## **Tuesday April 16**

## Topics for this Lecture:

- Thermodynamics
  - Kinetic Theory
  - Ideal Gas Law
  - Laws of Thermodynamics
  - PV diagrams & state transitions

## Ideal Gas:

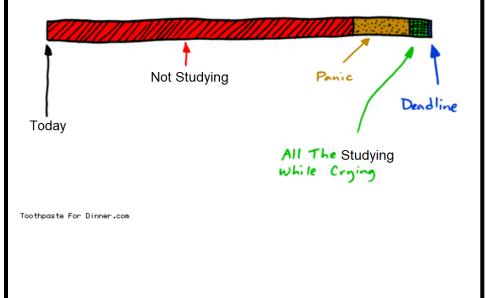
- PV=nRT=Nk<sub>B</sub>T • R=8.31 J/mol\*K • k<sub>B</sub> = R/N<sub>A</sub> = 1.38x10<sup>-23</sup>J/K • PV=(1/3)m(v<sub>rms</sub>)<sup>2</sup> •  $v_{RMS} = \sqrt{\overline{v^2}}$
- 1<sup>st</sup> law of thermodynamics: •ΔU = Q-W<sub>BySystem</sub>

Work by a gas = area under PV-curve

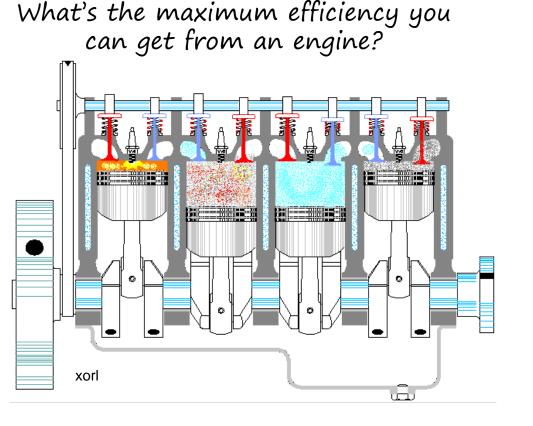
- •Assignment 13 due Friday
- Pre-class due 15min before class

The comprehensive final is Monday April 29<sup>th</sup> 2:30-4:30pm

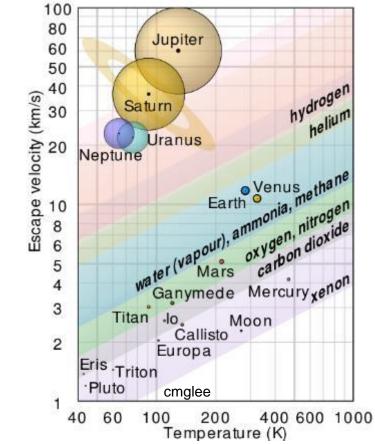
What not to do:



#### Thermodynamics



Why has Jupiter retained its atmospheric hydrogen, while Earth hasn't?



# Thermodynamics: Definitions

- •Gas: Fluid which fills its container
- •Ideal Gas:
  - •Low density gas, such that only classical collisions occur between molecules
  - Every-day air around you is roughly like this ... so it's a useful approximation
  - •Usually can understand ideal gases by considering microscopic interactions
- At a given instant, a gas is in a "state" and is described by: "State Variables",
   E.g. pressure P, volume V, number of molecules N, temperature T, internal energy U, entropy S
- Lots of particles in a gas...so define the concept of a "mole"
  - 1mole =  $6.02 \times 10^{23}$  molecules =  $1 N_A$  of molecules Avogadro's Number
  - Periodic table notes the # of grams per mole for an atom, e.g. 28.09 grams of silicon is 1 mole of silicon atoms
  - The number of moles of an item is described by n



What is the mass in grams of 3 moles of  $CO_2$ ?



1. Mass/mole = 1\*(Carbon mass/mole) + 2\*(Oxygen mass/mole)

2. Mass/mole = 
$$1*12u + 2*16u = 44u$$

Mass of atoms in atomic mass units, "u". 1u = 1g/molHydrogen (H) 1u Helium (He) 4u Lithium (Li) 6u Beryllium (Be) 8u Boron (Bo) 10u Carbon (C) 12u Nitrogen (N) 14u Oxygen (O) 16u

Gas Laws: Relationships between state variables

• "Ideal Gas Law":

• *PV* = *nRT* 

- P = pressure, V = volume, n = number of moles,
  - R = Ideal Gas constant, T = temperature
- R = 8.31 J/(mol\*K)
- ...alternate form:
   *PV=Nk<sub>B</sub>T*
- N = number of molecules,

 $k_B = Boltzmann constant = R/N_A = 1.38x10^{-23} J/K$ 

- Special cases for Ideal Gases:
  - <u>Constant P & n</u>: "Charles' Law":  $\frac{V_i}{T_i} = \frac{V_f}{T_f}$ 
    - ...heating a gas will increase its volume
  - <u>Constant T & n</u>: "Boyle's Law":  $P_iV_i = P_fV_f$ 
    - ...squeezing a gas into a smaller volume will increase the pressure



Calvin & Hobbes

Use absolute SI units: i.e. [T] = Kelvin, [P] = Pascal [absolute] Consider two gas-filled cylinders which have the same volume and same temperature. Cylinder A is filled with  $O_2$ . Cylinder B is filled with  $CO_2$ . There are the same number of moles of molecules in each cylinder. Which cylinder has the greatest pressure?

(A) 
$$P_A > P_B$$
 (B)  $P_A = P_B$  (C)  $P_A < P_B$ 

- 1. PV=nRT ... irrespective of molecule type
- 2. P = (nRT)/V
- 3. Since n, T, & V are all the same, P is the same.

Fun Fact: 1 mole of any gas at "STP" (standard temperature and pressure, 1atm, 273K) occupies ~ 22 liters. Mass of atoms in unified mass units, "u". 1u = 1g/mol Hydrogen (H) 1u Helium (He) 4u Lithium (Li) 6u Beryllium (Be) 8u Boron (Bo) 10u Carbon (C) 12u Nitrogen (N) 14u Oxygen (O) 16u



Consider two gas-filled cylinders which have the same volume and same temperature. Cylinder A is filled with  $O_2$ . Cylinder B is filled with  $CO_2$ . There is the **same mass** in each cylinder. Which cylinder has the greatest pressure?

(A)  $P_A > P_B$  (B)  $P_A = P_B$  (C)  $P_A < P_B$ 

- 1. PV=nRT
- 2. Both cylinders contain the same mass, but CO<sub>2</sub> is heavier per molecule.
- 3. So, cylinder B must have fewer molecules (i.e. lower n)
- 4. For a fixed V and T, lower n means lower P.

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Mass of atoms in
unified mass units,
"". 1u = 1g/mol
Hydrogen (H)
              1u
Helium (He)
              4u
Lithium (Li)
              6u
Beryllium (Be) 8u
Boron (Bo)
              10u
Carbon (C)
              12u
Nitrogen (N)
              14u
Oxygen (O)
              16u
```



Suppose I triple the pressure of a gas and double the volume, while keeping the number of molecules same. What would be the ratio of temperatures,  $T_{After}/T_{Before}$ ?

(A) 1/6 (B) 2/3 (C) 3/2

1. PV=nRT2.  $T_B = P_B V_B / n_B R$ 3.  $T_A = P_A V_A / n_A R$ 4.  $P_A = 3^* P_B$ .  $V_A = 2^* V_B$ .  $n_A = n_B$ 5.  $T_A = (3^* P_B)^* (2^* V_B) / n_B R = 6^* T_B$ 6.  $T_A / T_B = 6$ 

## Kinetic Theory: A microscopic view of gases

- Gas properties can be thought of as arising from the interactions of its microscopic constituents
- Assume gas molecules are like billiard balls, bouncing off of the walls & each other
- The large number of interactions gives the gas molecules similar average properties, e.g. kinetic energy, which we can assign to a global property of the gas, e.g. temperature.

Percentage of molecule

speed interva

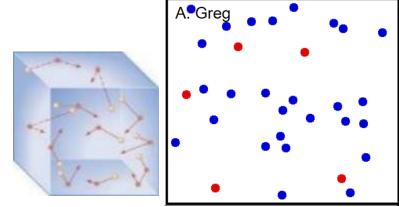
unit :

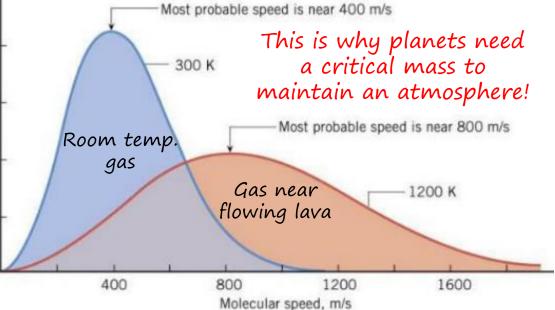
- For a given temperature, can define a typical velocity:
  - "Root mean square velocity"

• 
$$v_{RMS} = \sqrt{v^2}$$

 For a given temperature, the average kinetic energy for gas molecules is:

• 
$$\overline{KE} = \frac{1}{2}mv_{rms}^2 = \frac{3}{2}k_BT$$
  
•  $PV = \frac{1}{3}Nmv_{rms}^2$ 





Recall that massive objects have an associated "escape velocity", which is the speed required to overcome the gravitational pull of that object. Which type of gas is most likely to escape from our atmosphere?

(A) Hydrogen

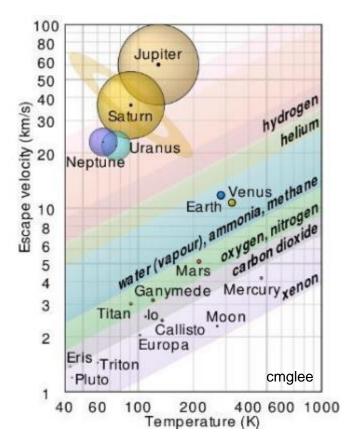
(B) Helium

(C) Neon

(D) Xenon

1. 
$$\overline{KE} = \frac{3}{2}k_BT = \frac{1}{2}mv_{rms}^2$$

- 2. For a given atmospheric temperature, all gas molecules will have the same average kinetic energy.
- 3. For the same KE, a smaller mass will lead to a larger velocity.
- 4. Therefore, hydrogen is the most likely to escape.



## Laws of Thermodynamics: Brief Overview

- 0<sup>th</sup> law:
  - Two systems in equilibrium with a third system are in equilibrium with each other.
  - Basically just **define temperature** here: if  $T_A = T_C$  and  $T_B = T_C$ ,  $T_A = T_B$ .
- 1<sup>st</sup> law:
  - When a system absorbs or emits energy (via work, heat, or matter), the internal energy of the system changes accordingly.
  - This is just a statement that **energy is conserved**.
- 2<sup>nd</sup> law:
  - Entropy (a.k.a. disorder) of interacting systems increases.
  - Consequence: Heat doesn't spontaneously flow from a cold object to a hot one
- 3<sup>rd</sup> law:
  - Entropy (a.k.a. disorder) of a system approaches 0 at 0K ("absolute zero").
  - Consequence: Engines have a limited maximum efficiency. And, since you would need an engine to do the cooling, you can't cool something to absolute zero.

Upshot: You can't get out more energy from a system than you put-in. i.e. there are no "perpetual motion" machines.

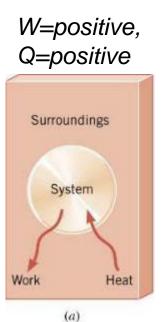


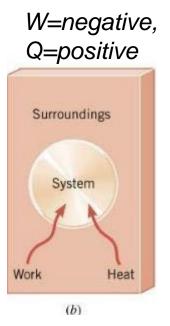
### 1st Law of Thermodynamics: The Math

- When a system absorbs or emits energy (via work, heat, or matter), the internal energy of the system changes accordingly.
- This is just a statement that **energy is conserved**.
- If we define U as the internal energy of a system, Q as heat added to the system (-Q if removed), and W as work done by the system (-W if work done on the system), then,

•  $\Delta U_{System} = Q_{ToSystem} - W_{BySystem}$ 

"system" = what we care about "surroundings" = everything else





Sect 15.1

A system containing 0.5 moles of diatomic nitrogen gas is placed over a hot plate, which adds 3000J of heat into the system. At the same time, the surroundings compress the gas, doing 1500J of work on the system. What is the change of internal energy of the gas in the system?

- 1.  $\Delta U = Q W$
- 2. Q is the heat added to the system. Here: 3000J.
- 3. W is the work done *by* the system.

For work done on the system, we use -W. So W = -1500 J.

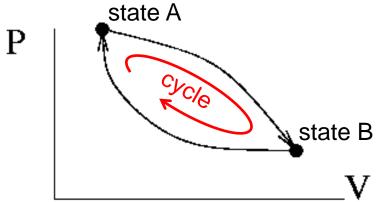
4. Therefore,

 $\Delta U = 3000 J - (-1500 J) = 4500 J$ 



#### **Transitions between states & PV diagrams**

- •A "state" of a system has a defined set of conditions, e.g. pressure, temperature, volume, number of molecules, internal energy
- Changing from one state to another is a "transition".
- •We will commonly represent transitions on diagrams indicating the pressure & volume for the system in the states and during the transitions. These are PV diagrams: state A
- Transitioning from one state to another (or many others) and back to the same initial state is a "cycle".
  For a full cycle: ΔU = 0



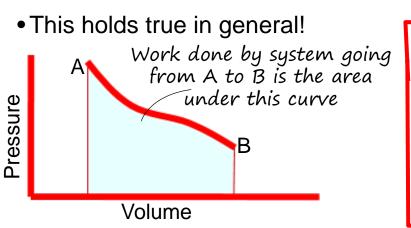
Sect 15.2

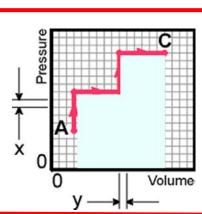
Work from a gas: Solution via PV diagrams

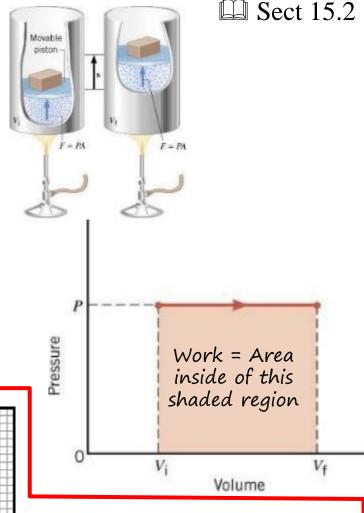
- Recall, Work = Force\*Displacement:  $W=F^*\Delta x$
- Recall, Force from a Gas = Pressure\*Area: F=P\*A
- So, the work done by a gas pushing-up a piston is,  $W = F^*\Delta x = P^*(A^*\Delta x) = P^*\Delta V$
- If the pressure is constant,

• "Isobaric Transition":  $\Delta U = Q - P^* \Delta V$ 

• On a PV diagram, can calculate work by integrating the area under the curve!

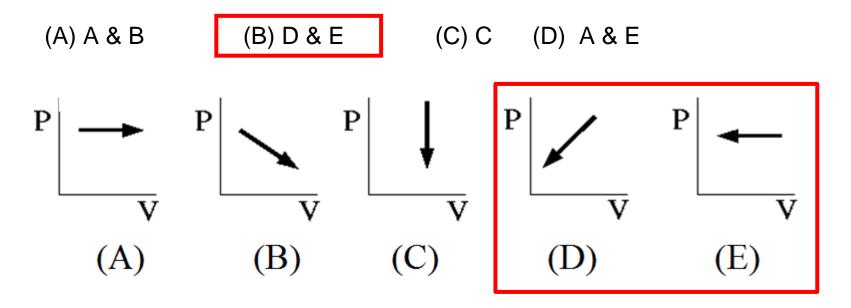






Can solve for work for more complex cases by integrating graphically. Which of the following PV diagrams correspond to **negative** work done by the system?



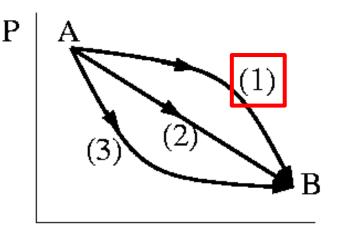


1. W =  $P^*\Delta V$ 

- 2. If a gas is expanding (i.e. V is increasing) it is doing work.
- 3. If a gas is contracting (i.e. V is decreasing) work is done on it, a.k.a. the gas is doing negative work.
- 4. (D) and (E) are gases contracting, so they are doing negative work.

Transitions 1, 2, and 3 all begin at state A and end at state B. For which transition is the work done by the system the greatest?

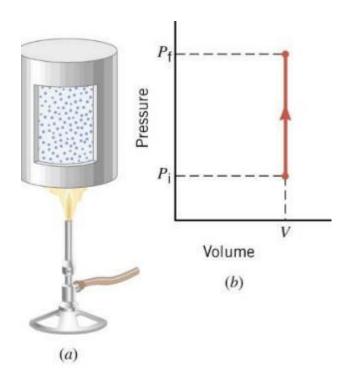
- 1. Work = area under the curve in a PV diagram
- 2. Greatest area = greatest work.
- 3. Transition 1 has the largest area below.



- Since each transition goes between the same pair of states, the internal energy change ( $\Delta U$ ) is the same.
- From the 1<sup>st</sup> law,  $\Delta U_{System} = Q_{ToSystem} W_{BySystem}$
- So,  $Q_{ToSystem} = \Delta U_{System} + W_{BySystem}$
- Therefore, transition 1 also has the greatest amount of heat added to the system.

#### Isochoric transition: Transition with no work

If a sealed container is heated, pressure increases, but volume is fixed.
W = P\*ΔV = P\*0 = 0 For isochoric
ΔU = Q - W = Q - 0 = Q transitions

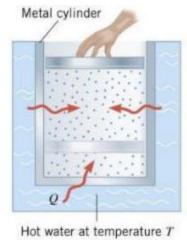


**Isothermal transition:** Transition with no internal energy change Sect 15.2

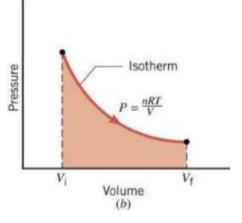
- If a gas in a container is slowly compressed, work will be done on the system without it heating up.
- For this transition type,  $\Delta T = 0$ ,
- So,  $\Delta U = 0$ .
- Therefore, 0 = Q W, i.e.

• W<sub>BySystem</sub> = Q<sub>ToSystem</sub> For isothermal transitions

• i.e. all the heat added goes into work done by the gas







## Adiabatic transition: Transition with no heat transfer

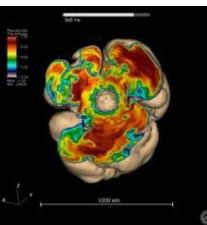
- If work (e.g. compression) is done on a thermally isolated system, heat will not be transferred, but the internal energy will change.
- For this transition type, Q = 0,
- So,  $\Delta U = Q W = 0 W = -W$

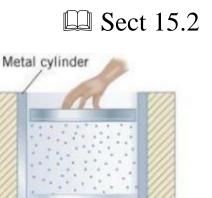
• $W_{BySystem} = -\Delta U_{System}$  For adiabatic transitions

• i.e. all the work done on a system changes the internal energy.

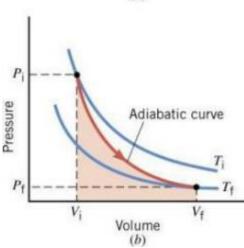
Or, only changes in the internal energy allow the system to do work.

- This can be a good approximation for really fast transitions, because there isn't time for heat exchange.
  - E.g. Supernova remnant expansion:



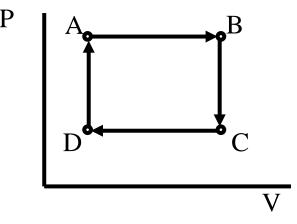


Insulating material (a)



Cycles: Transitions that form a loop in a PV diagram

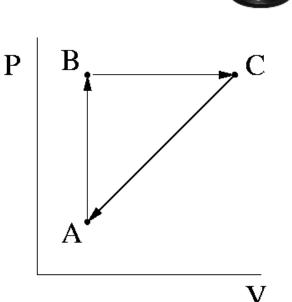
- For a full cycle: State A->B->C->D->A
  - $\Delta U_{net} = \Delta U_{AB} + \Delta U_{BC} + \Delta U_{CD} + \Delta U_{DA} = 0$
  - $W_{net} = W_{AB} + W_{BC} + W_{CD} + W_{DA}$
  - $Q_{net} = Q_{AB} + Q_{BC} + Q_{CD} + Q_{DA}$



- For example, for the cycle A->D on the right
  - $\Delta U_{net} = 0$ , as for all cycles
  - W<sub>net</sub> > 0, since the area under A->B is greater than the area under C->D
  - From the first law,  $\Delta U = Q-W = 0$ . So  $Q_{net} = W_{net} > 0$
- If the arrow direction were reversed (i.e. A->D->C->B->A), the signs would all flip! I.e. W<sub>net</sub> = Q<sub>net</sub> < 0</li>

In this picture,  $Q_{AB}$  is positive and  $\Delta U_{BC}$  is positive. What is the sign of of  $\Delta U_{CA}$ ?

1. Cycle: 
$$\Delta U_{net} = 0 = \Delta U_{AB} + \Delta U_{BC} + \Delta U_{CA} = 0$$
  
2.  $\Delta U_{AB} = Q_{AB} - W_{AB}$   
1. Area under A->B is zero, so  $W_{AB} = 0$   
2. So,  $\Delta U_{AB} = Q_{AB}$ , which we're told is >0.  
3. We're told  $\Delta U_{BC} > 0$   
4. Since  $\Delta U_{net} = 0$ , but  $\Delta U_{AB} > 0$  and  $\Delta U_{BC} > 0$ ,  
 $\Delta U_{CA} = must be < 0$ .



9

#### Examples of common engine cycles:

For cool animations, see: http://www.animatedengines.com/

