Physics 132- Fundamentals of Physics for Biologists II

Statistical Physics and Thermodynamics

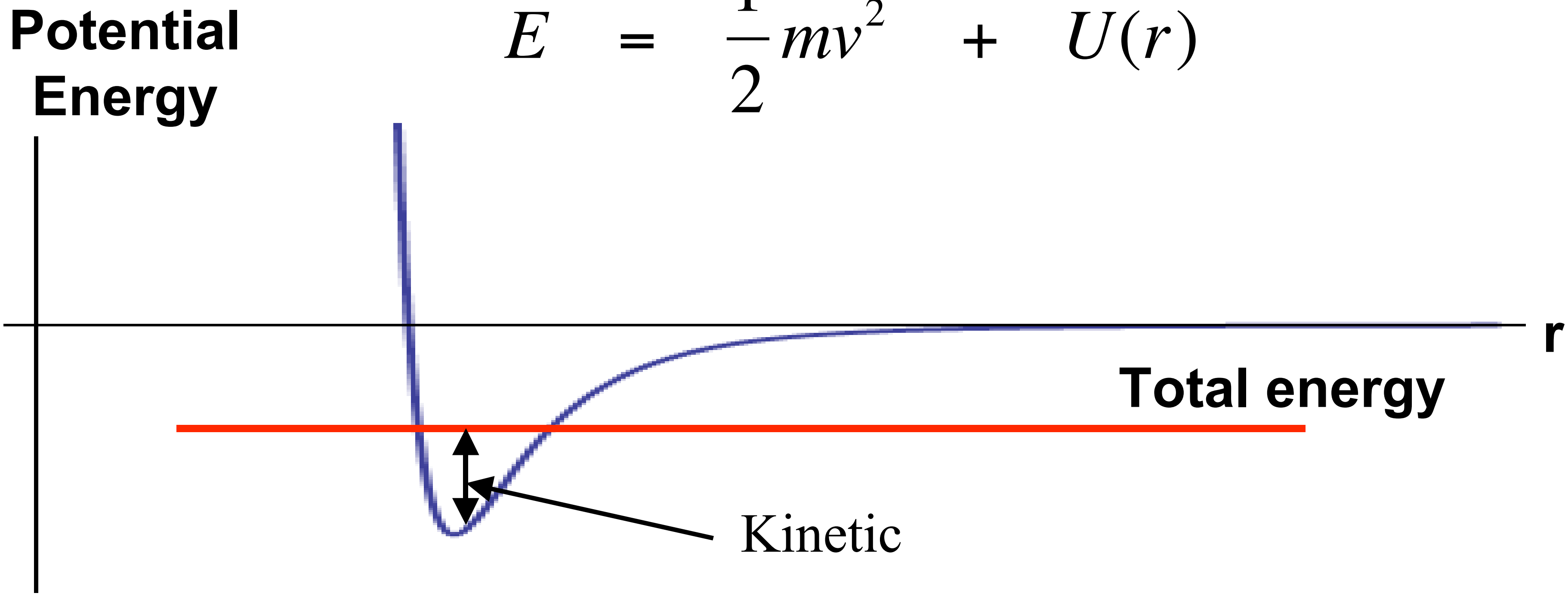
It’s all about energy

Classifying Energy

	Macroscopic Energy	Internal Energy
Kinetic Energy	Moving baseball	Vibrations and random motion of atoms
Potential Energy	Baseball high above earth	Interactions between atoms

Total Energy = Kinetic Energy + Potential Energy

$$E = \frac{1}{2}mv^2 + U(r)$$

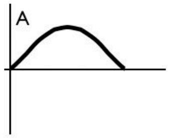


Draw r vs t

Draw v vs t

Sample Problem

1.2 (3 pts) Which of the following graphs could represent the kinetic energy as a function of time if we start observing the atoms when they are a distance r1 apart, and stop observing when they are again a distance r1 the next time?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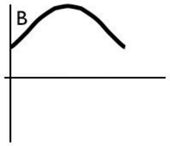
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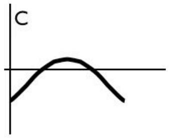
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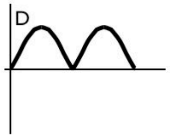
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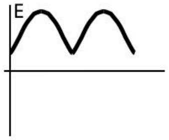
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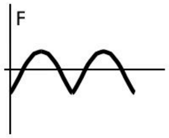
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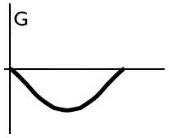
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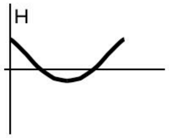
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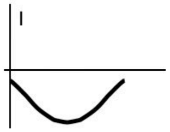
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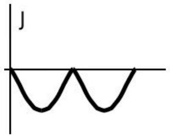
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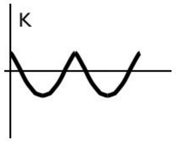
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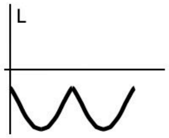
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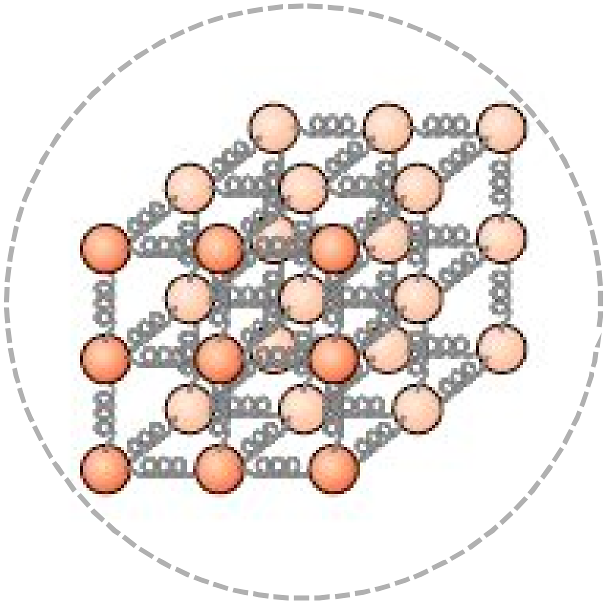
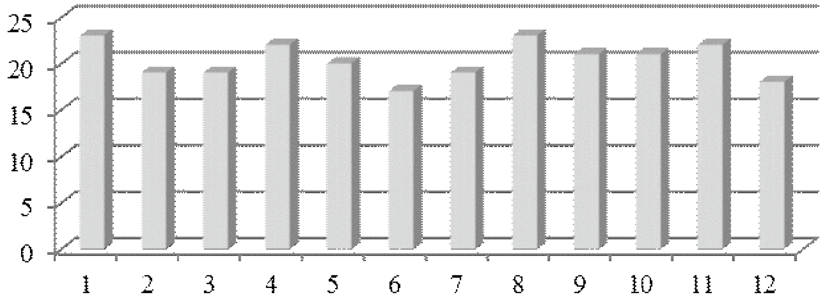
Temperature measuure of Internal Energy

Object A

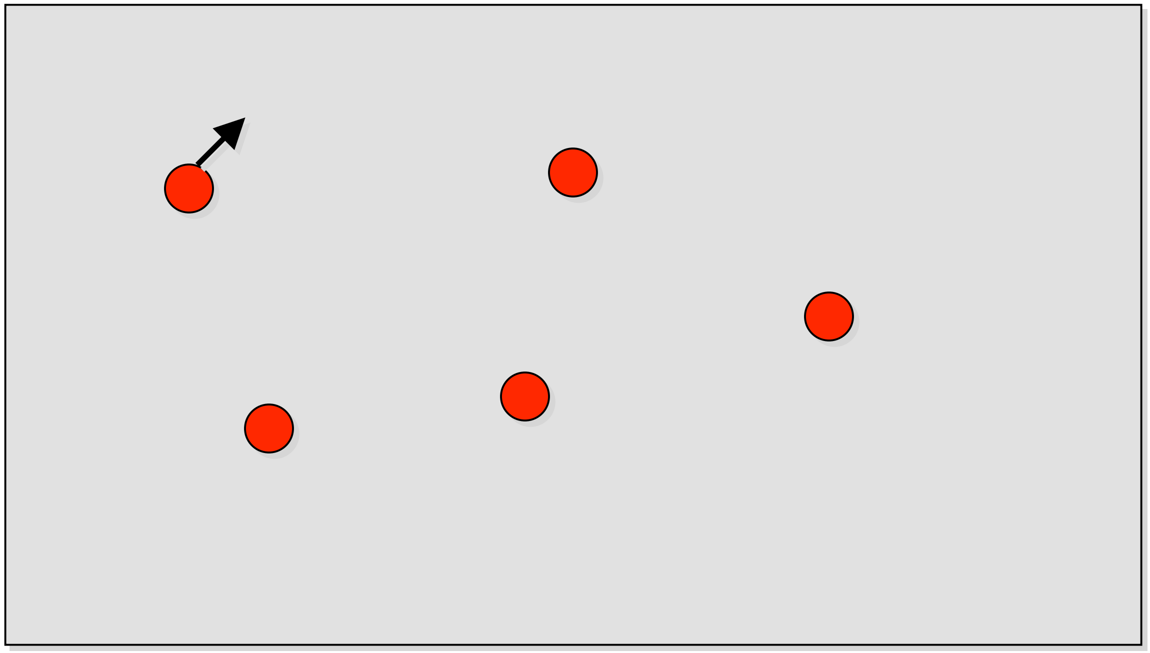


Object contains MANY **atoms (kinetic energy)** *and* **interactions (potential energy**)



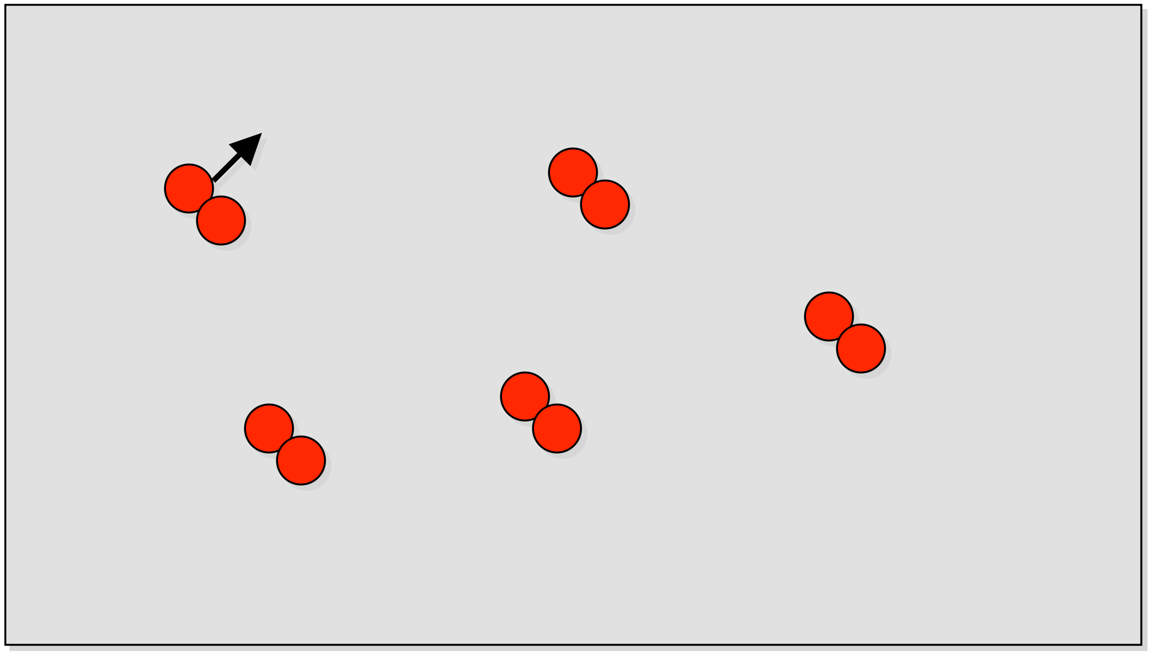
- **Temperature:** Measures the amount of energy in each atom or interaction – the key concept is that thermal energy is **on average** equally distributed among all these possible “bins” where energy could reside.
- Average Energy in each bin: 1/2 kT k - Botlzmann’s const

Thermal Energy 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

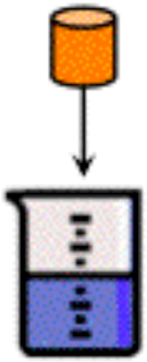
Thermal Energy in gas



N diatomic molecules, moving in 3D

Thermal Energy = (7/2) N kT

Sample Problem



1. (4 pts) A 200 g block of copper at a temperature of 55 °C is put into an insulated beaker of water at 20 °C. The two come to thermal equilibrium at a temperature of about 30 °C – much closer to the original temperature of the water than of the copper. (From the macroscopic point of view, the specific heat of water is about 1.0 J/g-°C while the specific heat of copper is only about 0.4 J/g-°C.) However, from the microscopic point of view…

1.1 (2 pts) From this you can conclude

A. There are more degrees of freedom in 200 g of copper than in 200 g of water.

B. There are fewer degrees of freedom in 200 g of copper than in 200 g of water.

C. There are about the same number of degrees of freedom in 200 g of copper as there are in 200 g of water.

D. The information given doesn't tell you anything about the number of degrees of freedom in the matter.

First Law of Thermodynamics

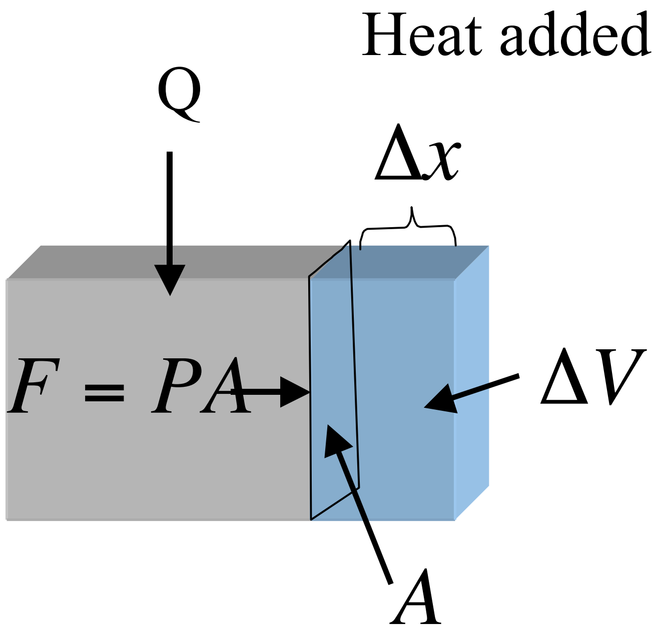
Total amount of energy in a system is unchanged, unless energy is put into the system or taken out of the system across the boundaries.

$$\Delta U = Q - W$$

Change in internal energy

Heat added

Work done by system on outside world



Work done by the system on the outside world

$$W = F\Delta x = P\Delta V$$

$$\Delta U = Q - W$$

What if P varies as volume changes ?

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

Sample Problem

The internal energy of an object at atmospheric pressure is observed to increase. At the same time its volume changes, but pressure is held constant. Which of the following is/are true?

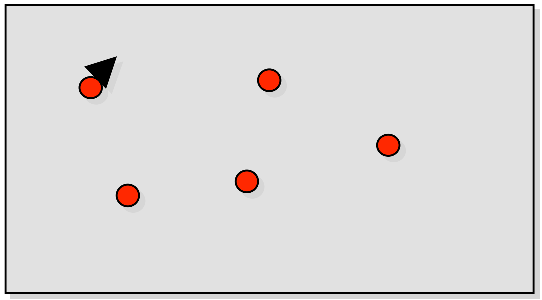
A. Heat must have been added to the system.

B. If the volume increased the system did positive work on its surroundings.

C. Since pressure is constant, enthalpy is conserved.

D. If the volume increased heat must have been added to the system.

E. If the enthalpy is constant, the volume must have decreased.



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

Equations of State (EOS)

You specify 3

EOS tells the other 2

Requires a model for the system

$P=NkT/V$

$U = (3/2)\ NkT$

for ideal monatomic gas

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)?

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

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

$H = U + PV$

$F = U - TS$
$G = H - TS$

Sample Problem

2. (3 pts) A number N of H_2 molecules and N/2 O_2 molecules react to make H_2O, and all three are in the (ideal) gas phase. Which of the following is true?

A. There are now N-H_2O molecules

B. If the reaction takes place at constant temperature and pressure the final volume will be smaller than the initial volume

C. If the reaction takes place at constant temperature and volume the final pressure will be lower than the initial pressure

D. If the reaction takes place at constant volume in an insulating box temperature must go down.

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

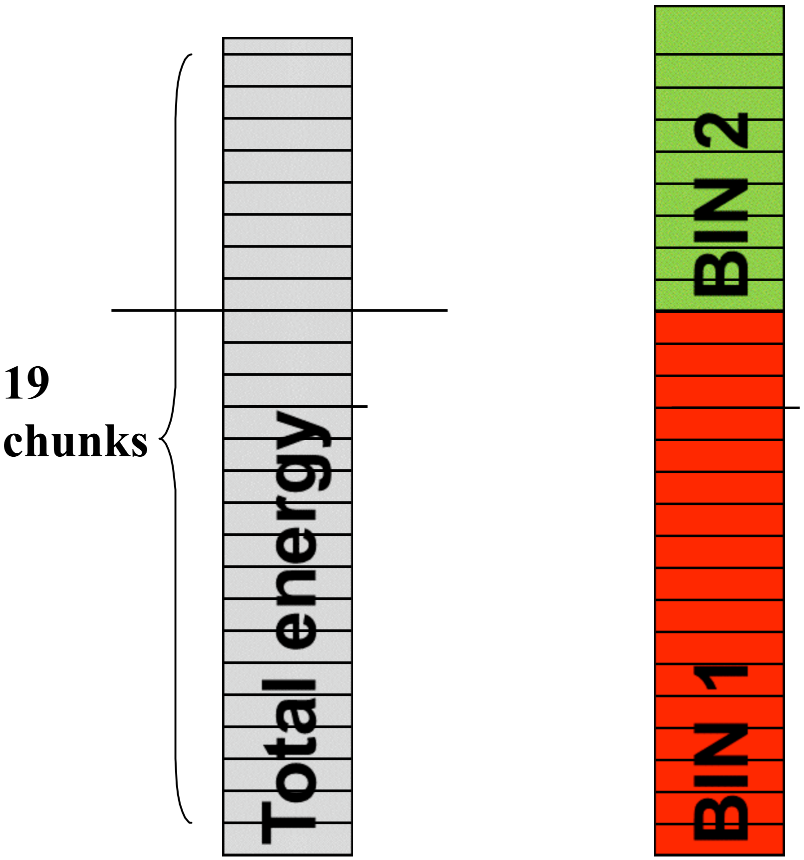
- ***Internal energy resides in "bins"*** , KE or PE associated with degrees of freedom.
- ***Thermodynamic equilibrium is dynamic*** – Energy moves from bin to bin, changes keep happening in each bin, but total energy remains unchanged.
- ***Key Assumption*** - All sharing arrangements among bins are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

Now lets calculate!

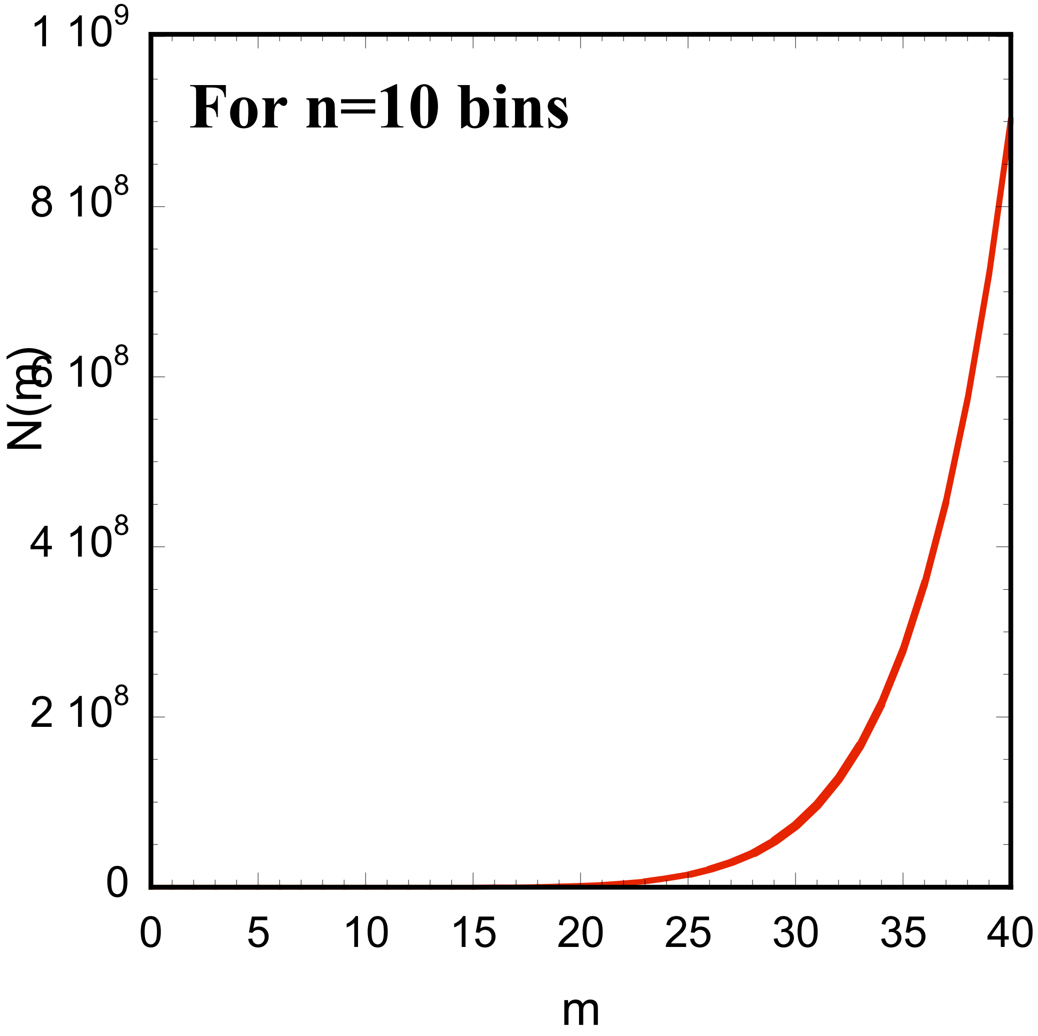
Two energy “bins” divide up 19 *chunks* of energy randomly



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

Q: How many ways can this be done?

How many different ways can *m* chunks of energy be shared by *n*=10 bins



$$N(m,n) \quad \frac{m^{n-1}}{(n-1)!}$$

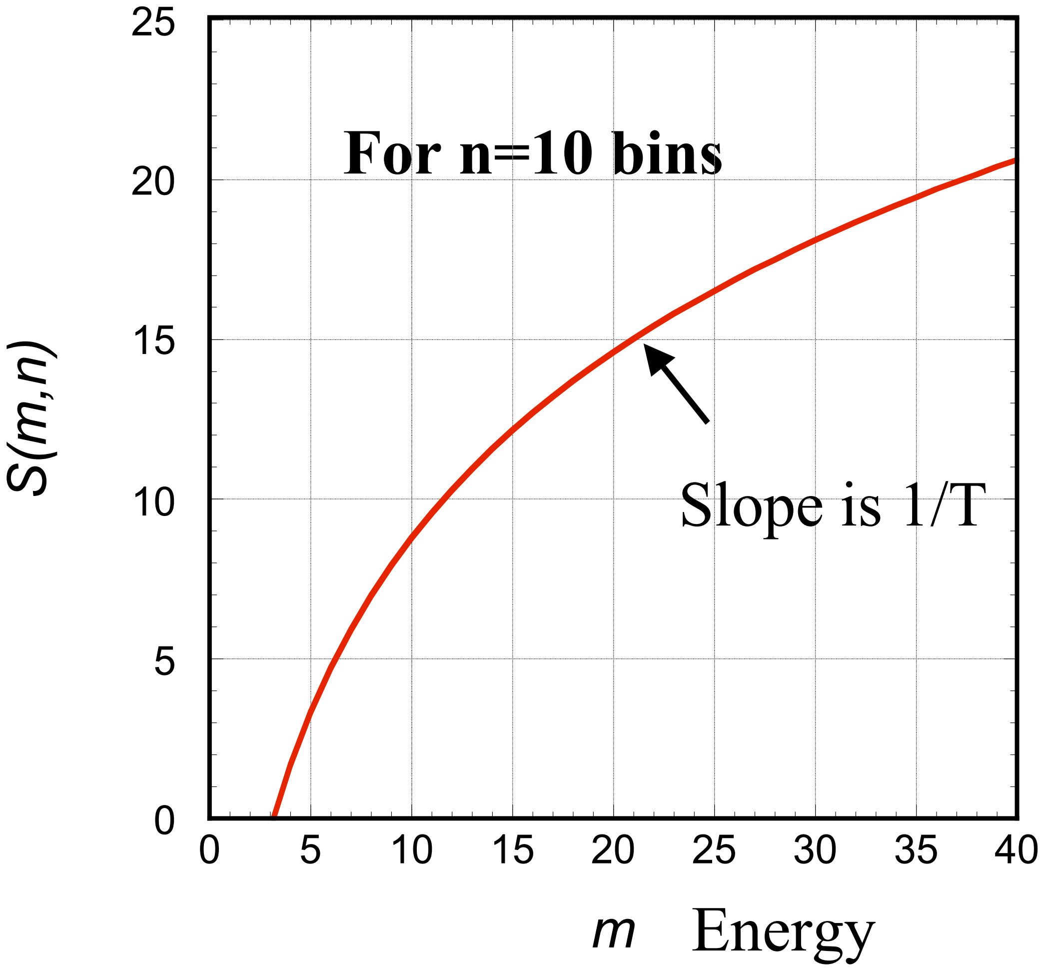
There are many ways!

Increases fast with *m.*

Maybe we should plot it differently?

Suggestions?

$$S(m,n) = \ln N(m,n) \qquad \frac{1}{kT} = \frac{dS(U)}{dU}$$



Remember:

m **represents total internal energy**

n **represents number of bins**

N represents number of arrangements.

Add 11th Bin and Assume 40 shared packets

How many ways can the 11th bin have *m* packets?

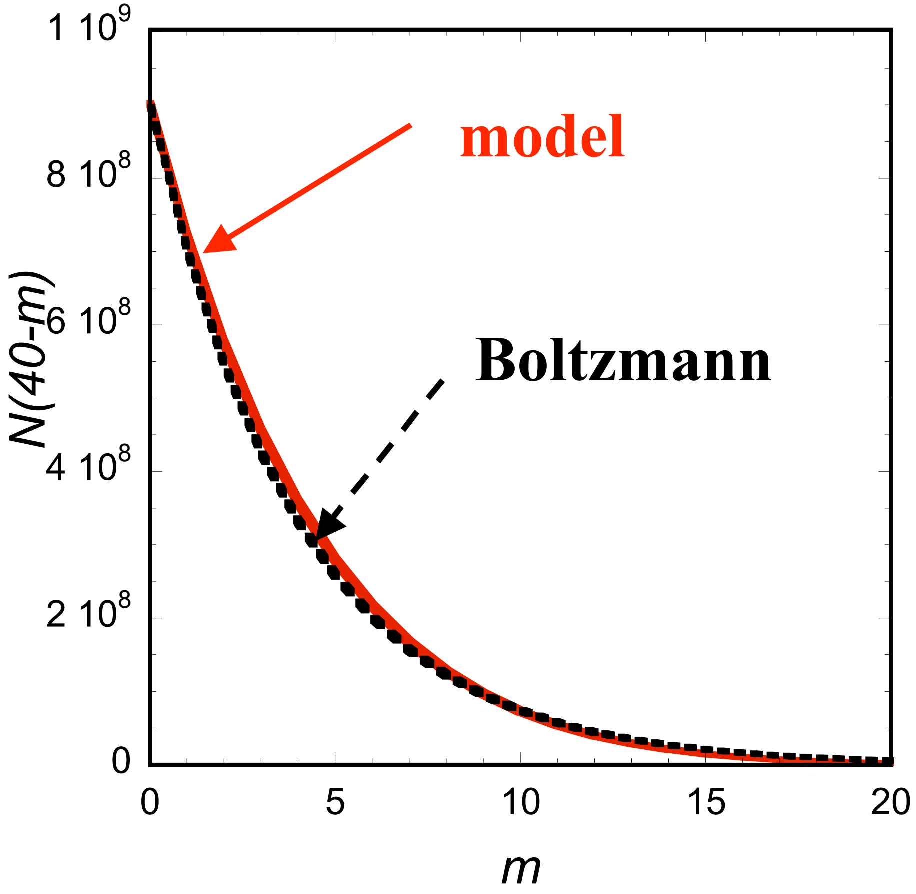
$$N(40-m) \quad \frac{(40-m)^9}{(9)!}$$

can show

$$N(40-m) \quad N(40)\exp(-\frac{m}{T})$$

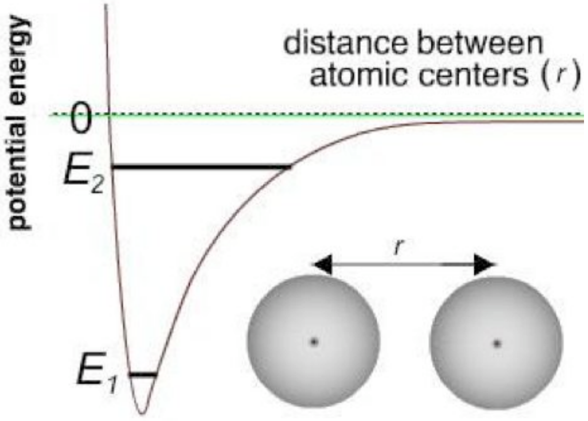
where

$$\frac{1}{T} = \left.\frac{dS(m)}{dm}\right|_{m=40} \qquad \Delta U = T\Delta S$$



This is the definition of temperature !

Sample Problem



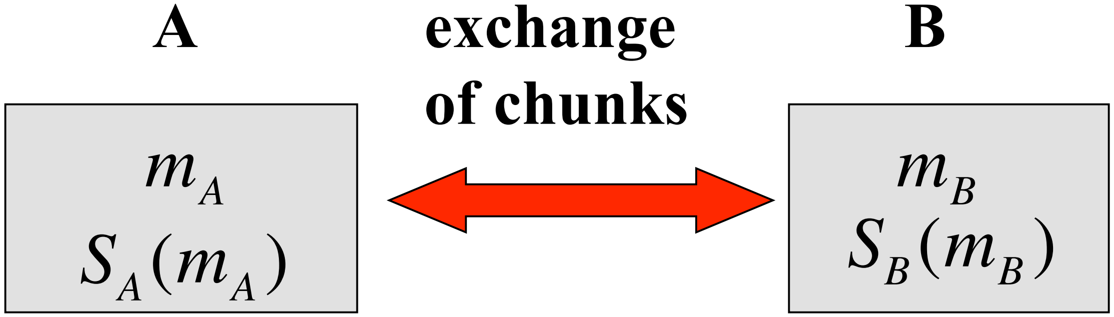
3. (4 pts) A gas of molecules at room temperature interacts with the potential shown at the right. Each molecule can be in the state E_1 or E_2. If the gas is at room temperature and E_2 - E_1 = 50 meV (milli-eV), then at equilibrium, the number of molecules found in the state E_2 divided by the number of molecules found in the state E_1 will be (2pts)

1. About 1
2. About 1/10
3. About 10
4. Much, much larger than 1
5. Much, much smaller than 1

6. Cannot be determined from the information given

(Note: The following numbers might be of use: At STP $k_B T$ = 1/40 eV/molecule; RT = 2.4 kJ/mole)

Condition for Maximum Entropy



A

m_A

$S_A(m_A)$

exchange of chunks

B

m_B

$S_B(m_B)$

no longer identical systems

$$m_A + m_B = m$$

$$S_T = S_A(m_A) + S_B(m_B = m - m_A)$$

Total entropy maximum when $\dfrac{dS_T}{dm_A} = 0$

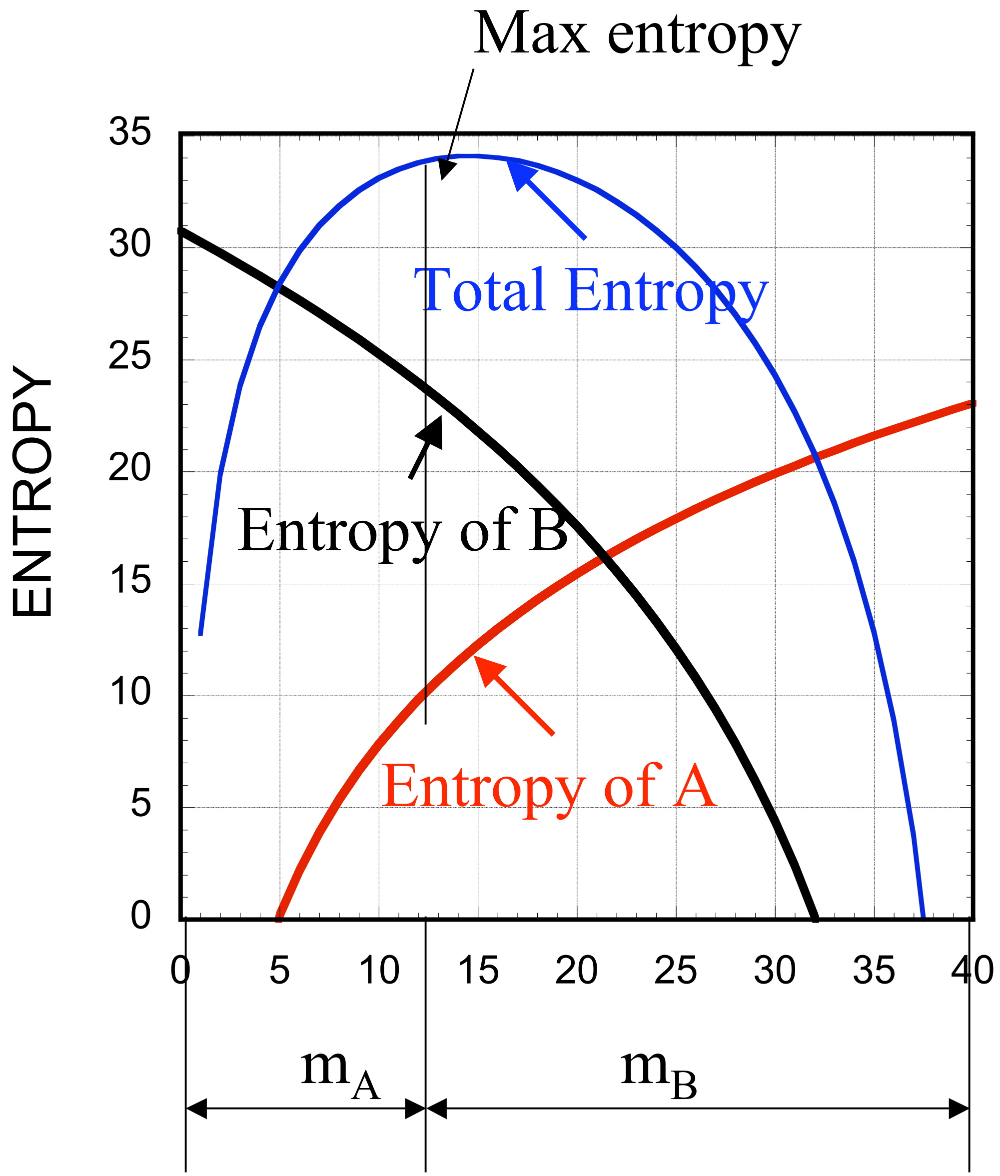
Temperatures equal $T_A = T_B$

Two systems share 40 chunks of energy

System A
12 bins

System B
20 bins

Who will wind up with more chunks of energy?



Foothold ideas: Entropy

- Entropy – an extensive measure of how well energy is spread in a system.
- Entropy measures
  - The number of microstates in a given macrostate

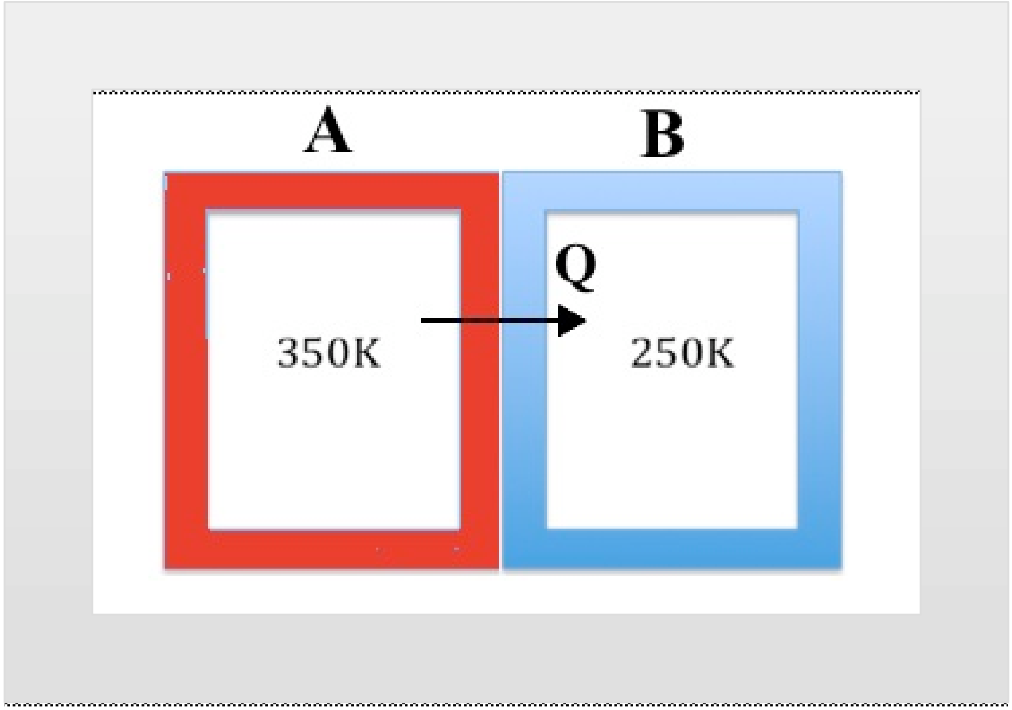
$$S = k_B \ln(W)$$

  - The amount that the energy of a system is spread among the various degrees of freedom
- Change in entropy upon heat flow

$$\Delta S = \frac{Q}{T}$$

A small amount of heat Q flows out of a hot system A (350K) into a cold system B (250K). Which of the following correctly describes the entropy changes that result? (The systems are thermally isolated from the rest of the universe.)

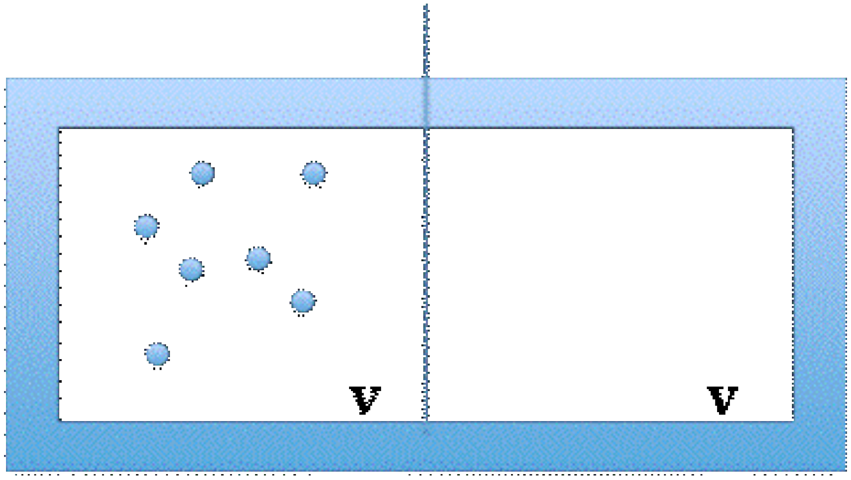
1. $|\Delta S_A| > |\Delta S_B|$
2. $|\Delta S_B| > |\Delta S_A|$
3. $|\Delta S_A| = |\Delta S_B|$
4. It cannot be determined from the information given

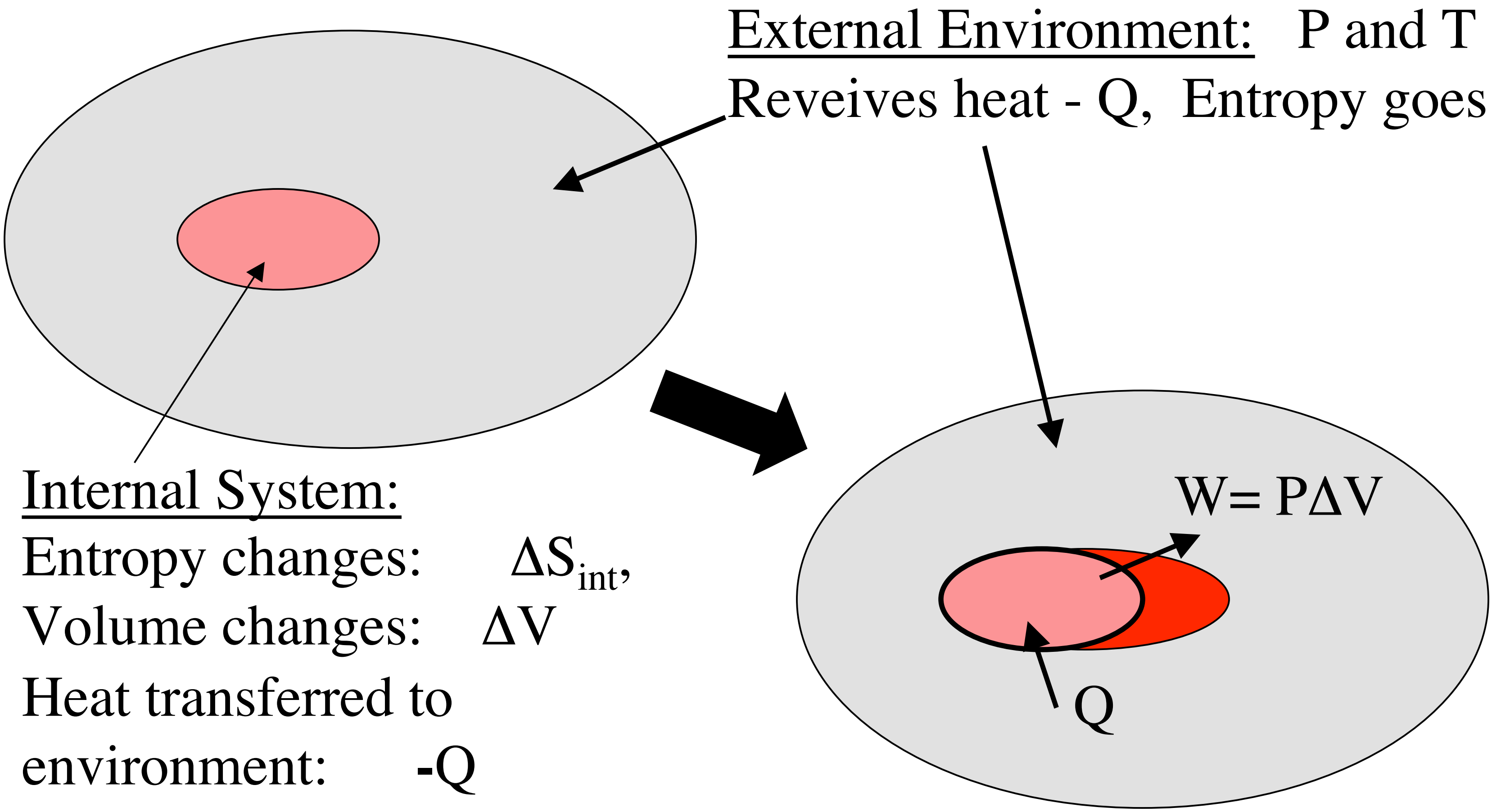


Suppose an isolated box of volume 2V is divided into two equal compartments. An ideal gas occupies half of the container and the other half is empty.

When the partition separating the two halves of the box is removed and the system reaches equilibrium again, how does the new **internal energy** of the gas compare to the internal energy of the original system?

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





External Environment: P and T fixed.
Reveives heat - Q, Entropy goes up

Internal System:
Entropy changes: ΔS_{int},
Volume changes: ΔV
Heat transferred to
environment: -Q

Change can happen if $T(\Delta S_{int} + \Delta S_{ext}) \geq 0$
But, $T\,\Delta S_{ext} = -Q = -\Delta H$

$T\Delta S_{int} - \Delta H \geq 0$ or $\Delta G = \Delta(H-TS) \leq 0$