

# CHE 1302

## Basic Principles of Modern Chemistry II

### Week 13

Hello and welcome to the weekly resources for Chemistry 1302! This resource covers topics typically taught by professors during the 13<sup>th</sup> week of classes.

On our website, <https://baylor.edu/tutoring>, you'll find the following links:

“Online Study Guide Resources” – If you don't see the topics you're learning right now, click here to find the weekly resources for the rest of the semester!

“How to Participate in Group Tutoring” - See if there is a Chemistry 1302 group tutoring session being hosted this semester – these are weekly question/answer sessions taught by our master tutors!

You can also view tutoring times for your course or schedule a private 30-minute appointment! Check out the website to learn more. You can also give us a call at (254)710-4135, or drop in. Our hours are Monday-Thursday 9 am – 8 pm on class days.

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**KEY WORDS: Spontaneous Processes, Enthalpy (H) Entropy (S), Free Energy (G)**

## TOPIC OF THE WEEK: Spontaneous Processes and Free Energy, G

A spontaneous process is one that occurs without any external influence. It does not have to do with speed but with energy. Even if it takes awhile, and even if it takes a “spark” of energy to get started, a process is considered **spontaneous** if the “free energy” at the end of the reaction is greater than the free energy at the beginning.

What is free energy? It's a measure of the amount of ability a reaction has to do work. A reaction with more free energy has more potential to give off heat and is more likely to react. What you need to know about free energy is what **makes it change**:

1. Free energy changes when heat is given off
2. Free energy changes when entropy (degree of disorderliness) changes... and entropy has more of an effect at higher temperatures!

These effects can be summarized in this equation:  $\Delta G = \Delta H - T\Delta S$

The highlights will elaborate on the right side of this equation. Let's start by looking at the left.

Ways to calculate:

1. If given  $\Delta G_f^\circ$  for each reactant and product, or the amount of free energy that it takes to form each reactant and product, you can **calculate the total  $\Delta G$** , as follows:
  - a.  $\Delta G^\circ = \sum \Delta G_f^\circ n_p - \sum \Delta G_f^\circ n_r$
  - b. The superscripted circle next to the G means “**standard**.” This equation applies when the free energy is being calculated at standard temperature and pressure, at equilibrium.
  - c. If the free energy being calculated is not “standard,” it can be derived from the standard:
    - d.  $\Delta G = \Delta G^\circ + RT \ln Q$ , where  $R = 8.3145 \text{ J/mol K}$
    - e. This same equation can be used to relate free energy, temperature, and the equilibrium constant. At equilibrium,  $\Delta G = 0$ , and  $Q = K$ . So,
      - f.  $\Delta G^\circ = -RT \ln K$ . Plug this back into  $\Delta G = \Delta G^\circ + RT \ln Q$ , and you get  $\Delta G = -RT \ln K + RT \ln Q = RT \ln \left( \frac{Q}{K} \right)$

## Highlight 1: Enthalpy, H

Enthalpy can be thought of as heat. It is measured in J/mol or kJ/mol. (Note on units: Make sure that, if  $\Delta H$  is in kJ/mol,  $\Delta G$  is also in kJ/mol, and  $\Delta S$  is in kJ/mol K. If one of them is in J/mol, the others should also use J.)

Just like  $\Delta G$ ,  $\Delta H$  can be calculated by subtracting that necessary to form the reactants from that necessary to form products.  $\Delta H_f^\circ = \sum \Delta H_f^\circ n_p - \sum \Delta H_f^\circ n_r$

Think of it this way: a certain **amount of heat is necessary to form the products**, and **another amount of heat is necessary to form the reactants**. Some, all, or more than all of the heat necessary to form the products comes from the heat that formed the reactants.

If some, but not all, of the heat comes from the reactants, the reaction is **endothermic**; it needs more heat, from an outside source, to fuel its product formation.

If more than all of the heat comes from the heat that formed the reactants, the reaction has extra heat that it does not need to fuel itself. This heat is released, and the reaction is called **exothermic**.

## Highlight 2: Entropy, S

**Entropy** is the degree of disorderliness/randomness of a system.

Entropy is related to the **number of possible arrangements of particles**. If you have 10 items in a bag, they can be arranged many more ways than 2 items in a bag. It is also related to the **number of possible levels at which the free energy can exist**. For example, if free energy is 4 J/mol, but this energy is contained in a 3 J level and a 1 J level, there are two energy levels at which the free energy can exist.

The different ways that the energy can be arranged are called “microstates.” The number of microstates is calculated based on the *number of energy levels*, the *energy of these levels*, and the *number of particles*.

One type of question you might be asked is whether **entropy increases or decreases in certain situations**.

Entropy increases with the following:

- **Increased volume**
  - Why: More possible arrangements (*and energy levels closer together*)
- **Heating**
  - Solids become liquids
  - Liquids/solids become gases
- **Solution** or mixture formed
  - *Unless: dissolving a gas in a liquid, or making a solution of electrolytes*
- **Decreased bond strength**
  - This happens if either: (1) charges decrease or (2) distances increase
- **Increased molecule flexibility**
  - Increases the number of vibrations
- \*You know that entropy **increased if  $S_{\text{reactants}} < S_{\text{products}}$**

Entropy, just like free energy and enthalpy, can be calculated by subtracting reactant values from product values:

$$\Delta S^{\circ} = \sum n_p S_{\text{products}}^{\circ} - \sum n_r S_{\text{reactants}}^{\circ}$$

If given enthalpy, temperature, and  $\Delta G$  (if given that you are at equilibrium,  $\Delta G=0$ ), you can calculate  $\Delta S$  as well.

### The Second Law of Thermodynamics

The second law of thermodynamics states that all spontaneous processes are associated with an increase in the entropy of the universe. All spontaneous processes increase the entropy of the universe.

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

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## Highlight 3: “Is the following reaction spontaneous?”

This kind of question shows up a lot! If given the signs of enthalpy change and entropy change, you can usually determine spontaneity based on the equation  $\Delta G = \Delta H - T\Delta S$ . For example, if enthalpy change is negative and entropy change is positive, free energy change will be negative, because a negative minus a positive is always a negative. (Think of this in terms of a number line: Start left of zero. Subtracting means moving to the left.) A negative minus a negative, however, could either be negative or positive. (Start left of zero. Move to the left negative digits – in other words, move to the right).

$\Delta H$	$\Delta S$	$\Delta G$
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-	+	-
+	-	+
-	-	Low T - High T +
+	+	Low T + High T -

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## Check Your Learning

1. Is  $\Delta S > 0$  or  $< 0$  for these reactions?
  - a.  $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$
  - b.  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
2. If  $\Delta H$  is \_\_\_\_ and  $\Delta S$  is \_\_\_\_,  $\Delta G$  is \_\_\_\_?
  - a. -, +
  - b. -, - (at low T)

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## Things You May Struggle With

1. If the forward reaction is spontaneous, the reverse reaction will be non-spontaneous, and vice versa.
2. Always convert temperature to Kelvin. Make sure that G, H, and S are all in J, or all in kJ, etc.
3. Forgetting to account for the number of moles of a particular reactant or product in calculating  $\Delta S'$  or  $\Delta G'$  from tabulated values
4. Remember, zero is the standard enthalpy (or free energy) of formation for elements
5. Be sure not to mix up  $\Delta G^\circ$  and  $\Delta G$ .

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That's all this week! Please reach out if you have any questions and don't forget to visit the Tutoring Center website for further information at [www.baylor.edu/tutoring](http://www.baylor.edu/tutoring). Answers to Check Your Learning are below.

1.
  - a.  $\Delta S < 0$
  - b.  $\Delta S < 0$
2.
  - a. -
  - b. -