Thermodynamics 8.7

Entropy

Spontaneous Processes

Spontaneous Process

- Proceeds without any assistance from outside the system.
  - Water evaporates at 25°C
  - Iron rusts in the presence of O_2 and H_2O
  - NaCl dissolves in water

Non-Spontaneous Processes

Non-Spontaneous Process

- Assistance from outside the system is necessary in order to induce the desired change.
  - Water does not boil at 75°C and 1atm.
  - Water does not freeze at 15°C.
  - $Fe_2O_{3(s)} + 3\ C_{(s)} \rightarrow 2\ Fe_{(s)} + 3\ CO_{(g)}$ at 25°C.

Spontaneous Processes

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

$H_2O_{(l)} \rightarrow H_2O_{(s)}$ at –10°C (spontaneous)
$H_2O_{(s)} \rightarrow H_2O_{(l)}$ at –10°C (non-spontaneous)

Spontaneous Processes

Exothermic reactions are often spontaneous

- Nature tends to favors 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.

Spontaneous Processes

Endothermic reactions can be spontaneous

- Evaporation is spontaneous.
  $H_2O_{(l)} \rightarrow H_2O_{(g)}$ $\Delta H^o = +40.7$ kJ
  $C_3H_{8(l)} \rightarrow C_3H_{8(g)}$ $\Delta H^o = +16.7$ kJ
- Dissolving soluble compounds is spontaneous.
  $NaCl_{(s)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$ $\Delta H^o = +3.9$ kJ

Entropy *(S)*

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

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

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

1st Law of Thermodynamics

The energy contained within the universe is constant.

2nd Law of Thermodynamics

The entropy of the universe is constantly increasing.

Entropy is a State Function

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

The degree of disorder contained within the reactants is a constant.

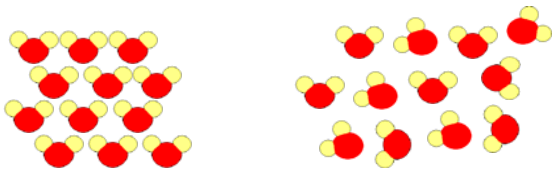
The degree of disorder contained within the products is a constant.

The route that was taken is not important.

$\Delta S > 0$ 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
- Reactions that produce more random phases
- Making most solutions
- Adding heat

$\Delta S > 0$ when melting

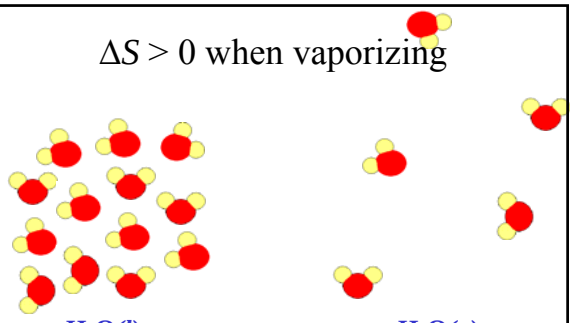


$H_2O(s)$ → $H_2O(l)$

Very Organized → Less Organized

Small *S* → **Larger *S***

$\Delta S > 0$ when vaporizing



$H_2O(l) \rightarrow H_2O(g)$

Relatively Low *S* **High *S***

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

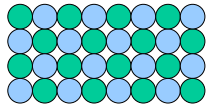
$4\ C_3H_5N_3O_{9(l)} \rightarrow 6\ N_{2(g)} + 12\ CO_{2(g)} + 10\ H_2O_{(g)} + O_{2(g)}$

- 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.

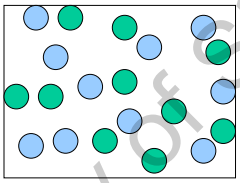
$\Delta S > 0$

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

- A ionic compound is very organized.

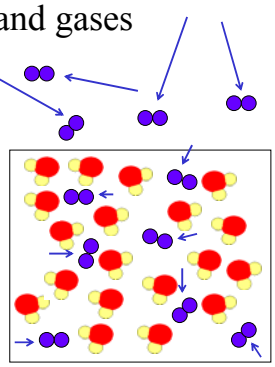


- A solution containing the same ions is much more disordered.



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

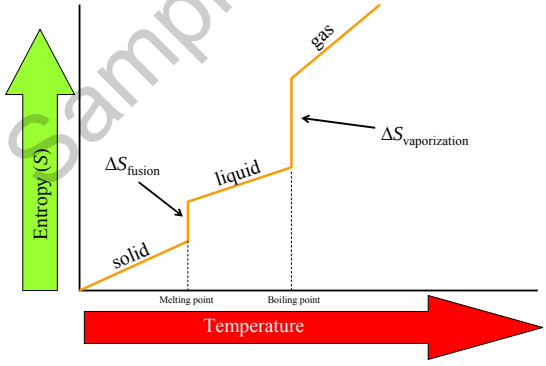
When dissolving a gas in a liquid the entropy will decrease.



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



Calculating ΔS

$$\Delta S^o_{rxn} = \Sigma\, n\, S^o_{(products)} - \Sigma\, n\, S^o_{(reactants)}$$

Sum of — stoichiometric coefficients

Ex) Calculating ΔS

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

$N_{2(g)} + 2\ O_{2(g)} \rightarrow N_2O_{4(g)}$

$\Delta S^o = \Sigma\ n\ S^o$ (products) - $\Sigma\ n\ S^o$ (reactants)

How can you tell if a process is spontaneous?

Exothermic Reactions are favorable.

$\Delta H < 0$

Systems that create disorder are favorable.

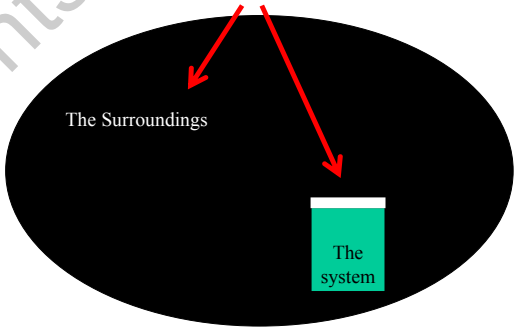
$\Delta S > 0$

Two methods for determining if a process is spontaneous

1) $\Delta S_{universe}$

2) ΔG (Gibbs Free Energy)

The Universe



$\Delta S_{universe}$

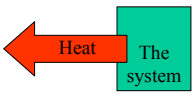
$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$

If $\Delta S_{universe} > 0$, the reaction is spontaneous.

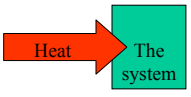
$\Delta S_{surroundings}$ and ΔH

Heat flow links the system to the surroundings.

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



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



$\Delta S_{universe}$

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

If a process:

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