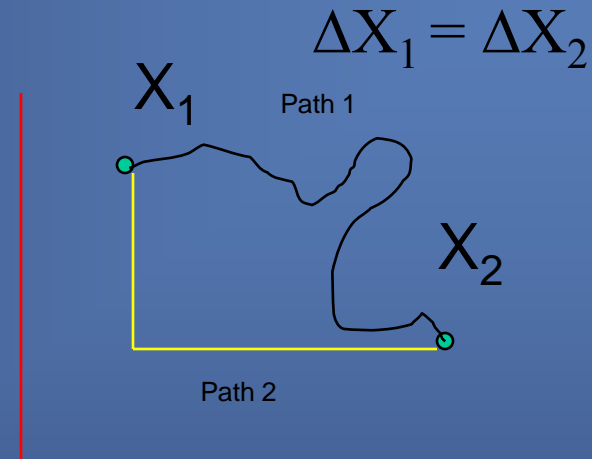


State Variables

- Examples of State Variables:

- Temperature
- Pressure
- Volume
- Entropy
- Enthalpy
- Internal Energy
- Mass
- Density



- **State Variables are Path Independent:** meaning that the change in the value of the state variable will be the same no matter what path you take between the two states. This is not true of either the work W or the heat Q .
- If a system is carried through a cycle that returns it to its original state, then a variable will only be a state variable if variable returns to its original value.
- If X is a State Variable then: $\int dX = 0$
- State Variables are only measurable when the system is in Equilibrium.

Definitions

- Entropy: A measure of the extent to which the energy of a system is unavailable. A mathematically defined thermodynamic function of state, the increase in which gives a measure of the energy of a system which has ceased to be available for work during a certain process: $ds = (du + pdv)/T \geq dq/T$ where s is specific entropy; u is specific internal energy; p is pressure; v is specific volume; T is Kelvin temperature; and q is heat per unit mass. For reversible processes, $ds = dq/T$ In terms of potential temperature, $ds = c_p (d\theta/\theta)$ where c_p is the specific heat at constant pressure.
- Enthalpy: the sum of the internal energy E plus the product of the pressure p and volume V .

Equilibrium

- A System is in Equilibrium if its Properties or Variables do not change with time.
 - *Thermal Equilibrium*
No Temperature or Pressure Gradients in the System.
 - *Mechanical Equilibrium*
No Unbalanced Forces or Torques in the System.
 - *Chemical Equilibrium*
No tendency of the System to undergo Chemical Reaction or Diffusion.
 - *Electrical Equilibrium*
No Electrical Potential Gradients in the System.

Thermodynamics

The 0th Law of Thermodynamics

If A and B are each in thermal equilibrium with a third body C, then A and B are in thermal equilibrium.

Thermal equilibrium means that two bodies are in states such that if they are connected, then their condition will not change.

Thermodynamics

The 1st Law of Thermodynamics

- Every thermodynamic system in an equilibrium state possesses a state variable called the internal energy U whose change in a differential process is given by

- $$dU = dQ - dW$$

- State variable: T , P , ρ , or mean molecular weight.
- dQ = change in the heat energy
- dW = work done on or by the system

Thermodynamics

The 2nd Law of Thermodynamics

- A transformation whose only final result is to transform into work heat extracted from a source that is at the same temperature throughout is impossible. (Kelvin -Planck statement)
- It is not possible for any cyclical machine to convey heat continuously from one body to another at a higher temperature without, at the same time, producing some other (compensating) effect. (Clausius statement)
- If a system goes from a state i to a state f , the entropy of the system plus environment will either remain constant (if the process is reversible) or will increase (if the process is irreversible). (Entropy statement)

Thermodynamic Variables

- $M = \text{Total Mass}$ (grams)
- $m = \text{Per Particle Mass}$ (grams)
- $V = \text{Volume}$ (cm^3)
- $\rho = \text{density}$ (gm/cm^3)
- $P = \text{Pressure}$ (dynes/cm^2)
- $T = \text{Temperature}$ (Kelvins)

Empirical Relations

Constant Mass Relations

- Boyle's Law: $P \propto 1 / V$ (Constant T)
- Charles' Law: $V \propto T$ (Constant P)
- $PV / T = \text{constant}$
- $\text{Constant} = \mu R$
- $\mu =$ number moles of gas (mass)
- $R =$ gas constant
- $R = 8.314 \text{ J mole}^{-1} \text{ K}^{-1}$ or $1.986 \text{ cal mole}^{-1} \text{ K}^{-1}$
- **$PV = \mu RT$ -- Perfect Gas Law**

Isothermal Work by Volume Expansion

$$W = \int_{v_i}^{v_f} p dV$$
$$= \int_{v_i}^{v_f} (\mu RT / V) dV$$

But $T = \text{Constant}$

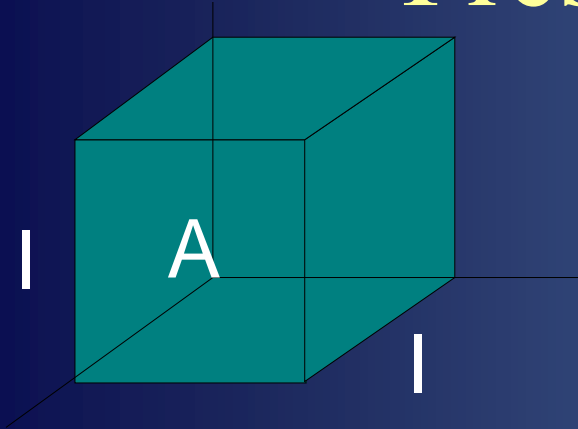
$$W = \mu RT \int_{v_i}^{v_f} dV / V$$
$$= \mu RT \ln(v_f / v_i)$$

An Ideal Gas

Macroscopic Description

- A gas consists of molecules: atoms / molecules.
- The motion is random and follows Newton's Laws (Brownian Motion).
- Number of molecules is large: statistics apply.
- Volume of molecules is small compared to the volume occupied by the gas.
- No appreciable forces except during collisions.
- Collisions are elastic and of negligible duration compared to the time between collisions.

Pressure Calculation



Cube of Side Length l and Side Area A and a molecule with velocity $= (v_x, v_y, v_z)$

- Consider v_x : At A an elastic collision occurs
 - $\phi p = p_f - p_i = (-mv_x) - mv_x = -2mv_x$ for the particle
 - For A : $\phi p = 2mv_x$ by conservation
- Now travel to the opposite wall and then back to A
 - The time to do this is $2l/v_x$ so it strikes A $v_x/2l$ times per unit time interval
- $dp/dt = 2mv_x (v_x/2l) = mv_x^2/l = F$

Pressure Calculation

- Pressure \equiv Force / Unit Area = F / l^2
- $P = m/l^3 (v_{1x}^2 + v_{2x}^2 + \dots)$
 - Let N = total number of particles
 - n = number particles per unit volume (number density)
 - $\implies nl^3 = N$
 - $\implies P = mn ((v_{1x}^2 + v_{2x}^2 + \dots) / N)$
 - But mn = mass per unit volume = ρ
 - $((v_{1x}^2 + v_{2x}^2 + \dots) / N) = \text{Average } v_x^2 = \langle v_x^2 \rangle$
 - $P/\rho = \langle v_x^2 \rangle$
 - Now $v^2 = (v_x^2 + v_y^2 + v_z^2)$
 - For random motion $v_x = v_y = v_z \implies \langle v^2 \rangle = 3\langle v_x^2 \rangle$ so:
- $P = \rho \langle v_x^2 \rangle = 1/3 \rho \langle v^2 \rangle$
 - But $\langle v^2 \rangle$ is the RMS Speed!

Kinetic Interpretation of Temperature

$$P = (1/3)\rho V_{\text{RMS}}^2$$

$$PV = 1/3 V\rho V_{\text{RMS}}^2$$

$V = \text{Volume}$

$$\rho = M/V = \mu M/V$$

$M = \text{total mass}$ $M = \text{Mass/mole}$ $\mu = \text{number of moles}$

$$PV = 1/3 \mu M V_{\text{RMS}}^2$$

$1/2 \mu M V_{\text{RMS}}^2 = \text{total kinetic energy}$ and $PV = \mu RT$

$$\mu RT = 1/3 \mu M V_{\text{RMS}}^2$$

$$3/2 RT = 1/2 M V_{\text{RMS}}^2$$

The total translational KE per mole is proportional to T

A Change Of Variable

- $3/2 RT = 1/2 M V_{\text{RMS}}^2$
- Divide by $N_0 = \text{Avogadro's Number}$
- $3/2 (R/N_0)T = 1/2 (M/N_0) V_{\text{RMS}}^2$
 - $(M/N_0) = \text{Mass / particle} = m$
 - $(R/N_0) = k = \text{Boltzman Constant } (1.38621(10^{-23}) \text{ J/K})$
- $3/2 kT = 1/2 m V_{\text{RMS}}^2$
- Rewrite the Ideal Gas Law:
- $PV = \mu RT = (N_0 \mu) (R/N_0)T = nkT$
 - $N_0 \mu = n = \text{Number of particles (total) in } V.$

Mean Free Path

- Cross Section: πd^2 where the mean diameter is d .
 - In calculation consider 1 particle of diameter $2d$ and the others as point masses.
- Volume Swept in time t : $vt \pi d^2$
- Particle Density = $n \implies nvt\pi d^2 = \text{number of collisions}$
- Mean Free Path: $l = vt / nvt\pi d^2 = 1 / n\pi d^2$
 - There are actually two different v 's here!
 - Numerator $v = \text{Mean } v \text{ with respect to container}$
 - Denominator $v = v \text{ with respect to other molecules}$
- Mean Free Path: $l = 1 / \sqrt{2} n\pi d^2$
- For the Solar Atmosphere:
 - $d \sim 2(10^{-8}) \text{ cm}$; $n \sim 6(10^{16}) \implies l \sim 0.01 \text{ cm}$.

The Hydrostatic Equation

- The Downward Gravitational Force is
- $(Gm(r) 4\pi r^2 \rho(r) dr) / r^2$
- The Pressure Force Upwards is
- $4 \pi R^2 dP$
- $dP =$ pressure difference across dr
- In Equilibrium
- $(G m(r) 4\pi r^2 \rho(r) dr) / r^2 = -4 \pi R^2 dP$
- $dP/dr = -G m(r) \rho(r) / r^2$
- The sign on dP/dr is negative as P decreases with increasing r . If $m(r) =$ total mass ($r =$ total radius) then $dP/dr = -g \rho(r)$.
- $dP = -g \rho(r) dr$
- If $\rho \neq f(r)$ then $P = P_0 + \rho g r$

