal Process in an Ideal gas (Work Done):

$$\text{đ}W = -p\,dV$$

Very slow compression. Thermalised with the environment.

$$p = \frac{nRT}{V}, \quad T \text{ is constant}$$

$$\Rightarrow dT = 0.$$

$$\Rightarrow \text{đ}W = -nRT \frac{dV}{V}$$

$$\Rightarrow W = -nRT \int_{V_i}^{V_f} \frac{dV}{V}$$

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

If $V_f > V_i \Rightarrow W < 0$
(Work done by the system).

If $V_f < V_i \Rightarrow W > 0$
(Work done on the system).

Heat: Spontaneous flow of energy due to difference in temperature (non-mechanical means of energy transfer).

Energy in transit (like work).

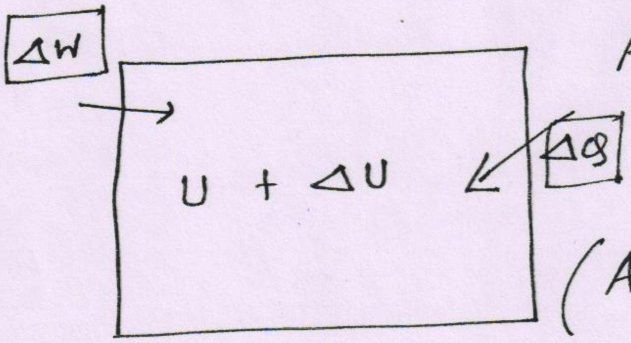
Heat $, \Delta Q,$ is a path function and does not depend on the thermodynamic coordinates in equilibrium (of the system).

Needs the Zeroth Law of Thermodynamics.

Internal Energy Function:

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

Internal Energy is a State function. How? | Joule's experiment.



A heat reservoir outside. (A large body that absorbs or rejects - transfers - an unlimited amount of heat without suffering any change in its thermodynamic coordinates).

ΔQ amount of heat changes the internal energy of the system.

Heat entering the system is positive.

Heat leaving the system is negative.

In an adiabatic process, $\Delta Q = 0$.

ΔW in this case becomes an exact differential (a state function, and NOT a path function).

- The result of Joule's experiment

$\Rightarrow$ $U \rightarrow$ Internal energy is a state function.

Can measure only the DIFFERENCE between two states.

$\Rightarrow$ U depends only on the thermodynamic coordinates of the system.

Under thermodynamic equilibrium, $f(P, V, T) = 0$.
(for example in the hydrostatic system).

$\Rightarrow$ $U \equiv U(P, T)$ or $U \equiv U(V, T)$

(In general U depends on any two thermodynamic coordinates, but temperature is kept as one). Why?

In differential form,

$$\boxed{dU = \text{đ}Q + \text{đ}W}$$

Mathematical statement of
THE FIRST LAW OF THERMODYNAMICS

Energy conservation.

Salient features of the First Law :

1/. Energy is Conserved (Julius Mayer).

2/. Heat is transitory energy due to temperature difference.

3/. Internal energy is a state function and depends on the thermodynamic coordinates.

4/. $\text{đ}Q$ and $\text{đ}W$ are inexact differentials.

5/. $\text{đ}Q$ is controlled by T in the (X, Y, T) format.

6/. $\text{đ}W$, under quasi-static conditions is controlled by the X, Y coordinates in the (X, Y, T) format.

7/. For a hydrostatic system, $\text{đ}W = -p\,dV$ (quasi-statically).

$$\therefore \boxed{dU = \text{đ}Q - p\,dV}$$

$$du = \text{đ}Q - p\,dV$$

In an isochoric process.

$$dV = 0 \quad \Rightarrow \quad dU = \text{đ}Q$$

In an isobaric process.

p is a constant.

$$\text{đ}Q = du + p\,dV$$

$$\Rightarrow H = \int dU + p\int dV \qquad \Bigg| \; \text{đ}Q \equiv H$$

$$\Rightarrow H = U + PV$$

<u>Enthalpy, H:</u>

PV is the work done to create the system (initial energy investment) | Minimum Interface

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Internal Energy :

$$U \equiv U(P, T)$$
$$U \equiv U(V, T)$$

$$dU = \left(\frac{\partial U}{\partial P}\right)_T dp + \left(\frac{\partial U}{\partial T}\right)_P dT$$

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

Now $$\text{đ}Q = dU + p\,dV$$

$$\Rightarrow \text{đ}Q = \left[\left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT\right] + p\,dV$$

$$\Rightarrow \text{đ}Q = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$\Rightarrow \frac{\text{đ}Q}{dT} = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \frac{dV}{dT} + \left(\frac{\partial U}{\partial T}\right)_V$$

When $dV = 0$ (isochoric process)

$$\frac{\text{đ}Q}{dT} = \left(\frac{\partial U}{\partial T}\right)_V = C_V$$

$dU = \text{đ}Q$ when $dV = 0$

Heat (Internal Energy) Capacity at constant volume.

By the <u>Equipartition Theorem</u>

in an ideal gas,

$U \equiv U(T)$ only. How? | <u>Kinetic Theory</u>

$$U = \frac{1}{2} f N k_B T = N f \left(\frac{1}{2} k_B T\right)$$

$f \rightarrow$ No. of quadratic degrees of freedom, each contributing $\frac{1}{2} k_B T$ per molecule.

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

$\Rightarrow \quad dU = C_V \, dT$ | $dU = 0$ for an isothermal process

$$\Rightarrow \quad đQ = dU + p\,dV$$

$$\Rightarrow \quad đQ = C_V \, dT + p\,dV$$

Now $\quad pV = nRT$

$$\Rightarrow \quad p\,dV + V\,dp = nR\,dT$$

$$\Rightarrow \quad p\,dv = nR\,dT - v\,dp$$

$$\Rightarrow \quad \text{đ}Q = C_v\,dT + nR\,dT - v\,dp$$

$$\Rightarrow \quad \text{đ}Q = (C_v + nR)\,dT - v\,dp$$

$$\Rightarrow \quad \frac{\text{đ}Q}{dT} = C_v + nR - v\frac{dp}{dT}$$

When $dp = 0$ (isobaric process).

$$\left(\frac{\text{đ}Q}{dT}\right)_p = C_p = C_v + nR$$

$C_p > C_v$ (Why?)

Heat Capacity at constant pressure, C_p.

$$\boxed{C_p - C_v = nR}$$

$c_p = \frac{C_p}{n}$

$c_v = \frac{C_v}{n}$

Molar specific heats.

Molar specific heats: $c_p - c_v = R$

Adiabatic Process :

$$đq = c_v\, dT + p\, dV$$

$$đq = c_p\, dT - v\, dp$$

For an adiabatic process, $đq = 0$.

$$\Rightarrow \quad c_p\, dT = v\, dp$$

and $$c_v\, dT = -p\, dv$$

$$\Rightarrow \quad \frac{c_p}{c_v} = -\frac{v}{p}\frac{dp}{dv}$$

$$\Rightarrow \quad \frac{dp}{p} = -\frac{c_p}{c_v}\frac{dv}{v}$$

define $\gamma = c_p/c_v$

$$\Rightarrow \quad \frac{dp}{p} + \gamma \frac{dv}{v} = 0$$

$$\Rightarrow \quad \int \frac{dp}{p} + \gamma \int \frac{dv}{v} = \text{constant}$$

$$\Rightarrow \quad \ln p + \gamma \ln V = \text{constant}$$

$$\Rightarrow \quad \boxed{pV^{\gamma} = \text{Constant}}$$

For an ideal gas

$$p = \frac{nRT}{V} \quad \left(\text{or} \quad V = \frac{nRT}{p} \right)$$

$$\Rightarrow \quad \frac{nRT}{V} V^{\gamma} = \text{constant}$$

$$\Rightarrow \quad TV^{\gamma-1} = \frac{\text{constant}}{nR}$$

$$\Rightarrow \quad \boxed{TV^{\gamma-1} = \text{Constant}}$$

and

$$p \cdot \frac{(nR)^{\gamma} T^{\gamma}}{p^{\gamma}} = \text{constant}$$

$$\Rightarrow \quad \boxed{p^{1-\gamma} T^{\gamma} = \text{constant}}$$

Calculating γ

$$\text{đ}Q = dU + p\,dV$$

For an adiabatic process, $\text{đ}Q = 0$.

$$\Rightarrow \quad dU = -p\,dV$$

$f = 3$ (translation)
$= 5$ (translation + rotation)
$= 7$ (translation + rotation + vibration)

<u>Kinetic Theory:</u>

$$U = Nf\left(\frac{1}{2}k_B T\right)$$

$$\Rightarrow \quad dU = \frac{1}{2}k_B N f\,dT$$

$$p = \frac{nRT}{V} \equiv \frac{N k_B T}{V}$$

$$\Rightarrow \quad \frac{1}{2}\cancel{k_B}\cancel{N}f\,dT = -\frac{\cancel{N}\cancel{k_B}T}{V}\,dV$$

$$\Rightarrow \quad \frac{f}{2}\frac{dT}{T} + \frac{dV}{V} = 0$$

$$\Rightarrow \quad \frac{f}{2}\int\frac{dT}{T} + \int\frac{dV}{V} = \text{constant}$$

$$\frac{f}{2} \ln T + \ln V = \text{Constant}$$

$$\Rightarrow \quad V T^{f/2} = \text{constant}$$

$$\Rightarrow \quad T V^{2/f} = \text{Constant}$$

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

$$\Rightarrow \quad \gamma - 1 = 2/f \quad \Rightarrow \quad \boxed{\gamma = 1 + \frac{2}{f}}$$

$$\Rightarrow \quad \gamma > 1$$

Alternative Approach

$$C_p - C_v = nR \quad , \quad C_v = \frac{dU}{dT} = \frac{1}{2} N f k_B$$

$$\Rightarrow \quad \frac{C_p}{C_v} - 1 = \frac{nR}{C_v} \quad \Rightarrow \gamma = 1 + \frac{nR}{C_v}$$

$$nR = \frac{N}{N_A} R = N k_B \quad \Rightarrow \gamma = 1 + \frac{N k_B}{\frac{1}{2} N f k_B}$$

$$\Rightarrow \quad \boxed{\gamma = 1 + \frac{2}{f}}$$

$f = 3$ (monatomic particles).

$f = 5$ (diatomic particles). Why?

Adiabatic Work Done :

When $đq = 0$, $dU = đw$

But $dU = \frac{f}{2} N k_B \, dT$

$$\Rightarrow \Delta W = \int dU = \frac{f}{2} N k_B \int_{T_i}^{T_f} dT$$

$$\Rightarrow \Delta W = \frac{f}{2} N k_B \left(T_f - T_i \right)$$

$$T_f = T_i \left(\frac{V_i}{V_f} \right)^{\gamma - 1}$$

$$\Rightarrow \Delta W = \frac{f}{2} N k_B T_i \left[\left(\frac{V_i}{V_f} \right)^{\gamma - 1} - 1 \right]$$

Adiabatic Work Done :

$$W = -\int_{v_i}^{v_f} p\, dv \quad \text{and} \quad p = c\, V^{-\gamma}$$

$$\Rightarrow W = -c \int_{v_i}^{v_f} V^{-\gamma}\, dv = -c \left. \frac{V^{1-\gamma}}{1-\gamma} \right|_{v_i}^{v_f}$$

$$\Rightarrow W = \frac{c}{\gamma-1}\left[v_f^{1-\gamma} - v_i^{1-\gamma} \right], \quad c = p_i v_i^{\gamma}$$

$$\Rightarrow W = \frac{p_i v_i^{\gamma}}{\gamma-1} v_i^{1-\gamma} \left[\left(\frac{v_f}{v_i} \right)^{1-\gamma} - 1 \right]$$

$$\Rightarrow W = \frac{p_i v_i}{\gamma-1} \left[\left(\frac{v_i}{v_f} \right)^{\gamma-1} - 1 \right]$$

But $P_i V_i = nRT_i$ and $nR = \frac{NR}{N_A} = Nk_B$

and $\gamma = 1 + \frac{2}{f} \Rightarrow \gamma - 1 = \frac{2}{f} \Rightarrow \frac{f}{2} = \frac{1}{\gamma-1}$

$$\Rightarrow W = \frac{f}{2} N k_B T_i \left[\left(\frac{V_i}{V_f} \right)^{\gamma-1} - 1 \right]$$

Isothermal and Adiabatic Compression (Expansion):

$$dU = đQ + đW$$

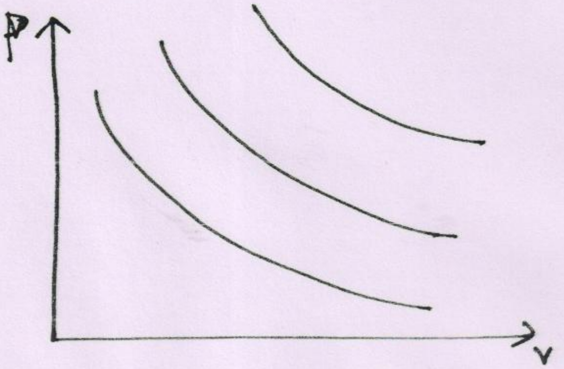
For an isothermal process, $dU = 0$

$$\Rightarrow \quad đQ = -đW$$

Energy enters as work and leaves as heat, in a slow compression process.

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

$p = \frac{nRT}{V}$ (T is constant) $\Rightarrow$ $pV = \text{constant}$



$$p\,dV + V\,dp = 0$$

$$\Rightarrow \frac{dp}{dV} = -\frac{p}{V}$$

In an adiabatic process.

$$\text{đ}Q = 0 \quad \Rightarrow \quad dU = \text{đ}W$$

Work enters the system and increases it's internal energy in a fast compression process.

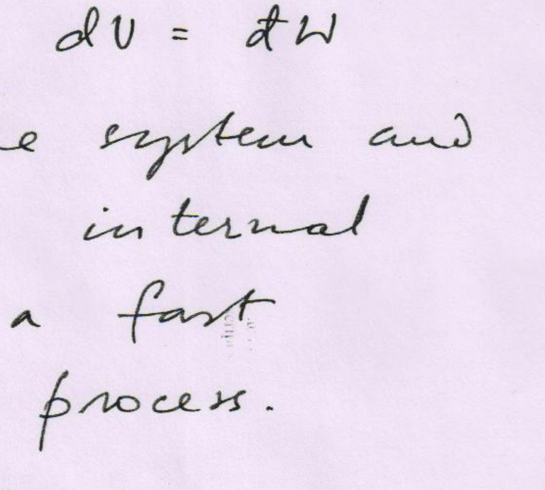
$$pv^{\gamma} = \text{constant}.$$

$$\Rightarrow \quad \frac{dp}{p} + \gamma\frac{dv}{v} = 0$$

$$\Rightarrow \quad \frac{dp}{dv} = -\gamma\frac{p}{v}$$

$\gamma > 1$

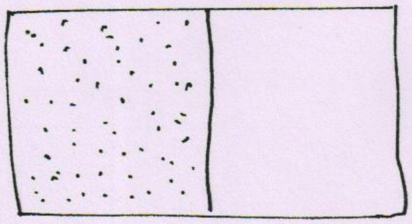
Adiabatic curves have a steeper slope.



[Curves DO NOT touch the line P = 0]

Free Expansion : Joule Expansion

Removing the partition results in adiabatic free expansion of the gas.



$đW = 0$ (No resistance to work against).

$đQ = 0$ (No temperature difference, i.e. no particles in vacuum).

$\Rightarrow dU = 0$ ($\because$ U is a function of temperature only for an ideal gas).

U is a function both of the temperature and pressure for a real gas.

Two Mathematical Theorems

$f(x, y, z) = 0$ as in $PV - nRT = 0$

or $x \equiv x(y, z)$ as in $P = \frac{nRT}{V}$

$$\Rightarrow dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

Similarly $y \equiv y(x, z)$ as in $V = \frac{nRT}{P}$

$$\Rightarrow dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz$$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left[\left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \right] + \left(\frac{\partial x}{\partial z}\right)_y dz$$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_z \right] dz$$

$$dx = a\,dx + b\,dz$$

$$\Rightarrow \quad a = 1 \quad \text{and} \quad b = 0$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1$$

$$\Rightarrow \boxed{\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{(\partial y/\partial x)_z}}$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y = 0$$

$$\Rightarrow \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y = \frac{-1}{(\partial z/\partial x)_y}$$

$$\Rightarrow \boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1}$$