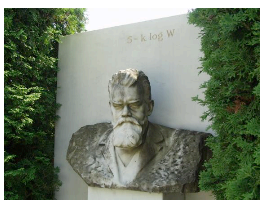
Entropy and The Second Law of Thermodynamics

Entropy (S)

- Entropy is often related to "disorder" – but not strictly correct
- Entropy is a measure of the number of possible arrangements for a given state
- The more possible arrangements – the higher the **probability** of that state.
- S= k log W (where W = number of arrangements)
- Units J/K



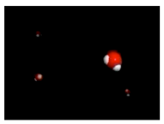
The Second Law of Thermodynamics

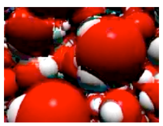
- **For any change the *total* entropy of the Universe must increase.**
- (you cant get as much energy back when a change occurs as you put in – some is always lost – spread out as thermal energy – unusable)
- $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$

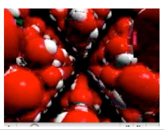
Question

- If entropy must always increase – does that mean there was a time when the entropy was zero?
- Sometimes entropy changes are called the "arrow of time" can you think why?

Which has more distinguishable arrangements?







Which has more entropy

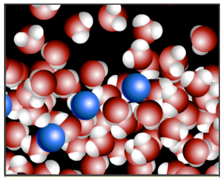
- A deck of cards in order or a shuffled deck?
- Separated dye and water or mixed dye and water?
- $CaCO_3$(s) or CaO(s) + CO_2(g)
- $H_2O_{(l)}$ (at 25 °C) or $H_2O_{(l)}$ (at 50 °C)

Web activities on entropy

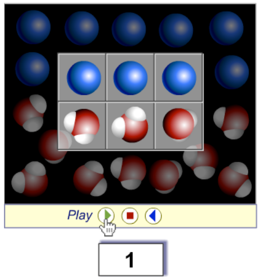
(Do 8.3 and 8.5)

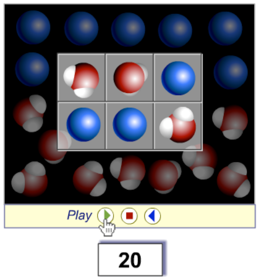
Mixing

- Why does the dye mix
- Will it unmix?
- Why not?
- When the dye mixes there are more arrangements than unmixed



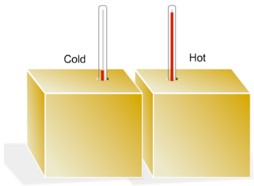
There are more distinguishable arrangements when dye molecules mix. (positional entropy)





Entropy tells which way energy

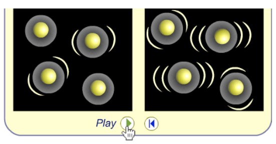
- Energy is quantized
- Energy quanta will transfer to the most probable state (the one with the most arrangements)



initial

two pieces of copper metal at different temperatures, what determines the direction of energy transfer?

As a model of two copper pieces at different temperatures, imagine two identical four-atom solids, one having two quanta of energy, and the other having six. Since temperature is a measure of the energy content of a substance, the four-atom solid with six energy quanta has a higher temperature than the four-atom solid with two energy quanta.



Representation of two pieces, with exaggerated relative movement of the copper atoms, at different temperatures.

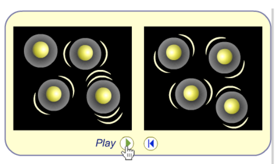
The total number of arrangements in a system, W_{tot}, is the product of the number of arrangements possible in each component of the system. In this case, there are two objects, so

$$W_{tot} = W_{(2\ quanta)} \times W_{(6\ quanta)}$$
$$= 10 \times 84$$

final

When two quanta are transferred from the warm to the cool object, there is an increase in the number of ways that energy quanta can be distributed between the two objects.

There are more ways to arrange the energy quanta when both solids have four quanta compared to when one solid has two and the other has six.



Atoms vibrating in this representation of one of the 1225 possible arrangements of quanta for the two pieces at the same temperature.

When both metals have four quanta,

$$W_{tot} = W_{(4\ quanta)} \times W_{(4\ quanta)}$$
$$= 35 \times 35$$
$$= 1225$$

The transfer of energy from hot to cold

Can you think of examples where the

Entropy of system increases

- Ice melting
- Water boiling
- Dye mixing with liquid

Entropy of system decreases

- Water freezing
- Water condensing
- Oil and water don't mix (even if you shake them up – they unmix)

How can this be? - we just said the Second Law is a Law (no exceptions!)

Hint: the Second Law refers to the

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

We have to take the surroundings into

- What effect does a more ordered system have on the surroundings?
- Why don't living systems violate the second law?

Phase changes and entropy

What is the correct value of $\Delta S_{l \to s}$?

$S_{gas} > S_{liquid} > S_{solid}$

therefore

- ☐ $\Delta S_{l \to s} < 0$
- ☐ $\Delta S_{l \to s} = 0$
- ☐ $\Delta S_{l \to s} > 0$

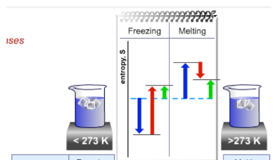
If liquids have a higher entropy why is

Hint: it is temperature dependent AND we have to consider the surroundings

Phase changes and entropy

- What is the sign of system entropy change when water melts
- What is the sign of system entropy change when water freezes
- How can a change where the entropy change is negative occur?
- (don't forget the surroundings)

Do phase change activity 8.7



	Freezing		Melting
ΔS_{sys}	< 0	is equal to	> 0
ΔH_{sys}	< 0	is equal to	> 0
ΔH_{surr}	> 0	is equal to	< 0
ΔS_{surr}	> 0	is less than	< 0
ΔS_{net}	> 0	not necessarily equal to	> 0

Freezing water

- Exothermic – increases the entropy of the surroundings!
- Do phase change activity 8.7
- Remember – Second law – **total** entropy change is important
- ΔStotal = ΔSsystem + ΔSsurroundings

Phase changes are always accompanied

ΔH of phase change

- $\Delta H_{freezing} = -\Delta H_{melting}$
- Same for condensation and boiling
- You can predict relative magnitudes of heats for phase change from molecular structures.
- Eg which would have a higher ΔH_{vap}?
- CH_3OH or CH_3CH_3?
- Why?