

## 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 O<sub>2</sub> and H<sub>2</sub>O
  - NaCl dissolves in water

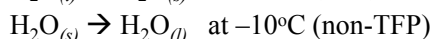
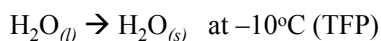
### Non-Thermodynamically Favored Process

#### 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)

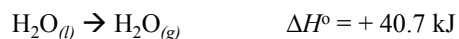
#### Exothermic reactions are often thermodynamically favored

- 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.

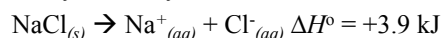
### Thermodynamically Favored Process (TFP)

#### 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  $\Delta S$  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 a maintaining a perfect lawn
- Spilling a glass of milk
- Breaking a window

### Laws of Thermodynamics

#### 1<sup>st</sup> Law of Thermodynamics

The energy contained within the universe is constant.

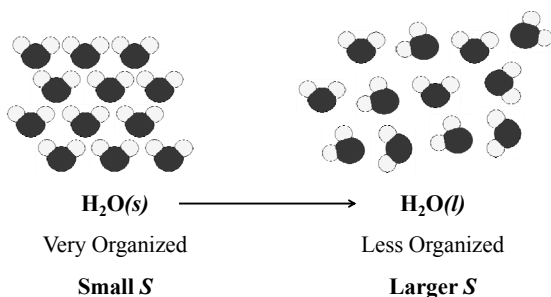
#### 2<sup>nd</sup> Law of Thermodynamics

The entropy of the universe is constantly increasing.

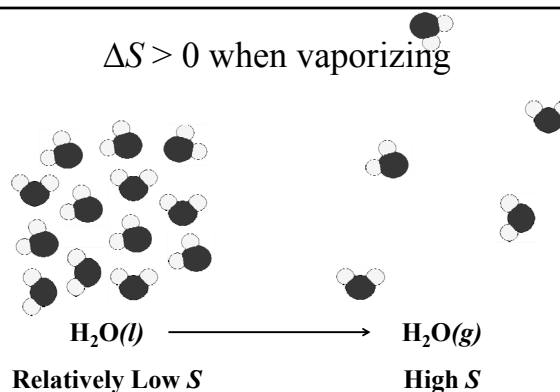
### $\Delta S > 0$ for the following processes:

- 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

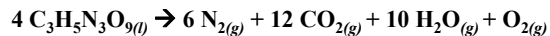
### $\Delta S > 0$ when melting



### $\Delta S > 0$ when vaporizing



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

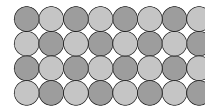


- 4 liquid molecules are converted into 29 gaseous molecules.
- Increasing the number of moles increases the number of potential arrangements.
- Changing from liquid to gas increases the number of potential arrangements.

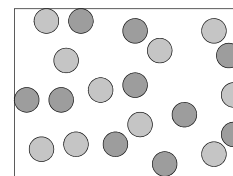
$$\Delta S > 0$$

$\Delta S > 0$  (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.

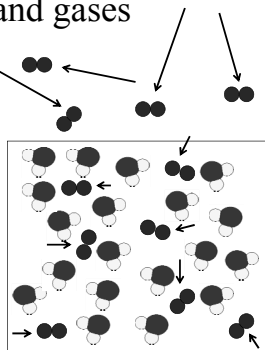


$\Delta S < 0$  when making solutions with liquids and gases

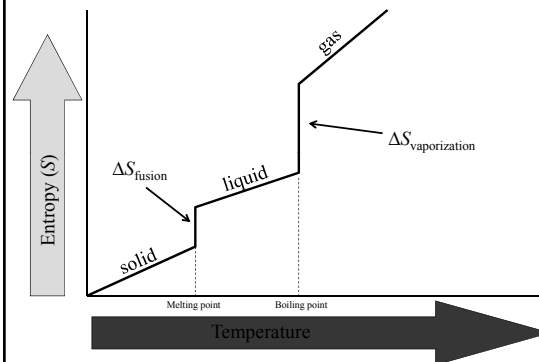
When dissolving a gas in a liquid the entropy will decrease.

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

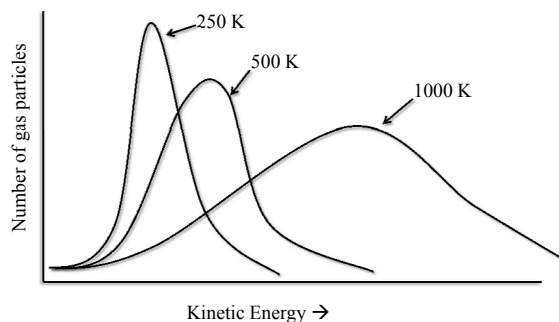
$$\Delta S < 0$$



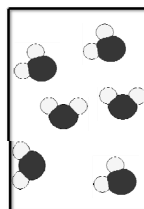
$\Delta S > 0$  when adding heat



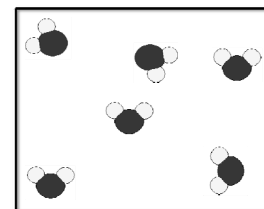
$\Delta S > 0$  when adding heat, as the distribution of KE increases



$\Delta S > 0$  when volume increases



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



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

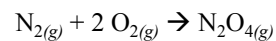
### Calculating $\Delta S$

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

Sum of  $\swarrow$   $\nwarrow$  stoichiometric coefficients

### Ex) Calculating $\Delta S$

Ex) Calculate  $\Delta S$  for the following reaction at 298K.



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

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.

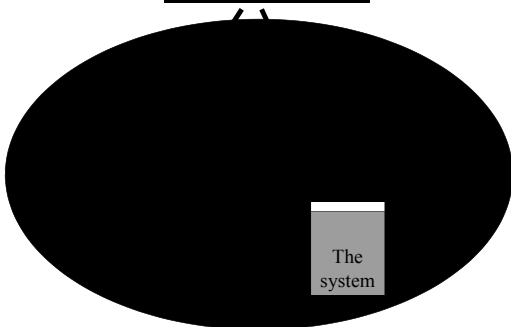
$$\Delta S > 0$$

Two methods for determining if a process is thermodynamically favored

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

2)  $\Delta G$  (Gibbs Free Energy)

### The Universe



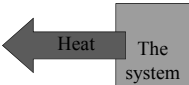
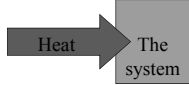
$$\Delta S_{\text{universe}}$$

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

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

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

Heat flow links the system to the surroundings.

- **Exothermic Reactions**  
 $-S_{\text{surr}}$  increases ( $\Delta S_{\text{surr}} > 0$ ) 
- **Endothermic Reactions**  
 $-S_{\text{surr}}$  decreases ( $\Delta S_{\text{surr}} < 0$ ) 

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

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

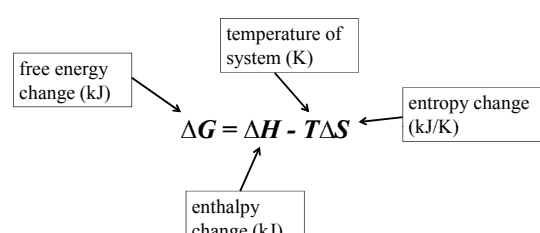
If a process:

- 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

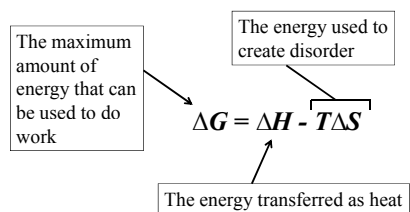
- 1)  $\Delta S_{\text{universe}}$
- 2)  $\Delta G$  (Gibbs Free Energy)

**Gibbs Free Energy ( $G$ )**



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

**Gibbs Free Energy ( $G$ )**



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

Two Methods for Calculating  $\Delta G$

- 1)  $\Delta G = \Delta H - T \Delta S$ 
  - Calculate  $\Delta H$  using calorimetry, Hess's Law, or enthalpy of formation values.
  - Calculate  $\Delta S$  using entropy values.
  - Calculate  $\Delta G$  using  $\Delta G = \Delta H - T \Delta S$
- 2) Calculate  $\Delta G$  using  $\Delta G_f^\circ$  values.

Ex1) Gibbs Free Energy ( $\Delta G$ )Ex1) Find  $\Delta G$  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?

Ex2) Gibbs Free Energy ( $\Delta G$ )

Ex2) At what temperature does the previous reaction become thermodynamically favored? Assume that  $\Delta H$  and  $\Delta S$  do not change as temperature changes?

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

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

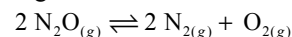
## Temperature and Thermodynamic Favorability

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

$\Delta H$	$\Delta S$	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.

Two methods for calculating  $\Delta G$ 

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

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

2) Calculate  $\Delta G$  using  $\Delta G_f^\circ$  values.

## Free Energy of Formation

$\Delta G_f^\circ$  is the free energy change that occurs when one mole of a compound is made from its elements in their standard states.

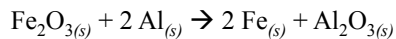
$\Delta G_f^\circ$  for an element in its standard state is zero.

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

Sum of
Stoichiometric Coefficients

### Ex) Free Energy of Formation Problem

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



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

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.

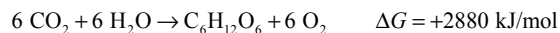
e.g. Oxidizing is a TFP.

- 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  $\text{CO}_2$  and  $\text{H}_2\text{O}$  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 the metabolic breakdown of glucose

