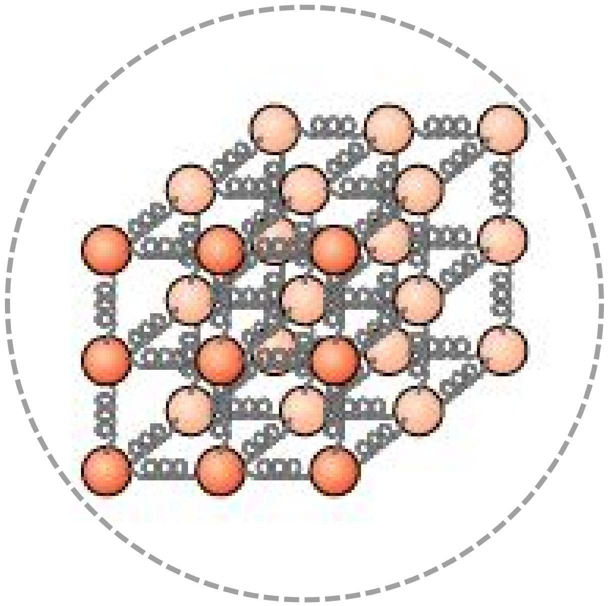
Physics 132- Fundamentals of Physics for Biologists II

Statistical Physics and Thermodynamics

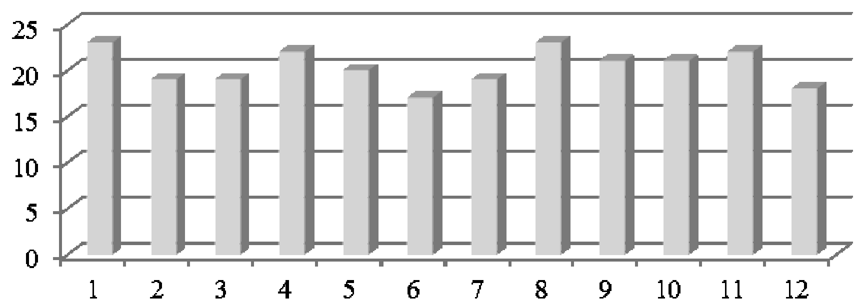
A confession

Temperature

Object A

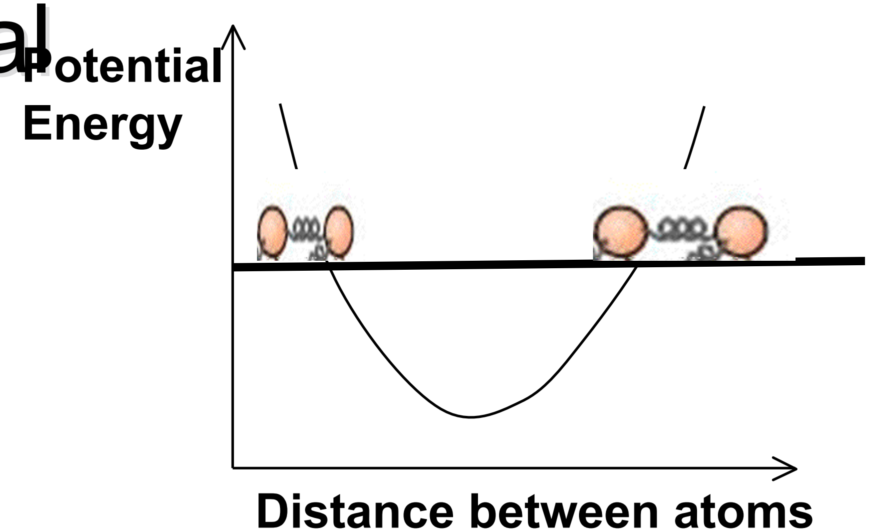


Object contains MANY **atoms (kinetic energy)** *and* **interactions (potential energy**)



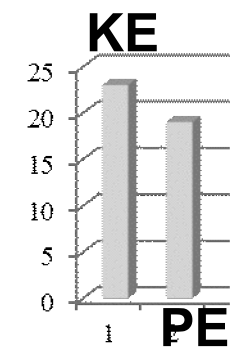
- **Temperature:** Measures the amount of energy in each atom or interaction – the key concept is that thermal energy is **on average** equally distributed among all these possible "bins" where energy could reside.
- Average Energy in each bin: 1/2 kT   k - Botlzmann's const

Thermal Energy can be either Kinetic or Potential



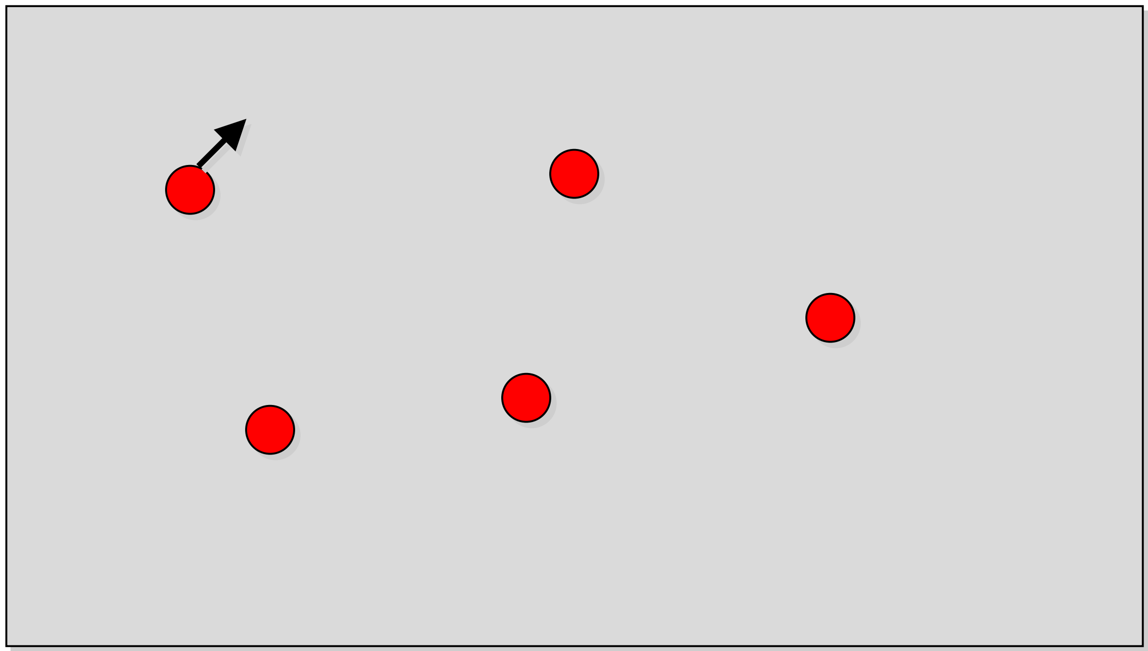
2 Bins: 1D KE PE

- **Let's define the zero of potential energy as the minimum of the Potential Energy Curve.**
- **With this definition, energy is ON AVERAGE the <u>same for both potential and kinetic energy</u>**



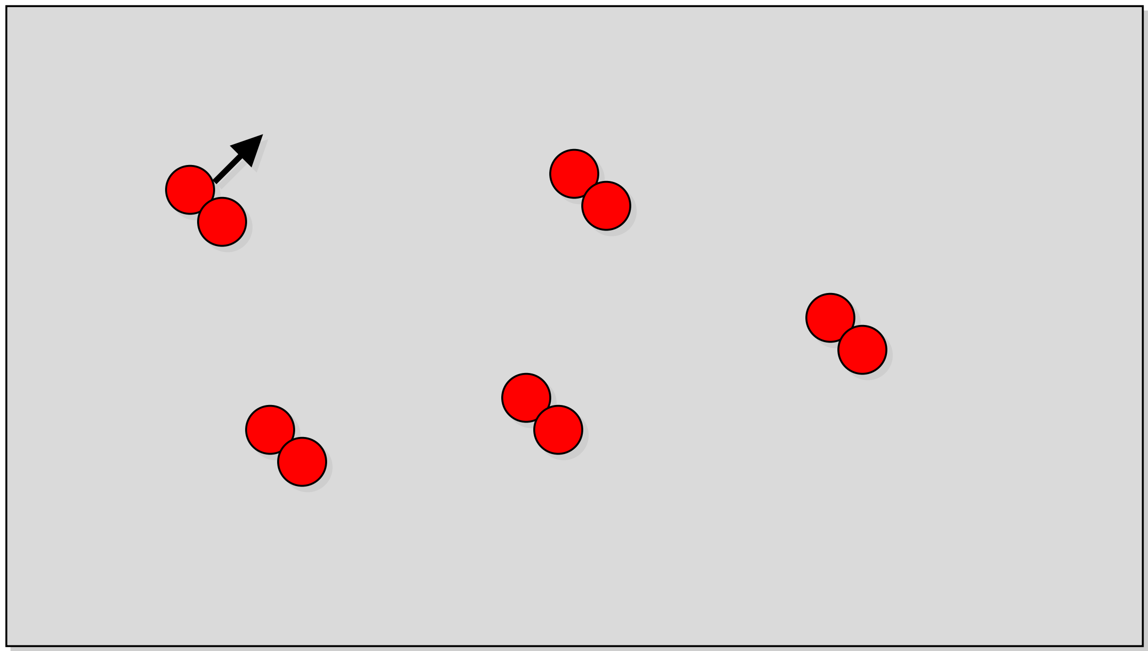
N oscillators, Thermal Energy = (2/2) N kT

Thermal Energy in an ideal gas



N monatomic molecules, moving in 3D
Each molecule has 3 Bins - 3 directions No PE
Thermal Energy = (3/2) N kT

Thermal Energy in gas



N diatomic molecules, moving in 3D

Thermal Energy = (?/2) N kT

Whiteboard, TA & LA

First Law of Thermodynamics

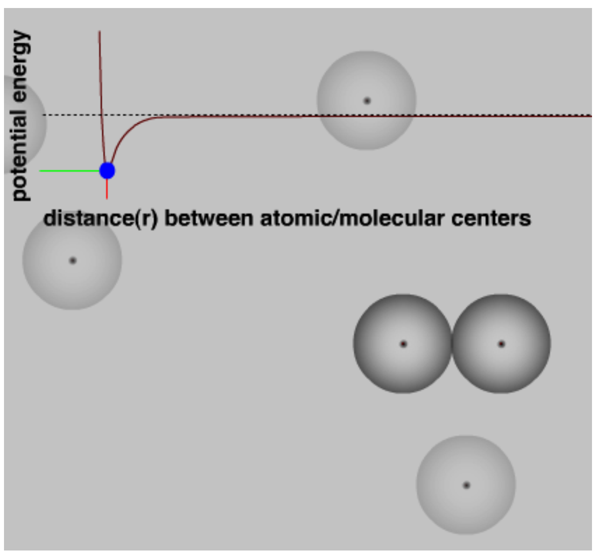
Total amount of energy in a system is unchanged, unless energy is put into the system or taken out of the system across the boundaries.

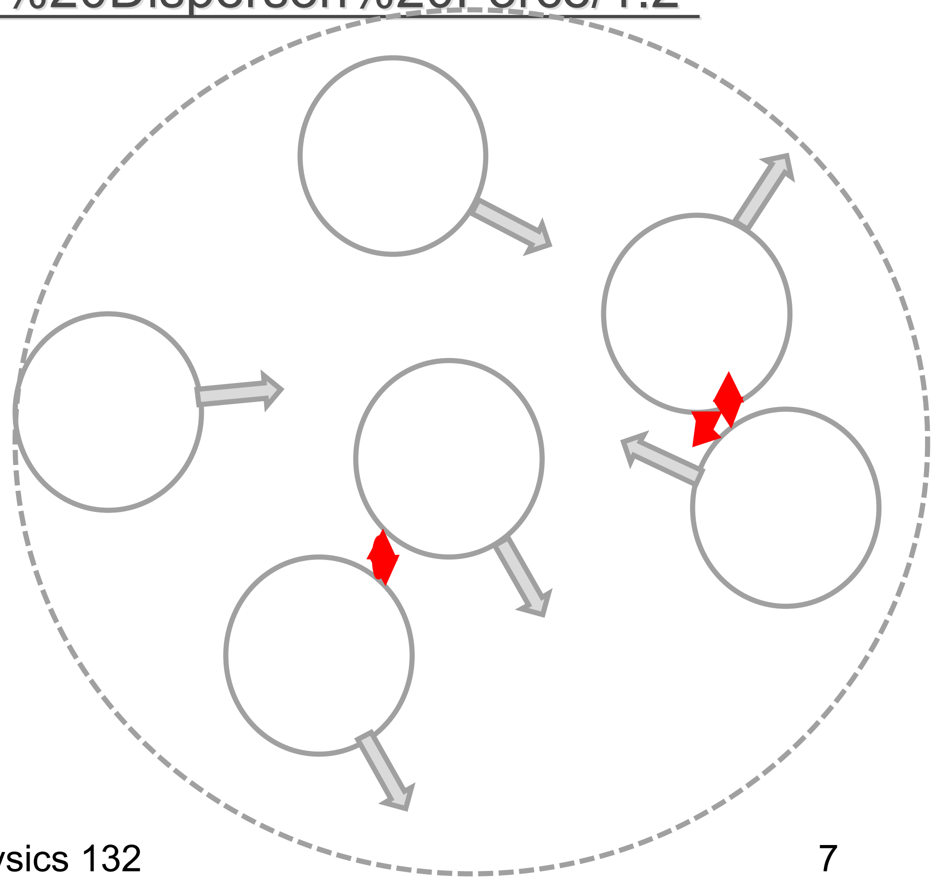
We need to separate two questions:

- How does energy move within the system?
- How can the energy of the system change?
- If the first law states that energy is conserved, how do we apply this law to an open system when energy is being exchanged? **

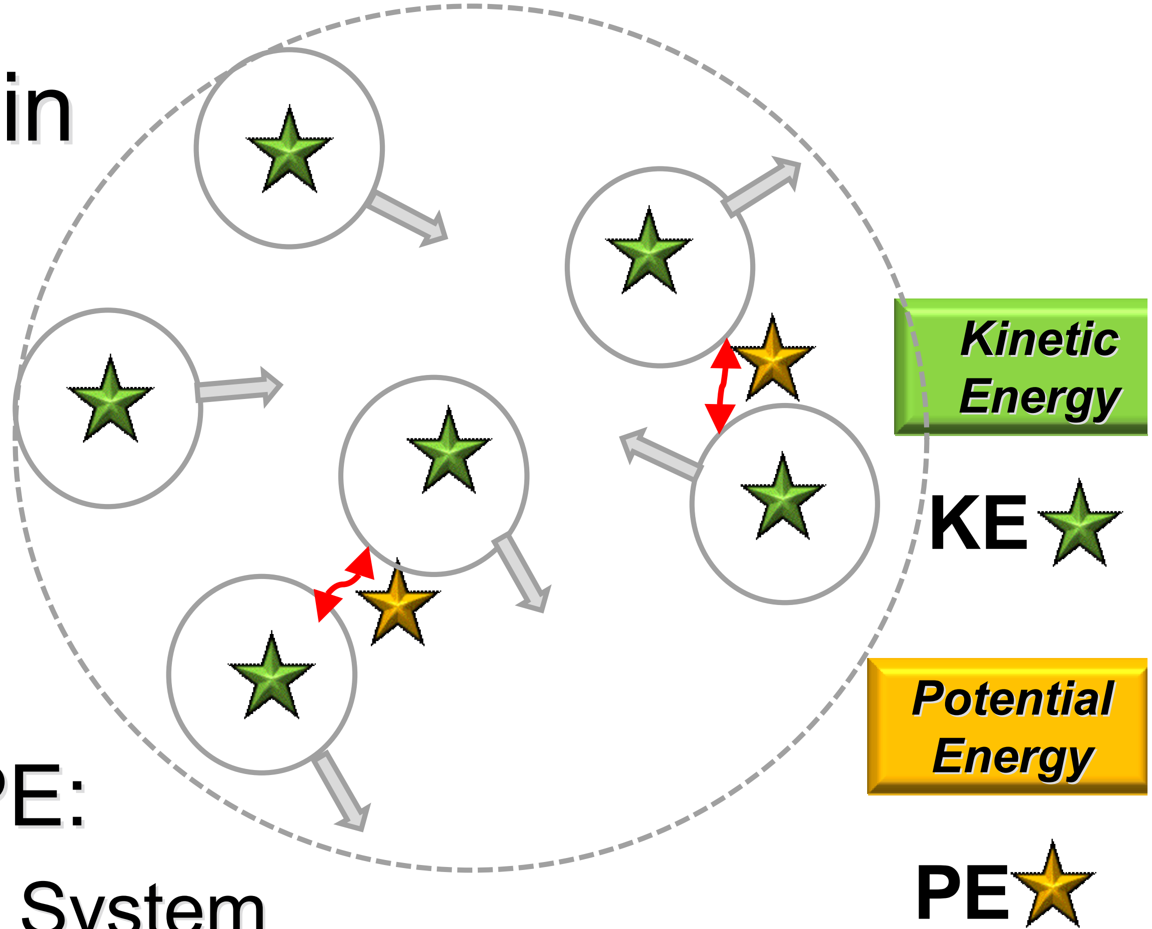
A simple 6 atom system

- http://besocratic.colorado.edu/CLUE-Chemistry/CLUE-STUDENT/chapter-1/London%20Disperson%20Force/1.2-interactions-2.html





Where is energy in this system?



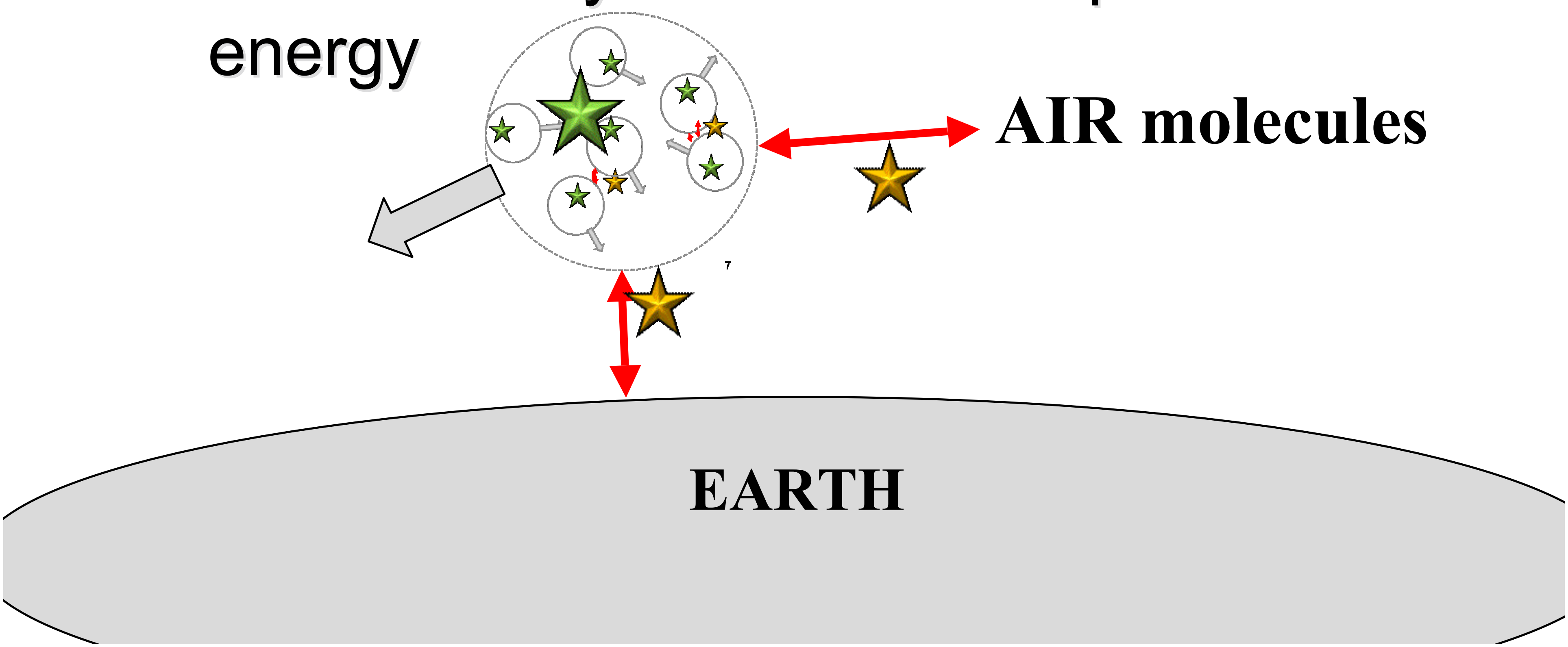
Kinetic Energy KE

Potential energy PE:

- Internal energy of a System
- Related to interactions (forces) within the System
- Can turn into KE (or other energy) when the objects in the system move
- **Stored in INTERACTION (line between objects)**

ZOOM out – the six atoms interact with their surrounding

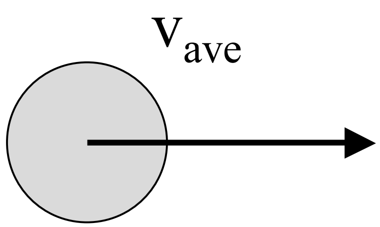
- The whole system can move and have kinetic energy
- The whole system can have potential energy



Classifying Energy (macro vs micro)

Macroscopic kinetic energy requires all molecules to move in the same direction, i.e., exhibit coherent motion. Finally the objects in our system also have chemical energy associated with the internal kinetic and potential energies of the electrons in atoms and the binding of atoms into molecules.† We will write the total result of both of these internal energies as $U_{internal}$. With this, the total energy of our system can be written

$$E = KE + PE + U_{internal}$$



total velocity of a part

$$v_T = v_{ave} + v_{rand}$$

$$K_T = (1/2)\,\Sigma\, m\, v_T^2$$

Moving object with many parts. Each part has a different velocity

$$K_T = (1/2)\,\Sigma\, m\, v_{ave}^2 + (1/2)\,\Sigma\, m\, v_{rand}^2$$

$$K_T = K_{ave} + K_{rand}$$

macroscopic internal

Question: In a hurricane which is greater ?

$$v_T = v_{ave} + v_{rand}$$

1. Average velocity of an air molecule (wind speed)
2. Average random speed of an air molecule (thermal speed)

First Law of Thermodynamics

Total amount of energy in a system is unchanged, unless energy is put into the system or taken out of the system across the boundaries.

We need to separate two questions:

- How does energy move within the system?
- How can the energy of the system change?

■If the first law states that energy is conserved, how do we apply this law to an open system when energy is being exchanged? **

Total energy of a macroscopic object changes when the object interacts with the rest of the universe

Heat (Thermal Energy) added to system

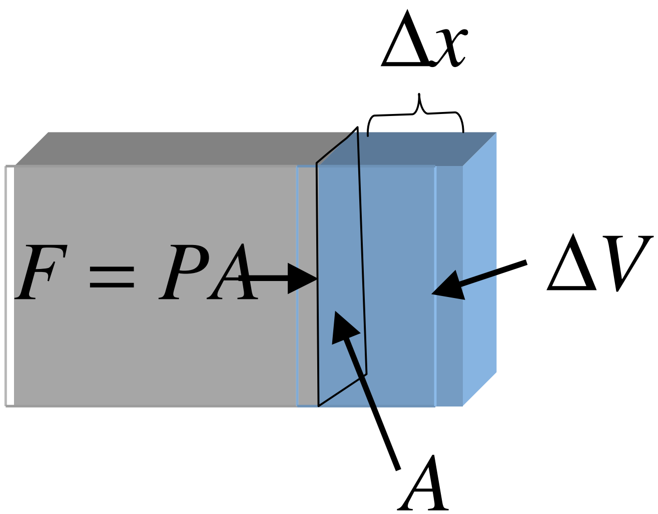
$$\Delta E = Q - W$$

Sign choice: Work done by the object on outside

Chemistry: Chemical processes usually do not involve motion of the whole object. Thus the macroscopic potential and kinetic energy usually do not change:

$$\Delta E = \Delta U = Q - W$$

- W is work which you learned about in the first semester - missing modifier
- Q is heat –Energy that flows from one system to another when the systems are free to exchange energy eg heat conduction
  - To understand why internal energy flows from one system to another system, we should first understand how internal energy moves within the sytem



Work done <u>by</u> the system <u>on</u> the outside world

$$W = F\Delta x = (PA)\Delta x = P(A\Delta x) = P\Delta V$$

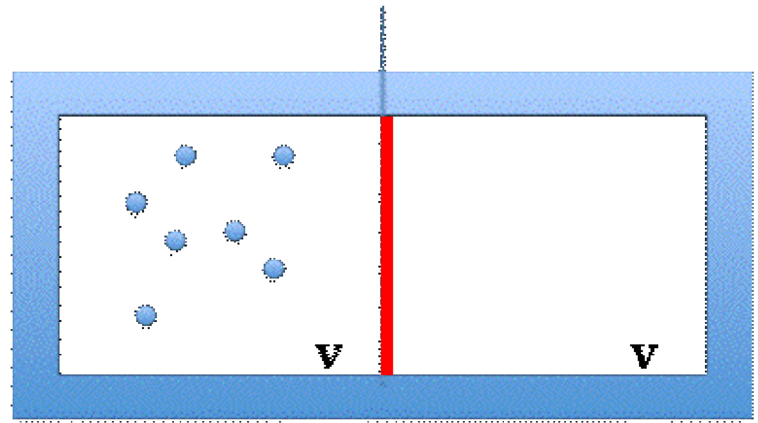
$$W = P\Delta V$$

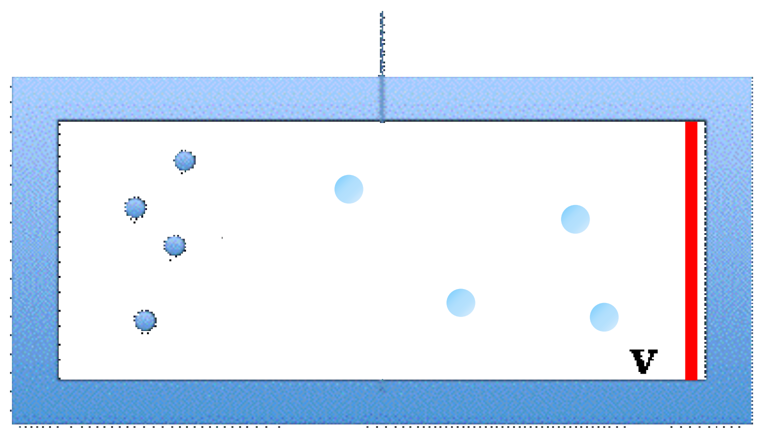
What if P varies as volume changes ?

$$W = \int_{V_1}^{V_2} P dV$$

Suppose an isolated box of volume 2V is divided into two equal compartments. An ideal gas occupies half of the container and the other half is empty. The partition is quickly removed without friction. How does the **energy** of the gas at the end compare to the **energy** of the gas at the start?

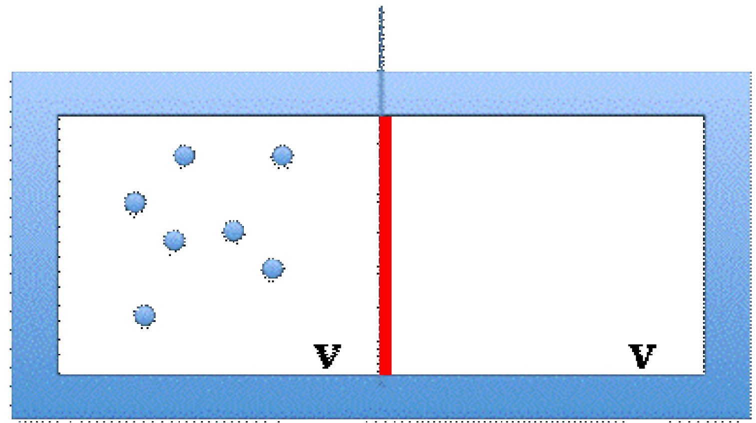
1. The internal energy increases
2. The internal energy decreases
3. The internal energy stays the same
4. There is not enough information to determine the answer



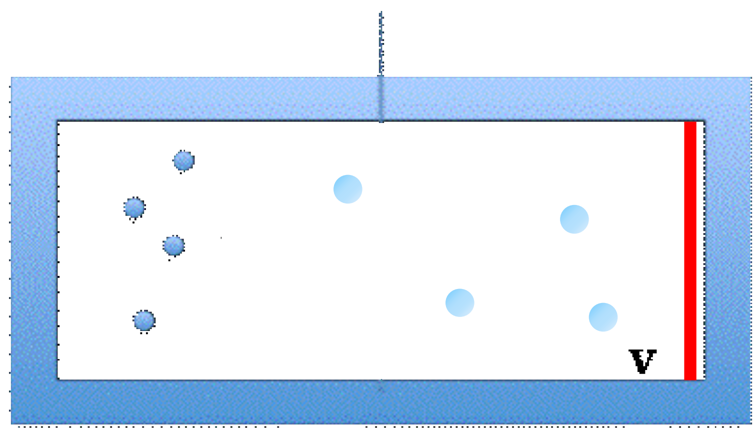


Follow - on How quick is quickly?

Suppose an isolated box of volume 2V is divided into two equal compartments. An ideal gas occupies half of the container and the other half is empty. The partition separating the two halves has some friction F when it slides and is gradually pushed away by the gas. How does the **energy** of the gas at the end compare to the **energy** of the gas at the start?

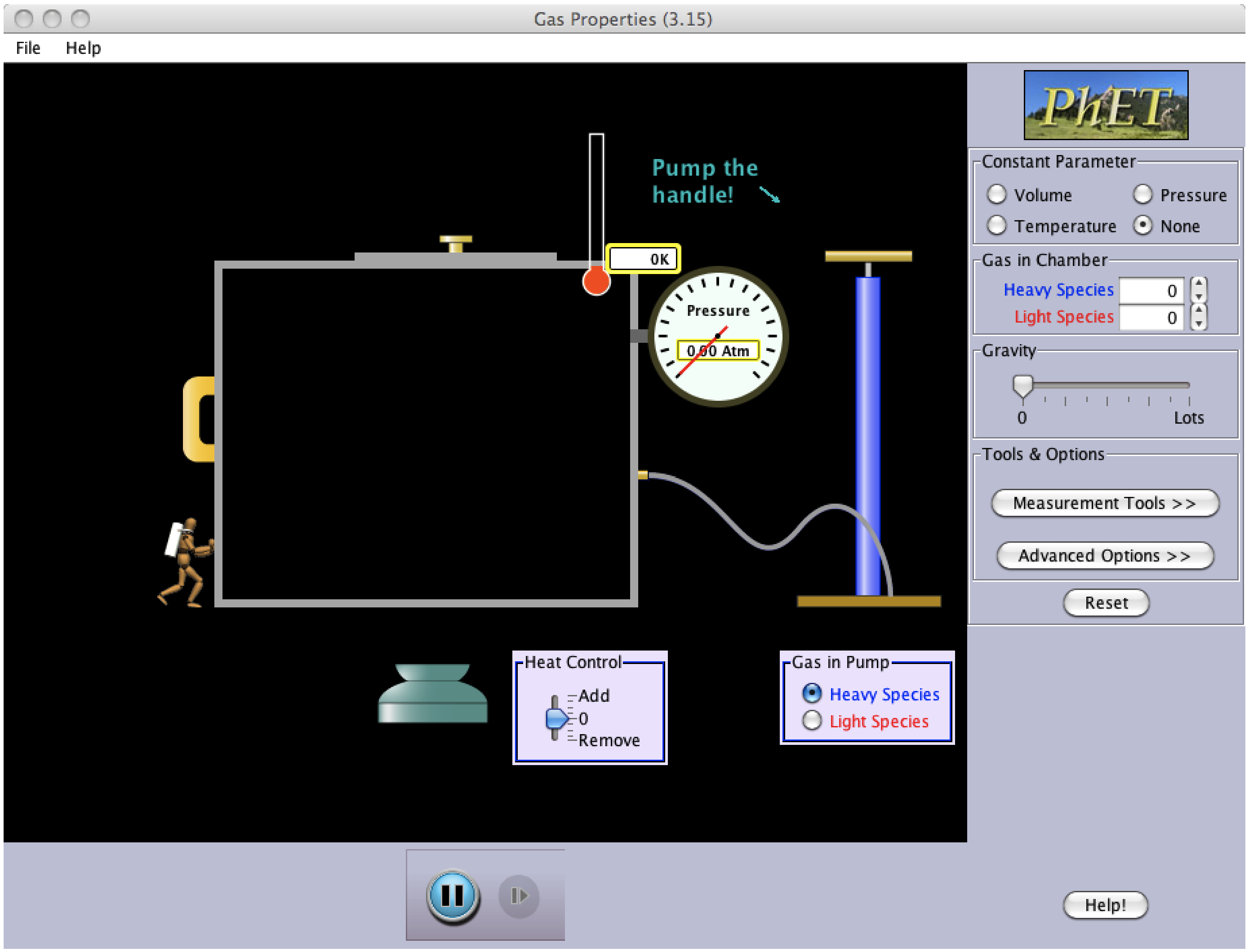


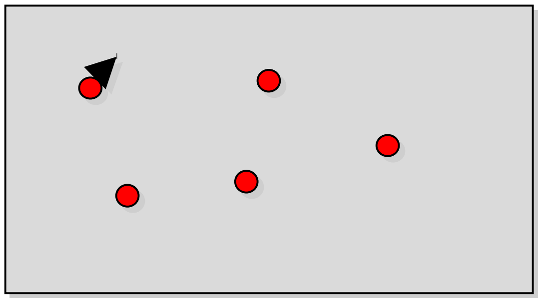
1. The internal energy increases
2. The internal energy decreases
3. The internal energy stays the same
4. There is not enough information to determine the answer



- W is work which you learned about in the first semester
- Q is heat – Internal Energy that flows from one system to another when the systems are free to exchange energy
  - To understand how internal energy flows from one system to another system, we should first understand how internal energy moves within the sytem

Changes in Internal Energy of an ideal Gas





State variables: Suppose I have an ideal gas

Which variables are needed to prescribe the conditions in this gas?

A. N- number of atoms
B. T - Temperature
C. P - Pressure
D. V - Volume
E. U - Internal Energy

$P=NkT/V$

$U = (3/2)\ NkT$

1. A, B
2. A, B, C, D
3. All
4. Any three
5. Any four

Equations of State (EOS)

A. N- number of atoms
B. T - Temperature
C. P - Pressure
D. V - Volume
E. U - Internal Energy

You specify 3

EOS tells the other 2

Requires a model for the system

To make life simple fix N

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

What is the missing equation in the case U(T,P)?

$$V=V(T,P) \quad \text{eg.} \quad V= NkT/P$$

Whiteboard, TA & LA

More Variables: The more the merrier !

A. N- number of atoms
B. T - Temperature
C. P - Pressure
D. V - Volume
E. U - Internal Energy
F. H - Enthalpy
G. S - Entropy
H. F - Helmholtz free energy
I. G - Gibbs free energy

$$H = U + PV$$

$$F = U - TS$$

$$G = H - TS$$

Enthalpy

- A measure of the total energy in a thermodynamic system.

$$H = U + PV$$

- Looking at energy exchanged, the change in enthalpy can be viewed:

$$\Delta H = \Delta U + \Delta(PV)$$

from first law

If **pressure is constant** then

$$\Delta H = \Delta U + P\Delta V = (Q - P\Delta V) + P\Delta V = Q$$

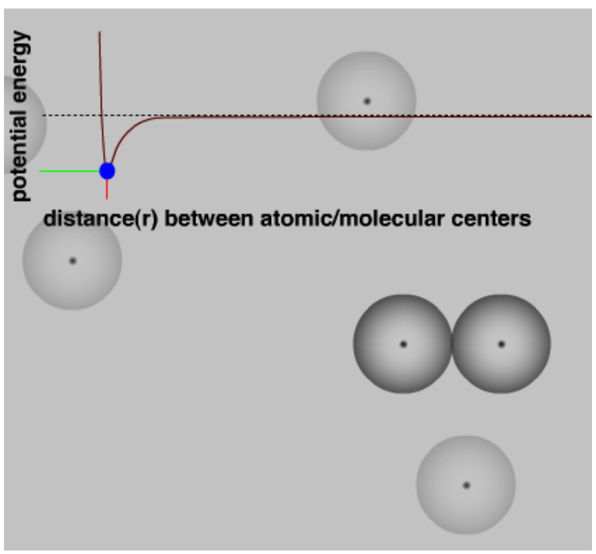
Enthalpy

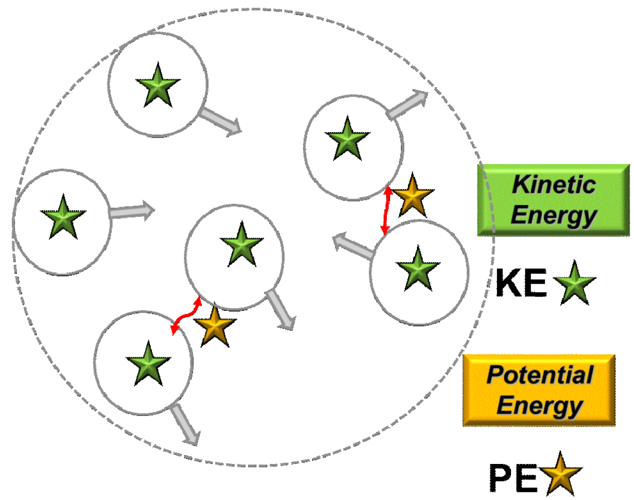
Since most chemical reactions take place under constant pressure

$+\Delta H \rightarrow$ Endothermic reaction

$-\Delta H \rightarrow$ Exothermic reaction

How does internal energy move within the system?





http://besocratic.colorado.edu/CLUE-Chemistry/CLUE-STUDENT/chapter-1/London%20Disperson%20Force/1.2-interactions-2.html

How does energy move within the system?

- physical description – forces and motion of colliding atoms/molecules
  - The loss of energy of one of the colliding atoms/molecules equals the gain of the other colliding atom/molecule

- Statistical description – what happens on average in many collisions or other interactions

Statistical Description: Thermal Equilibrium

- ***Internal energy resides in "bins"*** , KE or PE associated with degrees of freedom.
- ***Thermodynamic equilibrium is dynamic*** – Energy moves from bin to bin, changes keep happening in each bin, but total energy remains unchanged.
- ***Key Assumption*** - All sharing arrangements among bins are equally likely to occur.

Let's build a simple model of sharing energy

- Total amount of energy is conserved, Energy is divided into small *chunks*, shared among *bins.*
- Each *bin* can have an arbitrary number of *chunks* (but the total number of chunks for all bins is fixed).
- We are going to count, in how many ways this slicing of energy into *chunks* can be done.
- Each way of slicing is assumed to be equally likely.

This simple physical model of sharing of energy will give you a new way to think about the following concepts that are used in chemistry and biology

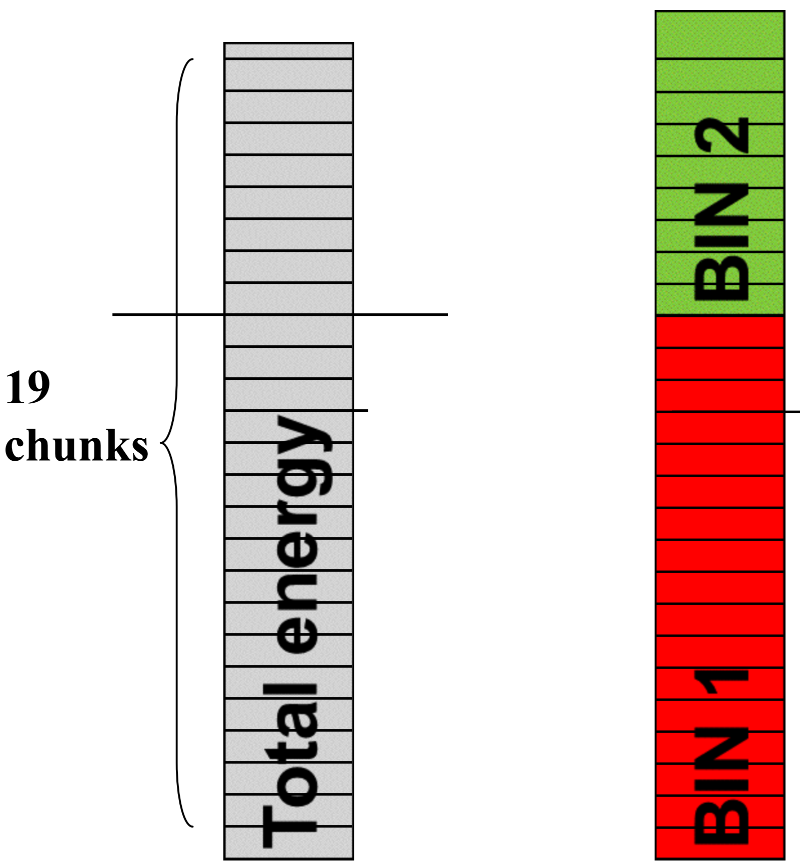
- Entropy – what is it, and why does it always seem to increase?
- Temperature - Why do two bodies in thermal equilibrium have the same temperature?
- Boltzmann distribution - why does the probability of having a certain energy decrease exponentially?

$$P(E) = e^{-\frac{E}{k_B T}}$$

All in a few lectures…

Now lets calculate!

Two energy "bins" divide up 19 *chunks* of energy randomly



After a "collision", the energy is RANDOMLY divided between Bin 1 and Bin 2

Q: How many ways can this be done?

Giving leftover energy to Bin 2

Bin 2 has the following energy	How many ways can this happen
0	1
1	1
2	1
3	1
4	1
…	
19	1

TOTAL number of "Scenarios": 20

Whiteboard, TA & LA

Giving Leftovers to Bin 3

Bin 3 has the following energy (1&2 have the rest)	How many ways can this happen
0	20
1	19
2	18
3	17
4	16
19	1

TOTAL number of "Scenarios": 210

Whiteboard, TA & LA

Three bins – m *chunks* of energy

Bin 3 has the following energy	How many ways can this happen
0	m+1
1	m
2	m-1
3	m-2
4	m-3
m	1

TOTAL number of "Scenarios": $\frac{(m+1)^2}{2} \approx \frac{m^2}{2}$

Whiteboard, TA & LA

Now let's add Bin 4

Bin 4 has the following energy	**How many ways can this happen**
0	$(m+1)^2/2$
1	$(m)^2/2$
2	$(m-1)^2/2$
3	$(m-2)^2/2$
4	$(m-3)^2/2$
m	

TOTAL number of "Scenarios": $\approx (m)^3/(3\cdot 2)$

Whiteboard, TA & LA

Now let's consider n Bins

- 2 bins: $(m+1)$
- 3 bins: $\frac{(m+1)^2}{2} \approx \frac{m^2}{2}$
- 4 bins: $\approx \frac{(m)^3}{(3 \cdot 2)}$

n bins

Students fill in!

Remember

$$\frac{m^{n+1}}{n+1} = \int_0^m dm\, m^n$$

Whiteboard, TA & LA