

# Kinetic Theory of Gases

**Modern Physics**

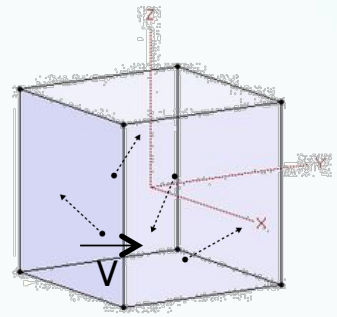
*September 7 and 12, 2016*



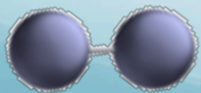
# Intro

- In this section, we will relate macroscopic properties of gases (like Pressure, Temperature) to the behavior of the microscopic components (atoms, molecules)
- This will also serve as an introduction to the topic of Statistical Mechanics
  - We apply Newton's laws of motion to a very large collection of objects, e.g., 1,000 grams of  $\text{H}_2$  gas  $\sim 6 \times 10^{26}$  molecules
  - Newton's laws apply, for instance, to a collision of a single atom / molecule with the walls of the gas container, or to each other, and from that we will derive expressions for the Pressure / Temperature of a volume of gas, specific heat, etc.
- We will deal with (ideal) gases, i.e., those where the interactions between atoms/molecules are very weak
- The model of an ideal gas is what is known as the kinetic theory of gases. We will treat an ideal gas as follows ==>

# Model

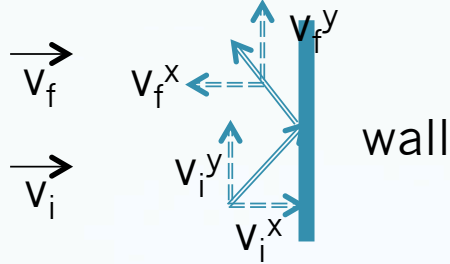


- Gas: composed of point-like atoms/molecules
- In a cube of dimension  $d$ , there is a very large number of atoms/molecules, and separation between them is much larger than their size
- The atoms/molecules will obey Newton's laws.
- Each atom/molecule can move in any direction at any speed  $\Rightarrow$  isotropic
- Atoms/molecules interact via short-range forces during elastic collisions with the walls or with each other
- I am talking about atomic (or molecular) gases
  - For atomic gases, the atoms only have translational motions (or degrees of freedom)
  - Molecular gases also have rotational and/or vibrational degrees of freedom

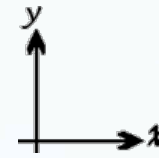


A molecule



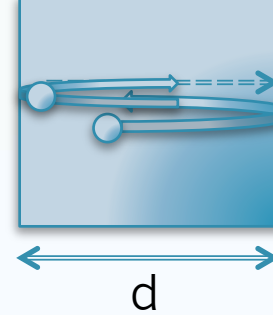


# Math



- Since the collision is elastic  $|\vec{v}_i| = |\vec{v}_f|$  and  $v_f^x = -v_i^x$  and  $v_f^y = v_i^y$ 
  - To make the rest of the discussion simpler, I'm going to drop the suffixes i and f and instead label  $\vec{v}$  of an atom / molecule as  $\vec{v}_k$ , where k means the  $k^{\text{th}}$  element “element”
- In this collision,  $v_k^y$  remains unchanged, but  $v_k^x$  is reversed
- Recall  $\vec{p}$ , i.e., momentum =  $m\vec{v}$
- $\Rightarrow \Delta p_k^x = -m_0 v_k^x - (m_0 v_k^x) = -2 m_0 v_k^x$  all of the elements have the same mass,  $m_0$
- Also, recall that  $\vec{F} = d\vec{p}/dt$  [  $= d(m\vec{v})/dt = m d\vec{v}/dt = m\vec{a}$  ]
- If the collision lasts for time  $\Delta t_c$ , then  $\vec{F}_k$  (on element) \*  $\Delta t_c = \Delta p_k^x = -2 m_0 v_k^x$ 
  - Average force that wall exerts on the  $k^{\text{th}}$  element

# Force



- If the element collides with one wall and then the other wall and then back at the 1st, then it has travelled a distance  $2d$ 
  - $\Delta t$  (between collisions) =  $2d / v_k^x$
- We want to get the average force over many collisions, i.e., as the element goes back and forth
- The momentum change only happens during collisions with the wall, and so we are able to write
  - $\vec{F}_k \Delta t = \vec{F}_k (2d/v_k^x) = -2m_0 v_k^x$
  - $\vec{F}_k = -2m_0 v_k^{x^2} / (2d) = -m_0 v_k^{x^2} / d$
- Therefore, by Newton's 3<sup>rd</sup> Law, the  $k^{\text{th}}$  element exerts an average force of  $+m_0 v_k^{x^2} / d$  on the container wall
- Total average force  $\vec{F} = \sum_{k=1}^N m_0 v_k^{x^2} / d = m_0 / d \sum v_k^{x^2}$  exerted by all of the elements upon the container wall

# Pressure

- If  $v_k^x$  is the speed of the  $k^{\text{th}}$  element along the x-direction, then the (RMS) speed averaged over all of the elements is

- $\overline{v_x^2} = \sum_{k=1}^N v_k^{x^2} / N \Rightarrow \sum_{k=1}^N v_k^{x^2} = N * \overline{v_x^2}$

- $F = (m_0/d) N \overline{v_x^2}$

- In reality, each element is free to move in any direction, with any speed, thus

- $v_k^2 = v_k^{x^2} + v_k^{y^2} + v_k^{z^2}$  and  $\vec{v}_k = v_k^x \mathbf{i} + v_k^y \mathbf{j} + v_k^z \mathbf{k}$   
 $\Rightarrow |\vec{v}_k|^2 = \text{mag. of vector}$

- $\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$

- Since the motion of the element is isotropic,  $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$  or  $\overline{v^2} = 3 * \overline{v_x^2}$

- Our equation then becomes  $\overline{F} = (1/3)(m_0/d)N\overline{v^2}$

Volume  
of box =  
 $V = d^3$

- Now Pressure =  $(F/A) = (F/d^2) = (1/3)(m_0/d^3)N\overline{v^2} = (1/3)(N/V)m_0\overline{v^2} = (2/3)(N/V)(1/2)m_0\overline{v^2}$

# Homework

TURN IT IN RIGHT NOW

# Temperature

average translational KE of gas

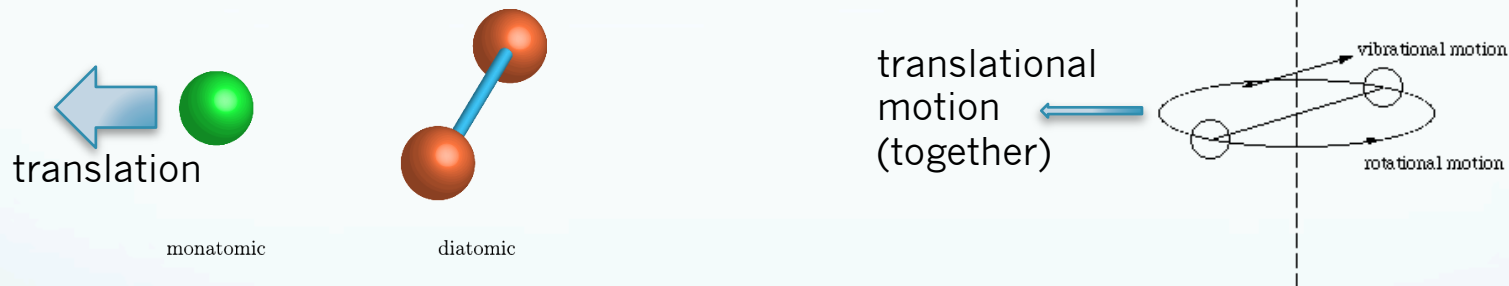
- We get  $P = (2/3)(N/V)(1/2)m_0\overline{v^2}$ . Some comments:
  - Keeping  $N$  and  $v^2$  fixed  $\Rightarrow P \propto 1/V$  (alpha is “prop. to”)
  - Keeping  $V$  and  $v^2$  fixed  $\Rightarrow P \propto N$
  - Keeping  $V$  and  $N$  fixed  $\Rightarrow P \propto v^2$  (average bar omitted)
- In the chapter on temperature, we had said that the equation governing an ideal gas was
  - $P V = n R T = (N / N_A) R T = N k_B T$ 

$n$  is #moles  
 $N_A$  is Avogadro's #,  $R$  const.  
 $k_B$  is Boltzmann's constant =  $1.38e-23$  J/K
- Above equation has  $PV = (2/3)N(1/2)m_0v^2 = Nk_B T$  or  $T = (2/(3k_B))(1/2)m_0v^2$  or  $(1/2)m_0v^2 = (3/2)k_B T$
- If that is the average translational KE per element, then  $KE_{\text{tot}} = (3/2)Nk_B T = (3/2)nRT$  (a BIG RESULT)



# Freedom

- Since an element (atom/molecule) can move in 3-d  
=> average translational KE, per degree of freedom =  $(1/2)k_B T$
- As it turns out, one can show we get the same result, whether we are talking about translational, rotational, or vibrational degrees of freedom



- We can re-write this and say that each degree of freedom **contributes  $(1/2)k_B T$  to energy of system**
- EQUIPARTITION of energy -> a very important result.
  - We will re-visit this later on in the course

# Example

- A tank of He has volume =  $0.3 \text{ m}^3$  and contains 2.0 moles of gas at  $20^\circ\text{C}$  (assume that helium is a mono-atomic ideal gas).
  - (a.) What is the total  $\text{KE}_{\text{trans}}$ ?
  - (b.) What is the average KE per atom?
  - (c.) What is the RMS (root-mean-squared) velocity (magnitude)? Try putting in units you know (like mph) Surprised??
- You will need to remember how many protons and neutrons there are in He (2 and 2), and approximate mass of 1 nucleon (p or n) by itself ( $1.67\text{e-}27 \text{ kg}$ )

# Mean Free Path

- Just want to point out that the gas atoms also encounter other atoms as they are zipping around the container
- These collisions cause the original atom's direction to change
- There is a concept called Mean Free Path, which estimates the average distance between collisions
  - We will come back to this later as needed
  - This will also be in your text reading assignment
- As number of atoms increases or the volume of a container decreases (or  $P$  increases) then the MFP will decrease

# Distribution of Speeds of Atoms/Molecules of an Ideal Gas

- In the previous discussion, we simply said that atoms/molecules can have any speed in any direction. From the previous example, it is clear that the *average speed* depends on  $T$ ,  $V$ , # of moles.
  - How are individual speeds distributed around this value?
- $n_V(E) = n_0 e^{-E/(k_B T)}$  is # density (**Boltzmann Distribution**)
  - $n_V(E)dE$  is the number of atoms/molecules per unit volume with energies in between  $E$  and  $E + dE$
  - $n_0 dE$  is the number between  $E = 0$  and  $dE$
- **Maxwell-Boltzmann's speed distribution function** is  $N_v = 4 \pi N (m_0 / (2\pi k_B T))^{3/2} v^2 e^{-m_0 v^2 / (2k_B T)}$ 
  - $N_v dv$  is # of atoms/mols. with speeds between  $v$  and  $v + dv$

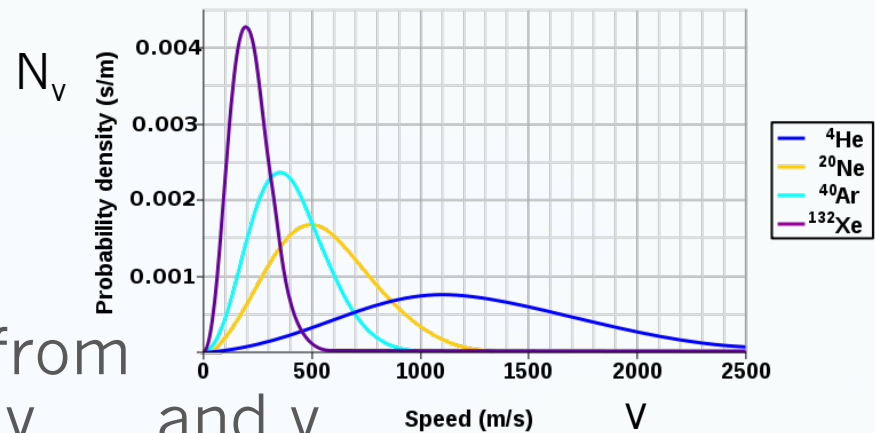
$E_2$  \_\_\_\_\_

$E_1$  \_\_\_\_\_

# Example

- Consider a system where atoms can occupy 2 different energy levels  $E_1$  and  $E_2$ , which are separated by 1.5 eV, that is,  $1.5 * 1.602e-19$  J. The gas is at a temperature of 2,500 Kelvin.
  - (a.) Determine the ratio of the # of atoms in the higher to the lower energy states.
  - (b.) With respect to every 1,000 atoms in the lower energy state, approximately how many atoms are in the higher energy state, at 2500 K?
  - (We shall discuss these issues in greater detail)

# Various Speeds



- Using the expression from slide 11 we'll get  $v_{\text{avg}}$ ,  $v_{\text{rms}}$ , and  $v_{\text{mp}}$ 
  - All three give you an idea about this distribution (**MB**).
- $v_{\text{mp}}$  is where  $dN_v/dv = 0$ . It is  $1.41 \sqrt{[(k_B T) / m_0]}$
- $v_{\text{avg}} = \int_0^{\infty} (v N_v dv) / N = 1.60 \sqrt{[(k_B T) / m_0]}$
- $v_{\text{rms}} = \sqrt{v^2} = \sqrt{[\int_0^{\infty} (v^2 N_v dv) / N]} = 1.73 \sqrt{[(k_B T) / m_0]}$
- Example: in a cup of how water, water molecules will have a spread of speeds
  - The higher ones can escape from the surface, thereby lowering the mean value of the distribution => lower  $T$  or cooling (although liquid not perfectly Maxwellian)

# Specific Heat of an Ideal Gas

- Things get a bit more complicated compared to solid and liquids in this case at least, because we can transfer heat to a gas in many different ways
  - P changes but Volume is constant
  - P is constant but Volume changes
  - Both Pressure and Volume can change(An isothermal P vs. V diagram example curve: on whiteboard)
- Since  $\Delta T$  is same in all three cases  $\Rightarrow \Delta E_{\text{int}}$  is same
  - Recall discussion from last chapter
- From 1<sup>st</sup> Law of Thermo:  $\Delta E_{\text{int}} = Q + W$ ,  $W = - \int P \, dV$
- Depending on which path we take, W will differ
  - However, since  $\Delta E_{\text{int}}$  same then the Q will be different, depending on the path which we take (W is *on* gas)



# Molar Specific Heats

- We define  $Q_V = nC_V\Delta T$  and  $Q_P = nC_P\Delta T$ . Let's derive  $C_V$ 
  - Specific heats at const. volume and const. pressure
  - It turns out that  $Q_P > Q_V$
- At constant volume  $W = - \int P \, dV = 0$ , while at constant pressure  $W = - \int P \, dV = -P \int dV = -P (V_f - V_i) = P (V_i - V_f)$ 
  - So, to keep  $\Delta E_{\text{int}}$  the same,  $Q$  is larger for latter case
- $C_V$ : molar specific heat @ constant volume
  - If we transfer heat into this system, its internal  $E$  will increase  $\Rightarrow$  temperature will increase
  - For a mono-atomic gas  $\Rightarrow$   $KE_{\text{translational}}$  will increase (which is equal to  $(3/2)Nk_B T = (3/2)nRT$  )
- $E_{\text{int}} = (3/2)Nk_B T = (3/2)nRT$ . As  $W=0$  here,  $Q = \Delta E_{\text{int}}$ 
  - $Q = (3/2)Nk_B \Delta T = (3/2)nR\Delta T \Rightarrow C_V = (1/n)(Q_V/\Delta T) = (1/n)(\Delta E_{\text{int}}/\Delta T) = (1/n)(3/2)nR = (3/2)R = 12.5 \text{ J}/(\text{mol}\cdot\text{K})$



# $C_P$ , the Molar Specific Heat at Constant Pressure



for an ideal gas.

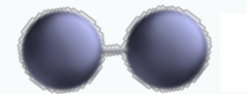
- $\Delta E_{\text{int}} = Q + W = nC_P\Delta T + (-P\Delta V)$ 
  - $\Delta E_{\text{int}}$  depends only on temperature, so  $\Delta E_{\text{int}} = nC_V\Delta T$  (from previous slide).
  - In both cases,  $T \rightarrow T + \Delta T$ , so  $\Delta E_{\text{int}}$  is the same.
- $nC_V\Delta T = nC_P\Delta T - P\Delta V$ 
  - For an ideal gas,  $PV = nRT \Rightarrow P\Delta V = nR\Delta T$
- $nC_V\Delta T = nC_P\Delta T - nR\Delta T$ 
  - Or  $C_P - C_V = R \Rightarrow C_P = C_V + R$
  - $C_P = 12.5 + 8.1 \sim 20.6 \text{ J / ( mol } \cdot \text{ K )}$
- It would seem that both  $C_P$  and  $C_V$  are constant, regardless of the gas with which we deal.
  - This works for mono-atomic gases such as He, Ar, or Ne
  - But for di-atomic/tri-atomic  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{SO}_2$  the values of  $C_P$  &  $C_V$  are different, yet  $C_P - C_V \sim R$  still!

Experimental Values (at some temp.)

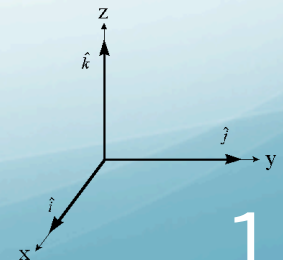
	C <sub>P</sub>	C <sub>V</sub>	C <sub>P</sub> - C <sub>V</sub>
Mono-atomic gases	~20.8	~12.5	~8.3
Di-atomic gases	~30	~21.7	~8.3
Tri-atomic gases	35-40	27-31	~8.5

# C<sub>V</sub> and C<sub>P</sub> *continued*

- What's going on with diatomic/triatomic?
  - We alluded to this: a mono-atomic gas will only have translational degrees of freedom
  - However, di-atomic and tri-atomic gases will also have rotational and vibrational d.o.f. (Deg. of Freedom)




- Consider a di-atomic gas,
  - It can rotate along 3 axes and so  $KE_{rot} = (1/2) I \omega^2$  ( $I$  = moment of inertia).
  - However,  $I_y = 0$ , so we have 2 degrees of freedom
- Ignore vibration for now
  - So,  $E_{int} = 3N(1/2)k_B T + 2N(1/2)k_B T = (5/2)Nk_B T = (5/2)nRT$  instead of a  $(3/2)$  !



# Degrees of Freedom Revisited

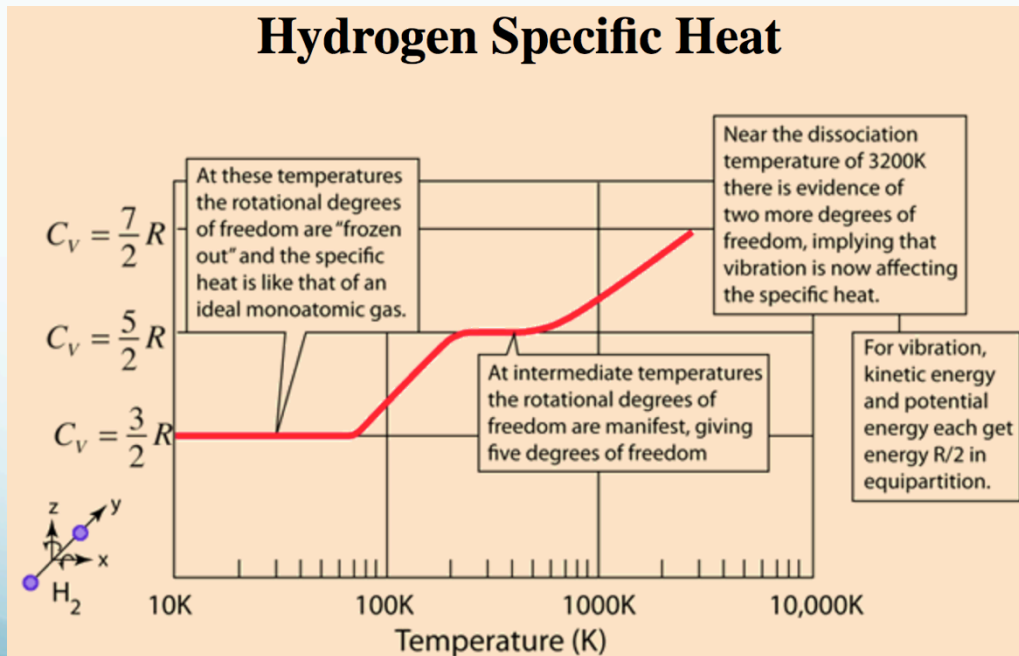
- $C_V = (1/n)dE_{\text{int}}/dT = (5/2)R = 20.8 \text{ J}/(\text{mol}\cdot\text{K})$
- $C_P = C_V + R \sim 28.9 \text{ J}/(\text{mol}\cdot\text{K})$ 
  - This agrees pretty well with the previous slide
  - But why, since we have ignored vibrational modes?
- So, we should have had  $E_{\text{int}} = 3N(1/2)k_B T + 2N(1/2)k_B T + 2N(1/2)k_B T$ 
  - $C_V = (7/2)R = 29.1 \text{ J}/(\text{mol}\cdot\text{K})$
  - $C_P = C_V + R = 37.2 \text{ J}/(\text{mol}\cdot\text{K})$
- This disagrees with the numbers for di-atomic gases
  - But, this seems to agree well with the tri-atomic ones??
- One can conclude that our model sort of works, but not exactly, which is not very surprising (Why?)

 -> there are two

# Empirical Data

- This is unsurprising because we have only relied on classical physics, and have also ignored interactions *between* the gas atoms and molecules
  - We need Quantum Mechanics (QM) in order to do that

## Hydrogen Specific Heat



HyperPhysics

- But actually to be more fair, as you increase  $T$ , more and more degrees of freedom come into play
  - And our simple model seems to be holding up!
- Life is complicated!
  - At times we can get by with simple models, but when they cannot explain data, then we need to modify the initial model
  - We will return to this when we get into QM

# Example

- A 1.0 liter insulated bottle is full of hot tea at  $90^{\circ}\text{C}$ . You pour out 1 cup of tea and immediately put the stopper back. Estimate the temperature of the remaining liquid, assuming that you replace the one cup of tea with air at room temperature.
  - Assume that the tea is mostly water (density =  $1 \text{ g/mL}$ )
  - 1 cup is about 6 oz. or 180 cc or  $\text{cm}^3$  Call it  $\sim 200 \text{ mL}$
  - What is room temperature? For simplicity let's say  $20^{\circ}\text{C}$
  - Assume air is an ideal but di-atomic gas ( $\text{N}_2$  mostly)
- Hint on answer: It will not be much of a change in  $T$

# Adiabatic Process for Ideal Gas

- This is when no heat transferred in/out of system
  - That is,  $Q = 0$ , and this can happen when you compress a volume of gas very quickly (e.g., in a car engine)
  - Or, it can happen if you have a system insulated from its surroundings (time assumed not to be a factor here)
- In such a process, all ( $P$ ,  $V$ , and  $T$ ) change (board ex.)
  - $E_{\text{int}}$  only depends on  $T$ , so  $\Delta E_{\text{int}}$  is proportional to  $\Delta T$
  - From previous discussion,  $\Delta E_{\text{int}} = nC_V\Delta T$  and from first law  $\Delta E_{\text{int}} = W + Q \Rightarrow nC_V\Delta T = -P dV$   
 $W = -\int P dV$  or  $dW = -P dV$ ;  $Q=0$
- The equation for an ideal gas is  $P V = n R T$ 
  - $P dV = V dP = n R dT$
  - $P dV + V dP = -n R P dV / (n C_V) = (-R / C_V) P dV$

# Adiabatic cont.

- Writing  $R = C_p - C_v$  and dividing by  $P$  times  $V$ ,
  - $dV / V + dP / P = - [ (C_p - C_v) / C_v ] (dV / V)$
  - $dV / V + dP / P = (1 - \gamma) (dV / V)$ 
    - Where  $\gamma = C_p / C_v$ , a.k.a. the specific heat ratio
  - $dP / P = - \gamma (dV / V)$  or  $dP / P + \gamma dV / V = 0$
- Integrating, we get  $\ln P + \gamma \ln V = \text{constant}$ .
  - Or,  $\ln P + \ln (V^\gamma) = \text{constant}$  or  $\ln (PV^\gamma) = \text{constant}$  or  
 **$PV^\gamma = \text{constant}$**  ADIABATIC
- In contrast, for an isothermal process
  - **$PV = \text{constant}$**  (And you know what constant is)

# New Assignment