

# Thermo Intro

temperature

Fahrenheit

Celcius

Rankine

Kelvin

Room temp  $20^{\circ}\text{C}$  ( $\sim 70^{\circ}\text{F}$ )

$\downarrow$   
293K

$$\Delta F = \frac{9}{5} \Delta C$$

$$T_F = \frac{9}{5} T_C + 32$$

$$T_K = T_C + 273.15$$

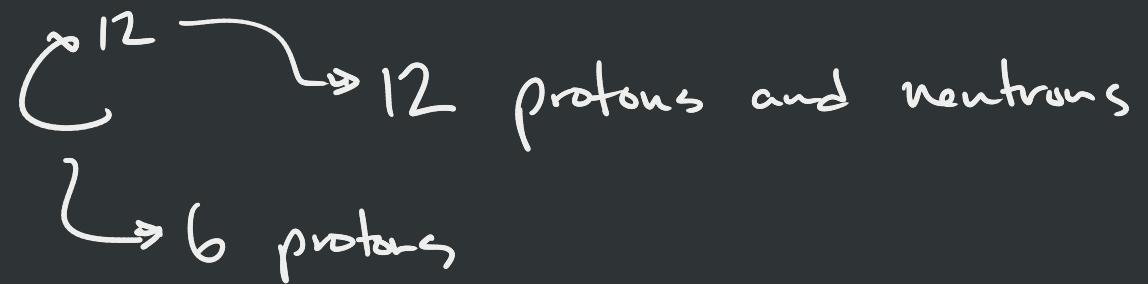
Number, moles, molar mass, density

1 mole of things =  $6.022 \cdot 10^{23}$  things

particle  
atom  
molecule

$N \rightarrow$  number of particles

$n \rightarrow$  number of moles



Ex. mass of one proton?

$$\text{mass of one proton} \times \text{number of proton} = \frac{\text{mass of collection}}{\text{collection}}$$

1 mole is a gram of protons and neutrons

$M$  → total mass of a collection

$m$  → mass of one particle

$$m \times N = M$$

$$m = \frac{M}{N} = \frac{1 \text{ gram}}{N_A}$$

$N_A \approx \text{Avogadro's number } 6.022 \cdot 10^{23}$

$$m = 1.7 \cdot 10^{-24} \text{ grams}$$

$$= 1.7 \cdot 10^{-27} \text{ kg}$$

What about  $N_2$ ?

$$1 \text{ mole of } N_2 = 2 \cdot (14 \frac{\text{g}}{\text{mol}}) = 28 \text{ g}$$

Dry air?

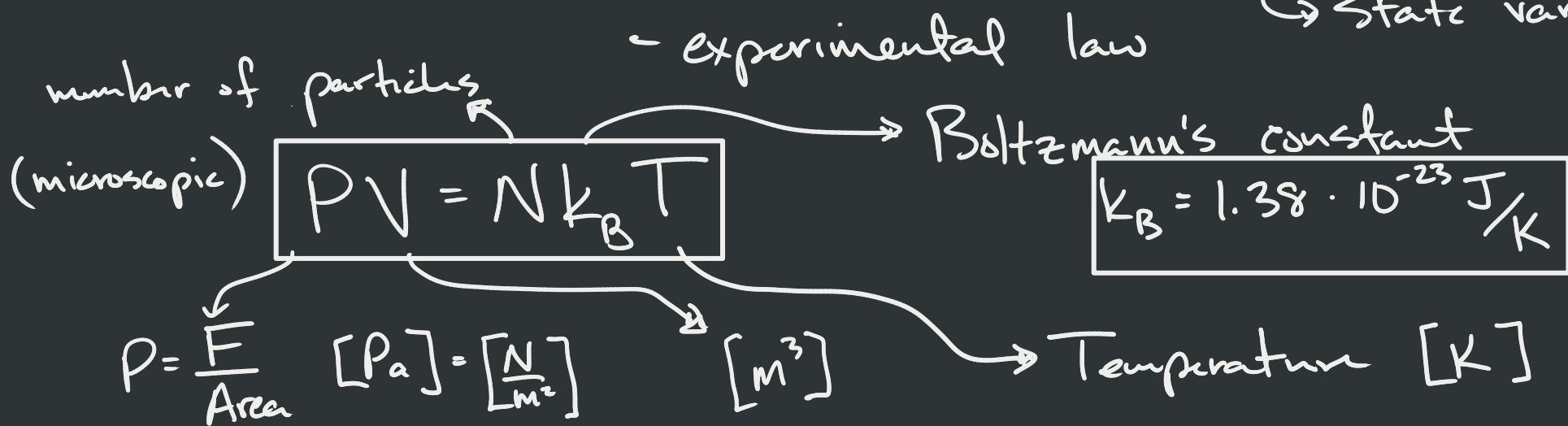
78%  $N_2$ , 21%  $O_2$ , 1% Ar

$$0.78 \cdot (28 \frac{\text{g/mol}}{\text{mol}}) + 0.21 (32 \frac{\text{g/mol}}{\text{mol}}) + 0.01 (40 \frac{\text{g/mol}}{\text{mol}}) = 29 \frac{\text{g/mol}}{\text{mol}}$$

---

Ideal Gas Law  $\rightarrow$  an equation of state

$\hookrightarrow$  state variables



Alternative form  $\rightarrow PV = nRT$  (macroscopic)

↗ universal gas constant

$$N k_B = n \cdot R$$

$$\left. \begin{array}{l} \\ N = n \cdot N_A \end{array} \right\} \leftarrow \text{definition of moles}$$

$$\cancel{n} \cdot N_A \cdot k_B = \cancel{n} \cdot R$$

$$N_A \cdot k_B = R = 6.022 \cdot 10^{23} \frac{\cancel{\text{part}}}{\cancel{\text{mol}}} 1.38 \cdot 10^{-23} \frac{\text{J}}{\text{K}}$$

$$R = 8.31 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

Volume of 1 mole of air at room temp and atmospheric pressure

293K or 300K

$$\hookrightarrow 1 \text{ atm} = 1.013 \cdot 10^5 \frac{\text{Pa}}{\text{bar}}$$

$$V = \frac{nRT}{P} = \frac{1 \text{ mol} \cdot 8.31 \frac{\text{J}}{\text{K} \cdot \text{mol}} \cdot 300 \text{ K}}{10^5 \text{ Pa}} = 0.024 \text{ m}^3$$

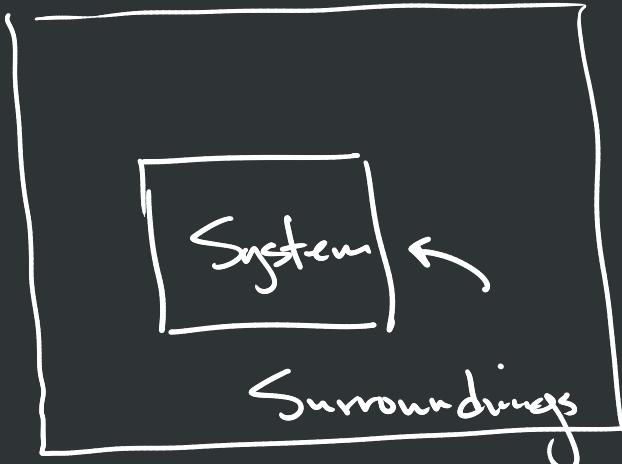
$$\nabla_{\text{cub}} = \delta^3$$
$$\sqrt[3]{0.024 \text{ m}^3} = \delta = 0.288 \text{ m}$$

$\sim 30 \text{ cm}$

## Laws of Thermodynamics

0. Thermometers work
1. Conservation of Energy
2. Heat flows from high temp to low temp  
Entropy is maximized  
No perpetual motion machine
3. You can't reach absolute zero

# 1<sup>st</sup> Law $\rightarrow$ Conservation of Energy



Energy of a system can change

Work

Heat

Force applied  
over distance

Spontaneous flow  
of energy due  
to a difference  
in temperature

$$dU = Q + W$$

$$\rightarrow dU = \delta Q + \delta W$$

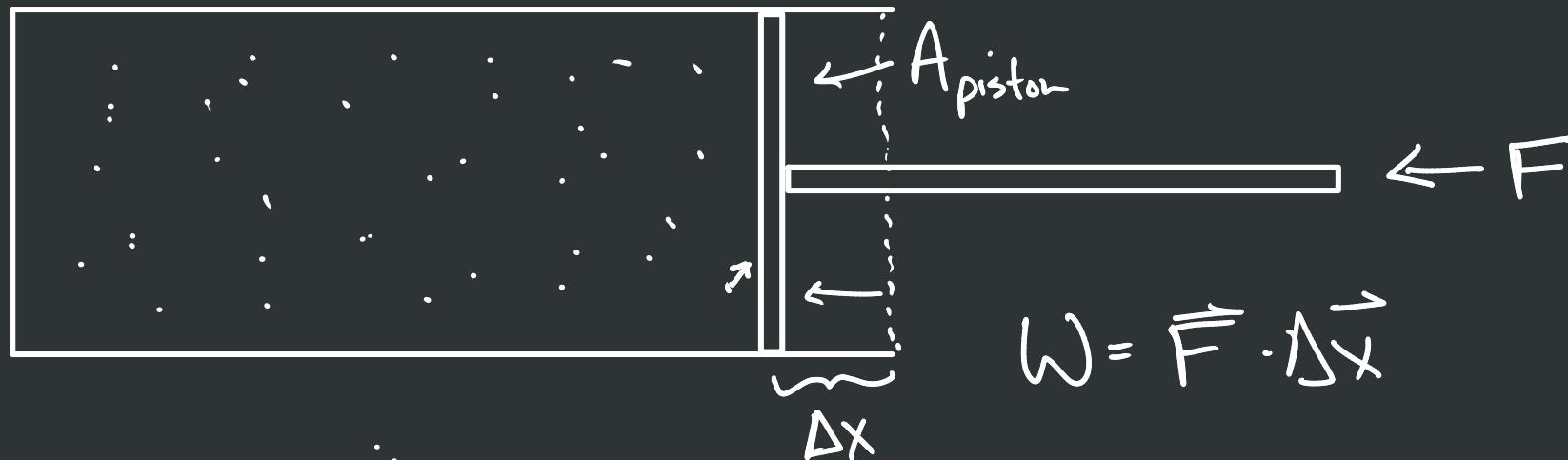
↑ inexact differential

~~$$dQ = Q(x+dx) - Q(x)$$~~

$$dU = \delta Q + \delta W$$

↳ internal energy of the system, heat is added  
or work is done to the system they are positive

# Compression Work (or Expansion)



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

assuming pressure is  
uniform throughout the  
chamber  
↳ compression (expansion)  
must happen quasistatically

$$P_{\text{gas}} = \frac{F_{\text{gas}}}{A_{\text{piston}}}$$

$$W = P_{\text{gas}} \cdot A_{\text{piston}} \cdot \Delta x$$



$\Delta V$   
 $\Delta V$  is (-) in  
compression but  
energy is  
increasing

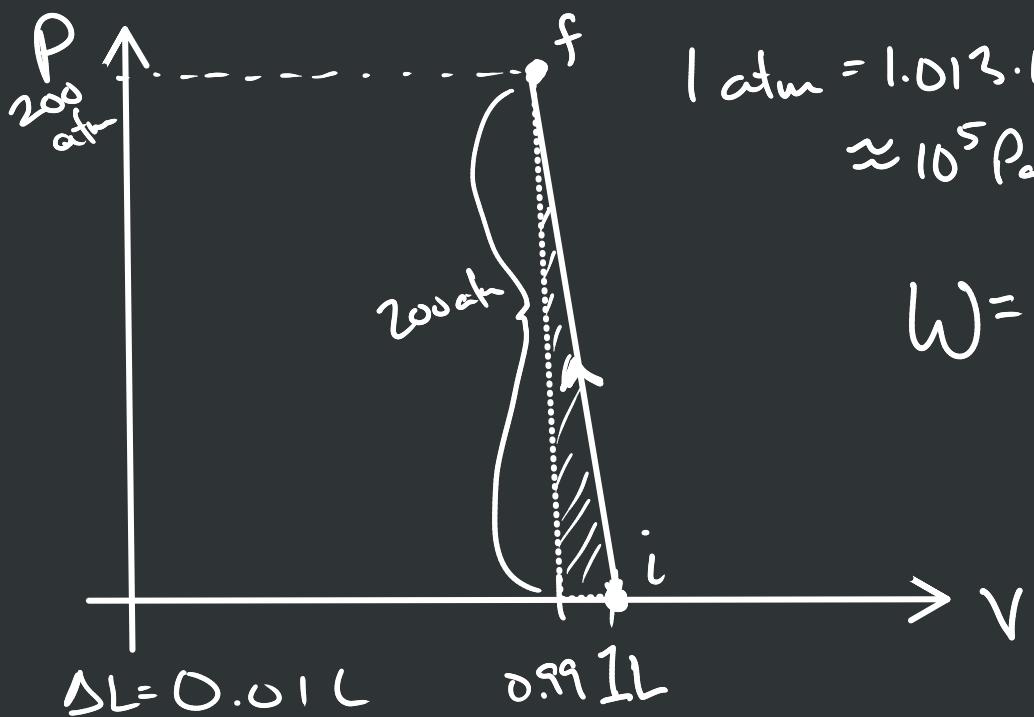
$$W = -P \Delta V$$

$$dU = dQ + dW$$

$$dW = -PdV$$

$$\underline{W = \int -PdV}$$

**Problem 1.32.** By applying a pressure of 200 atm, you can compress water to 99% of its usual volume. Sketch this process (not necessarily to scale) on a  $PV$  diagram, and estimate the work required to compress a liter of water by this amount. Does the result surprise you?



$$1 \text{ atm} = 1.013 \cdot 10^5 \text{ Pa}$$

$$\approx 10^5 \text{ Pa}$$

$$W = -\int P dV$$

$$P_{\text{abs}} = P_{\text{gauge}} + P_{\text{atm}}$$

$$\Delta V = 0.01 \text{ L} = 10^{-5} \text{ m}^3$$

$$0.01 \text{ L} \cdot \frac{1 \text{ m}^3}{1000 \text{ L}} = 10^{-5} \text{ m}^3$$

$$A_D = \frac{1}{2} b h \Rightarrow W = \underline{\underline{\frac{1}{2} P \Delta V}}$$

$$W = \frac{1}{2} (200 \cdot 10^5 \text{ Pa}) \cdot 10^{-5} \text{ m}^3 = \underline{\underline{100 \text{ J}}}$$

$$1 \text{ L} \cdot \frac{10^3 \text{ mL}}{1 \text{ L}} \cdot \frac{1 \text{ cm}^3}{1 \text{ mL}} \cdot \frac{(1 \text{ m})^3}{(100 \text{ cm})^3} = 1 \cdot 10^{-3} \text{ m}^3 = 0.001 \text{ m}^3$$

$$(10^2)^3 = 10^6$$

$$\boxed{1000 \text{ L} = 1 \text{ m}^3}$$

Slope - intercept

$$y = mx + b$$

$m = \frac{\Delta p}{\Delta V}$

↑  
y-int

point - slope

$$y - y_1 = m(x - x_1)$$

$$m = \frac{y_2 - y_1}{x_2 - x_1} = \frac{200}{-0.01} = -2 \cdot 10^4 \text{ atm/L}$$

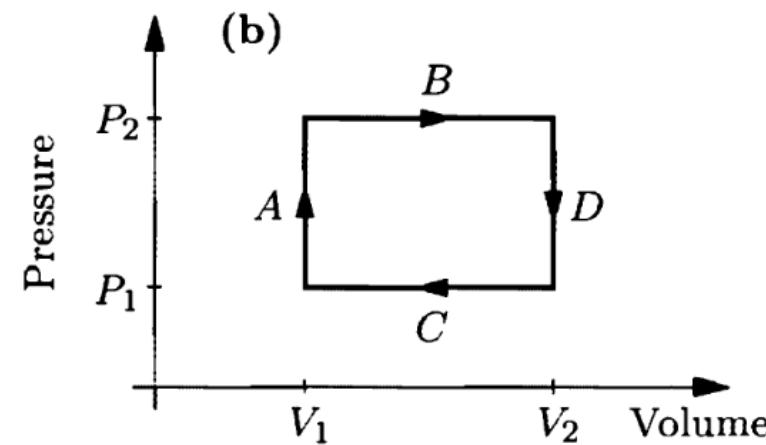
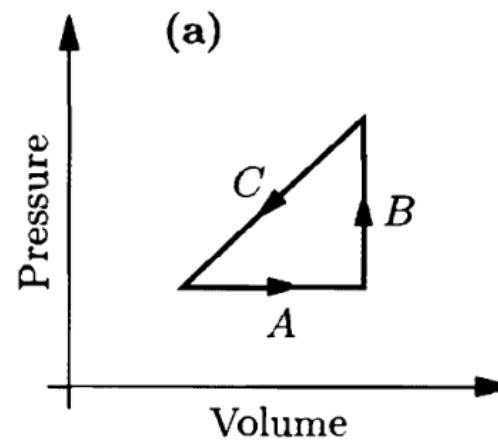
$$P - P_0 = -2 \cdot 10^4 \frac{\text{atm}}{\text{L}} (V - V_0)$$

$$P = -2 \cdot 10^4 \frac{\text{atm}}{\text{L}} \cdot V + 2 \cdot 10^4 \text{ atm}$$

1.33]

1.33

**Problem 1.33.** An ideal gas is made to undergo the cyclic process shown in Figure 1.10(a). For each of the steps *A*, *B*, and *C*, determine whether each of the following is positive, negative, or zero: (a) the work done on the gas; (b) the change in the energy content of the gas; (c) the heat added to the gas. Then determine the sign of each of these three quantities for the whole cycle. What does this process accomplish?



**Figure 1.10.** *PV* diagrams for Problems 1.33 and 1.34.

Come back!

# Proportionality

$$PV = Nk_B T$$

$$P_1 V = Nk_B T_1$$

$$\frac{P_2 V = Nk_B T_2}{P_1 V = Nk_B T_1}$$

$$P_2 V = Nk_B T_2$$

$$\frac{P_2}{P_1} = \frac{T_2}{T_1}$$

$$\frac{T_2}{T_1} = 2$$

$$P = \frac{Nk_B}{V} T$$

$$\begin{array}{c} P \propto T \\ \downarrow \\ P = C \cdot T \end{array}$$

↳ constant of proportionality

$$\frac{P_2}{P_1} = \frac{N_2}{N_1} \rightarrow P \propto N^{\prime} \rightarrow P = C_2 N$$

$$\hookrightarrow \frac{P_2}{P_1} = \left( \frac{N_2}{N_1} \right)^{\prime}$$

$$PV = N k_B T$$

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

$$P \propto N' T' V^{-1}$$

$$P \propto V^{-1} \rightarrow P = C_2 V^{-1} = \frac{C_2}{V}$$

$$\hookrightarrow \frac{P_2}{P_1} = \left( \frac{V_1}{V_2} \right)^{-1} = \frac{V_1}{V_2}$$

$$F_G \propto r^{-2} \rightarrow F_G = C_3 \cdot r^{-2}$$

↓

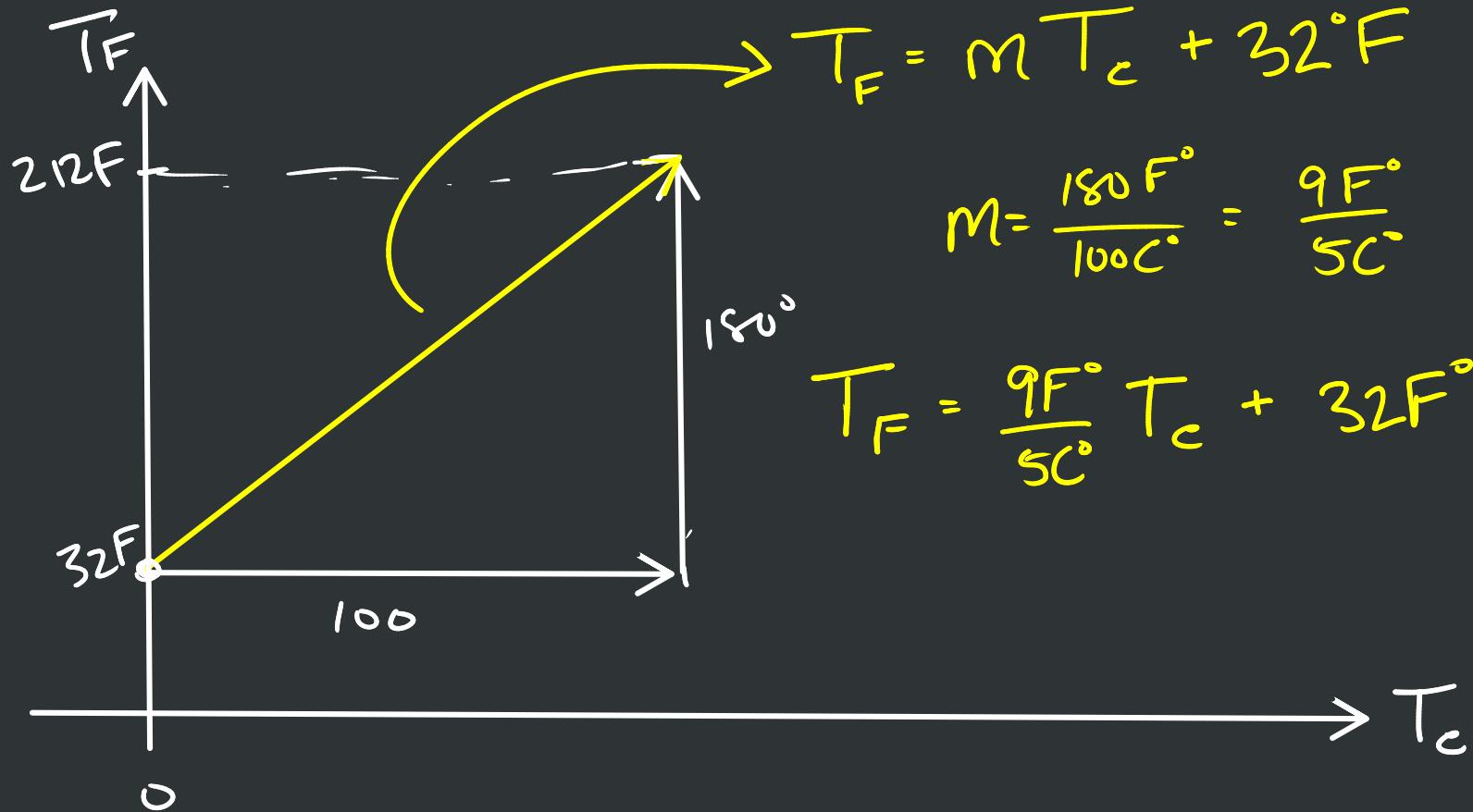
$$\frac{F_2}{F_1} = \left(\frac{r_2}{r_1}\right)^{-2} = \frac{C_3}{r^2}$$

$$\frac{F_2}{F_1} = \frac{r_1^2}{r_2^2}$$

$$T = \frac{PV}{k_B N}$$

$$\rho \propto N^{\prime} T^{\prime} V^{-1}$$

$$\frac{P_2}{P_1} = \left(\frac{T_2}{T_1}\right)^{\prime} \cdot \left(\frac{V_2}{V_1}\right)^{-1}$$



Heat  $\rightarrow$  flow of energy due to a difference in temperature

$$\Delta U = Q + \cancel{W} \quad [\text{Joules}] \quad [\text{calorie}] \quad 1 \text{ cal} = 4.186 \text{ J}$$

vs.

Calorie  $\leftarrow$  food

$$\frac{Q}{\Delta T} = C \leftarrow \text{heat capacity} \quad \left[ \frac{\text{J}}{\text{K}} \right] \quad | C_{\text{cal}} = 1000 \text{ calorie}$$

①

$$\frac{C}{m} = c \leftarrow \text{specific heat capacity} \quad \left[ \frac{\text{J}}{\text{gK}} \right] = \left[ \frac{\text{kJ}}{\text{kgK}} \right] \quad | \overline{Q = mc \cdot \Delta T}$$

②

$$\frac{C}{n} = C_{v,p} \leftarrow \text{molar heat capacity at constant volume}$$

molar heat capacity at constant pressure

$$Q = nC_v \cdot \Delta T$$

③  $\frac{C}{V} \leftarrow$  volumetric heat capacity

---

Phase change

$$\frac{Q}{m} = L \leftarrow \text{Latent Heat}$$

→ Latent Heat of fusion -  $L_f$   
solid  $\leftrightarrow$  liquid

→ Latent Heat of vaporization -  $L_v$   
liquid  $\leftrightarrow$  gas

---

Calorimetry - when multiple objects are in thermal contact  
at what temperature is thermal equilibrium

$$\Delta U = Q = Q_1 + Q_2 + Q_3 + \dots$$



objects changing temp or phase transitions occurring

Ex:  $\left| \begin{array}{l} 5\text{kg of Al at } 500^\circ\text{C} \\ 5\text{kg of Pb at } 75^\circ\text{C} \end{array} \right|$  What is equil temp?

$\hookrightarrow 490^\circ$  How much heat was given off?  
 $\equiv$

$$C_{Al} = 0.9 \frac{\text{kJ}}{\text{kgK}}$$

$$C_{Pb} = 0.13 \frac{\text{kJ}}{\text{kgK}}$$

$$Q = mc\Delta T = mc(T_f - T_i)$$

$$= 5\text{kg} \cdot 0.9 \frac{\text{kJ}}{\text{kgK}} (490^\circ\text{C} - 500^\circ\text{C})$$

$$= 5\text{kg} \cdot 0.9 \frac{\text{kJ}}{\text{kgK}} \cdot (-10\text{K})$$

$$Q = -45 \text{ kJ} \quad \xrightarrow{+45 \text{ kJ}} +45 \text{ kJ} = 5\text{kg} \cdot 0.13 \frac{\text{kJ}}{\text{kgK}} \cdot \Delta T$$

$$\Delta T = 69.2 \text{ K}$$

$$T_f = 145^\circ\text{C}$$

$$Q_1 + Q_2 = 0$$

$$m_{Al} \cdot C_{Al} \cdot \Delta T_{Al} + m_{Pb} \cdot C_{Pb} \cdot \Delta T_{Pb} = 0$$

$$m_{Al} \cdot C_{Al} \cdot (T_f - 500) + m_{Pb} \cdot C_{Pb} \cdot (T_f - 75) = 0$$

solve for  $T_f$

$$T_f = 446 \text{-ish } {}^{\circ}\text{C}$$

HW: 1.7, 1.16, 1.17

$$1.7 \quad \beta = \frac{\Delta V}{V} / \Delta T$$

$$\beta = \frac{1}{5500} \text{ K}^{-1} = 1.81 \cdot 10^{-4} \text{ K}^{-1}$$

$$r = \frac{1}{2} \text{ cm}$$

$$A = \pi \left(\frac{1}{2} \text{ cm}\right)^2 = \frac{\pi}{4} \text{ cm}^2$$

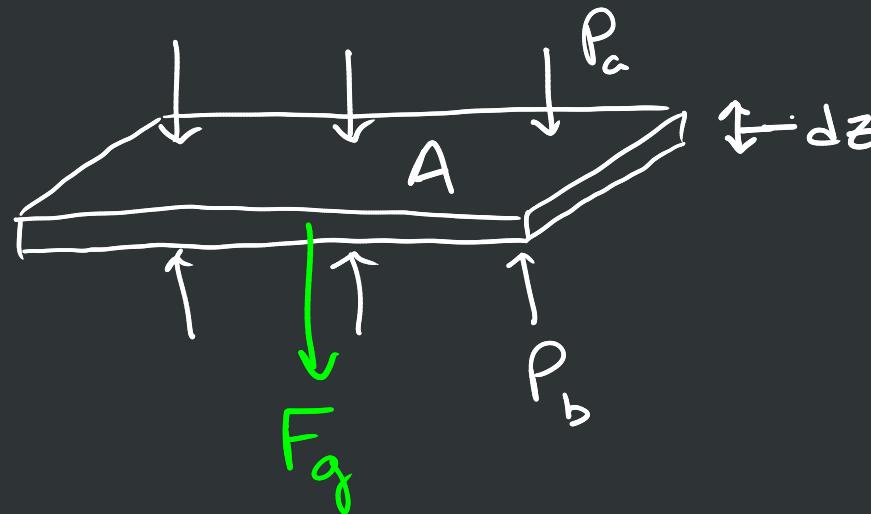
$$V = A \cdot h = \frac{\pi}{2} \text{ cm}^3$$

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

$$\Delta z = 1 \text{ mm} \approx 1 \text{ K}$$

$$1.16 \quad \rho = \frac{M}{V}$$

"rho"  
Volumetric mass density



a)  $P = \frac{F}{A}$

$$+ P_b \cdot A - P_a \cdot A - M \cdot g = 0$$



$$\frac{dP}{dz} = \underbrace{\rho}_{\text{pressure}}$$

b)  $PV = Nk_B T$

$$\rho = \underbrace{\frac{P}{T}}_{m} \leftarrow \text{Avg Mass of air molecules}$$

$$m = 29 \text{ g/mol}$$

$$N = m \cdot n$$

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

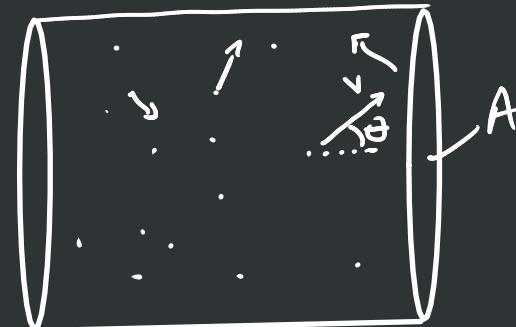
$\left(1 - \frac{nb}{V}\right)^{-1} \rightarrow$  apply the binomial expansion

1.2b

# Kinetic Theory and Equipartition of Energy

pressure  $\longleftrightarrow$  kinetic energy  $\longleftrightarrow$  temperature

$$\text{pressure} = \frac{F}{A} = \frac{\Delta p}{A \Delta t} \xleftarrow{\substack{2mv \cos \theta \\ \Delta p \text{ for each} \\ \text{collision w/} \\ \text{the wall in} \\ \Delta t \text{ amount} \\ \text{of time}}}$$



$$d(\text{pressure}) = \frac{2mv \cos \theta}{dA \cdot dt} \cdot \underbrace{\text{number of particles hitting area } dA}_{w/ v \text{ velocity in } dt} \} \text{ integrate over all velocities + } \theta \}$$

Number of atoms traveling in a particular direction w/ a particular speed      fraction of them that are within striking distance of the surface of  $dA$

# Probability

$$P(x) = \frac{\text{desired outcomes}}{\text{total outcomes}}$$

$N(x) \leftarrow$  number of desired outcomes

total outcomes  $\rightarrow N = \sum_{x=0}^{\infty} N(x)$

average  $P(x) = \frac{N(x)}{N}$

$$N(x) = P(x) \cdot N$$

normalized

$$\sum_{x=0}^{\infty} P(x) = 1$$

$$\langle X \rangle = \sum_{x=0}^{\infty} x \cdot P(x)$$

↑

average value  
expectation value  
(not the same  
as the most probable)

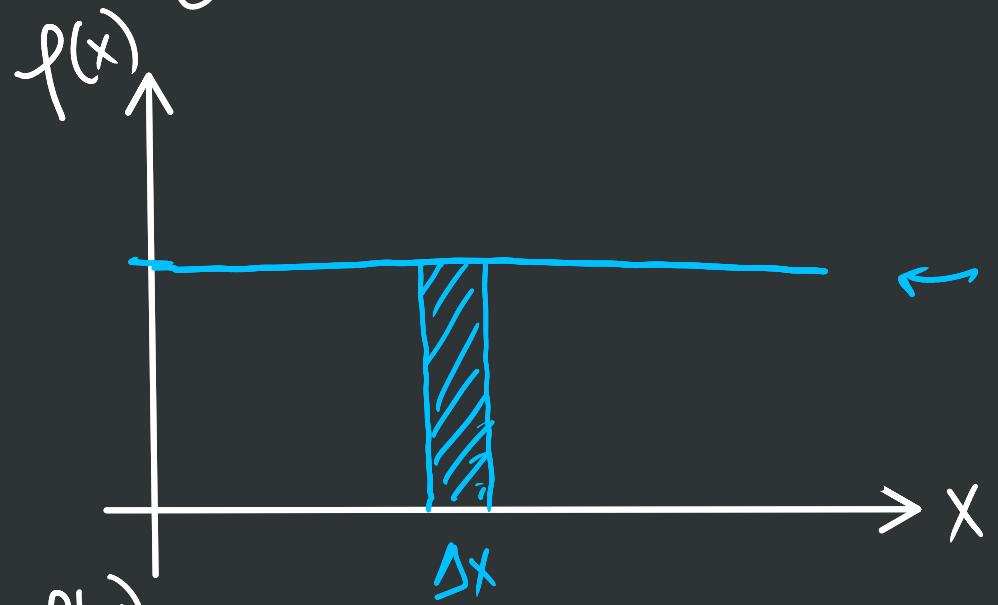
$$\langle X^2 \rangle = \sum_{x=0}^{\infty} x^2 \cdot P(x)$$

$$\langle f(x) \rangle = \sum_{x=0}^{\infty} f(x) \cdot P(x)$$

weighted average  
by probability

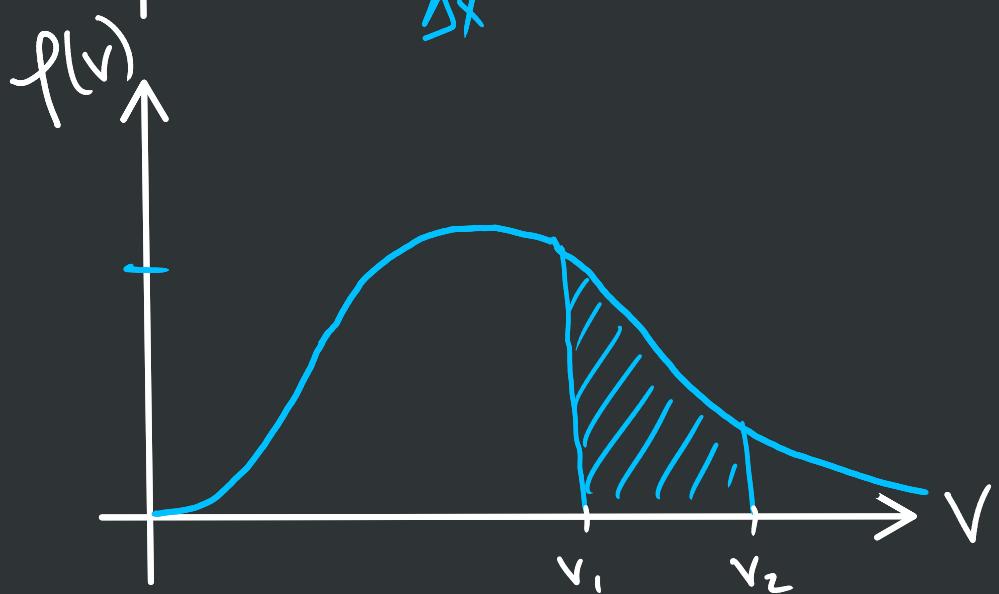
## Continuous variable

$$\left\{ \begin{array}{l} \text{probability that an individual} \\ \text{value lies between } x \text{ and } x+dx \end{array} \right\} = f(x) \cdot dx$$



← uniform  
prob  
function

- probability density function
- probability distribution



$$P(v_1, v_2) = \int_{v_1}^{v_2} f(v) \cdot dv$$

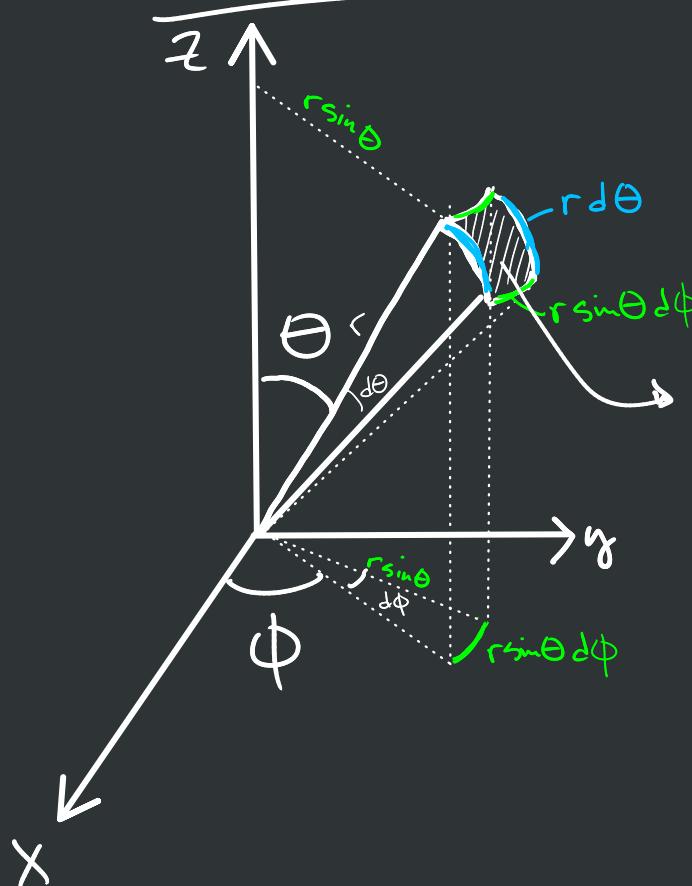
$$\int_{-\infty}^{+\infty} f(v) dv = 1 \quad \leftarrow \text{normalization}$$

$$\langle v \rangle = \int_{-\infty}^{\infty} v \cdot f(v) \cdot dv$$

$$\langle v^2 \rangle = \int_{-\infty}^{\infty} v^2 \cdot f(v) \cdot dv$$

$$\langle f(v) \rangle = \int_{-\infty}^{\infty} f(v) \cdot f(v) \cdot dv$$

number of atoms  
traveling in a  
particular direction  
w/ a particular  
speed



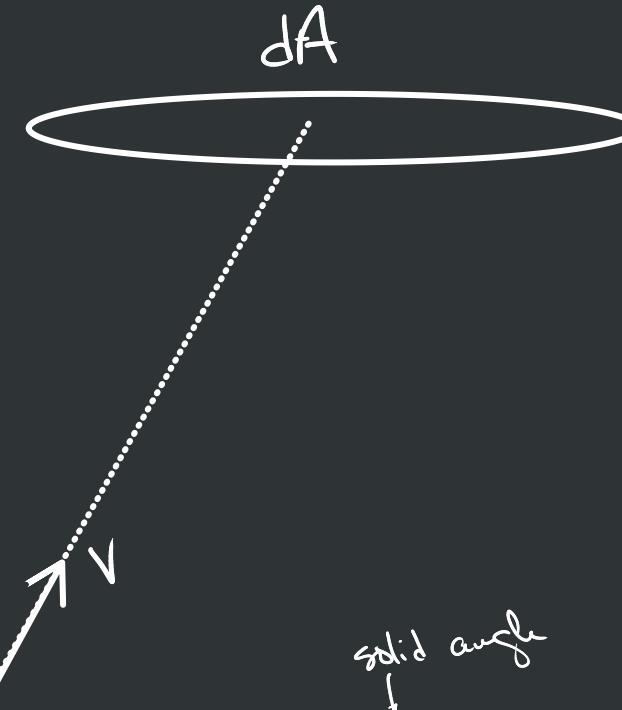
$$dA = r^2 \sin\theta \, d\theta \, d\phi$$

$$\begin{aligned} d\Omega &= \frac{dA}{r^2} \\ &= \frac{r^2 \sin\theta \, d\theta \, d\phi}{r^2} \end{aligned}$$

$$d\Omega = \sin\theta \, d\theta \, d\phi$$

Probability of a particle  
moving in a direction of  $\Theta, \Phi$

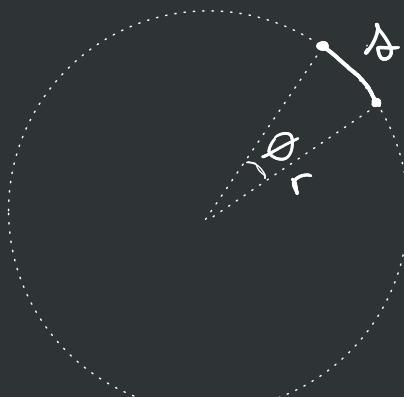
$$\frac{d\Omega}{4\pi} = \frac{\sin\theta \, d\theta \, d\phi}{4\pi}$$



solid angle

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

$A = 4\pi r^2$   
total solid angle  
of a sphere  $4\pi$   
(steradians)

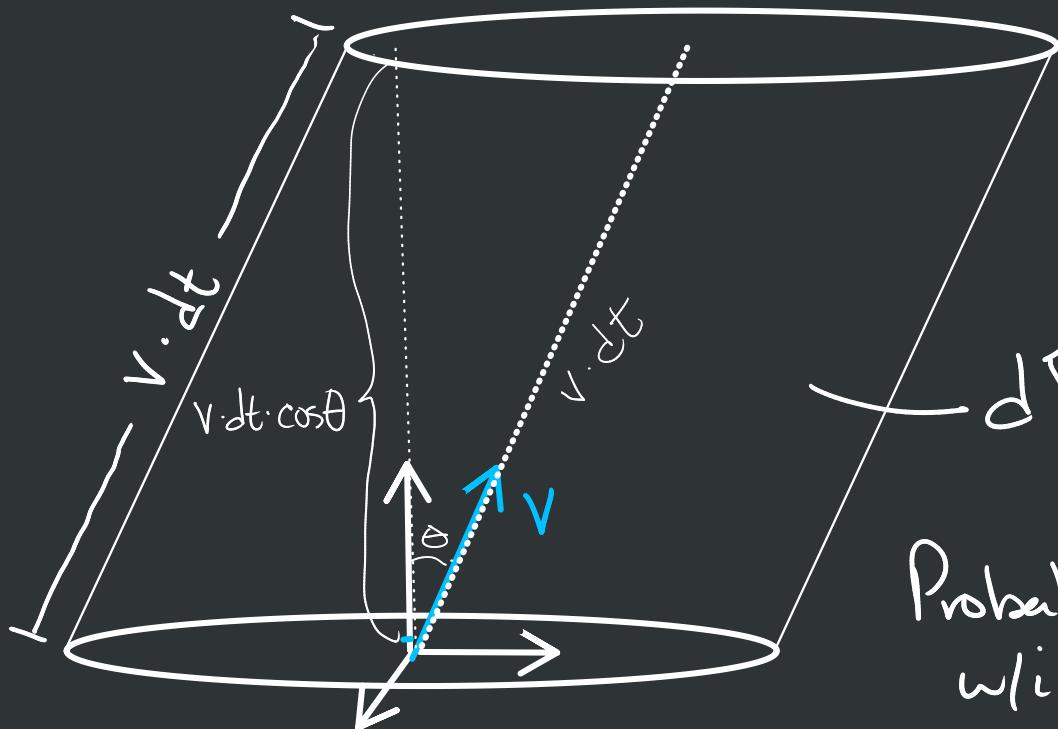


$$\begin{aligned} \Theta &= \frac{\delta}{r} \\ d\Theta &= \frac{ds}{r} \\ C &= 2\pi r \end{aligned}$$

Number of particles  
travelling w/ speed  $v$  in the direction of  $\Theta, \phi$   $\rightarrow \frac{\sin\Theta d\Theta d\phi}{4\pi} \cdot \rho(v) \cdot dv \cdot N$

## NEXT PIECE

$dA$  of the wall



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

Probability of being w/i striking distance =  $\frac{dV}{V}$

$$= \frac{v \cdot dt \cdot dA \cdot \cos\theta}{V}$$

$$d\text{pressure} = \frac{2mv \cos \theta}{dA dt} \cdot \frac{\sin \theta d\theta d\phi}{2\pi} \cdot \varphi(v) \cdot dv \cdot N \cdot v \frac{dt \cdot dA \cos \theta}{V}$$

$$P = \frac{N \cdot m}{2\pi V} \int_0^\infty r^2 \varphi(v) dv \underbrace{\int_0^{\pi/2} \cos^2 \theta \cdot \sin \theta d\theta}_{\gamma_3} \underbrace{\int_0^{2\pi} d\phi}_{2\pi}$$

$\langle v^2 \rangle$

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

$$PV = \frac{Nm \langle v^2 \rangle}{3} \quad \longleftrightarrow \quad PV = Nk_B T$$

$$\frac{m \langle v^2 \rangle}{3} = k_B T$$

$$\langle v \rangle^2 \stackrel{?}{=} \langle v^2 \rangle$$

$$\langle K \rangle = \frac{1}{2} m \langle v^2 \rangle$$

$$m \langle v^2 \rangle = 3k_B T$$

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$$

$$\langle K \rangle = \frac{3}{2} k_B T$$

$$\langle v^2 \rangle = \frac{3k_B T}{m}$$

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

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

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

•  $U = \frac{3}{2} N k_B T$  monatomic ideal gas

•  $U = \frac{3}{2} n R T$

{  $\begin{array}{l} \text{Ex: "average" speed of air} \\ \text{air} \rightarrow 29 \text{ g/mol} = 0.029 \text{ kg/mol} \\ m = \frac{0.029 \text{ kg}}{N_A} \end{array}$  }

$$\langle K \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} m \langle v_x^2 + v_y^2 + v_z^2 \rangle$$

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

$$= \frac{1}{2} m \langle v_x^2 \rangle + \frac{1}{2} m \langle v_y^2 \rangle + \frac{1}{2} m \langle v_z^2 \rangle$$

$$= \frac{1}{2} m \langle v_x^2 \rangle + \frac{1}{2} m \langle v_y^2 \rangle + \frac{1}{2} m \langle v_z^2 \rangle$$

$$= \frac{3}{2} m \langle v_x^2 \rangle = \frac{3}{2} k_B T \quad \frac{1}{2} m \langle v_x^2 \rangle = \frac{1}{2} k_B T$$

→ 3 could be thought of as the  
# of degrees of freedom of a monatomic ideal  
gas  
ways that energy can be possessed

$$v_{rms, \text{air}} = \sqrt{\frac{3 N_A k_B \cdot 293 K}{0.029 \text{ kg}}}$$

$$= \sqrt{\frac{3 \cdot 8.31 \cdot 293}{0.029}}$$

$$v_{rms, \text{air}} = 501 \text{ m/s}$$

### 1.3 Equipartition Theorem

$$\rightarrow U_{\text{thermal}} = N \cdot f \cdot \frac{1}{2} k_B T$$

↑ degrees of freedom (quadratic)

- $\frac{1}{2}mv_x^2, \frac{1}{2}mv_y^2, \frac{1}{2}mv_z^2$  (translational)

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

- $\frac{1}{2}kx^2, \dots$

ideal gases { monatomic  $\rightarrow f=3$   
diatomic  $\rightarrow f=5$  (near room temperature)

solid  $\rightarrow f=6$

revisit 1.4 + 1.5: 1<sup>st</sup> Law and P-V diagrams

$$dU = dQ + dW$$

$$dU = dQ - pdV$$

(1<sup>st</sup> Law)

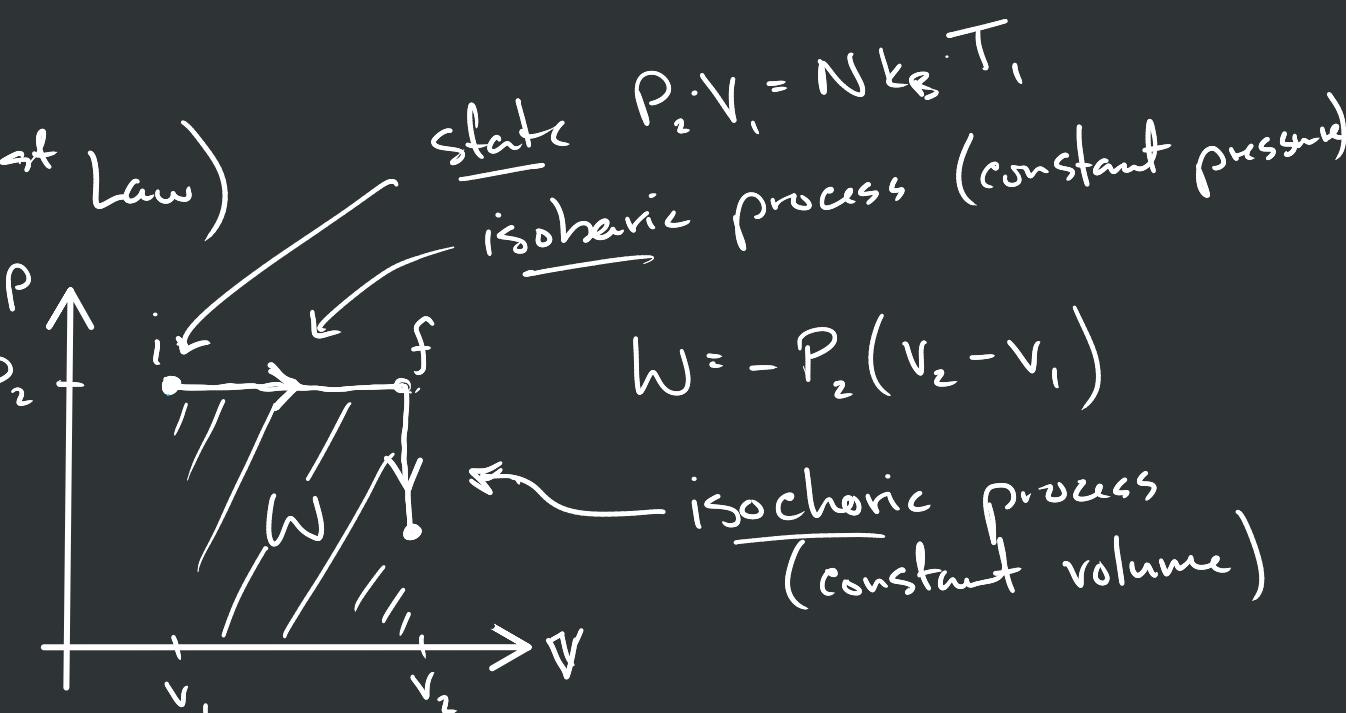
$$U = \frac{f}{2} N k_B T$$

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

$$U_f - U_i = \frac{f}{2} N k_B T_f - \frac{f}{2} N k_B T_i$$

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

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



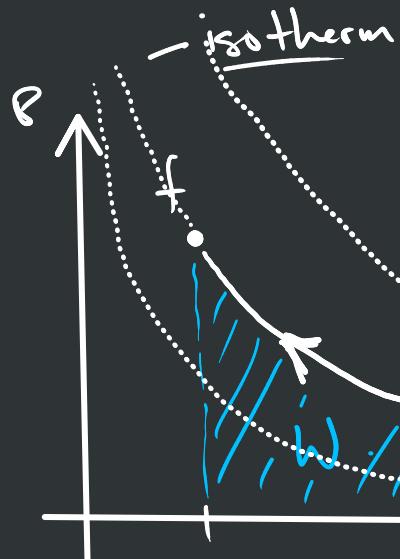
$$PV = N k_B T$$

$$P_f V_f - P_i V_i = N k_B T_f - N k_B T_i$$

isobaric process  $\rightarrow P_2 \Delta V = N k_B \Delta T$

Isothermal

→ compression



$$\delta U = \delta Q + \delta W$$

$$\delta W = -\delta Q$$

$$PV = Nk_B T$$

↓ all constant

$$P = \frac{Nk_B T}{V}$$

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

only true for  
isobaric

by extension:

$$\Delta U = \frac{f}{2} N k_B \Delta T = \frac{f}{2} \Delta P \cdot V$$

only true  
for isochoric

$$\delta W = -P dV$$

$$W = - \int_{V_i}^{V_f} P dV$$

$$W = - \int_{V_i}^{V_f} \frac{Nk_B T}{V} dV$$

$$dW = - \frac{1}{c} dQ$$

$$W = - Nk_B T \int_{V_i}^{V_f} \frac{dV}{V}$$

$$Q = - W$$

$$W = - Nk_B T \ln(V) \Big|_{V_i}^{V_f}$$

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

$$W = - Nk_B T (-\ln V_f + \ln V_i)$$

$$Q = PV \ln\left(\frac{V_f}{V_i}\right)$$

$$W = Nk_B T (\ln V_i - \ln V_f)$$

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

Work done  
during an  
isothermal  
process

$$PV = Nk_B T$$

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

Adiabatic Process (isentropic) → no heat added/removed  
 compression → still quasistatic  
 → super insulated  
 → quick

first law:  $dU = \cancel{dQ} + dW$

$$dU = dW$$

$$\Delta U = W$$

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

↑  
 what is the final temp?

$$dW = -pdV \quad \text{not const}$$

$$W = - \int \frac{N k_B T}{V} dV \quad \text{not const}$$

$$dU = dW$$

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

$$\frac{f}{2} N k_B dT = -pdV$$

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

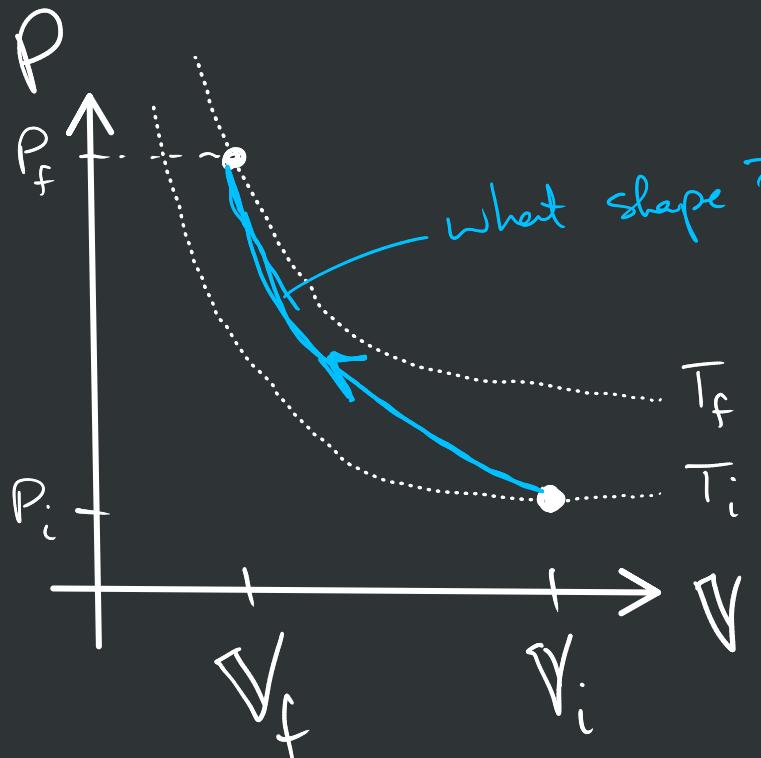
$$\frac{f}{2} \int_{T_i}^{T_f} \frac{dT}{T} = - \int_{V_i}^{V_f} \frac{dV}{V}$$

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

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

$$\rightarrow \underbrace{\left| \left(\frac{T_f}{T_i}\right)^{\frac{f}{2}} = \frac{V_i}{V_f} \right|}_{\text{constant}} \Rightarrow V \propto T^{-f/2}$$

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



$$P(V) \quad P_f(v_f)$$

$$V \cdot T^{f/2} = \text{constant} \iff \left( \frac{T_f}{T_i} \right)^{\frac{f}{2}} = \frac{V_i}{V_f}$$

$$PV = Nk_B T$$

$$T_i = \frac{P_i V_i}{N k_B}$$

$$\left( \frac{P_f V_f}{P_i V_i} \right)^{f/2} = \frac{V_i}{V_f}$$

$$\frac{T_f = \frac{P_f V_f}{N k_B}}{T_i = \frac{P_i V_i}{N k_B}}$$

$$\frac{P_f V_f}{P_i V_i} \propto \left( \frac{V_i}{V_f} \right)^{f/2}$$

$$P(V) = P_i \left( \frac{V_i}{V} \right)^{\gamma}$$

ideal gas:  $f = 3 \leftarrow \text{monatomic} \rightarrow \gamma = 5/3$   
 $f = 5 \leftarrow \text{diatomic} \rightarrow \gamma = 7/5$

$$\frac{P_f}{P_i} = \left( \frac{V_i}{V_f} \right)^{\gamma} \left( \frac{V_i}{V_f} \right)^{f/2}$$

$$\frac{P_f}{P_i} = \left( \frac{V_i}{V_f} \right)^{1 + f/2}$$

$$d\omega = -p dV$$

$$\omega = - \int p dV$$

$$= - \int p_i \left( \frac{V_i}{V} \right)^\gamma dV \quad \text{and } \underline{\text{integrate}}$$

$$\gamma = 1 + \frac{2}{f}$$

$$\gamma = \frac{f+2}{f}$$

## Revisit section 1.6 | - Heat Capacity

$$\text{1st Law} \rightarrow dU = \cancel{\pm Q} + \underbrace{\pm W}_{-\rho dV}$$

$$dU = \pm Q - \rho dV$$

$$\rightarrow \pm Q = dU + \rho dV$$

$\downarrow$        $U(T, V)$  or  $U(T, P)$

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

↑  
constant  
volume

$$\pm Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + \rho dV$$

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

Two cases : ① constant volume  
                  ② constant pressure

① constant volume

$$dV = 0$$

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

heat capacity at constant volume

② constant pressure

$$C_P = \left( \frac{dQ}{dT} \right)_P = C_V + \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] \left( \frac{dV}{dT} \right)_P$$

$$C_P = C_V + \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] \left( \frac{dV}{dT} \right)_P$$

for an ideal

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

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

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

$$\frac{C_V}{n} = \frac{f}{2} R$$

$$\frac{\frac{3}{2} R}{K_{mol}} = \frac{12.5 J}{K_{mol}}$$

$$\left| \begin{array}{l} \text{solid} \\ f=6 \end{array} \right.$$

$$\frac{\frac{5}{2} R}{K_{mol}} = \frac{20.8 J}{K_{mol}}$$

$$\frac{\frac{6}{2} R}{K_{mol}} = \frac{25 J}{K_{mol}}$$

$$C_P = C_V + \left[ \underbrace{\left( \frac{\partial U}{\partial V} \right)_T}_{U = \frac{f}{2} n_m R T} + P \right] \left( \frac{dV}{dT} \right)_P$$

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

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

$$\left( \frac{dV}{dT} \right)_P = \frac{n R}{P}$$

$$C_P = C_V + n R$$

$$\frac{C_P}{n} = \frac{C_V}{n} + R$$

$$\xrightarrow{\text{monatomic}} \frac{C_P}{n} = \frac{3}{2} R + R = \frac{5}{2} R$$

$$\xrightarrow{\text{diatomic}} \frac{C_P}{n} = \frac{7}{2} R = 29 J/K_{mol}$$

$$C_p - C_v = \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] \left( \frac{\partial V}{\partial T} \right)_P$$

end 1.b | - Enthalpy

$$dU = \pm Q + \pm W$$

$$\underbrace{- P dV}_{\text{other}} + W_{\text{other}}$$

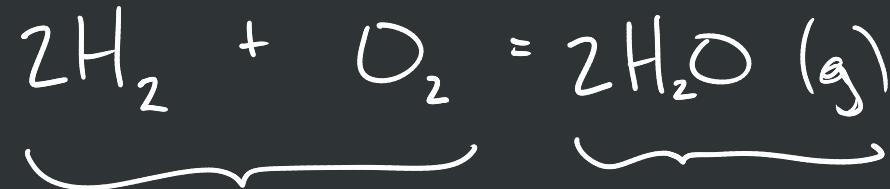
$$dU + P dV = \pm Q + W_{\text{other}}$$

enthalpy  $\rightarrow$  heat content

$$U + PV = H$$

$$\Delta U + P \Delta V = \Delta H \leftarrow \text{at } \underline{\text{constant pressure}}$$

Ex:



$$\sum \Delta H_{\text{reactants}} = 0$$

$$\Delta H_{\text{H}_2\text{O(g)}} = -241.82 \text{ kJ/mol}$$

$$\sum \Delta H_{\text{products}} = 2(-241.82 \text{ kJ/mol})$$

$$\Delta H = \Delta H_f - \Delta H_i = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$$

$$\underline{\underline{\Delta H = -483 \text{ kJ}}} \leftarrow \text{heat given off}$$

How much work is done on gas by atmosphere?

$$\underbrace{P \Delta V}$$

$$\Delta V = V_f - V_i$$

$$PV = nRT$$

$$1 \cdot 10^5 P_0 \cdot V = (3 \text{ mol}) \cdot 8.31 \cdot (298 \text{ K})$$

$$V = 0.0743 \text{ m}^3 \rightarrow 74.3 \text{ L}$$

$$\nabla \propto n$$

$$\frac{V_f}{V_i} = \frac{n_f}{n_i} = \frac{2}{3}$$

$$V_f = \frac{2}{3} \cdot V_i = \frac{2}{3} \cdot 0.0743 \text{ m}^3 = 0.0495 \text{ m}^3 \\ = 49.5 \text{ L}$$

$$\rightarrow \Delta V = 0.0495 - 0.0743$$

$$= -0.0248 \text{ m}^3$$

$$W = -P V \left. \begin{array}{l} \text{const} \\ \text{pressure} \end{array} \right\}$$

$$= -10^5 \text{ Pa} \cdot (-0.0248 \text{ m}^3)$$

$$= 2.48 \cdot 10^3 \text{ J} \quad 2.48 \cdot 10^{-2}$$

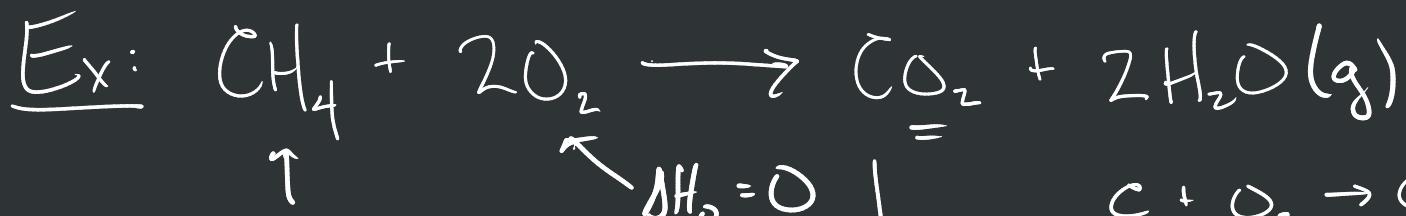
$$W = 2.48 \text{ kJ}$$

$$\hookrightarrow Q = -2.48 \text{ kJ}$$

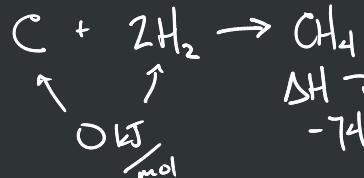
$$\Delta H = -483 \text{ kJ} = \Delta U + P \nabla$$

$$\Delta U = -483 \text{ kJ} - 2.48 \text{ kJ}$$

$$= -485.5 \text{ kJ}$$



$$\Delta_f H_{\text{CH}_4} = -74.81 \text{ kJ/mol}$$



$$\Delta H \rightarrow -74.81 \text{ kJ/mol}$$



$\uparrow$  takes  $74.81 \text{ kJ/mol}$  of heat  
to do this

$$\Delta H_{\text{O}_2} = 0$$



$$\Delta H = -393.51 \text{ kJ}$$



$$\Delta H = -483 \text{ kJ}$$

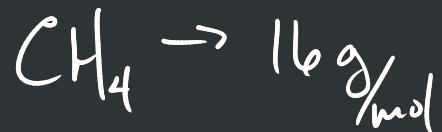
$$\Delta H = -483 \text{ kJ} - 393.51 \text{ kJ} - (-74.81 \text{ kJ})$$

$$= -802 \frac{\text{kJ}}{\text{mol CH}_4} \rightarrow 802 \text{ kJ of heat to surroundings}$$

How long does the sun last?

$$M_s = 2 \cdot 10^{30} \text{ kg}$$

$$\rho = 3.9 \cdot 10^{26} \text{ kg/m}^3 \Rightarrow t = \frac{Q}{P} \xrightarrow{?}$$



$$\frac{\text{CH}_4}{2\text{O}_2} = \frac{16}{64} = \frac{1}{4}$$

$\frac{1}{4} M_s$  is  $\text{CH}_4 \rightarrow 0.5 \cdot 10^{30} \text{ kg}$  of  $\text{CH}_4$

$$\frac{802 \text{ kJ}}{\text{mol} \cdot \text{CH}_4} \cdot \frac{1 \text{ mol}}{16 \text{ g}} \cdot \frac{1000 \text{ g}}{1 \text{ kg}} \cdot 0.5 \cdot 10^{30} \text{ kg} = \text{kJ}$$







1.47

$$Q_{\text{tea}} = m_{\text{tea}} \cdot c \cdot \Delta T_{\text{tea}}$$

$$Q_{\text{tea}} = 200 \text{ g} \cdot \left( 1 \frac{\text{cal}}{\text{g} \cdot \text{K}} \right) \cdot (-35 \text{ K})$$

$$Q_{\text{tea}} = -7000 \text{ cal}$$

$$\left\{ \begin{array}{l} Q_{\text{ice}} = +7000 \text{ cal} = M_{\text{ice}} \cdot C_{\text{ice}} \cdot (+15 \text{ K}) + M_{\text{ice}} \cdot L_f + M_{\text{ice}} \cdot C_{\text{water}} \cdot (65 \text{ K}) \\ \\ \end{array} \right.$$

1.17 a)  $P \cdot V = nRT \left( 1 + \frac{B}{V/n} \right)$

$\uparrow$   
2nd term  
in the expansion

calculate  $\frac{B}{V/n}$

$T \text{ (K)}$	$B \frac{\text{cm}^3}{\text{mol}}$	$\frac{n}{V} \cdot B$
100	-160	?
200	-35	
300	-4.2	

$$P \cdot V = nRT \left( 1 + \frac{n}{V} \cdot B \right)$$

$$P = \frac{n}{V} RT \left( 1 + \frac{n}{V} \cdot B \right) \rightarrow \text{solve for } \frac{n}{V}$$

$$P = \left(\frac{n}{V}\right)RT + \left(\frac{n}{V}\right)^2 BRT$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$0 = \left(\frac{n}{V}\right)^2 BRT + \left(\frac{n}{V}\right)RT - P$$

$$-RT \pm \sqrt{(RT)^2 + 4BRT \cdot P}$$

↑      ↑  
83.1 1 atm  
=

$$PV = nRT$$

$$\underbrace{P_{\text{atm}} \cdot 10^5}_{\substack{\uparrow \\ \uparrow}} \cdot \underbrace{V_{\text{cm}^3} \cdot 10^{-6}}_{\substack{\uparrow \\ \uparrow}} = nRT$$

$8.31 \frac{\text{J}}{\text{K} \cdot \text{mol}}$

$$\frac{P_{\text{atm}} \cdot V_{\text{cm}^3}}{10} = n \cdot R \cdot T$$

$$P_{\text{atm}} \cdot V_{\text{cm}^3} = n \cdot \underbrace{10 \cdot R}_{\substack{\uparrow \\ \uparrow}} T$$

$$R_{\text{atm} \cdot \text{cm}^3} = 83.1 \frac{\text{atm} \cdot \text{cm}^3}{\text{K} \cdot \text{mol}}$$

$$c) \left( P + \frac{an^2}{V^2} \right) (V - nb) = nRT \quad | \quad PV = nRT \left( 1 + \frac{n}{V} \cdot B + \left( \frac{n}{V} \right)^2 C \right)$$



goal  $\rightarrow \underline{\underline{B(a,b)}} + \underline{\underline{C(a,b)}}$

$$V \left( 1 - \frac{nb}{V} \right)$$

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

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

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

$$= nRT \left( \left( 1 - \frac{nb}{V} \right)^{-1} - \frac{n}{V} \frac{a}{RT} \right)$$

Hint!  $(1+x)^p \approx 1 + px + \frac{1}{2}p(p-1)x^2$

$$B(a, b, T)$$

