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

$C_1 = 100 \quad F_1 = 212$

$C = mF + b$

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

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

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

$T_F = 100°F$ $T_c = 10°F$ $\Delta T_F = 90°F$

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

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

$\Delta T_c = 50°C$

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

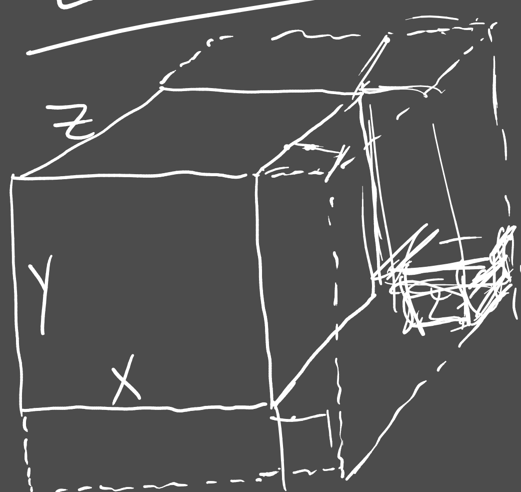
$\Delta L = \alpha \Delta T \cdot L$

$= 1.1 \cdot 10^{-5} \cdot 50°C \cdot 1000\ m$

$= 50000 \cdot 10^{-5}$

(c)

$L = .5\ m$



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

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

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

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

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

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

$$\beta\Delta T = \frac{\Delta V}{\underset{XYZ}{V}} = \frac{\Delta V}{XYZ} = \underbrace{\frac{\Delta Z}{Z}}_{\alpha_z \Delta T} + \underbrace{\frac{\Delta X}{X}}_{\alpha_x \Delta T} + \cancel{\frac{\Delta X \Delta Z}{XZ}}^{\approx 0} + \underbrace{\frac{\Delta Y}{Y}}_{\alpha_y \Delta T} + \cancel{\frac{\Delta Y \Delta Z}{YZ}}^{\approx 0} + \cancel{\frac{\Delta X \Delta Y}{XY}}^{\approx 0} + \cancel{\frac{\Delta X \Delta Y \Delta Z}{XYZ}}^{\approx 0}$$

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

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 is determined
by those

An equation that relates the thermodynamic coordinates
↳ equation 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 $n = \frac{N}{V}$ $\qquad \rho = \frac{M}{V}$

Form used in chemistry (useful large numbers + mixtures)

$$pV = n_m R \cdot T$$

R → gas constant

n_m → number of moles

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

$$N k_B = n_m R$$

or

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

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

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

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

$$PV = N k_B T$$

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

$N = N_A \quad T = 20°C = 293$

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

$$V = 0.024 \ m^3$$

↳ ~ 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

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

$$= 3.4\,nm$$

$$= 34\,\text{Å}$$

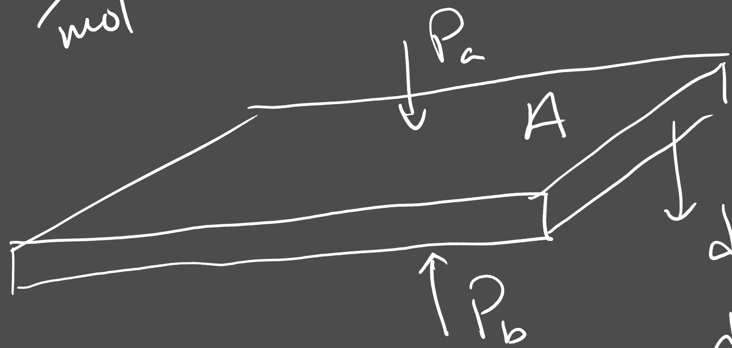
$H_2 = 289\ pm = 2.89\ \text{Å}$

$N_2 = 364\ pm = 3.64\ \text{Å}$

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)



$dM = \rho \, dV$

$dm = \rho A \cdot dz$

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

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

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

$P(z)$

$P_b = P(z)$

$P_a = P(z+dz)$

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

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

$PV = N k_B T$

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

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

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

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

$\boxed{17}$ c

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

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

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

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

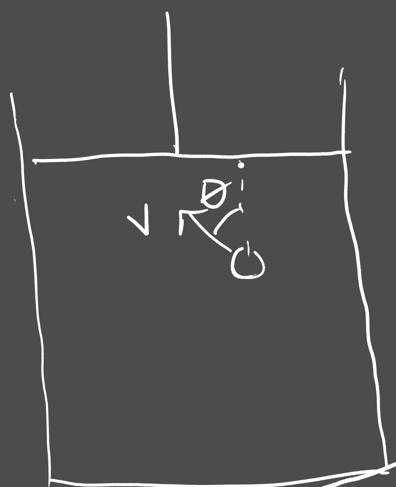
$$\rightarrow PV = \frac{nRT}{1-\frac{nb}{V}} - \frac{an^2}{V}$$

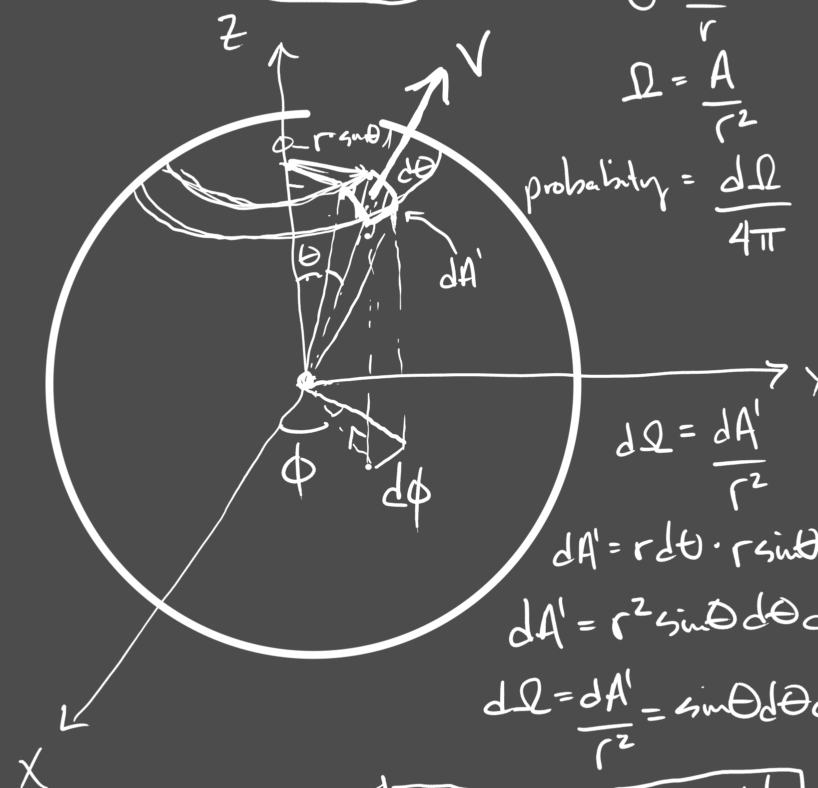
$$PV = nRT\left(\underbrace{\left(1-\frac{nb}{V}\right)^{-1}}_{\text{apply binomial}} - \frac{a \cdot n}{RTV}\right)$$

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

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

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





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

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

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

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

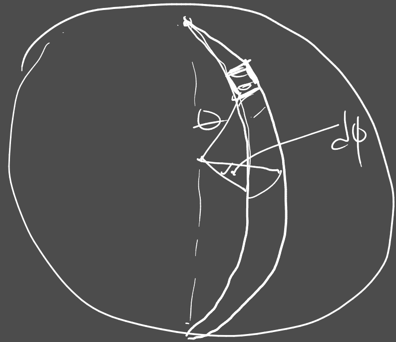
$dA' = r\,d\theta \cdot r\sin\theta\,d\phi$

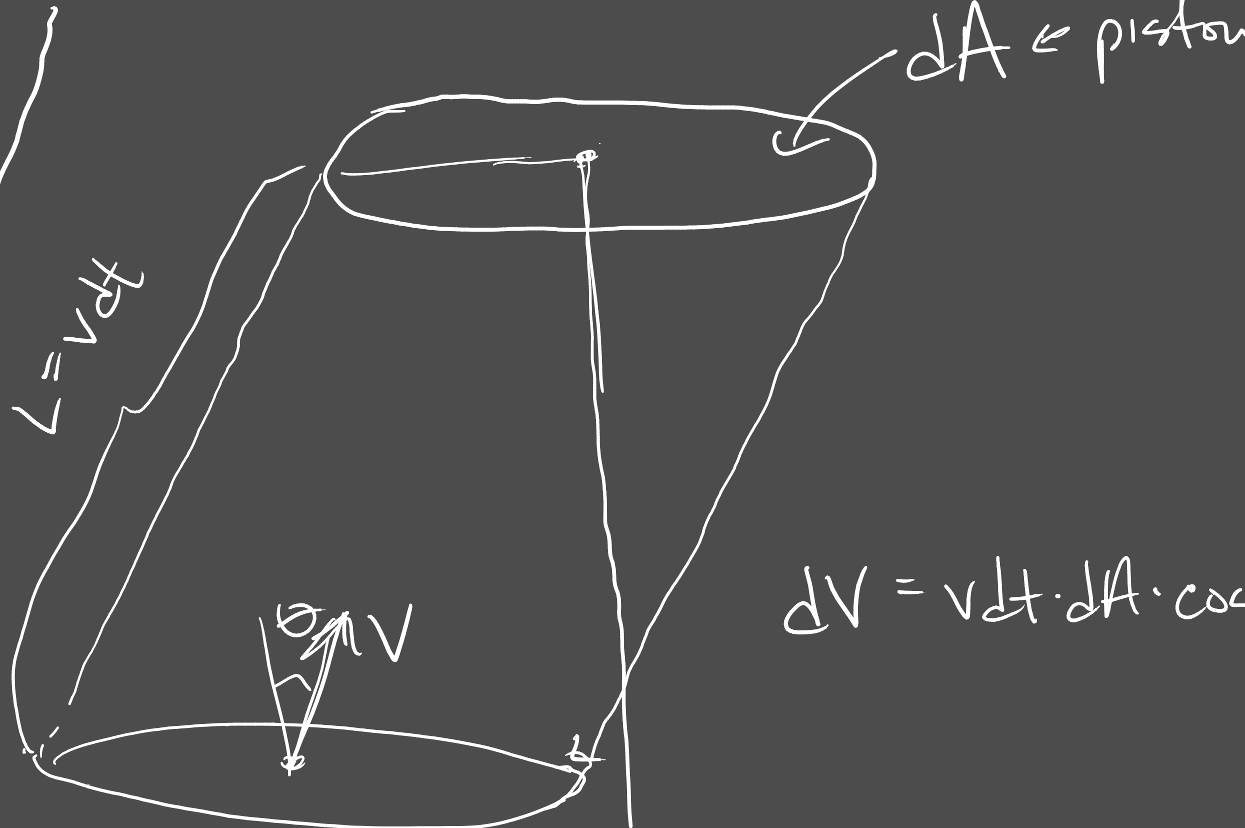
$dA' = r^2 \sin\theta\,d\theta\,d\phi$

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

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

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 $v+dv$

$f(v) \longrightarrow$ speed distribution function

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

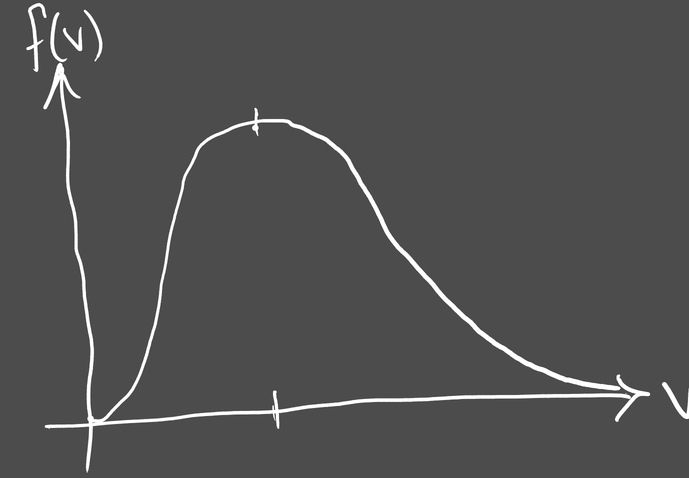
$$\longrightarrow f(v) \cdot dv$$

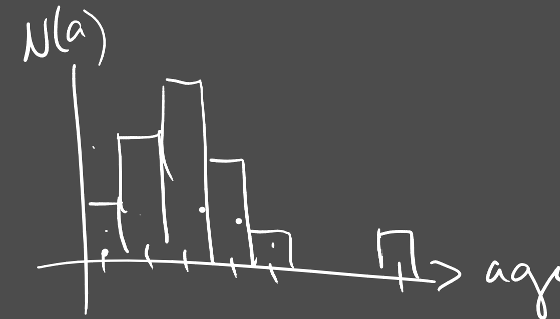
$$\int_0^\infty f(v)\, dv = 1$$

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

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

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





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

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

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

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

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

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

speed θ ϕ

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

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

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

$$pV = Nk_BT$$

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

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

<u>ideal gas</u>

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

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

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

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

#21, 22

Equipartition Theorem

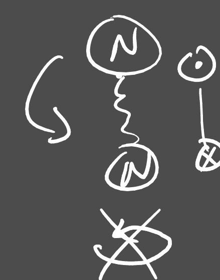
$$U_{thermal} = \frac{f}{2} N k_B T$$

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

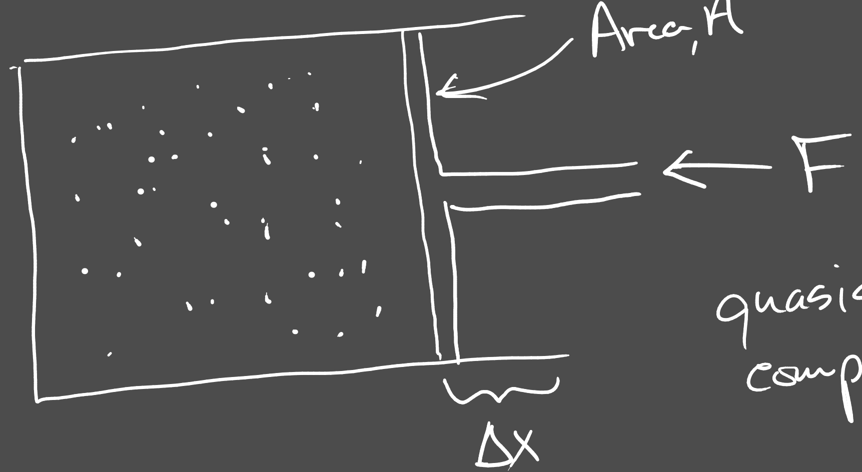
$dU = \delta Q + \delta W$

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

$$đW = -P\Delta V \rightarrow đW = -P(V,T)\,dV$$

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

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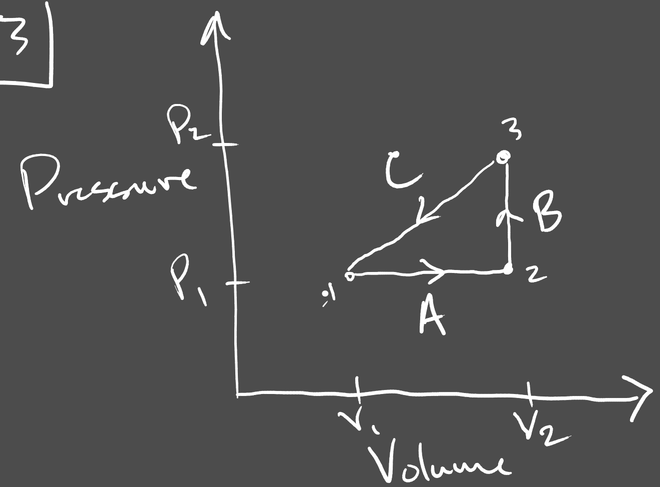
#23, 28, 32, 33, 34

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: $W > 0$

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

$U < 0$

$Q < 0$

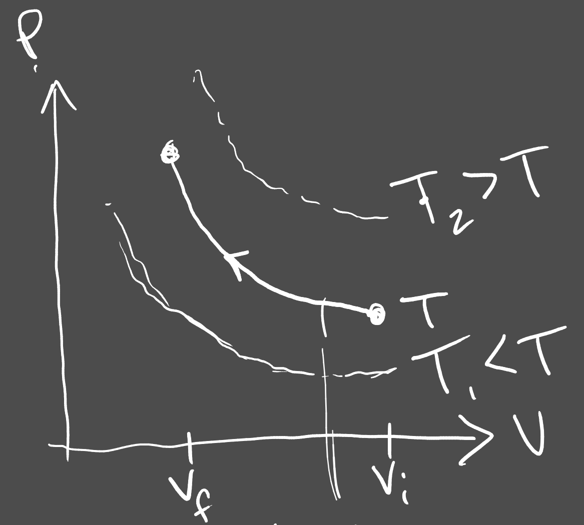
$$\underset{<0}{\Delta U} = \underset{<0}{Q} + \underset{>0}{W}$$

Isothermal Process + Adiabatic Process → expansion/compression

Isothermal → constant temperature

Adiabatic → no heat escape

Isothermal Compression



isotherm

$$PV = \underbrace{Nk_BT}_{\text{all constant}}$$

$$P = \frac{Nk_BT}{V}$$ hyperbola

$$W = -\int p\,dV = -Nk_BT\int_{V_i}^{V_f} \frac{1}{V}\,dV$$

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

$$W = Nk_BT\ln\left(\frac{V_i}{V_f}\right)$$

what about heat?

$$\Delta U = \frac{f}{2}Nk_B\Delta T$$

isothermic → $\Delta T = 0$

first law → $\cancel{dU}^{\,0} = đQ + đW$

$$đQ = -đW \rightarrow Q = Nk_BT\ln\left(\frac{V_f}{V_i}\right)$$

Adiabatic Compression → no heat added/removed

first law $dU = \cancel{dQ}^{\,0} + dW$

$$\boxed{dU = dW}$$

for ideal gas $U = \frac{f}{2} N k_B T$

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

$-pdV$

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

$PV = N k_B T$

$P = \frac{N k_B T}{V}$ $\quad -\int p dV$

$$\frac{f}{2} \frac{dT}{T} = -\frac{dV}{V}$$

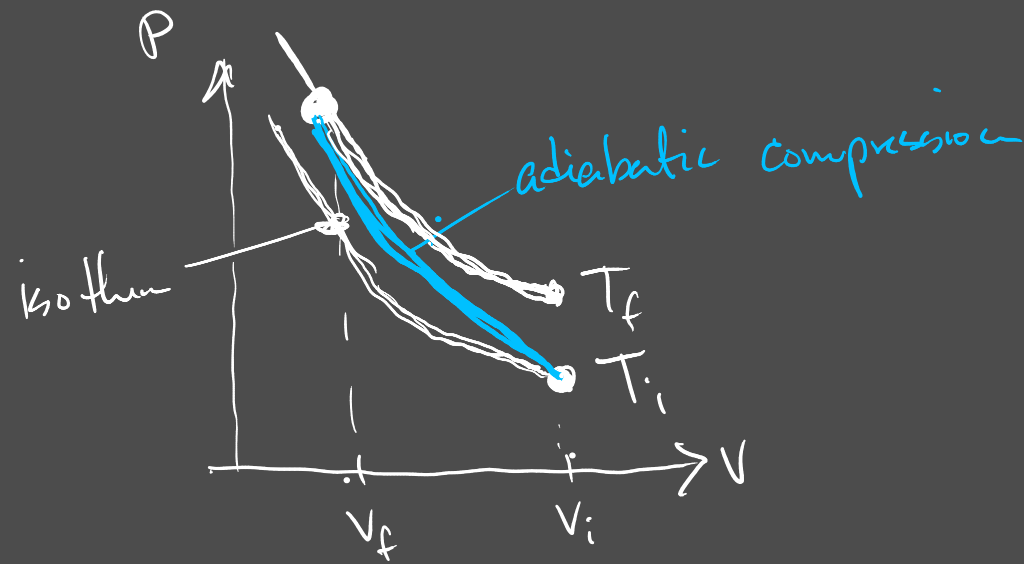
now integrate

$$\frac{f}{2} \ln\left(\frac{T_f}{T_i}\right) = -\ln\left(\frac{V_f}{V_i}\right) = \ln\left(\frac{V_i}{V_f}\right)$$

$$\left(\frac{T_f}{T_i}\right)^{f/2} = \frac{V_i}{V_f} \rightarrow V \propto \frac{1}{T^{f/2}} \rightarrow V \cdot T^{f/2} = \text{constant of prop.}$$

$$T_f^{f/2} \cdot V_f = T_i^{f/2} \cdot V_i$$

So we can get final temp now, what about final pressure?



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

$$PV = Nk_BT$$

$$T \propto PV$$

$$V \cdot (PV)^{f/2} = \text{new const}$$

$$V \cdot P^{f/2}\, V^{f/2} =$$

$$\frac{2}{f}\left(V^{1+f/2} \cdot P^{f/2}\right) = (\qquad)^{2/f}$$

$$V^{\frac{2}{f}+1} \cdot P = \text{new const.}$$

$$V^{(2+f)/f} \cdot P = \text{const}$$

$f = 3$, $\gamma = 5/3$

$f = 5$, $\gamma = 7/5$

$$\gamma = \frac{2+f}{f} \leftarrow \underline{\text{adiabatic exponent}}$$

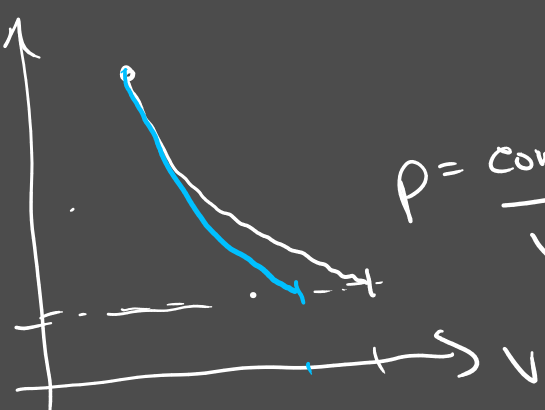
for an ideal gas

$$V^{\gamma} \cdot P = \text{const}$$

$$\downarrow$$

$$\left(\frac{V_f}{V_i}\right)^{\gamma} = \frac{P_i}{P_f}$$

Hint for #38



$$P = \frac{\text{const}}{V^{\gamma}}$$

not exactly 1.40

$$\frac{dT}{dp} = \frac{2}{f+2}\frac{T}{p} \quad \text{or} \quad \left(\frac{\gamma-1}{\gamma}\right)\frac{dT}{dp} = \frac{T}{p}$$

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

$$P(z) = P(0)\, e^{-\frac{mgz}{k_B T}}$$

depended on constant T w/ z

$$dU = \cancel{đQ}^{\,0} + đW$$

$$dU = đW$$

$$\frac{f}{2} N k_B dT = -p\, dV = -p \underbrace{\frac{dV}{dp}}_{?} dp$$

$$PV = N k_B T$$

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

product rule

$$\frac{dV}{dp} = -\frac{N k_B T}{p^2} + \frac{N k_B}{p}\frac{dT}{dp}$$

$$\frac{f}{2}\cancel{N}k_B dT = +\cancel{p}\frac{\cancel{N k_B} T}{p^{\cancel{2}}} dp - \cancel{p}\frac{\cancel{N k_B} dT}{\cancel{p}}$$

$$\left(\frac{f}{2}+1\right) dT = \frac{T}{p} dp$$

$$\left(\frac{f}{2}+1\right)\frac{dT}{dp} = \frac{T}{p} \implies \boxed{\frac{dT}{dp} = \frac{2}{f+2}\cdot\frac{T}{p}} = \frac{\gamma-1}{\gamma}\frac{T}{p}$$

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

$$\frac{dP}{dT} = \underbrace{\frac{\gamma}{\gamma-1} \frac{P}{T}}$$

$$\frac{dP}{dT} \cdot \frac{dT}{dz} = -\frac{mg}{k_B} \cdot \frac{P}{T}$$

$$\frac{\gamma}{\gamma-1} \cdot \frac{\cancel{P}}{\cancel{T}} \cdot \frac{dT}{dz} = -\frac{mg}{k_B} \cdot \frac{\cancel{P}}{\cancel{T}}$$

$$\frac{dT}{dz} = \underbrace{-\frac{mg}{k_B}\left(\frac{\gamma-1}{\gamma}\right)}_{\text{constant}}$$

linear change in temp w/ height

$$dU = \underbrace{đQ}_{T\,dS} + \underbrace{đW}_{-p\,dV}$$

integration factor

Heat Capacity

$$dU = đQ + \underbrace{đW}_{-pdV}$$

$$đQ = dU + pdV$$

$\underline{U(T,V)}$ or $U(T,P)$

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

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

We want to know how much heat is needed to change the temperature under certain conditions (constraints)

Two cases: (1) Constant volume

(2) Constant pressure

(1) Constant volume $\rightsquigarrow dV = 0$

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

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

↳ heat capacity at constant volume

ideal gas

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

$$U = \frac{f}{2} n_m R T$$

$$\frac{\partial U}{\partial T} = \frac{f}{2} n_m R$$

$\frac{C_V}{n_m}$ ← molar heat capacity / molar specific heat

$$\frac{C_V}{n_m} = \frac{f}{2} R \to \sim 12.5 \text{ monatomic}, \quad \to \sim 20 \text{ diatomic}$$

☆ ☆ ☆ ☆

#36, 38, 41, 45

② Constant pressure

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

$$C_p \equiv \left(\frac{đQ}{dT}\right)_p = \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{dV}{dT}\right)_p$$

$$\rightarrow C_p = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{dV}{dT}\right)_p$$

$$C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{dV}{dT}\right)_p .$$

ideal gas

$$U = \frac{f}{2} n_m R \cdot T$$

$$C_p = \frac{f}{2} n_m R + 0 + p\frac{dV}{dT}$$

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

for ideal gas

$$V = \frac{n_m R T}{p}$$

$$\frac{dV}{dT} = \frac{n_m R}{p}$$

$$C_p = \frac{f}{2} n_m R + n_m R$$

$$\underbrace{\frac{C_p}{n_m}}_{} = \frac{f}{2} R + R$$

(molar specific heat)
(molar heat capacity)

for monoatomic

$f = 3$

$C_V = \frac{3}{2} R$

$C_p = \frac{5}{2} R$

Schroeder's derivation of C_p (slightly beefed up)

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

$$đQ = dU + p\,dV$$

$$C_p = \left(\frac{đQ}{dT}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + \underbrace{\left(\frac{\partial U}{\partial P}\right)_T \frac{dp}{dT}}_{dp=0 \text{ at constant pressure}} + p\frac{dV}{dT}$$

$$C_p \equiv \left(\frac{đQ}{dT}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{dV}{dT}\right)_p \qquad C_p = \frac{\Delta U + p\Delta V}{\Delta T}$$

$$\gamma \equiv \frac{C_p}{C_v} \leftarrow \text{adiabatic index} = \frac{(f+2)}{f}$$

for ideal gas

Specific Heat Capacity

$$c_p = \frac{C_p}{M}$$ ← big see

little see

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

Latent Heat → during a phase change

$$C = \frac{dQ}{dT}$$ ← add some heat

← 0 change in temp

$$C = \infty$$

total heat to complete the phase change

$$\frac{Q}{M} = L$$ ← latent heat

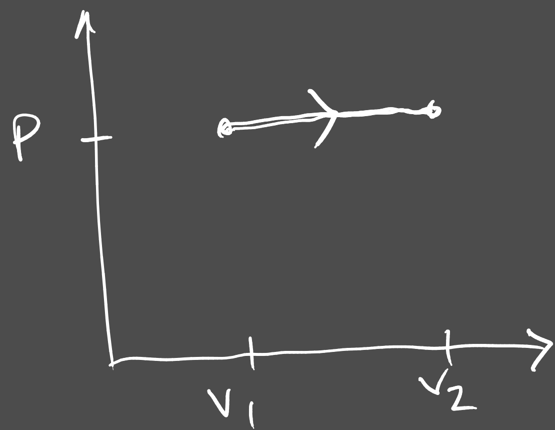
L_f → latent heat of fusion (solid ↔ liquid)

L_v → latent heat of vaporization (liquid ↔ gas)

Enthalpy

isobaric process → constant pressure

#1.34



$W: -P(V_2 - V_1)$

$\Delta U: \frac{f}{2} P\Delta V = \frac{f}{2} P(V_2 - V_1)$

$Q: \Delta U - W = \frac{f}{2} P(V_2 - V_1) + P(V_2 - V_1)$

heat at constant pressure → enthalpy

$$H = U - W$$

$$H \equiv U + PV$$

$$\Delta H = \underline{\Delta U + P\Delta V}$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P$$

☆ ☆
#47, 50

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O\ (l)$ $\}$ put this in a piston chamber

$\underline{\Delta H = -286\ kJ/mol}$

how much heat will be given off?

How much of this heat comes from the energy change in the bonds $\rightarrow \Delta U_{int}$

How much comes from the change in volume?

$\underline{1.49}$

$PV = n_m R T$

$10^5\ Pa \cdot V = 1.5\ mol\ (8.31\ J/K\,mol)(273\ K)$

$V = .034\ m^3$

$= 34$ liters

$W = -P\int_{34L}^{0L} dV = -10^5\ Pa \cdot (0\ m^3 - 0.34\ m^3) = 3400\ J$

$= 3.4\ kJ$

$\underline{\Delta H = -286\ kJ} = \Delta U - W \rightarrow \underline{\Delta U = -282.6\ kJ}$

1.50)

$$CH_4 + 2O_2 \longrightarrow CO_2(g) + 2H_2O(g)$$

$T = 298\ K \qquad P = 10^5\ Pa$

(a) $CH_4 \leftarrow C + 2H_2$

$-74.81\ kJ/mol \qquad 0\ kJ/mol \qquad 0\ kJ/mol$

so it would take 74.8 kJ/mol to convert $C + H_2$ to CH_4

(b) $C + O_2 \rightarrow CO_2$

$\Delta H = -393.51\ kJ/mol$

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O(g)$

$\Delta H = -241.82\ kJ/mol$

$\times 2$ for 2 moles of H_2O

$-483.64\ kJ$

(c) $\Delta H_{reaction} = +74.81\ kJ - 483.64 - 393.51$

$= -802.34\ kJ/mol\ CH_4$

(d) How much heat is given off to surroundings (at constant pressure) $\rightarrow$ 802.34 kJ

(e) $W=0$

$\Delta H = \Delta U = 802.34\,kJ$

if H_2O condenses to liquid

$p\Delta V = -4.9\,kJ$

$\Delta H \rightarrow H_2O(l)$ $\quad -285\,kJ/mol \times 2 = -571.64\,kJ$

$\Delta H_{react} = -890.34\,kJ = \Delta U + p\Delta V$

$\Delta U = -885.41\,kJ$

(f) $m = 2 \cdot 10^{30}\,kg$

$P = 3.9 \cdot 10^{26}$ Watts $= \dfrac{\Delta Q}{\Delta t} \leadsto t = \dfrac{\Delta Q}{P}$

$\Delta Q = 802\,kJ/mol \cdot \#mol$

$CH_4 + 2O_2$

$\downarrow \qquad \downarrow$

$16\,g/mol \quad 2 \cdot 32\,g/mol \quad = 80\,g/mol$

$$802\,\frac{kJ}{\cancel{mol}} \cdot \frac{1\,\cancel{mol}}{80\,\cancel{g}} \cdot \frac{1000\,\cancel{g}}{1\,kg} \cdot 2 \cdot 10^{30}\,kg = 2 \cdot 10^{34}\,kJ = 2 \cdot 10^{37}\,J$$

$$t = \frac{2 \cdot 10^{37}\,J}{3.9 \cdot 10^{26}\,W} = 5 \cdot 10^{10}\,s \cdot \frac{1\,hr}{3600\,s} \cdot \frac{1\,d}{24\,hr} \cdot \frac{1\,yr}{365\,d} = \underline{\underline{1585\,yr}}$$

1.36 (a) $V_1 = 1\text{ liter} = .001\,m^3$ $\quad P_1 = 1\,atm = 1\cdot 10^5\,Pa$

$V_2 = ?$ $\quad P_2 = 7\,atm = 7\cdot 10^5\,Pa$

γ for air $\frac{7}{5}$

$$\left(\frac{V_2}{V_1}\right)^{\gamma} = \frac{P_1}{P_2}$$

$$V_2 = V_1\left(\frac{P_1}{P_2}\right)^{1/\gamma} = 1\text{ liter}\left(\frac{1\,atm}{7\,atm}\right)^{5/7}$$

$$V_2 = 0.249 \text{ liters}$$

$$\frac{V_2}{V_1} = \frac{1}{4}$$

(b) $\boxed{p = \frac{c}{V^{\gamma}}}$

$pV^{\gamma} = \text{constant}$

$$\frac{P_2}{P_1} = \frac{V_1^{\gamma}}{V_2^{\gamma}}$$

$$p(V) = \frac{P_1 V_1^{\gamma}}{V^{\gamma}} \leftarrow \text{now its a function}$$

$$W = -\int p\,dV = -P_1 V_1^{\gamma}\int \frac{dV}{V^{\gamma}}$$

$dU = đW$

$\Delta U = W$

$\Delta U = \frac{5}{2} N k_B \Delta T = W \longrightarrow \frac{5}{2} N k_B (T_2 - T_1)$

?

$\frac{5}{2} \underbrace{N k_B T_1}_{P_1 V_1} \left(\frac{T_2}{T_1} - 1 \right)$

$10^5 \cdot .001\,m^3$

10^2

$\left(\frac{T_2}{T_1}\right)^{f/2} = \frac{V_1}{V_2}$

$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{2/f}$

$T_2 = 523\,K$

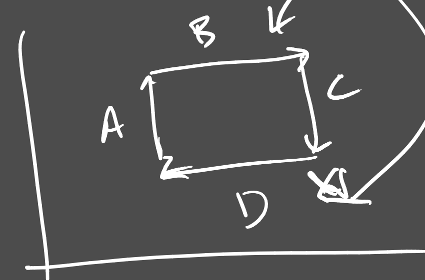
$\Delta T = 223\,K$

$\Delta U = 165\,J$

$N = \frac{P_1 V_1}{k_B T_1}$

constant pressure

isobaric compressions (B + D)



(A + C)

isochoric

constant volume