Chapter 1

Thermal equilibrium – state when the macroscopic variables of two objects stop changing

→ achieved by an exchange of energy ← claim

temperature – is a measure of the tendency of an object to spontaneously give up energy

How do we measure temperature?

- volume (constant pressure) (mercury/alcohol)
- pressure (constant volume)
- electrical resistance
- thermal emf (thermocouple)
- radiation

HW#1 | 1, 2, 7

1.) $C_0 = 0$ $\quad F_0 = 32$

$C_1 = 100$ $\quad F_1 = 212$

$C = mF + b$

$0 = m \cdot 32 + b$ | $100 = m(212) + b$

$m = \frac{5}{9}$ $\quad b = 32$

7.) $\beta = \frac{\Delta V / V}{\Delta T}$ $\rightsquigarrow$ fractional change in volume $\propto$ change in temp

$\frac{V_f - V_i}{V_i} = \frac{\Delta V}{V} = \beta \cdot \Delta T$

(a) estimate mercury bulb volume $\rightsquigarrow$ cylinder diameter

$\left(\frac{1}{4} \text{ cm diameter}\right)^3 \approx \frac{1}{64} \text{cm}^3 \cdot \frac{10^3 \text{ mm}^3}{1 \text{ cm}^3} = \underbrace{10 \text{ mm}^3 = V}$

≈ 100

ΔV from $1°C$

8] $\frac{\Delta L}{L} = \alpha \cdot \Delta T$ $\qquad T_F = 100°F \qquad T_c = 10°F \qquad \Delta T_F = 90°F$

$$\frac{\Delta T_F}{\Delta T_c} = \frac{9}{5} \qquad \frac{\Delta T_c}{\Delta T_F} = \frac{5}{9}$$

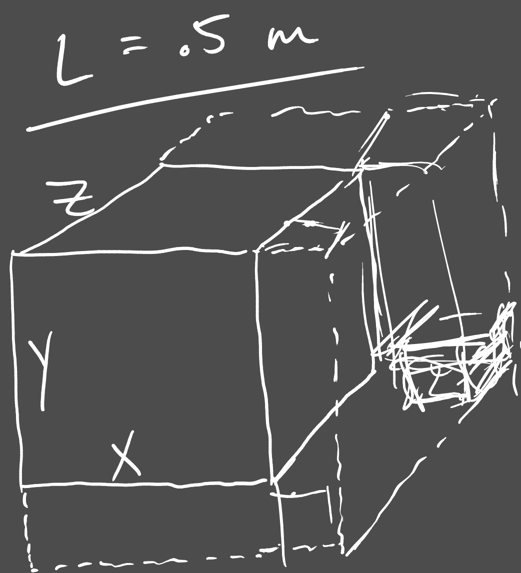
(a) $\alpha = 1.1 \cdot 10^{-5} K^{-1}$

$$\Delta T_c = \frac{5}{\cancel{9}}(\cancel{90}^{10}°F)$$

$$\Delta T_c = 50°C$$

$$\Delta L = \alpha \Delta T \cdot L$$
$$= 1.1 \cdot 10^{-5} \cdot 50°C \cdot 1000\, m$$
$$= 50000 \cdot 10^{-5}$$

(c)



$$\alpha \Delta T = \frac{\Delta L}{L}$$

$$\alpha_x \Delta T = \frac{\Delta x}{X}, \quad \alpha_y \Delta T = \frac{\Delta y}{Y}, \quad \alpha_z \Delta T = \frac{\Delta z}{Z}$$

$$\beta \Delta T = \frac{\Delta V}{V}$$

$$\Delta V = V_f - V_i = (X + \Delta x)(Y + \Delta y)(Z + \Delta z) - XYZ$$

$$\Delta V = (XY + Y\Delta x + X\Delta y + \Delta x \Delta y)(Z + \Delta z) - XYZ$$

$$\Delta V = \cancel{XYZ} + XY\Delta z + YZ\Delta x + Y\Delta x\Delta z + XZ\Delta y + X\Delta y\Delta z + Z\Delta x\Delta y + \Delta x\Delta y\Delta z - \cancel{XYZ}$$

$$\beta\Delta T = \frac{\Delta V}{\underset{XYZ}{V}} = \frac{\Delta V}{XYZ} = \underbrace{\frac{\Delta z}{z}}_{\alpha_z \Delta T} + \underbrace{\frac{\Delta x}{x}}_{\alpha_x \Delta T} + \cancel{\frac{\Delta x \Delta z}{xz}}^{\approx 0} + \underbrace{\frac{\Delta y}{y}}_{\alpha_y \Delta T} + \cancel{\frac{\Delta y \Delta z}{yz}}^{\approx 0} + \cancel{\frac{\Delta x \Delta y}{xy}}^{\approx 0} + \cancel{\frac{\Delta x \Delta y \Delta z}{xyz}}^{\approx 0}$$

$$\beta \cancel{\Delta T} = (\alpha_x + \alpha_y + \alpha_z)\cancel{\Delta T}$$

Macroscopic View

what we want to consider

Surroundings

boundary - can be open or closed to matter or energy

Goal: ① describe the behavior of system
② describe interactions w/ surroundings
③ BOTH!

Macroscopic description: variables at human scale or larger
↳ easy to measure in a lab

Microscopic description: variables at molecular scale or smaller
↳ very hard to measure directly

Take a cylinder of a gas: (what does it take to describe it)

- mass + composition
- volume
- pressure
- temperature

these form macroscopic coordinates

1. no special assumptions about structure of matter
2. fewest possible to provide description
3. fundamental → suggested by sensory perception.
4. directly measurable

Microscopic view treated w/ statistical mechanics has nearly the opposite of these conditions

P, V, T → two can be varied but third it determined by those

An equation that relates the thermodynamic coordinates
↳ <u>equation</u> of <u>state</u>

for a closed system, the equation of state relates temp to <u>two</u> other variables.

<u>Other examples</u>

stretched wire → force, length, temperature

1.2 The ideal gas law

$$p \cdot V = N \, k_B \, T$$

N → total number of particles

k_B → Boltzmann's constant → $1.381 \cdot 10^{-23}$ J/K

T → absolute temp → Kelvin

V → volume

p → pressure = $\frac{\text{Force}}{\text{Area}}$

This is experimental. An approximation of low density gases

$$p = n k_B T$$

n → number density $\quad n = \frac{N}{V} \qquad \rho = \frac{M}{V}$

Form used in chemistry (useful large numbers + mixtures)

$$pV = n_m R \cdot T$$

R → gas constant

n_m → number of moles

$$N = n_m \cdot N_A \rightsquigarrow n_m = \frac{N}{N_A}$$

$$N k_B = n_m R$$

$N_A = 6.022 \cdot 10^{23}$ things/mole

or

$k_B = 1.381 \cdot 10^{-23}$ J/K

$$R = k_B N_A = 8.31 \ \mathrm{J/K \cdot mol}$$

Problem 1.9. What is the volume of one mole of air, at room temperature and 1 atm pressure?

$$PV = N k_B T$$

$N = N_A \quad T = 20°C = 293$

$$V = \frac{N k_B T}{P}$$

$P = 1 \underline{atm} = 1.013 \cdot 10^5 \ \mathrm{Pa} \ \left[\frac{N}{m^2}\right] = [\text{Pascal}]$

$$V = 0.024 \ m^3$$

↳ ~ 30 cm cube

~ 24 liters

Problem 1.12. Calculate the average volume per molecule for an ideal gas at room temperature and atmospheric pressure. Then take the cube root to get an estimate of the average distance between molecules. How does this distance compare to the size of a small molecule like N_2 or H_2O?

1 mol at 1 atm at 293K, $V = 0.024\, m^3$
(N_A)

$$\frac{V}{N_A} = \frac{0.024\, m^3}{6.02 \cdot 10^{23}} = 4 \cdot 10^{-26}\ m^3/\text{molecule}$$

$\downarrow \sqrt[3]{\ }$

side length

$$\sqrt[3]{4 \cdot 10^{-26}} = 3.4 \cdot 10^{-9}\ m$$
$$= 3.4\ nm$$
$$= 34\ \text{Å}$$

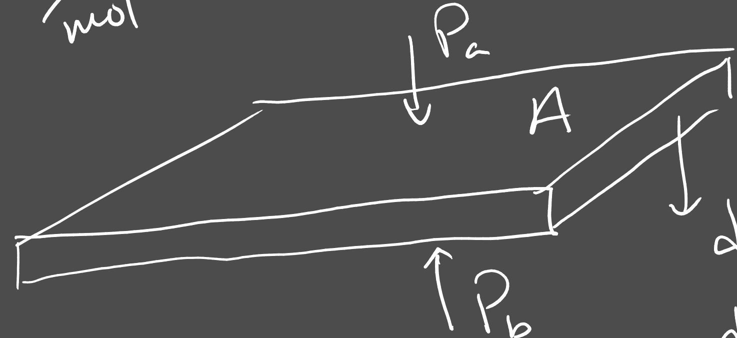
$H_2 = 289\ pm = 2.89\ \text{Å}$

$N_2 = 364\ pm = 3.64\ \text{Å}$

HW: 12☆, 13, 14☆, 16☆, 17☆

14) $2 \cdot 14\,g/mol \cdot .78 + 2 \cdot 16\,g/mol \cdot .21 + 40\,g/mol \cdot 0.01 = 29\,g/mol$

16)



$dM = \rho\, dV$

$dm = \rho A \cdot dz$

$$\underbrace{P_b \cdot \cancel{A} - P_a \cdot \cancel{A}}_{-dP} - \rho \cancel{A} dz \cdot g = 0$$

$$-dP = \rho\, dz \cdot g$$

$$\frac{dP}{dz} = -\rho g$$

$P(z)$

$P_b = P(z)$

$P_a = P(z+dz)$

$$\frac{P_a - P_b}{dz} = \frac{P(z+dz) - P(z)}{dz}$$

$$= \frac{dP}{dz}$$

$PV = Nk_BT$

$$m\frac{N}{V} = \frac{mP}{k_BT} \Rightarrow \rho = \frac{mP}{k_BT}$$

$$\int \frac{dP}{P} = -\int \frac{mg}{k_B T}\, dz$$

$$\ln P = -\frac{mg}{k_B T} z$$

$$P(z) = e^{Az}$$

17 c

$$\left(P + \frac{an^2}{V^2}\right)\underbrace{\left(V - nb\right)}_{= V\left(1 - \frac{nb}{V}\right)} = nRT$$

$$PV = nRT\left(1 + \frac{B(T)}{(V/n)} + \frac{C(T)}{(V/n)^2}\right)$$

$$= nRT\left(1 + \frac{n}{V}B(T) + \frac{n^2}{V^2}C(T)\right)$$

$$PV + \frac{an^2}{V} = \frac{nRT}{\left(1 - \frac{nb}{V}\right)}$$

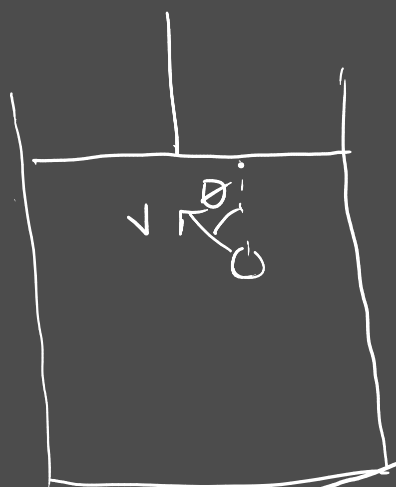
$$\rightarrow PV = \frac{nRT}{1 - \frac{nb}{V}} - \frac{an^2}{V}$$

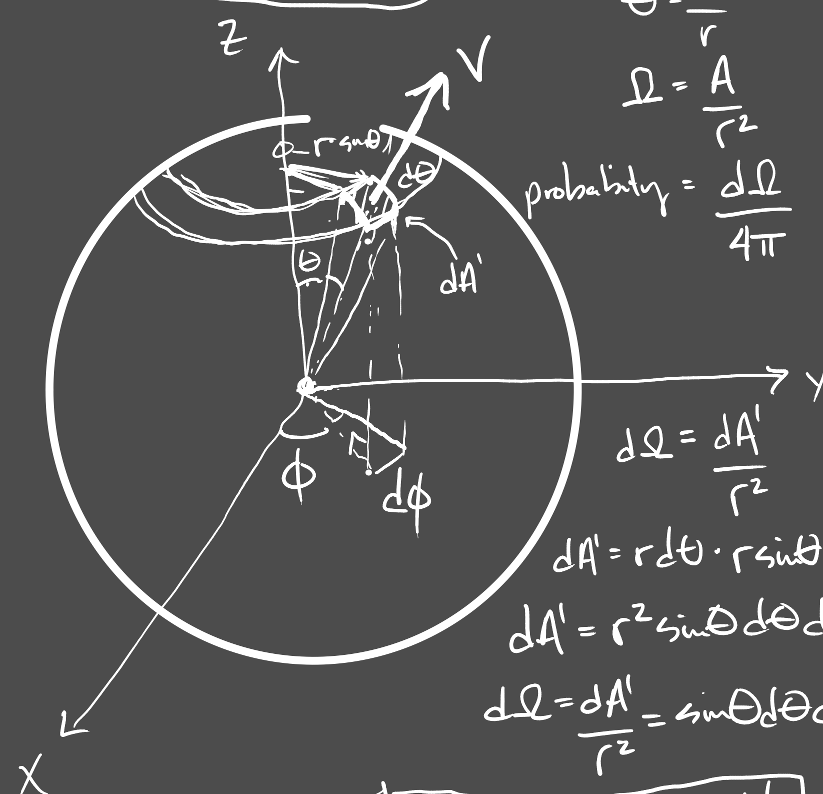
$$PV = nRT\left(\underbrace{\left(1 - \frac{nb}{V}\right)^{-1}}_{\text{apply binomial}} - \frac{a \cdot n}{RTV}\right)$$

we want pressure from a microscopic model:
(elastic collisions)

$$\text{pressure} = \frac{F}{A} = \frac{\Delta p}{A \cdot \Delta t} \rightarrow 2mv\underbrace{\cos\theta}_{v_y}$$

$$\text{pressure} = \frac{2mv\cos\theta}{dA\,dt} \cdot \underbrace{\text{number of particles hitting Area } dA \text{ w/ velocity } v \text{ in time } dt}$$





$\theta = \frac{A}{r}$

$\Omega = \frac{A}{r^2}$

$\text{probability} = \frac{d\Omega}{4\pi}$

$d\Omega = \frac{dA'}{r^2}$

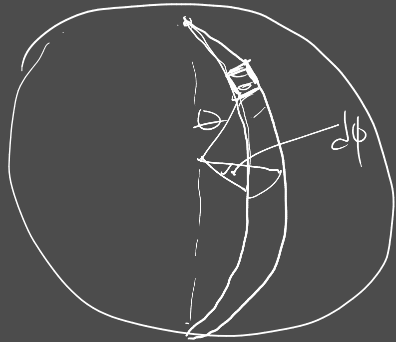
$dA' = r\,d\theta \cdot r\sin\theta\,d\phi$

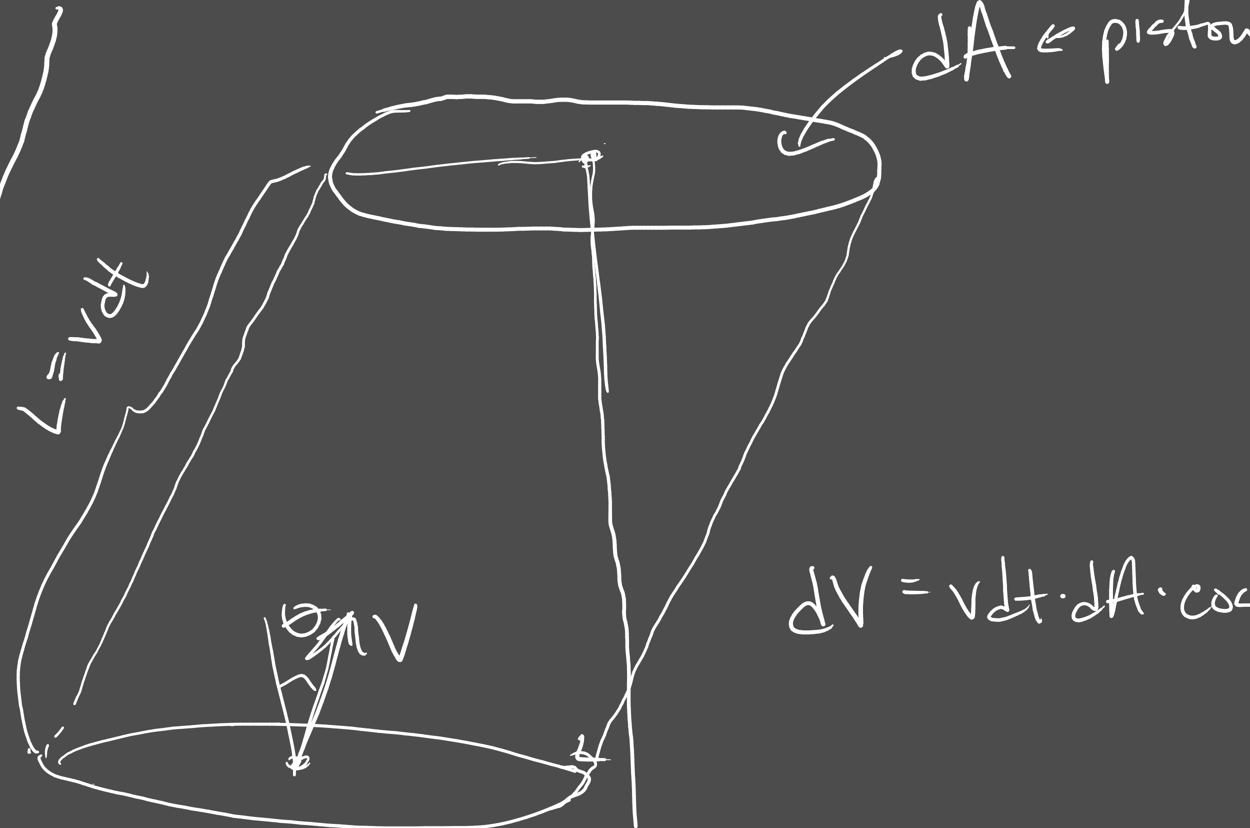
$dA' = r^2 \sin\theta\,d\theta\,d\phi$

$d\Omega = \frac{dA'}{r^2} = \sin\theta\,d\theta\,d\phi$

$$\boxed{\frac{d\Omega}{4\pi} = \frac{\sin\theta\,d\theta\,d\phi}{4\pi}}$$

number of atoms traveling in this particular direction in the entire volume. $\cdot$ fraction of those that are within striking distance in time dt.





$dV = v\,dt \cdot dA \cdot \cos\theta$

probability of an atom being in this volume

$$\frac{dV}{V} = \boxed{\frac{v\,dt\,dA\cos\theta}{V}}$$

$N \cdot \frac{d\Omega}{4\pi} \cdot \frac{dV}{V} \cdot$ number of particles having a particular speed between v and $v + dv$

$f(v) \rightarrow$ speed distribution function

fraction of particles w/ speeds between v and $v + dv$

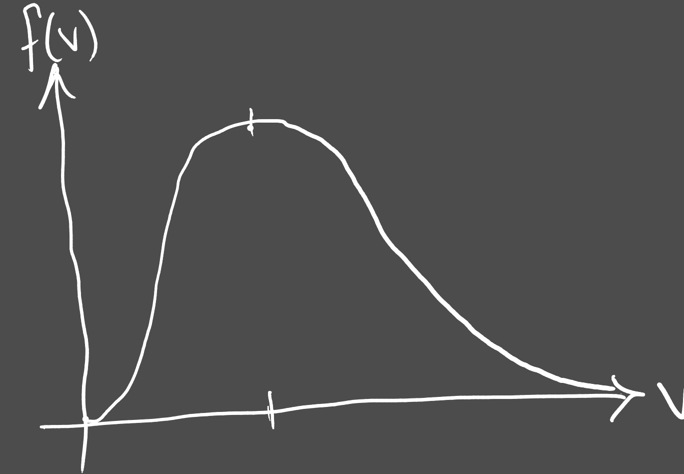
$$\rightarrow f(v) \cdot dv$$

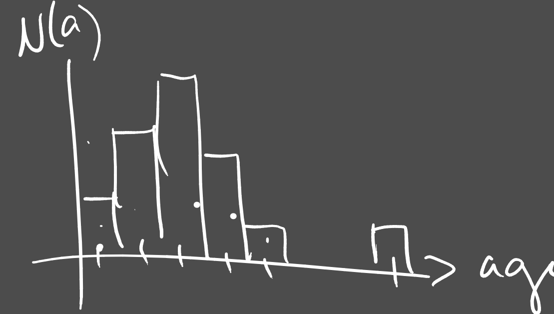
$$\int_0^\infty f(v)\, dv = 1$$

$$\langle v \rangle = \int_0^\infty v\, f(v)\, dv$$

$$\langle v^2 \rangle = \int_0^\infty v^2 f(v)\, dv$$

$$\langle g(v) \rangle = \int_0^\infty g(v)\, f(v)\, dv$$





$$\rho(\text{state}) = \psi^* \psi$$

$$1 = \int_{-\infty}^{\infty} \psi^* \psi\, dx$$

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^* \cdot x \cdot \psi\, dx$$

$$\text{pressure} = \frac{2mv\cos\theta}{dA\,dt} \cdot N \cdot \frac{d\Omega}{4\pi} \cdot \frac{dv}{V} \cdot f(v)dv$$

$$\int dp = \frac{2mv\cos\theta}{\cancel{dA}\,\cancel{dt}} \cdot N \cdot \frac{\sin\theta\, d\theta\, d\phi}{4\pi} \cdot \frac{v\cancel{dt}\,\cancel{dA}\cos\theta}{V} \cdot f(v)dv$$

$$\text{pressure} = \frac{2mN}{4\pi V} \int_0^{\infty} \int_0^{\pi/2} \int_0^{2\pi} v^2 f(v)\,dv \cdot \cos^2\theta \sin\theta\, d\theta \cdot d\phi$$

speed $\quad \theta \quad \phi$

$$\text{pressure} = \frac{mN}{\cancel{2}\pi V} \underbrace{\int_0^{\infty} v^2 f(v)dv}_{\langle v^2 \rangle} \cdot \underbrace{\int_0^{\pi/2} \cos^2\theta \sin\theta\, d\theta}_{1/3} \underbrace{\int_0^{2\pi} d\phi}_{\cancel{2\pi}}$$

$$p = \frac{mN}{3V} \cdot \langle v^2 \rangle$$

$$pV = N \boxed{\frac{m\langle v^2\rangle}{3}}$$

$$pV = N \boxed{k_B T}$$

$$3k_BT = m\langle v^2\rangle \longrightarrow \underline{V_{rms}} = \sqrt{\langle v^2\rangle} = \sqrt{\frac{3kT}{m}}$$

$$\frac{3}{2}k_BT = \underbrace{\frac{1}{2}m\langle v^2\rangle}_{\langle K\rangle}$$

ideal gas

$$U = \frac{3}{2}P \cdot V$$

$$U = N\langle K\rangle$$

$$\boxed{U = \frac{3}{2}Nk_BT} \longrightarrow T = \frac{2}{3k_B}\cdot\frac{U}{N}$$

$$\langle K\rangle = \frac{1}{2}m\left(\langle v_x^2\rangle + \langle v_y^2\rangle + \langle v_z^2\rangle\right)$$

#21, 22

Equipartition Theorem

$$U_{thermal} = \frac{f}{2} N k_B T$$

degree of freedom

quadratic energy terms

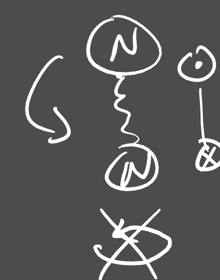
$\frac{1}{2} m v_x^2$, $\frac{1}{2} I \omega_x^2$, $\frac{1}{2} k x^2$

not the total energy

energy that changes when temp changes

$f = 3$ ← monoatomic gas

$f = 5$ ← diatomic gas (near room temp)



1.23 1 liter of He at room temp

Heat + Work

1^{st} Law of Thermo: Conservation of Energy

If the energy of system changes
it must come from the surroundings

So how? → heat + work

heat → spontaneous due to ΔT

work → force applied but also energy from current in a resistor

$$\underbrace{dU = đQ + đW}$$

→ inexact differential

can't do → $W = \int đW$

→ $\oint đW \neq 0$ ← path dependent

$\Delta U = Q + W$ ← book form

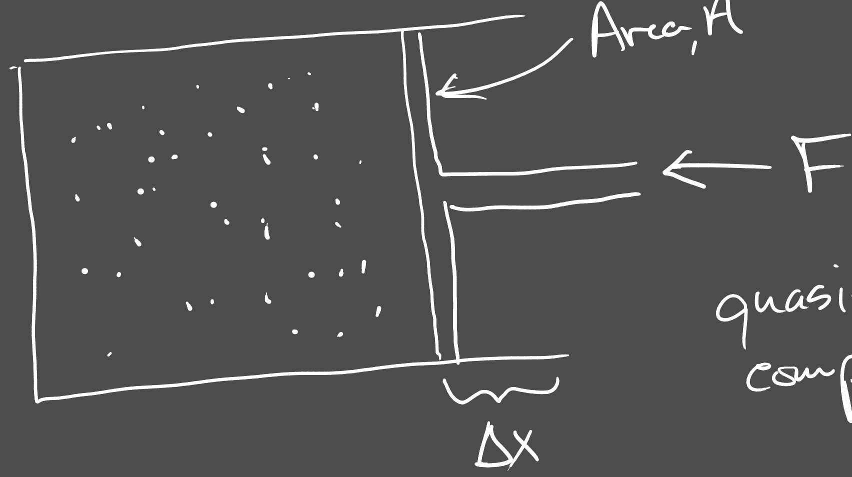
$dU = \delta Q + \delta W$

Engineering def:

$dU = \delta Q - \delta W$

↑ positive work is done on surroundings

Compression/Expansion Work



$$W = \vec{F} \cdot d\vec{r} = F \cdot \Delta x$$

$$\hookrightarrow = P \cdot A$$

quasistatic compression $\rightarrow W = P \cdot \underbrace{A \cdot \Delta x}_{-\Delta V}$

$$W = -P\Delta V$$

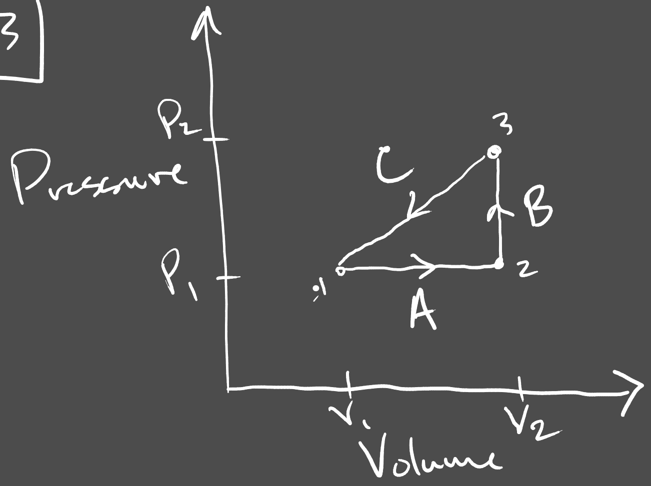
$\hookrightarrow$ constant pressure over ΔV

$$\text{đ}W = -P\Delta V \rightarrow \text{đ}W = -P(V,T)\,dV$$

$$\underline{\underline{W = -\int P\,dV}} \qquad \cancel{W = \int \text{đ}W}$$

#23, 28, 32, 33, 34

1.33



Sign: Work, energy, heat

A: $W = -\int_1^2 p\,dV = -p\int_1^2 dV = -p(V_2 - V_1)$

$W < 0$

$Q = ?$ $\leftarrow$ $Q > 0$

$\rightarrow U = \frac{f}{2} N k_B T = \frac{f}{2} PV$

$\Delta U > 0$ b/c $\Delta V > 0$

$$\boxed{\underset{>0}{\Delta U} = \underset{>0}{Q} + \underset{<0}{W}}$$

B: $W = 0$, $\Delta V = 0$

$\Delta U > 0$

$Q > 0$

C: $W > 0$

$\Delta U = U_f - U_i = \frac{3}{2}(\overset{\downarrow}{P_f}\overset{\downarrow}{V_f} - \overset{\uparrow}{P_i}\overset{\uparrow}{V_i})$

$U < 0$

$Q < 0$

$$\underset{<0}{\Delta U} = \underset{<0}{Q} + \underset{>0}{W}$$

Isothermal Process + Adiabatic Process

constant temprature

no heat escape

expansion/compression