Thermodynamics

Or, “will it happen?”

Questions to answer…

1. What is thermodynamics all about?
2. What are “spontaneous” reactions?
3. What does enthalpy have to do with predicting spontaneity?
4. What is entropy? What does it have to do with spontaneity?
5. How can I predict whether a reaction will be spontaneous?

Thermodynamics

- Deals with two fundamental ideas
  1. energy (enthalpy, Δ H)
  2. "distribution of microstates" (entropy, S)
- Tells us which reactions should and shouldn't happen by themselves
- Reaction **spontaneity**

Questions to answer…

1. What is thermodynamics all about?

Spontaneous Reactions
"Thermodynamically favored"

- Occur by themselves once the conditions are right

Examples

- phase change at the right T
- gravity effects
- rusting of Fe

- Nonspontaneous changes must be forced

Example

  - electrolysis of H_2O
  - $2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)}$
- some other spontaneous change must occur first
  - electricity will flow when the circuit is completed

Which is the “spontaneous” change?

Can the other be forced? How?

Everything that happens can be traced back to some spontaneous (thermodynamically favored) change….

Questions to answer…

1. What is thermodynamics all about?
2. What are “spontaneous” reactions?

When is a reaction spontaneous?

“thermodynamically favored”

When is a reaction spontaneous?

- When attractions are formed, energy is RELEASED from the system
- Exothermic reactions
- $\text{PE(system)} \Longrightarrow \text{KE (surroundings)}$
- More energy is released when new bonds in products are formed than it took to break the bonds in the reactants

When is a reaction spontaneous?

1. Reactions with a (-)ΔH tend to be spontaneous
   - This is how enthalpy fits in

Questions to answer…

1. What is thermodynamics all about?
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But…

- Spontaneous reactions can be either exothermic or endothermic!
- Therefore, an additional thermodynamic parameter is required to predict if a reaction is or is not spontaneous.
- **ENTROPY**

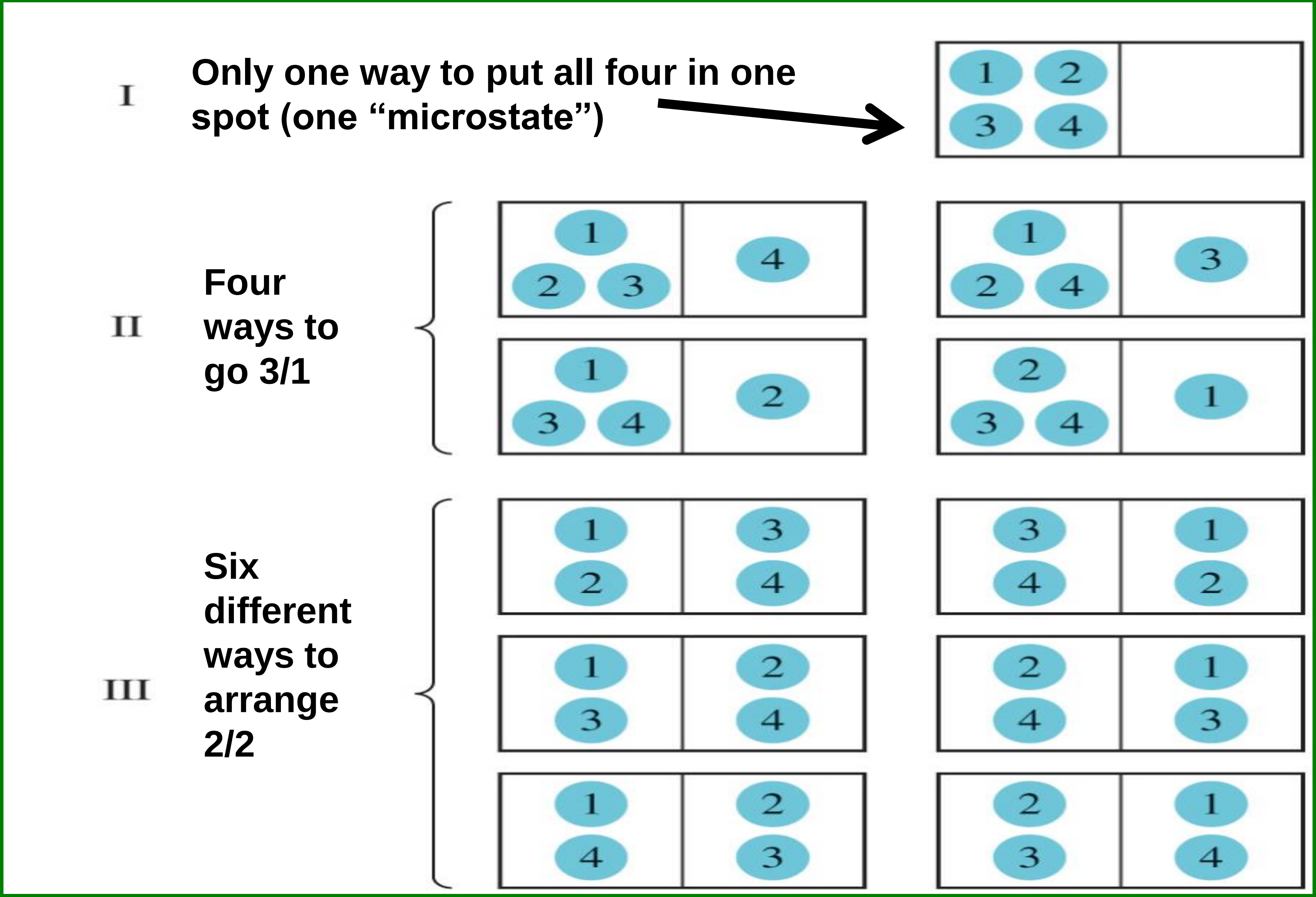
What is “Entropy”?

- Entropy (S) describes the amount of "distribution of microstates" in a system
- The *more centralized* or accumulated in one spot the matter is, the fewer the microstates, the *lower* the entropy
- The *more distributed or spread around*, the *higher* the entropy

What are "distributions of microstates"?

How many different ways can you distribute 4 objects among two containers?

Imagine four objects spread among two locations



Which process or “direction” tends to be the spontaneous change?

- a stone wall crumbles over time, or a loose pile of stones turns into a wall?
- ice melts at room temperature, or water freezes at room temperature?
- **What is the entropy change here? Increasing? Decreasing?**

2. Another principal driving force in a reaction is an **<u>increase in entropy</u>**

The **<u>second law of thermodynamics</u>** states that ***spontaneous processes always proceed in such a way that the entropy of the universe increases***.

The **third law of thermodynamics** states that ***the entropy of a pure crystal at 0 K is zero.***

- This simply means all "real world" substances have a positive S value
  - **S is measured in J/K**
- **S** is never a negative number, but Δ **S** can be!

Any event that is accompanied by an increase in entropy (Δ S is positive) tends to occur spontaneously

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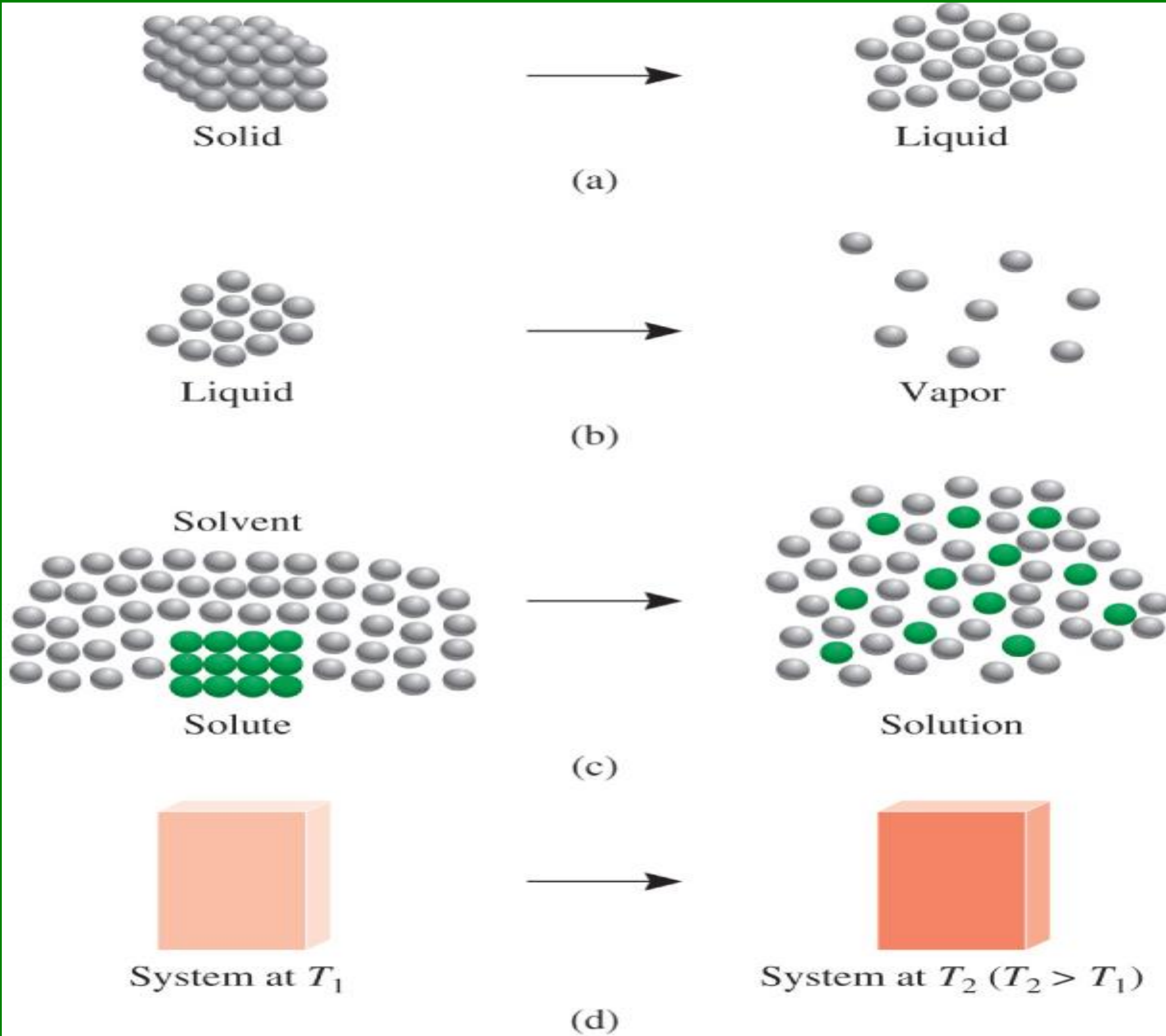
When is Δ S positive?

1. an increase in freedom of movement = an increase in entropy
   - solid to liquid
   - liquid to gas
   - dissolving a solid into a liquid
   - fewer molecules (particles) to more molecules

When is Δ S positive?

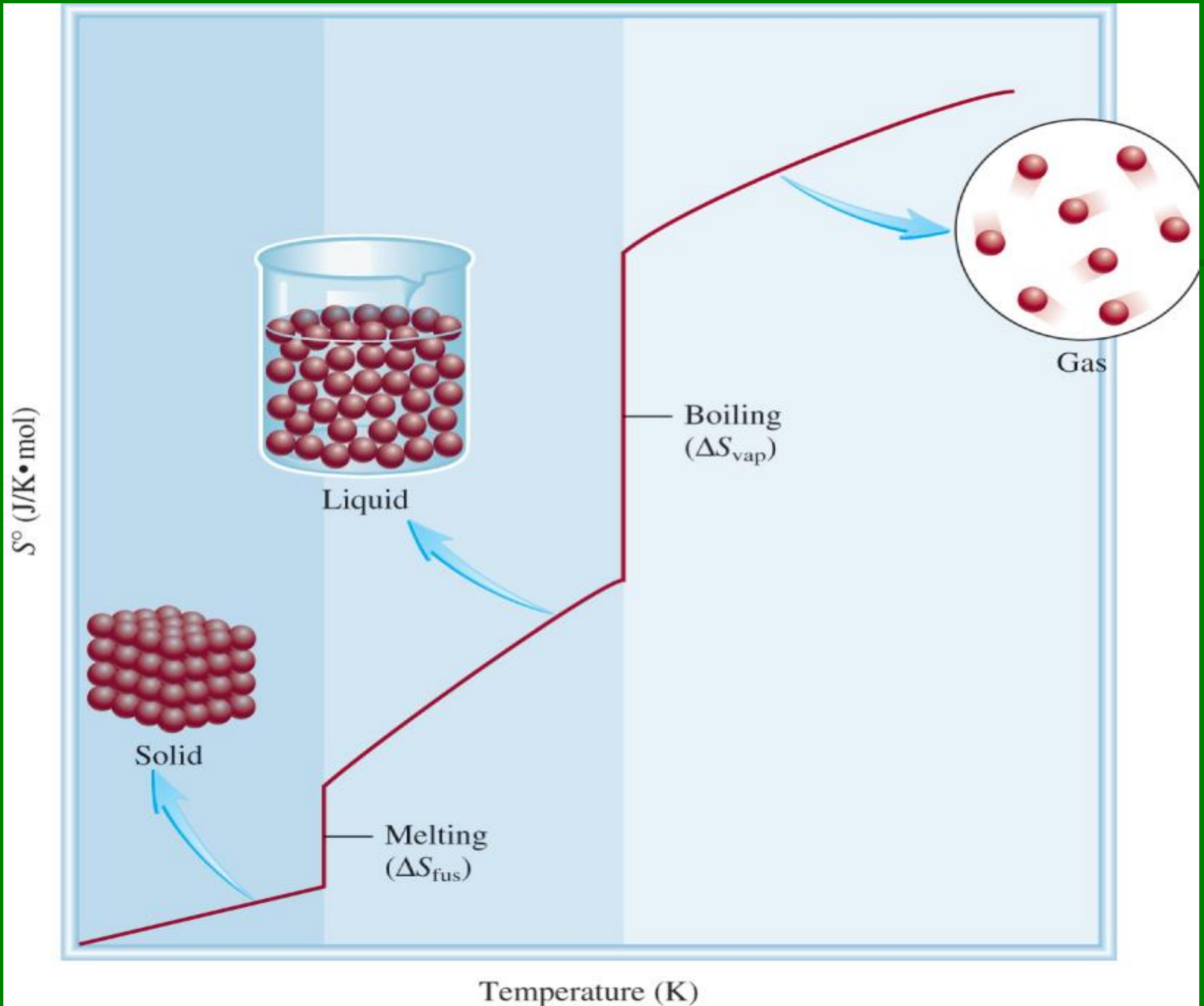
1. an increase in freedom of movement = an increase in entropy
   - solid to liquid
   - liquid to gas
   - dissolving a solid into a liquid
   - fewer molecules (particles) to more molecules
2. An increase in temperature means an increase in Entropy



Solid
Liquid
(a)
Liquid
Vapor
(b)
Solvent
Solute
Solution
(c)
System at T_1
System at T_2 ($T_2 > T_1$)
(d)

What would a graph look like if we plot temperature on the x axis and entropy on the y axis?

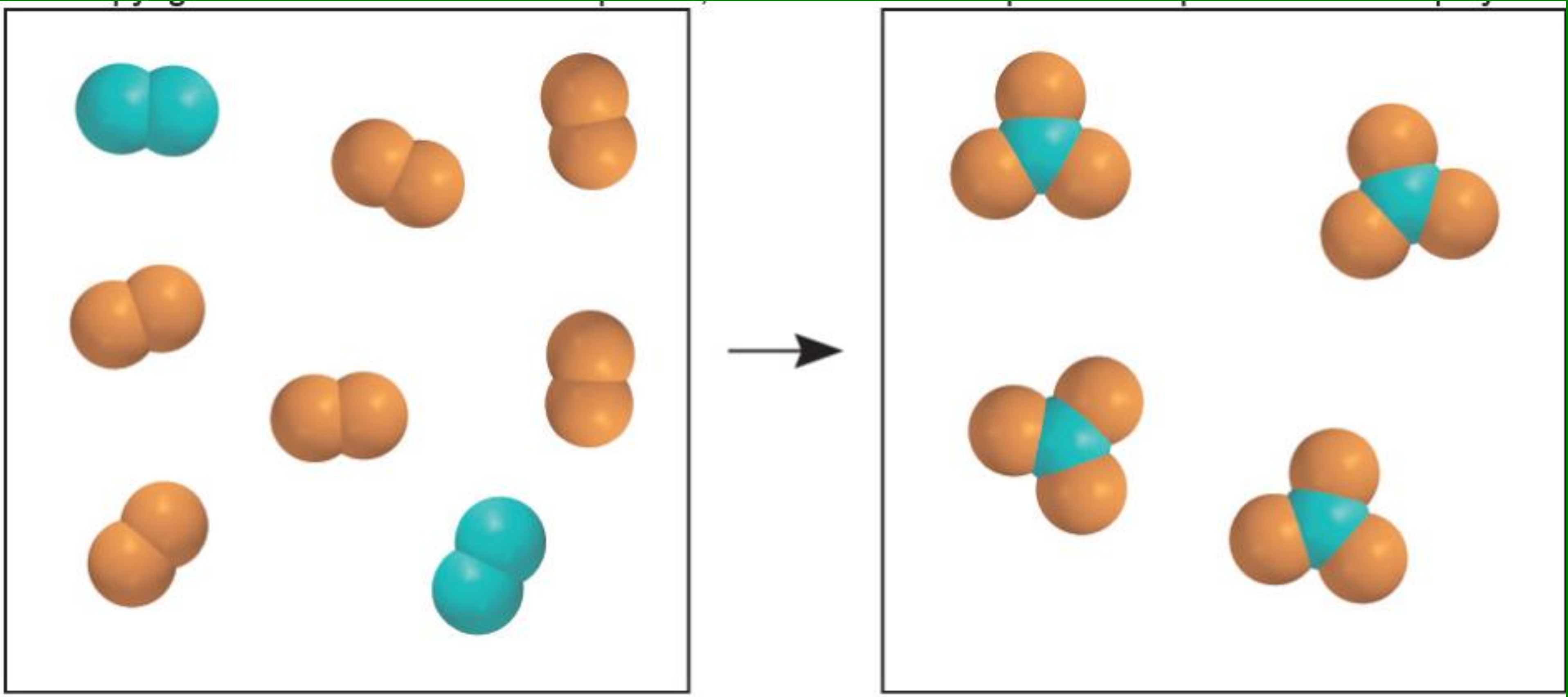
(assume the origin is 0,0)

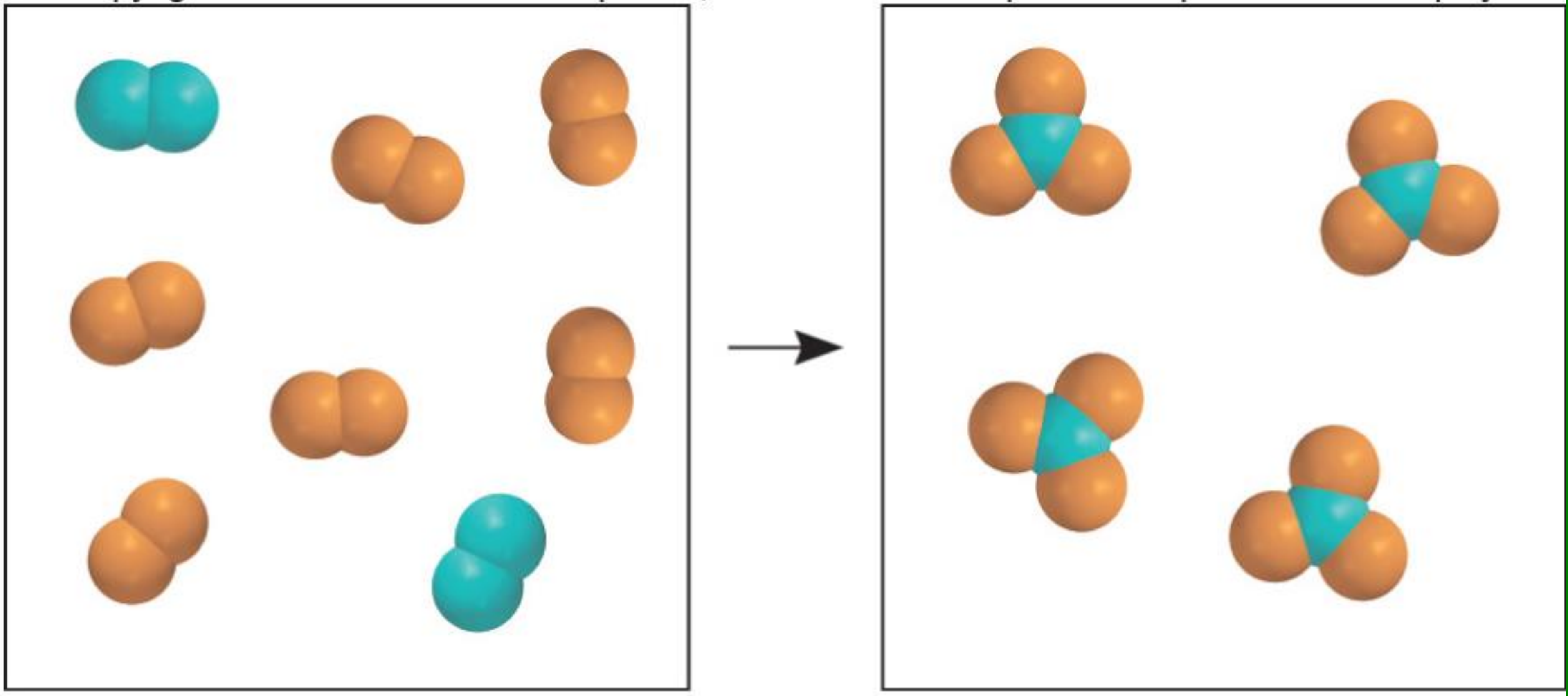

Gas
Liquid
Boiling
(ΔS_{vap})
Solid
Melting
(ΔS_{fus})
$S°$ (J/K•mol)
Temperature (K)

A few general rules…

1. If the reaction produces more moles of gas than it consumes, entropy increases (+ ΔS)
2. If there are more particles on the product side of the equation, entropy increases (+ ΔS)
3. If the reaction involves only liquids and solids, ΔS may be (+) or (-), but it will be small

Decide if Δ S is positive...





All substances are gases = no effect

8 molecules to 4 = less freedom of movement (less distribution)

Δ S is negative $\Rightarrow$ Entropy decreases

Decide if Δ S is positive…

2 $NO_{2(g)} \rightarrow N_2O_{4(g)}$

- gas to gas = no effect
- two molecules to one = less freedom of movement
- less distribution of energy/microstates
- Δ S is negative $\Rightarrow$ Entropy decreases

Decide if Δ S is positive…

$2\ SO_{2(g)} + O_{2(g)} \rightarrow 2\ SO_{3(g)}$

- gas to gas = no effect
- 3 molecules to 2 = lower freedom of movement
- Less distribution of energy/microstates
- ΔS is negative ⇒ Entropy decreases

Decide if Δ S is positive…

$2\ NaHCO_{3(s)} \rightarrow Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$

- solid to solid and gases
- 2 molecules to 3

more freedom of movement

More distribution of energy / microstates

- Δ S is positive

Decide if Δ S is positive…

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)}$$

- liquid to gas
- 2 molecules to 3
- more freedom of movement
- Δ S is positive
- Even so, this reaction is nonspontaneous - Why?

How are Δ H and Δ S related?

$$2H_2O_{(l)} + E \rightarrow 2H_{2(g)} + O_{2(g)}$$

- The reaction is *endothermic*
- Δ S is positive, but the reaction is nonspontaneous, because ΔH is also positive

"Will the reaction happen spontaneously?"

	"Yes"	"No"
Δ H	-	+
Δ S	+	-

Next up, we will look at the quantitative relationship between Δ H and Δ S

Free Energy "G"

- The Free Energy of a system is the energy that is available (free) to do useful work
- **A change can only be spontaneous if it is accompanied by a decrease in free energy**
  - **ΔG is negative**

Gibbs equation

- $G = H - TS$
- H is unknown; but it is ΔG that is important anyway…

$$\Delta G = \Delta H - T\Delta S$$

When is a reaction spontaneous?

- When ΔG is negative
- That is, when the result of ($\Delta H - T\Delta S$) is less than zero

When is ΔG negative?

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$
-	+	- no matter what T is
+	-	+ no matter what T is
+	+	- only if $T\Delta S > \Delta H$ (high T)
-	-	- only if $\Delta H > T\Delta S$ (low T)

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