

Lecture 17

Thermodynamics III

Entropy

Free Energy

Thermodynamically Favored Process (TFP)

Thermodynamically Favored Process

- Proceeds without any assistance from outside the system.
 - Water evaporates at 25°C
 - Iron rusts in the presence of O₂ and H₂O
 - NaCl dissolves in water

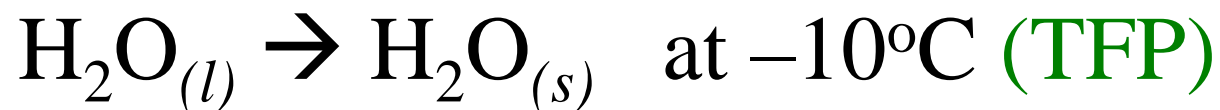
Non-Thermodynamically Favored Process

Non-Thermodynamically Favored Process

- Assistance from outside the system is necessary in order to induce the desired change.
 - Water does not boil at 75°C and 1 atm.
 - Water does not freeze at 15°C.
 - $\text{Fe}_2\text{O}_{3(s)} + 3 \text{C}_{(s)} \rightarrow 2 \text{Fe}_{(s)} + 3 \text{CO}_{(g)}$ at 25°C

Thermodynamically Favored Process (TFP)

A process that is thermodynamically favored in one direction is non-thermodynamically favored in the other direction.



Thermodynamically Favored Process (TFP)

**Exothermic reactions are often
thermodynamically favored**

- Nature tends to favor processes that cause a reduction in energy.
- In an exothermic reaction, the bonds in the products contain less energy than the bonds in the reactants. The excess energy is released as heat.

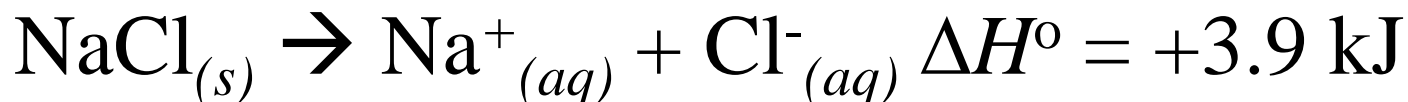
Thermodynamically Favored Process (TFP)

**Endothermic reactions can be
thermodynamically favored**

- Evaporation is thermodynamically favored.



- Dissolving soluble compounds is thermodynamically favored.



Entropy (S)

- A measure of the **disorder** of a system.
- A **greater** degree of **disorder** is **favorable**.
- A **positive** value for ΔS is **favorable**.

$$\Delta S = S_{(\text{products})} - S_{(\text{reactants})}$$

Increases in entropy are favored

- Your house gets dirty
- Making a stir-fry
- The impossibility of maintaining a perfect lawn
- Spilling a glass of milk
- Breaking a window

Laws of Thermodynamics

1st Law of Thermodynamics

The energy contained within the universe is constant.

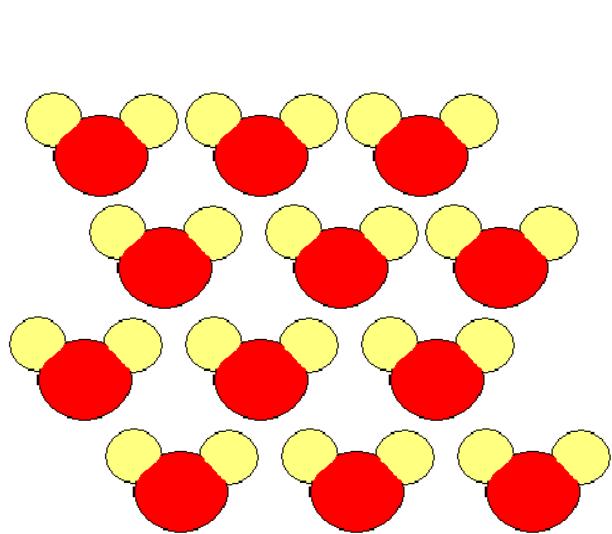
2nd Law of Thermodynamics

The entropy of the universe is constantly increasing.

$\Delta S > 0$ for the following processes:

- Melting
- Vaporization
- Reactions where the products are in the same phase as the reactants but contain more particles than the reactants
- Making most solutions
- Adding heat
- Increasing the volume of a gas

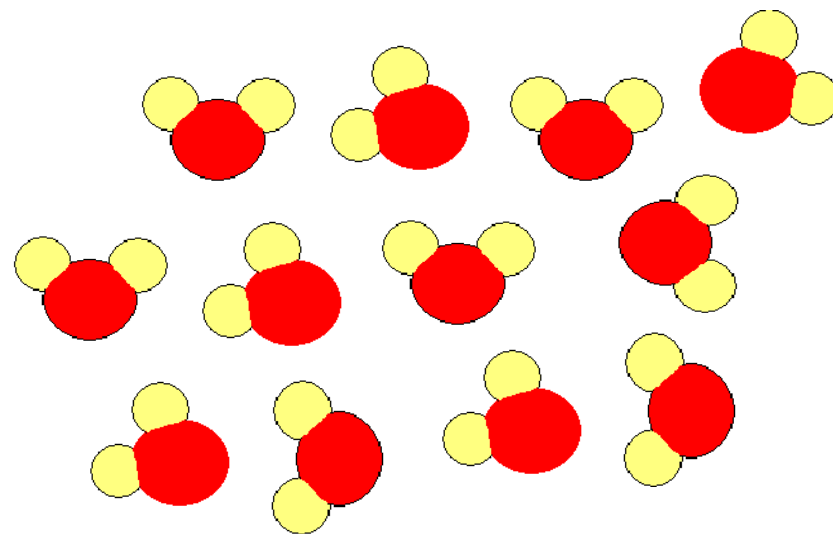
$\Delta S > 0$ when melting



$\text{H}_2\text{O}(s)$



$\text{H}_2\text{O}(l)$



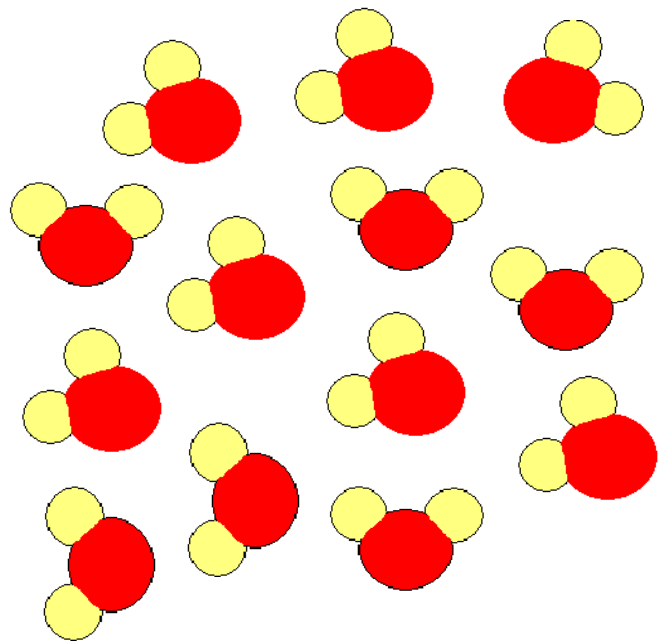
Very Organized

Less Organized

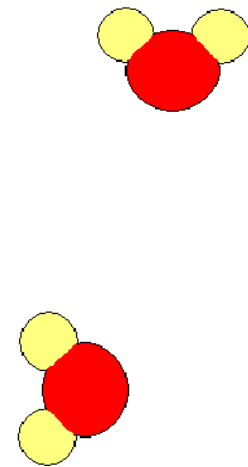
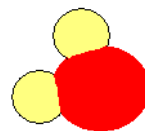
Small S

Larger S

$\Delta S > 0$ when vaporizing



$\text{H}_2\text{O}(l)$



$\text{H}_2\text{O}(g)$

Relatively Low S

High S

$\Delta S > 0$ when products have more
particles

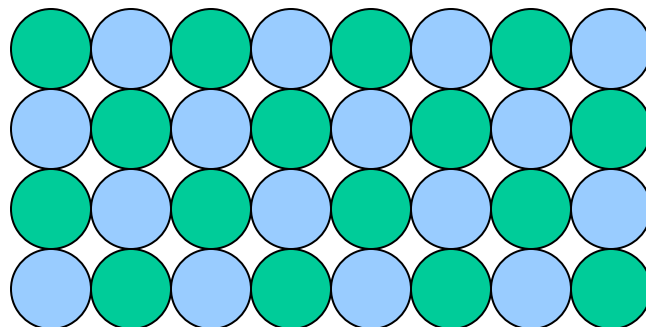


- 4 liquid molecules are converted into 29 gaseous molecules.
- Increasing the number of moles increases the number of potential arrangements.
- Changing from liquid to gas increases the number of potential arrangements.

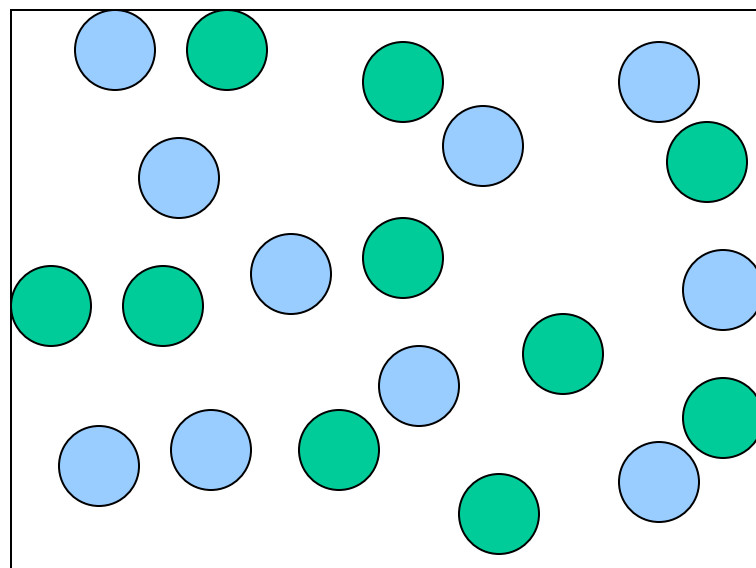
$$\Delta S > 0$$

$\Delta S > 0$ (*usually*) when making solutions with solids and/or liquids

- A ionic compound is very organized.

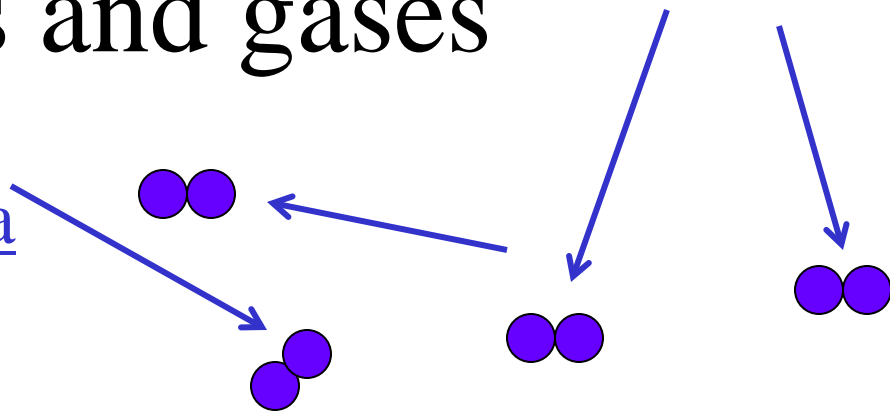


- A solution containing the same ions is much more disordered.

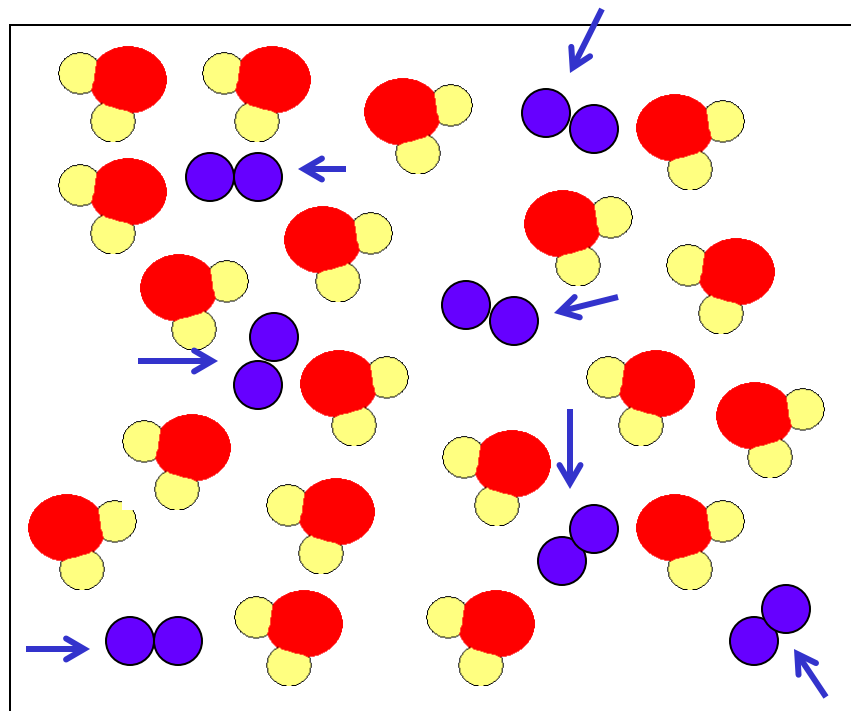


$\Delta S < 0$ when making solutions with liquids and gases

When dissolving a gas in a liquid the entropy will decrease.

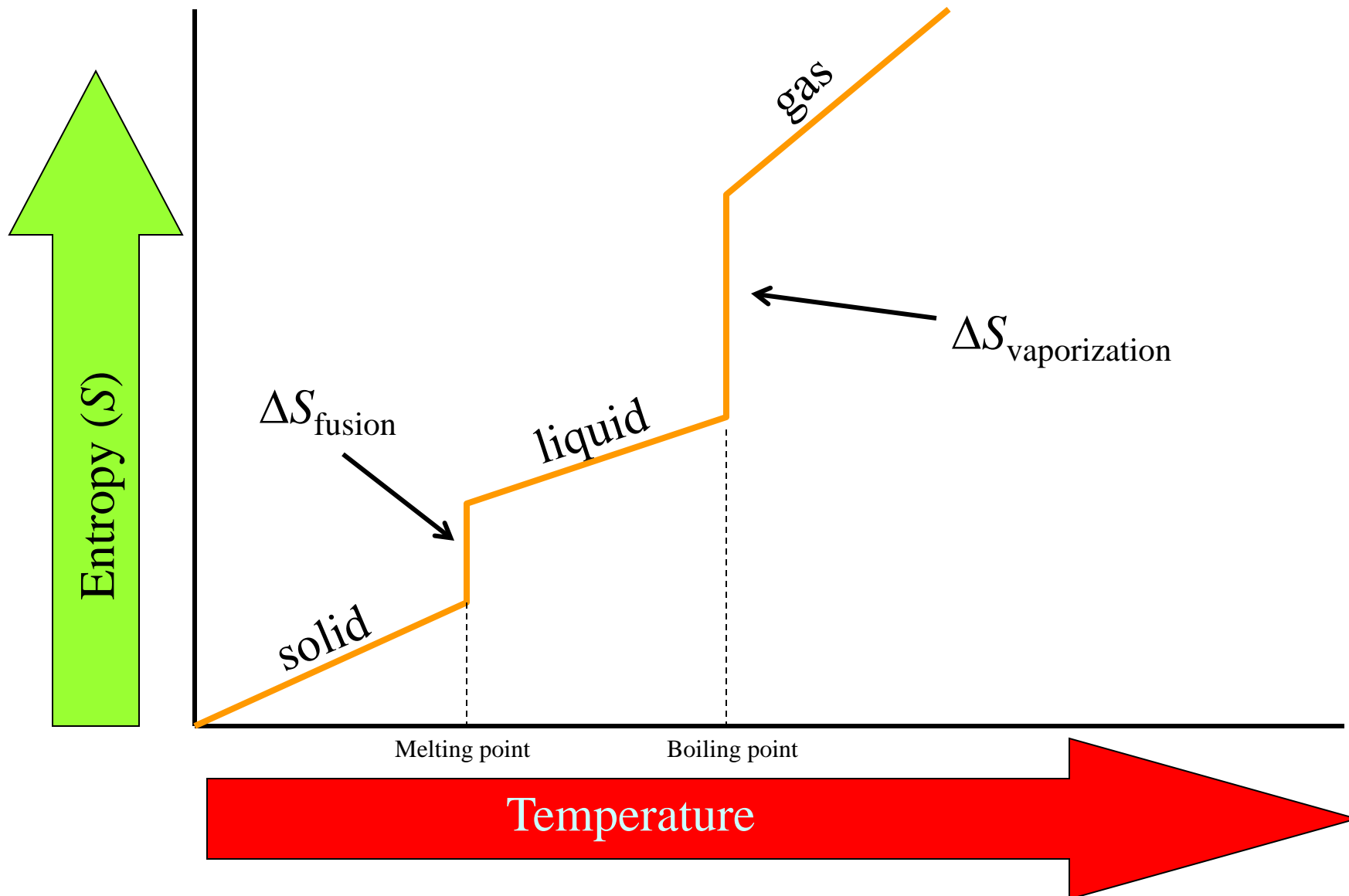


The rapid and chaotic movements of the gas particles are greatly reduced by the molecules in the solution.

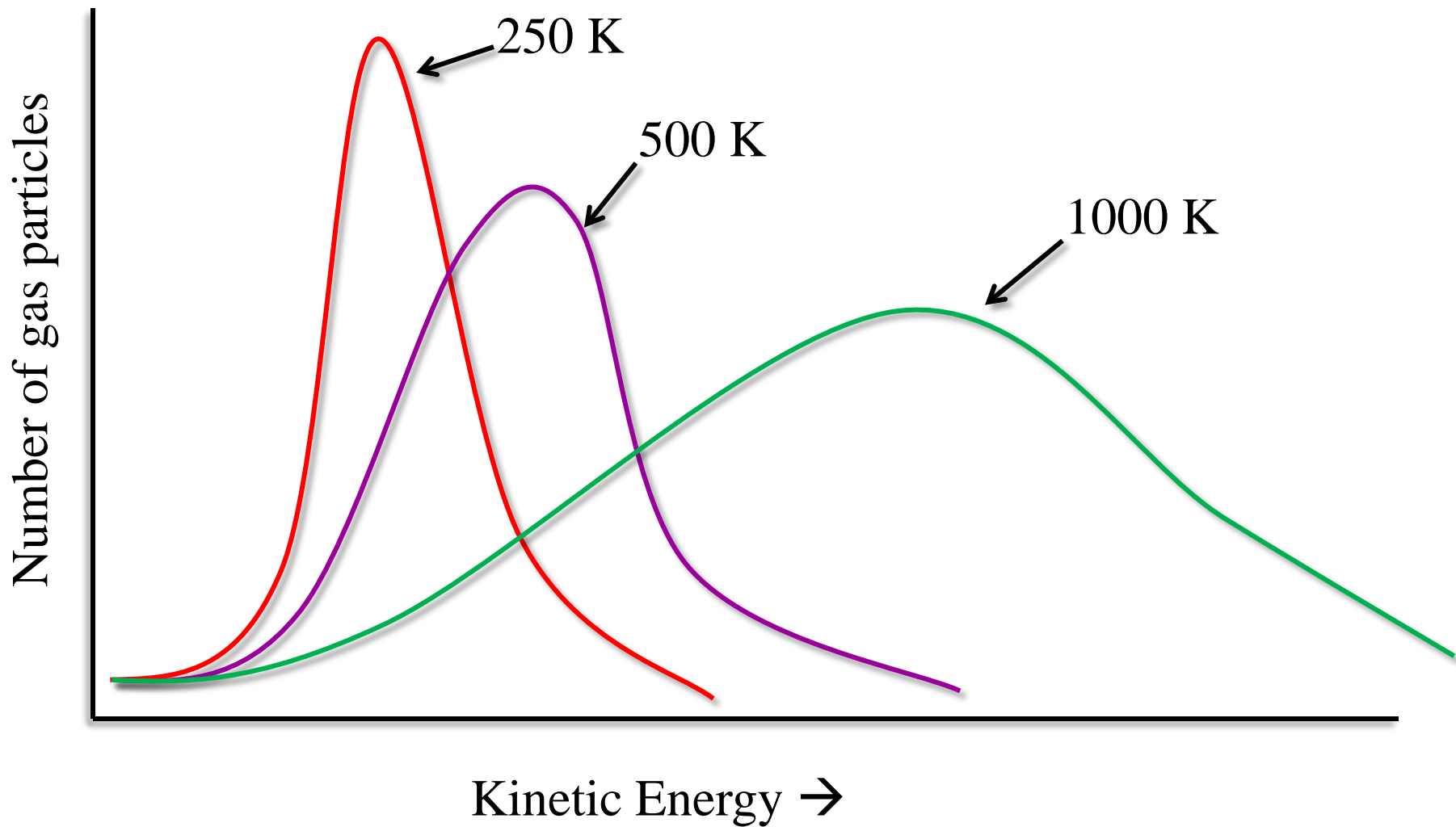


$$\Delta S < 0$$

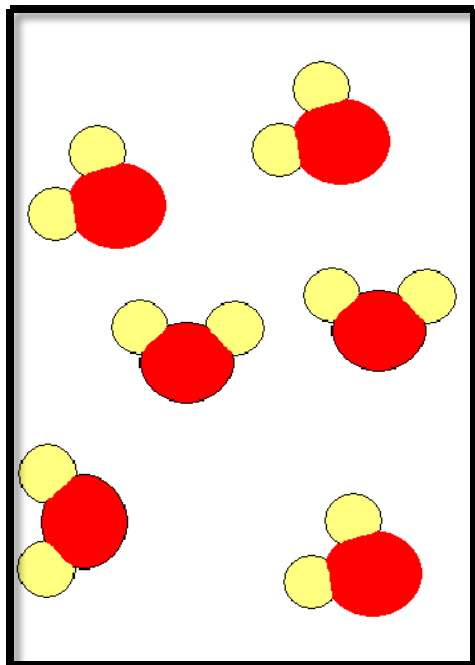
$\Delta S > 0$ when adding heat



$\Delta S > 0$ when adding heat, as the distribution of KE increases

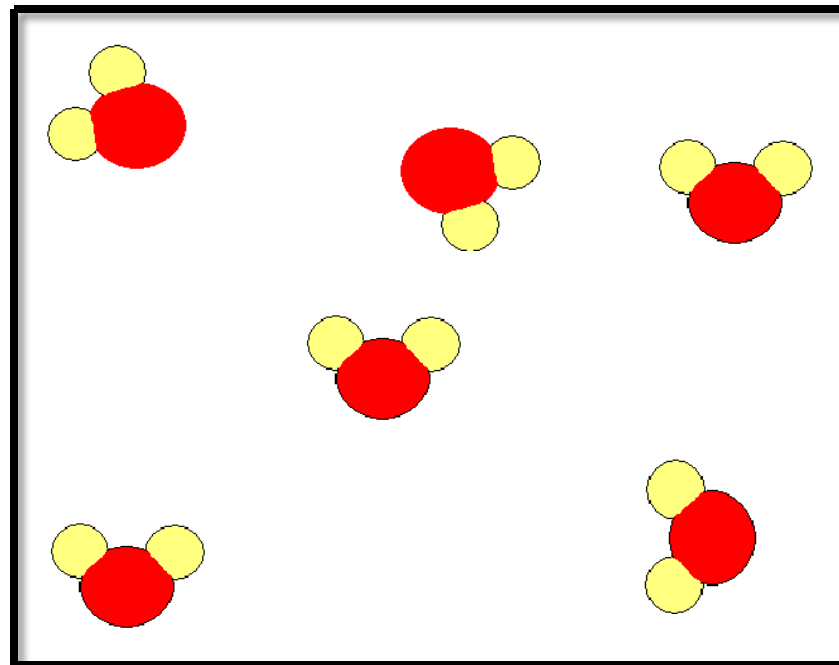


$\Delta S > 0$ when volume increases



$\text{H}_2\text{O}(g)$

High S



$\text{H}_2\text{O}(g)$

Higher S

Calculating ΔS

$$\Delta S_{\text{rxn}}^{\circ} = \sum n S^{\circ}_{\text{(products)}} - \sum n S^{\circ}_{\text{(reactants)}}$$

Sum of

stoichiometric
coefficients

Ex) Calculating ΔS

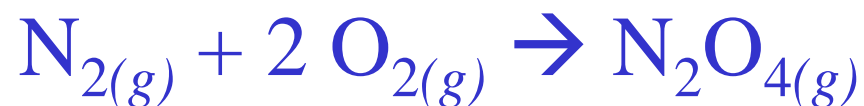
Ex) Calculate ΔS for the following reaction at 298K.



$$\Delta S^\circ = \sum n S^\circ (\text{products}) - \sum n S^\circ (\text{reactants})$$

Ex) Calculating ΔS

Ex) Calculate ΔS for the following reaction at 298K.

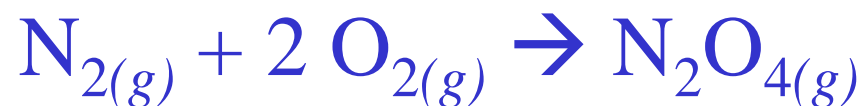


$$\Delta S^\circ = \sum n S^\circ (\text{products}) - \sum n S^\circ (\text{reactants})$$

$$\Delta S^\circ = [1(S^\circ (\text{N}_2\text{O}_{4(g)}))] - [1(S^\circ(\text{N}_{2(g)})) + 2(S^\circ(\text{O}_{2(g)}))]$$

Ex) Calculating ΔS

Ex) Calculate ΔS for the following reaction at 298K.



$$\Delta S^\circ = \sum n S^\circ (\text{products}) - \sum n S^\circ (\text{reactants})$$

$$\Delta S^\circ = [1(S^\circ (\text{N}_2\text{O}_{4(g)}))] - [1(S^\circ(\text{N}_{2(g)})) + 2(S^\circ(\text{O}_{2(g)}))]$$

$$\Delta S^\circ = [1(304.2)] - [1(191.5) + 2(205.0)]$$

$$\Delta S^\circ = - 297.3 \text{ J/K}\cdot\text{mol}$$

How can you tell if a process is thermodynamically favored?

Exothermic reactions are favorable.

$$\Delta H < 0$$

Producing a greater degree of disorder is favorable.

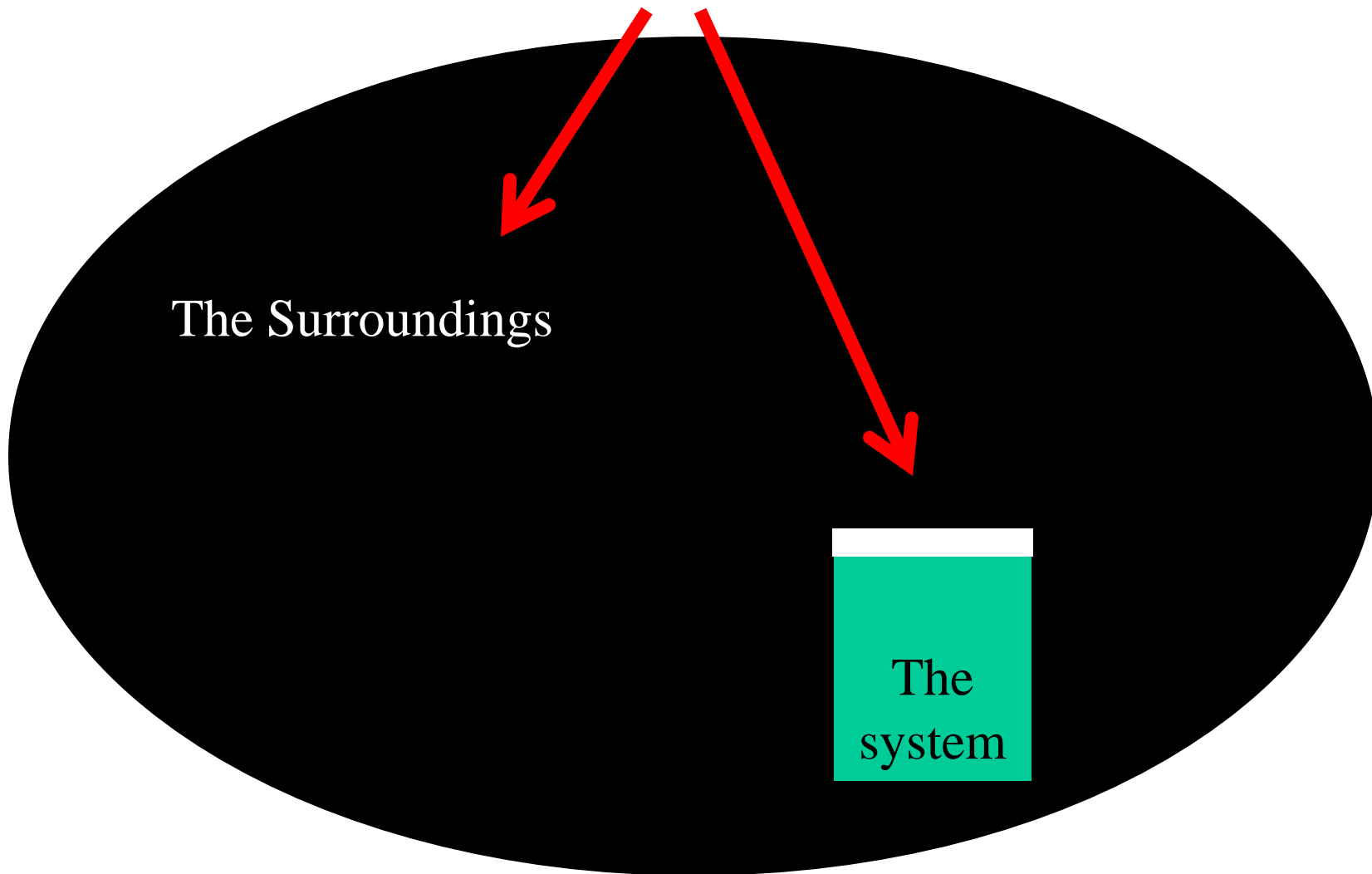
$$\Delta S > 0$$

Two methods for determining if a process is thermodynamically favored

1) $\Delta S_{\text{universe}}$

2) ΔG (Gibbs Free Energy)

The Universe



The Surroundings

The
system

$$\Delta S_{\text{universe}}$$

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

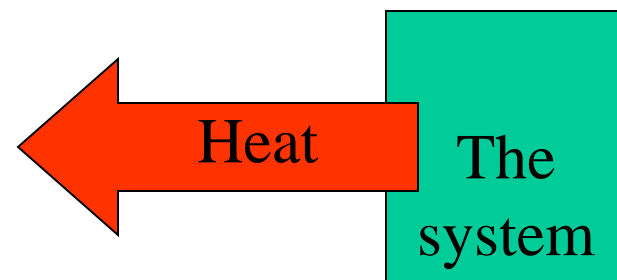
If $\Delta S_{\text{universe}} > 0$, the reaction is thermodynamically favored.

$\Delta S_{\text{surroundings}}$ and ΔH

Heat flow links the system to the surroundings.

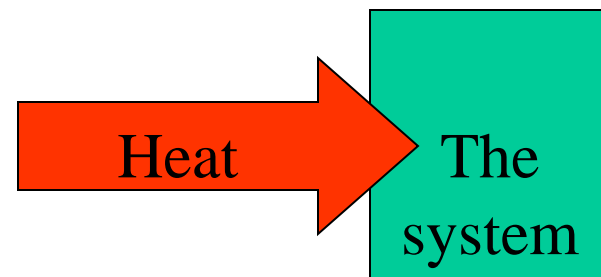
- **Exothermic Reactions**

– S_{surr} increases ($\Delta S_{\text{surr}} > 0$)



- **Endothermic Reactions**

– S_{surr} decreases ($\Delta S_{\text{surr}} < 0$)



$$\Delta S_{\text{universe}}$$

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

If a process:

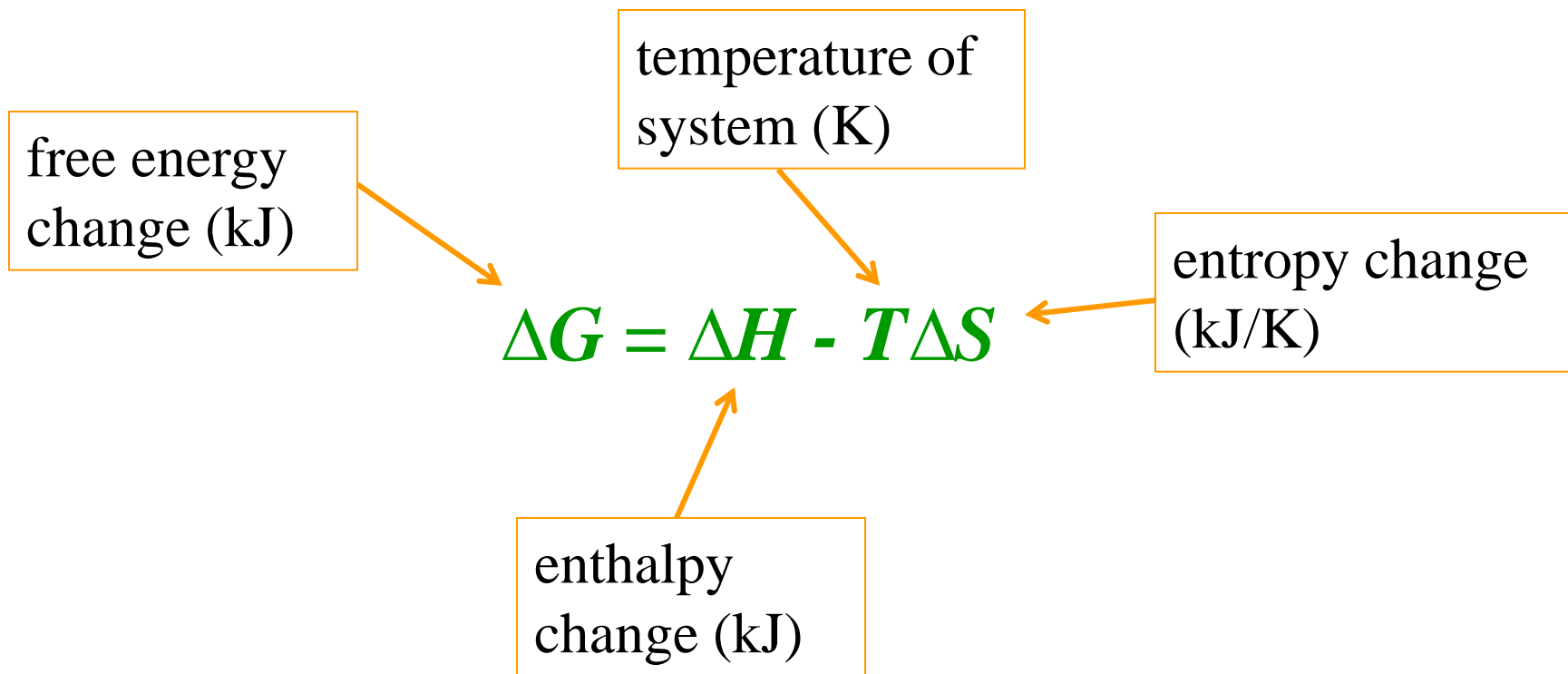
- increases the entropy of the system ($\Delta S_{\text{sys}} > 0$),
- and is exothermic ($\Delta S_{\text{surr}} > 0$),
- it must also be thermodynamically favored ($\Delta S_{\text{universe}} > 0$).

Two methods for determining if a process is thermodynamically favored

1) $\Delta S_{\text{universe}}$

2) ΔG (Gibbs Free Energy)

Gibbs Free Energy (G)



If $\Delta G < 0$, the reaction is thermodynamically favored.

Gibbs Free Energy (G)

The maximum amount of energy that can be used to do work

The energy used to create disorder

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

The energy transferred as heat

If $\Delta G < 0$, the reaction is thermodynamically favored.

Two Methods for Calculating ΔG

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

- Calculate ΔH using calorimetry, Hess's Law, or enthalpy of formation values.
- Calculate ΔS using entropy values.
- Calculate ΔG using $\Delta G = \Delta H - T\Delta S$

2) Calculate ΔG using ΔG_f° values.

Ex1) Gibbs Free Energy (ΔG)

Ex1) Find ΔG for a reaction if:

$$\Delta H = -218 \text{ kJ and } \Delta S = -765 \text{ J/K at } 32^\circ\text{C.}$$

Is the reaction thermodynamically favored?

Ex1) Gibbs Free Energy (ΔG)

Ex1) Find ΔG for a reaction if:

$$\Delta H = -218 \text{ kJ and } \Delta S = -765 \text{ J/K at } 32^\circ\text{C.}$$

Is the reaction thermodynamically favored?

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

$$\Delta G = -218 \text{ kJ} - (32 + 273 \text{ K}) (-765 \div 1000 \text{ kJ/K})$$

$$\Delta G = +15.3 \text{ kJ (non-thermodynamically favored)}$$

Ex2) Gibbs Free Energy (ΔG)

Ex2) At what temperature does the previous reaction become thermodynamically favored? Assume that ΔH and ΔS do not change as temperature changes?

$$\Delta G = \Delta H - T\Delta S = 0 \quad (\text{set } \Delta G = 0 \text{ and solve for } T)$$

$$T = \frac{\Delta H}{\Delta S} = \frac{-218 \text{ kJ}}{-0.765 \text{ kJ/K}} = 285 \text{ K}$$

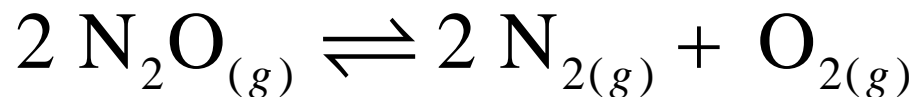
Temperature and Thermodynamic Favorability

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

ΔH	ΔS	Thermodynamic Favorability
–	+	TFP at all temperatures
+	–	non-TFP at all temperatures
–	–	TFP at low temperatures non-TFP at high temperatures
+	+	TFP at high temperatures non-TFP at low temperatures

Ex) Thermodynamic Favorability

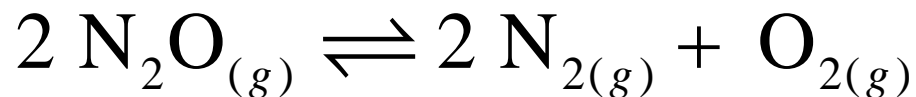
Ex) $\Delta H^\circ = -163 \text{ kJ}$ and $\Delta S^\circ = +148 \text{ J/K}$ for the following reaction.



Is this process thermodynamically favored?
Justify your answer.

Ex) Thermodynamic Favorability

Ex) $\Delta H^\circ = -163 \text{ kJ}$ and $\Delta S^\circ = +148 \text{ J/K}$ for the following reaction.



Is this process thermodynamically favored?
Justify your answer.

YES! $\Delta H < 0$ and $\Delta S > 0$

Two methods for calculating ΔG

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

- Calculate ΔH using calorimetry, Hess's Law, or enthalpy of formation values.
- Calculate ΔS using entropy values.
- Calculate ΔG using $\Delta G = \Delta H - T\Delta S$

2) Calculate ΔG using ΔG_f° values.

Free Energy of Formation

ΔG_f° is the free energy change that occurs when one mole of a compound is made from its elements in their standard states.

ΔG_f° for an element in its standard state is zero.

$$\Delta G_{\text{rxn}}^\circ = \sum n \Delta G_f^\circ (\text{products}) - \sum n \Delta G_f^\circ (\text{reactants})$$

Sum of

Stoichiometric

Coefficients

Ex) Free Energy of Formation Problem

Ex) Find $\Delta G_{\text{rxn}}^{\circ}$ for the thermite reaction under standard conditions.



$$\Delta G_{\text{rxn}}^{\circ} = \sum n \Delta G_{\text{f}}^{\circ} (\text{products}) - \sum n \Delta G_{\text{f}}^{\circ} (\text{reactants})$$

Ex) Free Energy of Formation Problem

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$$\Delta G_{\text{rxn}}^{\circ} = \sum n \Delta G_{\text{f}}^{\circ} (\text{products}) - \sum n \Delta G_{\text{f}}^{\circ} (\text{reactants})$$

$$\Delta G_{\text{rxn}}^{\circ} = [2 (\Delta G_{\text{f}}^{\circ}(\text{Fe}_{(s)})) + 1 (\Delta G_{\text{f}}^{\circ}(\text{Al}_2\text{O}_{3(s)}))] - [2 (\Delta G_{\text{f}}^{\circ}(\text{Al}_{(s)})) + 1 (\Delta G_{\text{f}}^{\circ}(\text{Fe}_2\text{O}_{3(s)}))]$$

Ex) Free Energy of Formation Problem

Ex) Find $\Delta G_{\text{rxn}}^{\circ}$ for the thermite reaction under standard conditions.



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$$\Delta G_{\text{rxn}}^{\circ} = [2(0) + 1(-1582)] - [2(0) + 1(-743.6)]$$

$$\Delta G_{\text{rxn}}^{\circ} = -838 \text{ kJ/mol}$$

Thermodynamically favored
process are not necessarily fast!

The rate of a reaction is determined by
chemical kinetics, not thermodynamics.

Many TFPs do not occur at a measurable rate.

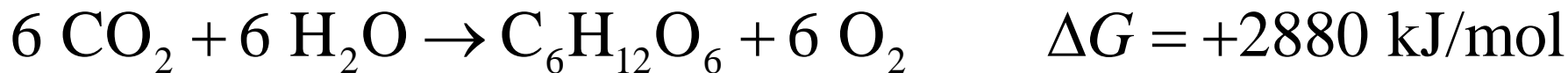
e.g. Oxidizing is a TFP.

- It can take several hundred years for an iron beam to rust away.

Using external energy when $\Delta G > 0$

External energy can drive reactions when $\Delta G > 0$

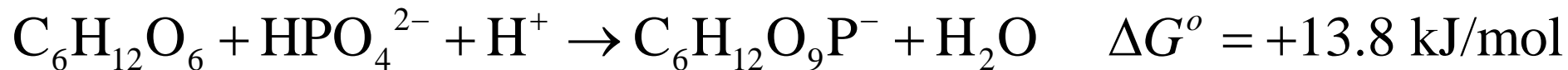
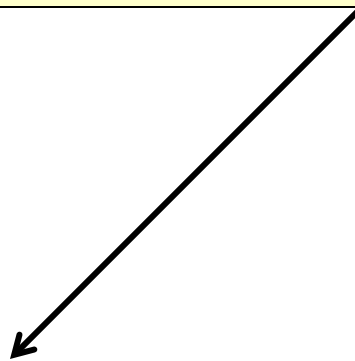
- Electricity can be used to recharge a battery.
- Photons can supply the energy required to remove electrons from atoms.
- e.g. The conversion of CO_2 and H_2O to glucose through photosynthesis.



- This occurs through multiple steps that are initiated by the absorption of several photons.

Coupling reactions when $\Delta G > 0$

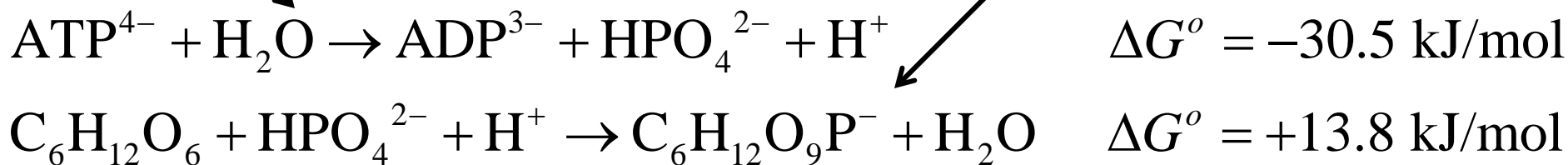
Initial step in metabolic breakdown of glucose



Coupling reactions when $\Delta G > 0$

Initial step in metabolic breakdown of glucose

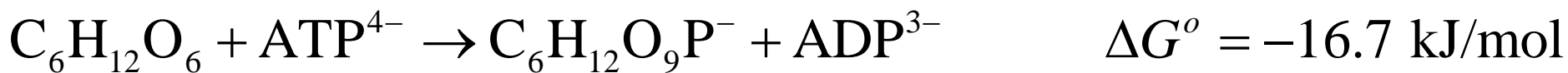
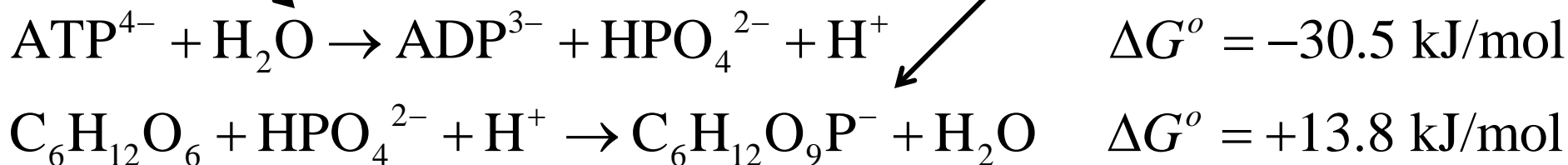
Conversion of ATP to ADP



Coupling reactions when $\Delta G > 0$

Initial step in metabolic breakdown of glucose

Conversion of ATP to ADP



Coupling a non-thermodynamically favored process with the conversion of ATP to ADP makes the overall process thermodynamically favored.