

# Chapter 15: Energy and Chemical Change

## Section 5: Reaction Spontaneity

**Spontaneous process:** any physical or chemical change that once begun, occurs with no outside intervention

- Rust is spontaneous.
- The formation of rust on iron is an exothermic and spontaneous reaction.

**Entropy (S):** a measure of the number of possible ways that the energy of a system can be distributed, and this is related to the freedom of the system's particles to move and number of ways they can be arranged.

- the number of possible arrangements available to a system increases under the following conditions:
  - volume increases
  - energy increases
  - number of particles increase
  - the particle's freedom of movement increases

**Second law of thermodynamics:** states that spontaneous processes always proceed in such a way that the entropy of the universe increases

- sometimes considered to be a measure of the disorder or randomness of the particles that make up a system
- particles that are more spread out have more disorder causing a greater entropy

$$\Delta S_{\text{system}} = S_{\text{products}} - S_{\text{reactants}}$$

- If entropy increases,  $S_{\text{products}} > S_{\text{reactants}}$  meaning  $\Delta S = +$
- If entropy decreases,  $S_{\text{products}} < S_{\text{reactants}}$  meaning  $\Delta S = -$

Predicting  $\Delta S_{\text{system}}$  is positive or negative:

- Entropy changes associated with changes in state can be predicted
  - Particle movement increases from solid  $\rightarrow$  liquid  $\rightarrow$  gas so if a physical change occurs from a (s)  $\rightarrow$  (l) or (l)  $\rightarrow$  (g), entropy is positive.
- The dissolving of a gas in a solvent always results in a decrease in entropy.
  - Gas particles have more entropy when they can move freely.
- Assuming no change in physical state occurs, the entropy of a system usually increases when the number of gaseous product particles is greater than the number of gaseous reactant particles.
  - $2 \text{SO}_3 (\text{g}) \rightarrow 2 \text{SO}_2 (\text{g}) + \text{O}_2 (\text{g}) \quad \Delta S_{\text{system}} > 0$
  - 3 moles of gaseous product  $>$  2 moles of gaseous reactant
- With some exceptions, entropy increases when a solid or a liquid dissolves in a solvent.
  - $\text{NaCl} (\text{s}) \rightarrow \text{Na}^+ (\text{aq}) + \text{Cl}^- (\text{aq}) \quad \Delta S_{\text{system}} > 0$
- The random motion of the particles of a substance increases as its temperature increases.

**Free energy (Gibbs free energy):** the energy that is available to do work at constant pressure and temperature

- free energy is useful energy
- Calculating whether a reaction is spontaneous or not
- $\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$ 
  - $\Delta G_{\text{system}}$  = change in Gibbs free energy measured in kJ or J
  - $\Delta H_{\text{system}}$  = change in enthalpy measured in kJ or J

- $T$  = temperature measured in Kelvin
- $\Delta S_{\text{system}}$  = change in entropy measured in Joules/Kelvin

<u><math>\Delta H_{\text{system}}</math></u>	<u><math>\Delta S_{\text{system}}</math></u>	<u><math>\Delta G_{\text{system}}</math></u>	<u>Reaction Spontaneity</u>
- (exo)	+	Always -	Always Spontaneous
- (exo)	-	- or +	Spontaneous At low temps
+ (endo)	+	- or +	Spontaneous At high temps
+ (endo)	-	Always +	Never spontaneous

- A **spontaneous reaction** is a reaction that favors the formation of products at the conditions under which the reaction is occurring.
  - Example: Combustion reaction in a bonfire
    - Enthalpy = decreases because it releases heat out to the surrounding =  $\Delta H_{\text{system}} = -$
    - Entropy = increases because you are getting gaseous products =  $\Delta S_{\text{system}} = +$
    - Meaning this combustion reactions (all combustion reactions) are spontaneous and will occur under normal conditions
- A **nonspontaneous reaction** is a reaction that does not favor the formation of products at the given set of conditions. In order for a reaction to be nonspontaneous, it must be endothermic, accompanied by a decrease in entropy, or both.
  - Example: Our atmosphere is made up of nitrogen gas and oxygen gas



- This is an endothermic reaction (heat is absorbed).
- The entropy remains fairly unchanged since it has 2 moles of gas on the product and 2 moles of gas on the reactant. (I looked it up and it states that it is slightly positive.)
- It is a spontaneous reaction at high temperatures and since our atmosphere is relatively cool, this reaction is nonspontaneous (it will not occur under normal conditions).

Do not confuse the term spontaneous with the notion that a reaction occurs rapidly.

A spontaneous reaction is one in which product formation is favored, even if the reaction is extremely slow.

A piece of paper will not suddenly burst into flames, although its combustion is a spontaneous reaction. What is missing is the required activation energy to get the reaction started. If the paper were to be heated to a high enough temperature, it would begin to burn, at which point the reaction would proceed spontaneously until completion.