N6 - THERMODYNAMICS

More About Entropy

Link to YouTube Presentation: https://youtu.be/I9S9UZAO5kA

N6 - THERMODYNAMICS

More About Entropy

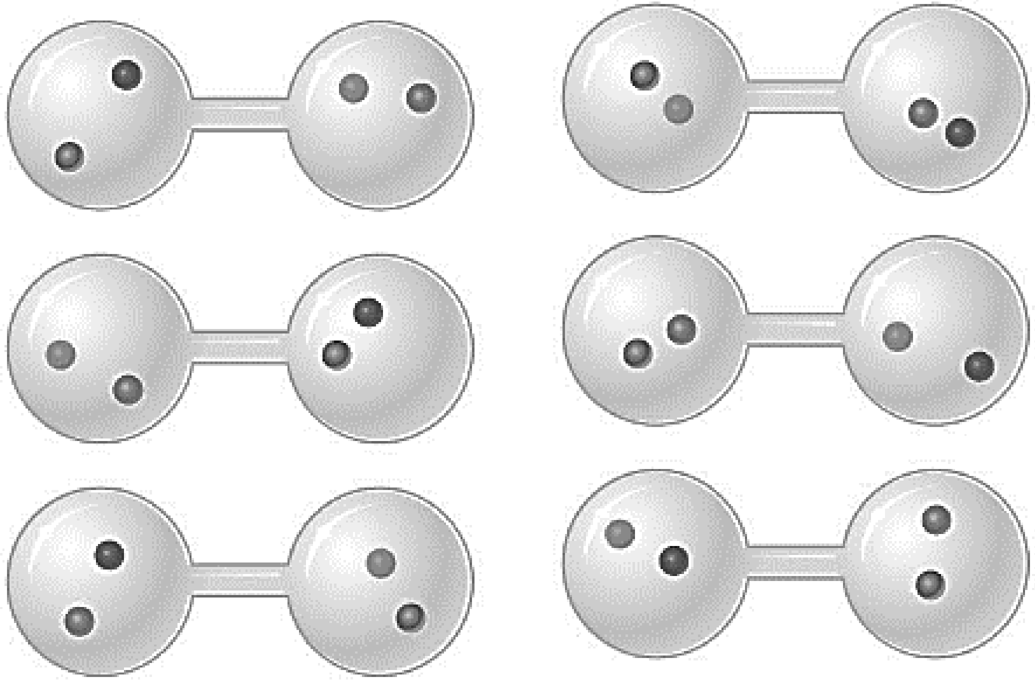
Target: I can describe entropy and ways that a reaction may have an increase (or decrease) in entropy.

Key Concepts about Entropy

#1 - a thermodynamic function that increases as the number of energetically equivalent ways of arranging the components **(microstates)** increases, S.

- Units are usually **J/K** or **J/mol•K**

Macrostate State vs Microstate



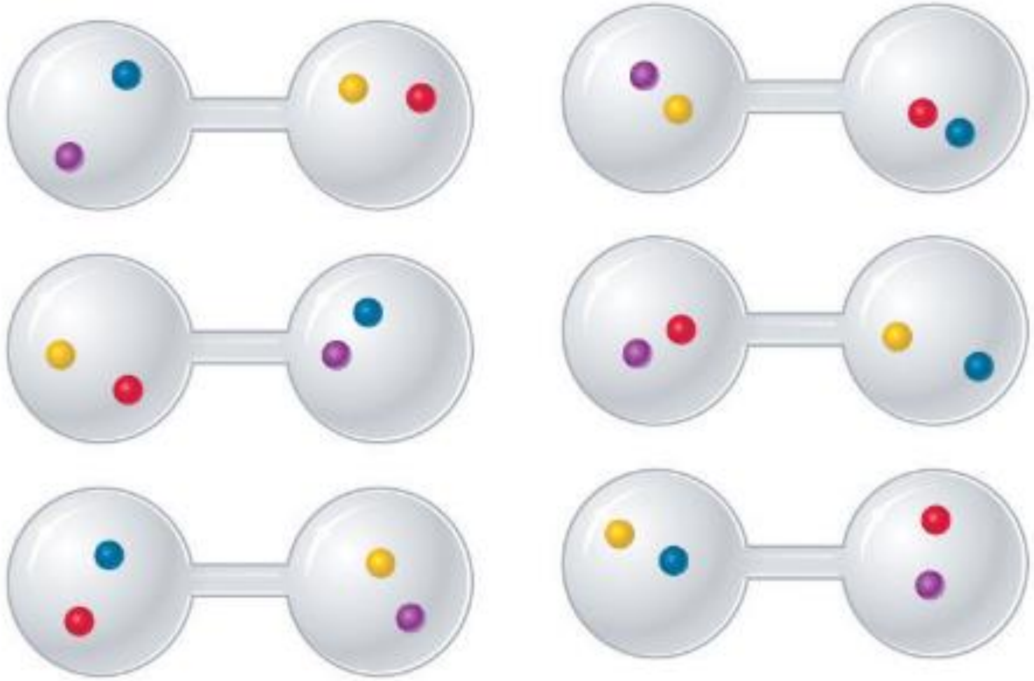
- Right now each of these systems should look the same.
- We don’t have a way to differentiate between particles.
- We end up looking at only the “Macrostate” – each side of each container has two particles in it.

Macrostate State vs Microstate

- These microstates all have the same macrostate.

- There are six different particle arrangements that result in the same macrostate.

- The individual unique particles make up the microstate, the overall “big picture” is the macrostate



Review of Concepts about Entropy

#2 – “Random” systems have more energy dispersal and are more energetically stable, lower energy, than ordered systems. Therefore, entropy change is **favorable** when the result is more energy dispersal, when there are more microstate arrangements.

- **When ΔS is positive.**

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

Review of Concepts about Entropy

#3 – Increase in entropy of the universe is the driving force for reactions.

Review of Concepts about Entropy

#4 – Nature proceeds toward the states that have the highest probabilities of existing. More microstates, more energy dispersal means more ways for the arrangement to be achieved, more likely to happen.

PARENTS: "YOUR ROOM IS MESSY!"

Standard Entropy Change, ΔS°

Standard entropy change - the difference in absolute entropy between the reactants and products under standard conditions.

$$\Delta S^{o}_{\text{reaction}} = \sum n S^{o}_{\text{products}} - \sum n S^{o}_{\text{reactants}}$$

Standard Entropy Change, $\Delta S°$

IMPORTANT

Standard enthalpy of formation, $\Delta H_f°$, of an element is 0 kJ/mol,
BUT the standard entropy, *S*°,
is **(almost) ALWAYS** positive, **NOT** zero!

The standard entropy of some **IONS** can be negative due to the inability to separate them and measure them independently. So $H^+(aq)$ is designated as a reference point of 0, so some ions might end up with a negative S°.

For the Rx: **$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$** $\Delta S^\circ_{rxn} = -146.5$ J/mol•K

Calculate the standard molar entropy of $O_2(g)$.

$S^\circ_{NO(g)} = 210.8$ J/mol•K , $S^\circ_{NO2(g)} = 240.1$ J/mol•K

A -175.8 J $mol^{-1}K^{-1}$

B 269.4 J $mol^{-1}K^{-1}$

C -205.1 J mol^{-1} K^{-1}

D 205.1 J mol^{-1} K^{-1}

E None of the above

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Calculate the standard molar entropy of $O_2(g)$.

$S°_{NO(g)}$ = 210.8 J/mol•K , $S°_{NO2(g)}$ = 240.1 J/mol•K

$$\Delta S_{rxn} = \Sigma\, \Delta n S_{Products} - \Sigma\, \Delta n S_{reactants}$$

$(-146.5) = [\ 2(240.1)\ ] - [\ 2(210.8) + S°_{O2}\ ]$

$S°_{O2} = 205.1\ Jmol^{-1}K^{-1}$

- A -175.8 $J\ mol^{-1}K^{-1}$
- B 269.4 $J\ mol^{-1}K^{-1}$
- C -205.1 $J\ mol^{-1}\ K^{-1}$
- D **205.1 $J\ mol^{-1}\ K^{-1}$**
- E None of the above

Some Changes that Increase Entropy

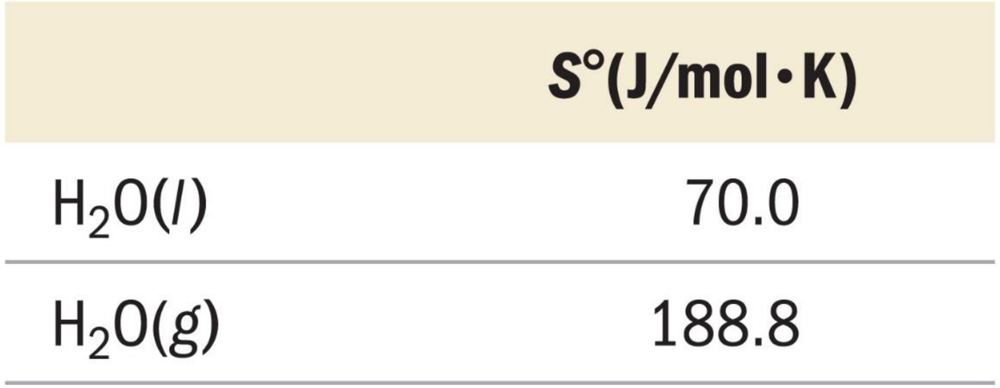
Some Changes that Increase Entropy

#1 - Products are in a more dispersed arrangement.

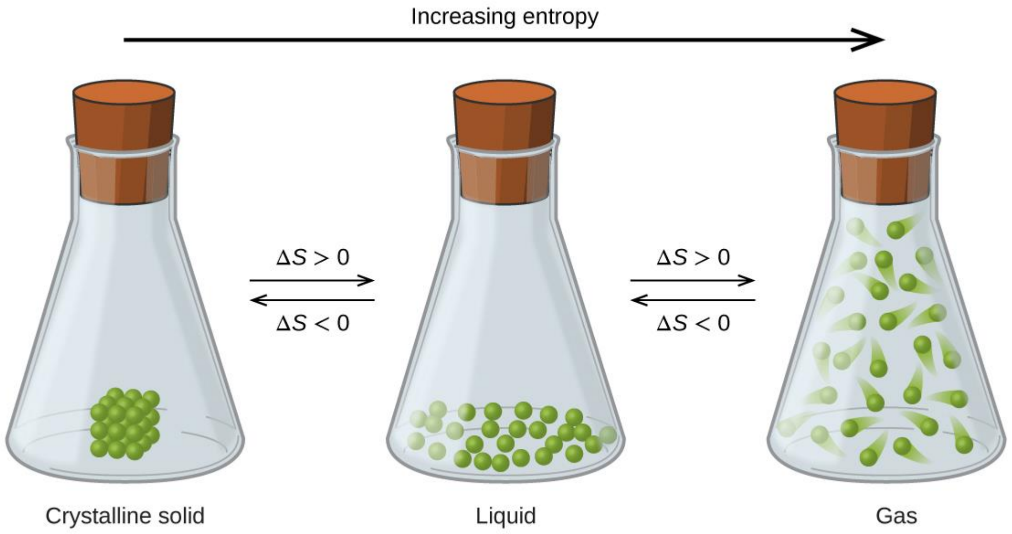
Example

State of Matter

- Solid < Liquid < Gas
- More arrangements possible



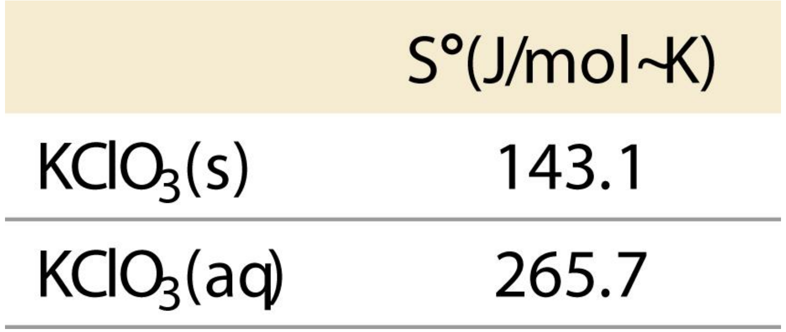
	$S°$(J/mol·K)
$H_2O(l)$	70.0
$H_2O(g)$	188.8



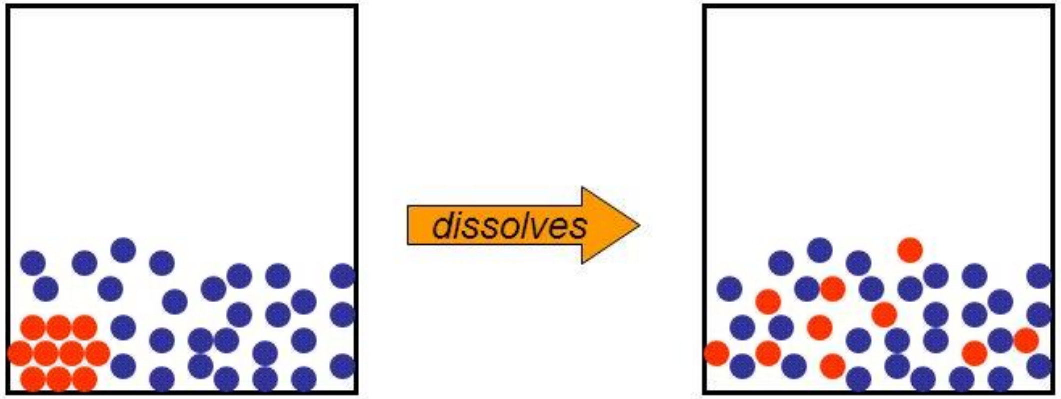
Example

Dissolution (s) → (aq)

- Dissolved solids usually have larger entropy, distributing particles throughout the mixture.



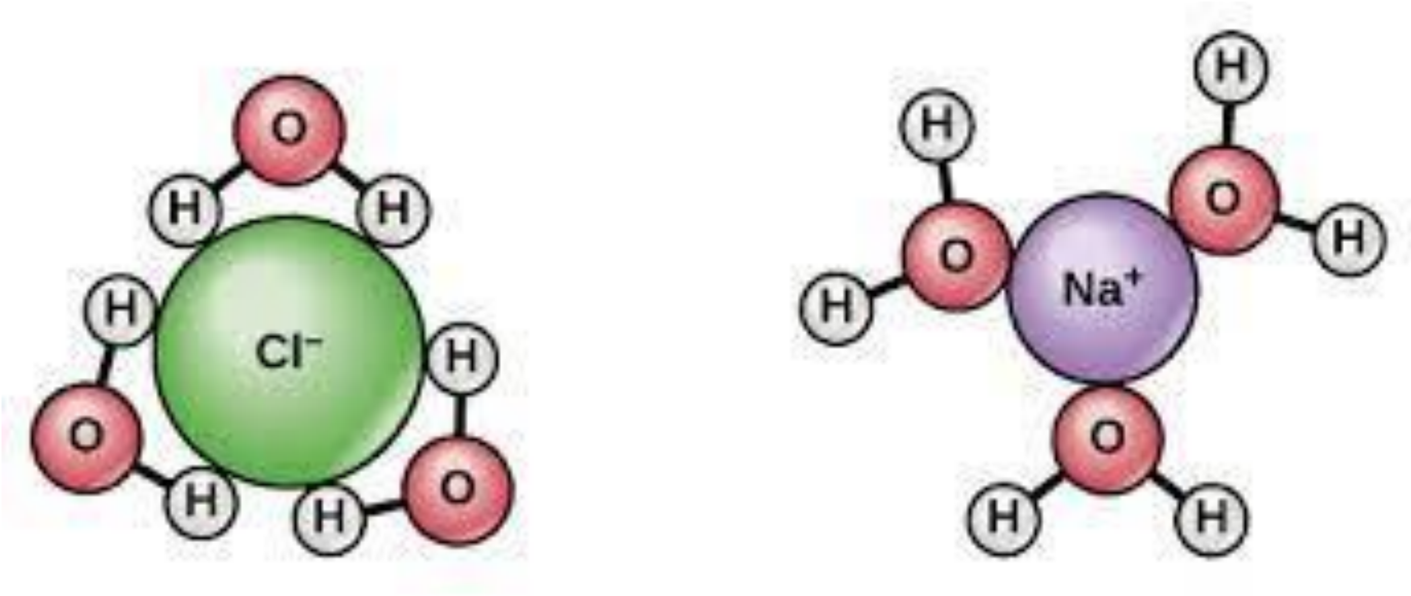
	S°(J/mol~K)
$KClO_3$(s)	143.1
$KClO_3$(aq)	265.7



Example

Aqueous solutions

- Sometimes it is trickier!
- “Sphere of hydration” can add order...DECREASE in entropy!



Some Changes that Increase Entropy

#2 - Larger numbers of product molecules than reactant molecules

$AB_2 \rightarrow A + 2B$

Some Changes that Increase Entropy

#3 - Rxn’s that have an increase in temperature (exothermic)

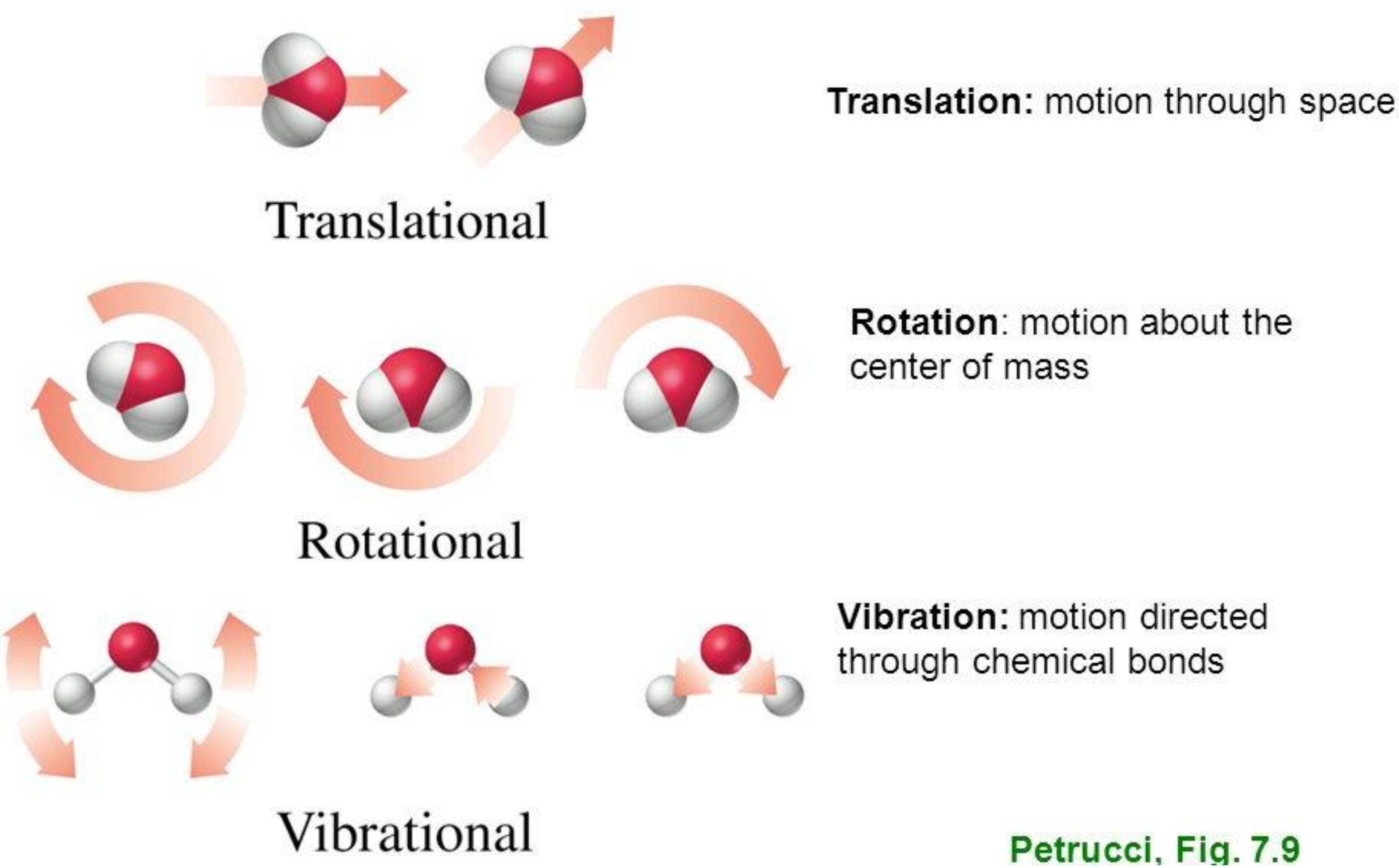
Some Changes that Increase Entropy

#4 – Products that have more degrees of movement

Example

Degree of Movement

- Lots of types of movement



Translation: motion through space

Rotation: motion about the center of mass

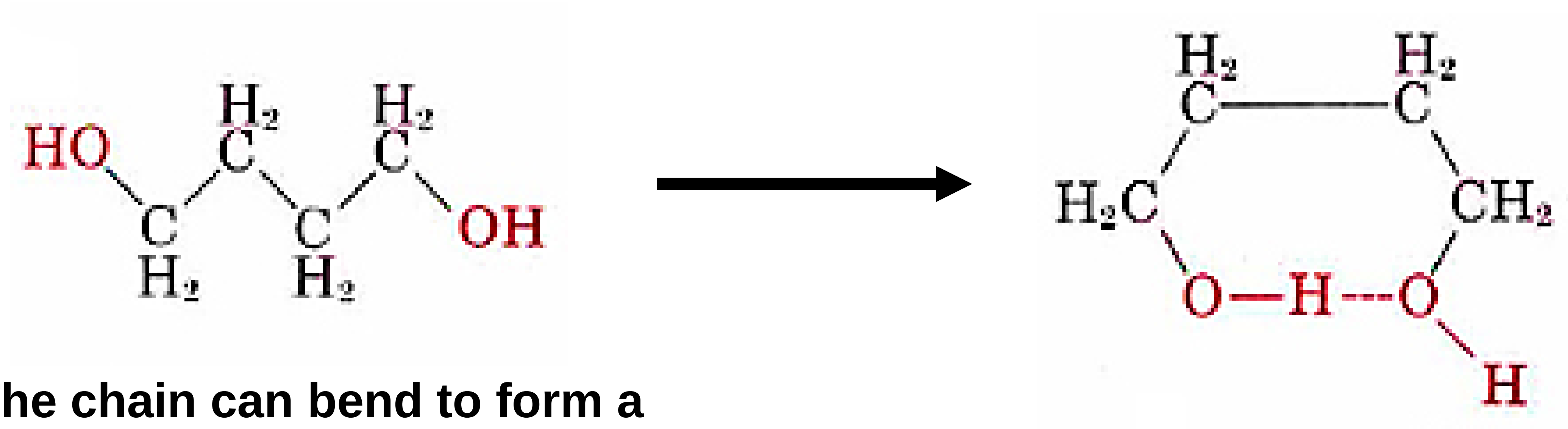
Vibration: motion directed through chemical bonds

Petrucci, Fig. 7.9

Example

Degree of Movement

- More degrees of movement results in more entropy.



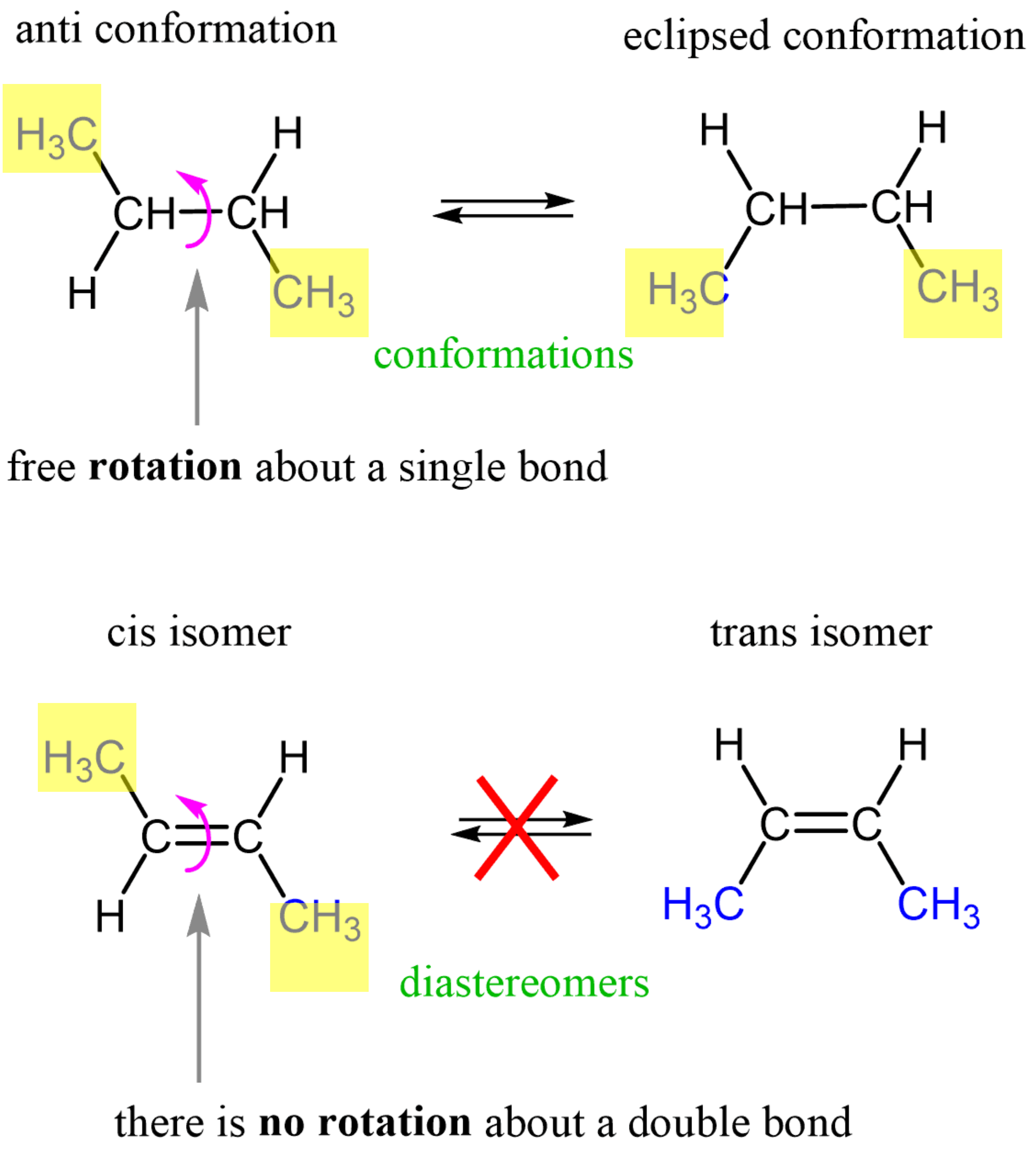
The chain can bend to form a hydrogen bond with itself

Now it has LESS entropy!

Example

Degree of Movement

- Single bonds rotate more than double/triple bonds can.



Some Changes that Increase Entropy

#5 – Products that have more molecular complexity

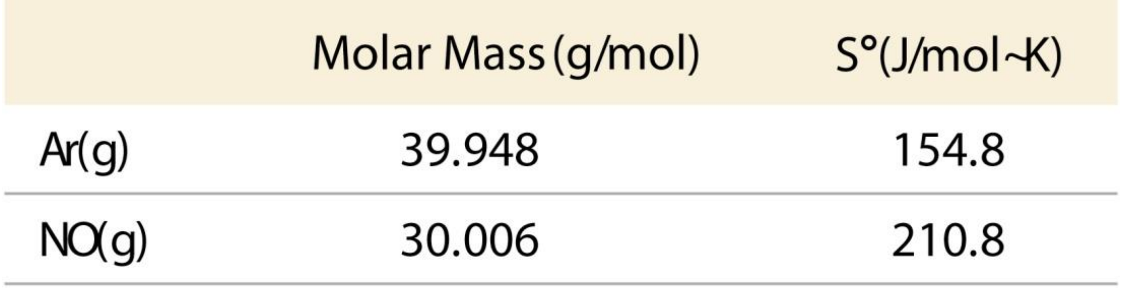
Changes in Entropy - Examples

Molecular Complexity

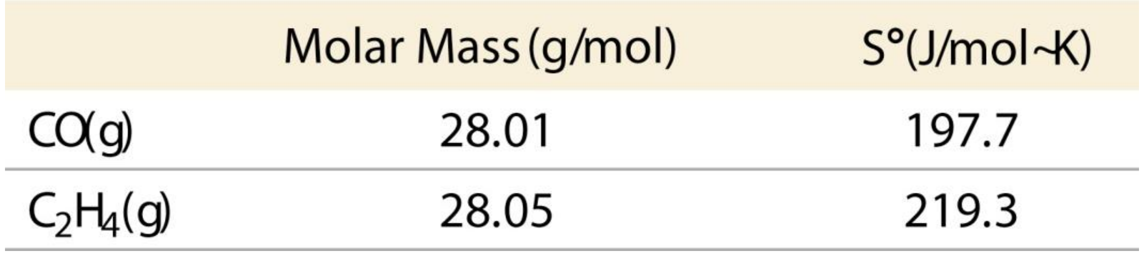
- Larger, more complex molecules generally have larger entropy.

Larger/Complex doesn't always mean molar mass!

- More energy levels/states are available, allowing more dispersal of energy through the states.



	Molar Mass (g/mol)	S°(J/mol~K)
Ar(g)	39.948	154.8
NO(g)	30.006	210.8

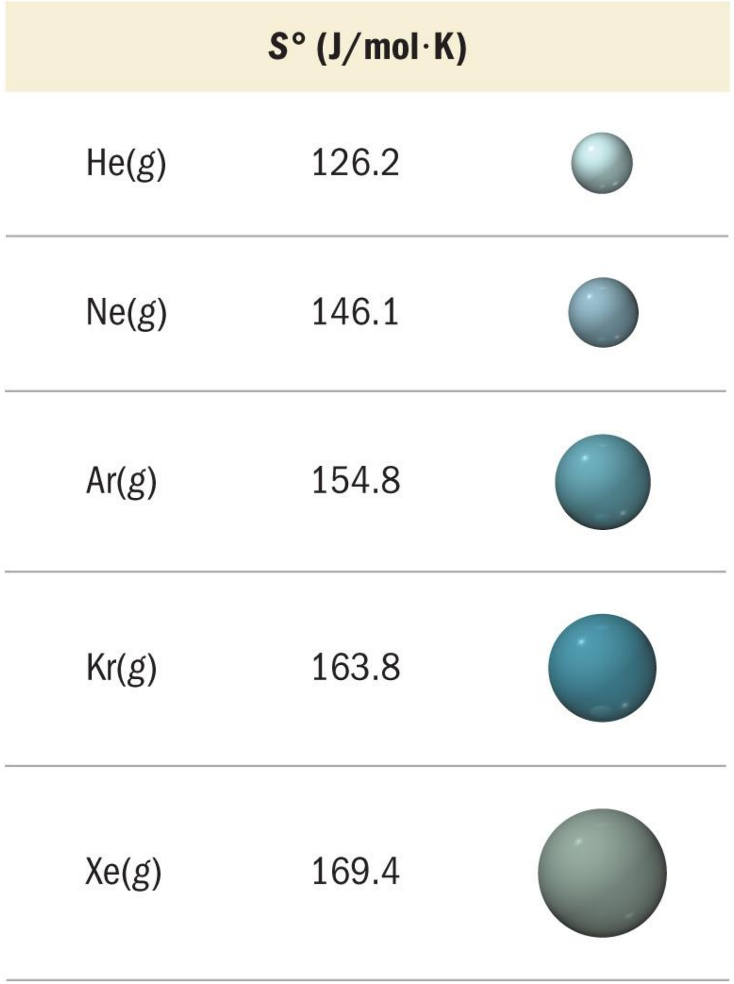


	Molar Mass (g/mol)	S°(J/mol~K)
CO(g)	28.01	197.7
C_2H_4(g)	28.05	219.3

Changes in Entropy - Examples

Molar Mass

- Commonly looks like the larger the molar mass, the larger the entropy...but the mass isn't the *direct* reason
- Seems a little counter intuitive…larger things can't have as many places to be arranged in the same among of space, right?

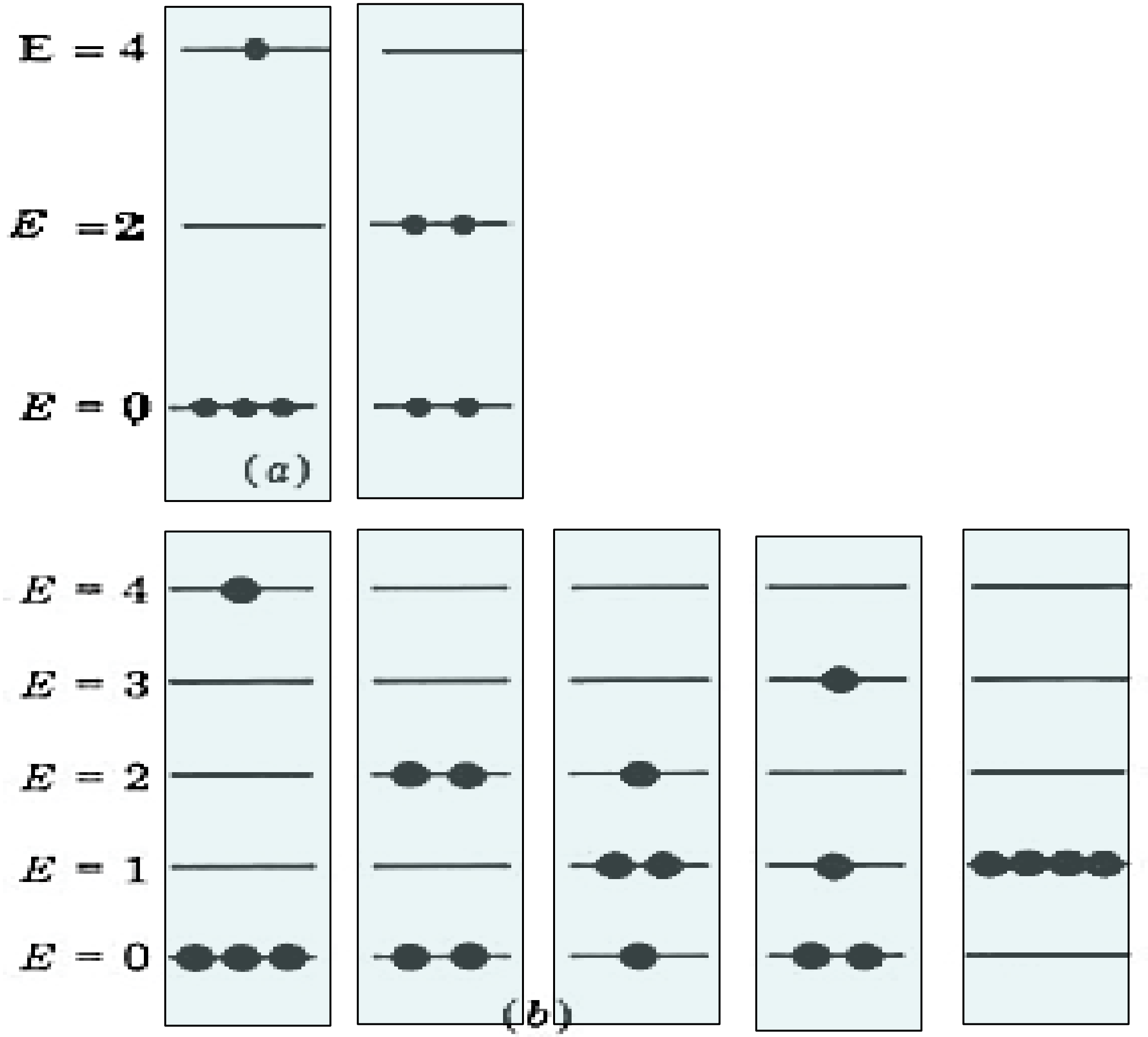


	S° (J/mol·K)	
He(g)	126.2	
Ne(g)	146.1	
Ar(g)	154.8	
Kr(g)	163.8	
Xe(g)	169.4	

Changes in Entropy - Examples

Molar Mass

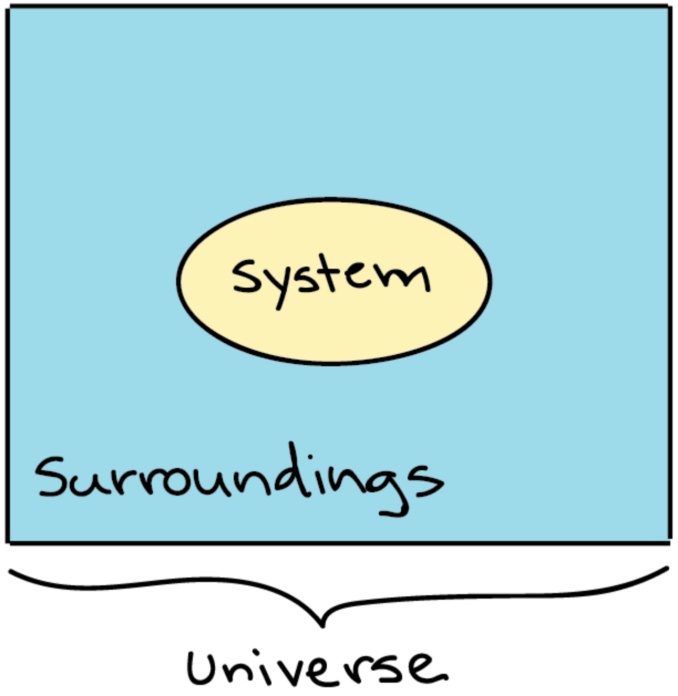
- It's because the mass affects the energy levels!
- The larger the molar mass, the closer the energy levels/states.
- The closer the energy states the more ways the energy can be dispersed through them.



A little bit about the “Entropy of the Universe”

2^{nd} Law of Thermodynamics

The total entropy change of the universe must be **positive** for a process to be spontaneous



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

Reversible process $\Delta S_{univ} = 0$
Irreversible spontaneous process $\Delta S_{univ} > 0$

Yes, you can still have negative ΔS_{system}

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

If the entropy of the system ↓

Then the entropy of the surroundings must ↑ by a ***larger*** amount.

Do not need to write this down!

2nd Law of Thermodynamics

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

When ΔS_{system} is negative,

$\Delta S_{surroundings}$ must be positive
AND bigger for a spontaneous process.

Do not need to write this down!

2nd Law of Thermodynamics

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

When $\Delta S_{surroundings}$ is negative,

ΔS_{system} must be positive
AND bigger for a spontaneous process.

Do not need to write this down!

Relating Entropy to Heat Energy

The entropy change in the surroundings is proportional to the amount of heat gained or lost.

$$q_{\text{surroundings}} = -q_{\text{system}}$$

(Equal but opposite sign)

(Sometimes it is easier to measure surroundings than the system, or vice versa – our lab experiments can exploit this fact sometimes to make our life more convenient – calorimetry!)

Relating Entropy to Heat Energy

The entropy change in the surroundings is also inversely proportional to its temperature.

Meaning the impact of ∆H on entropy is more noticeable at lower temperatures.

$$\Delta S_{surroundings} = \frac{-q_{system}}{T} = \frac{-\Delta H_{system}}{T}$$

**remember* in this class q = ∆H because we are not dealing with changes to P or V*

Can start to be creative with the equations

In my opinion, one of the things that makes topics like Thermodynamics difficult is that there is SO much substitution and rearrangement of equations.

Repetition and exposure helps these come more naturally and quickly. Sometimes a new equation isn't actually new!

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

$$= \Delta S_{system} + \frac{-\Delta H_{system}}{T}$$

YouTube Link to Presentation

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