

Thermochemistry Lecture Notes

During this unit of study, we will cover three main areas. A lot of this information is NOT included in your text book, which is a shame. Therefore, the notes you take in class (see below) are very important. The three main areas are

- **Reaction Energy:** Why is energy released by some reactions, and why is energy required to make other reactions occur?
- **Reaction Equilibrium:** Why don't all reactions convert 100% of the reactants to products? How can we describe and even change the ratio of products formed to reactants that remain?
 - **Reaction Rate:** What are the factors that affect the rate of a chemical reaction?

I. Reaction Energy

- a. The study of energy in chemical reactions is called **thermodynamics**, which literally means "changes in heat."
- b. The standard conditions for thermodynamics are
 - i. Standard temperature = 25 °C = 298 K
 - ii. Standard Pressure = 1 atm
 - iii. Notice that these are different than STP for gases (where ST=273 K and SP = 1 atm).
- c. All chemical reactions either release or require (absorb) energy when they occur. Another way to say this is that reactions either "give off" or "take in" energy.
- d. Heat energy is referred to in this course as **enthalpy (H)**.
 - i. Enthalpy is the heat absorbed or released by a system at constant pressure.
 - ii. It is impossible to measure enthalpy directly. Only changes in enthalpy are used in this course. We only use "ΔH" in this course. $\Delta H = H_{\text{final}} - H_{\text{initial}}$
 - iii. Units of heat energy. We will use joules (J) or kilojoules (kJ).
- e. System, surroundings, and universe
 1. The **system** is the chemical reaction under study.
 2. The **surroundings** is every place in the universe *except* the system.
 3. The **universe** is the system and the surroundings.
- f. Exothermic reactions.
 1. An **exothermic** reaction is a reaction in which heat is released by the system to the surroundings. From the perspective of the system, "heat is given off."
 2. For an exothermic reaction, the sign of ΔH is negative.
 3. When an reaction is exothermic (ΔH is negative), that is a **favorable** condition. Enthalpy is just one of the variables involved when predicting whether or not a reaction will occur, but reactions which release heat are more likely to occur than ones in which heat is required, all things being equal.
- g. Endothermic reactions
 1. An **endothermic** reaction is a reaction in which heat is absorbed by the system from the surroundings. From the perspective of the system, "heat is taken in."
 2. For an endothermic reaction, the sign of ΔH is positive.
 3. When an reaction is endothermic (ΔH is positive), that is an **unfavorable** condition. Enthalpy is just one of the variables involved when predicting

whether or not a reaction will occur, but reactions which absorb heat are less likely to occur than ones in which heat is released, all things being equal.

vii. Qualitative example problems

Example problem: Consider cooking a pot of soup over a stove's flame burner. Explain the transfer of heat using the terms learned in class.

Answer: The stove's gas is reacting with the air in an exothermic reaction. The soup is heated, and that is an endothermic process. So, if you consider the soup the system, this is an endothermic process. On the other hand, if the burner is considered the system, then the reaction is considered exothermic.

Example problem: When ice melts because you leave it out on the table, is this an endothermic or exothermic process?

Answer: As ice melts, it has to absorb heat. Therefore, if ice is defined as the system, then the melting of ice is endothermic.

Example problem: When water freezes after you put it in the freezer, is this an endothermic or exothermic process?

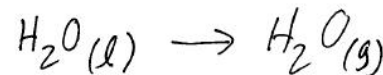
Answer: As water freezes, it must get rid of (release, give off) heat. Therefore, if the water is considered the system, then the freezing of water is exothermic.

viii. Quantitative example problems using enthalpy data

1. Enthalpy is impossible to measure.
2. However, the change in enthalpy, ΔH, is possible to measure through calorimetry.
3. We use ΔH[°]_f, the standard enthalpy of formation, to determine the change in enthalpy when a substance is formed from its elements in their standard states.
4. Therefore, each element in its standard state is assigned a value of "0" for its ΔH[°]_f.
5. All other reactions are computed by subtracting the sum of the reactants' ΔH[°]_f from the sum of the products' ΔH[°]_f.

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

Example problem #1: Consider the evaporation of water:



Find the standard change in enthalpy for this reaction, and state whether the reaction is exothermic or endothermic. Use the table of standard enthalpies of formation.

$$\Delta H_{\text{rxn}}^{\circ} = [\text{PRODUCTS}] - [\text{REACTANTS}]$$

$$= [-241.82] - [-285.83]$$

$$\Delta H = 44.01 \text{ kJ/mol}$$

ENDOTHERMIC, because heat is taken in (ΔH is positive).
THIS makes sense, because energy is required in order for liquid H_2O to become gaseous H_2O .

Example problem #2: Consider the condensation of water vapor:



Find the standard change in enthalpy for this reaction, and state whether the reaction is exothermic or endothermic. Use the table of standard enthalpies of formation.

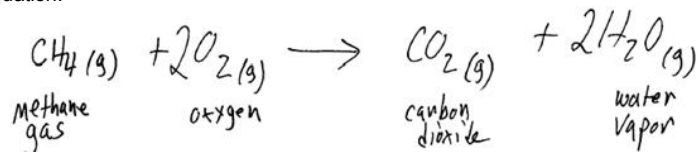
$$\Delta H_{\text{rxn}}^{\circ} = [\text{PRODUCTS}] - [\text{REACTANTS}]$$

$$= [-285.83] - [-241.82]$$

$$\Delta H^{\circ} = -149.73 = -44.01 \text{ kJ/mol}$$

EXOTHERMIC, because heat is released.
 ΔH is negative, which makes sense: you have to remove energy from water vapor/steam in order to make it a liquid.

Example problem #3: Burning natural gas in the lab is described by the following chemical equation.



Find the standard change in enthalpy for this reaction, and state whether the reaction is exothermic or endothermic. Use the table of standard enthalpies of formation.

$$\Delta H_{\text{rxn}}^{\circ} = [\text{PRODUCTS}] - [\text{REACTANTS}]$$

$$= [2 \times \text{H}_2\text{O}(\text{g}) + \text{CO}_2] - [\text{CH}_4 + 2 \times \text{O}_2]$$

$$= [2 \times (-241.82) + (-393.5)] - [(-74.8) + (2 \times 0)]$$

$$= [(-483.64) + (-393.5)] - [(-74.8) + 0]$$

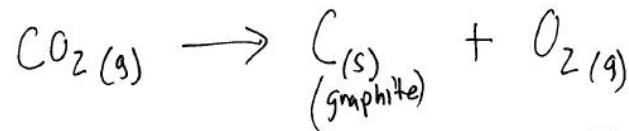
$$= [-877.14] - [-74.8]$$

$$= -877.14 + 74.8$$

$$\Delta H = -802.3 \text{ kJ/mol}$$

ΔH is (-), thus exothermic.
As you would expect, burning gas gives off heat!

Example problem #4: Consider the following chemical equation:



Find the standard change in enthalpy for this reaction, and state whether the reaction is exothermic or endothermic. Use the table of standard enthalpies of formation.

$$\Delta H_{\text{rxn}}^{\circ} = [\text{PRODUCTS}] - [\text{REACTANTS}]$$

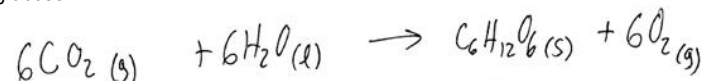
$$= [0 + 0] - [-393.5]$$

$$= 393.5 \text{ kJ/mol}$$

Extremely endothermic.
This huge endothermicity explains why carbon dioxide is unlikely to "break down" into carbon & oxygen gas.

Example problem #5: Consider the following chemical equation for the photosynthesis of

glucose:



Find the standard change in enthalpy for this reaction, and state whether the reaction is exothermic or endothermic. Use the table of standard enthalpies of formation.

$$\begin{aligned} \Delta H_{\text{rxn}}^{\circ} &= [\text{PRODUCTS}] - [\text{REACTANTS}] \\ &= [(\text{C}_6\text{H}_{12}\text{O}_6) + (6 \times \text{O}_2)] - [(6 \times \text{CO}_2) + (6 \times \text{H}_2\text{O})] \\ &= [(-1273.02) + (6 \times 0)] - [(6 \times -393.5) + (6 \times -285.8)] \\ &= [-1273.02] - [-2361 + -1714.98] \\ &= [-1273.02] - [-4075.98] \\ &= 2802.96 = \boxed{2803.0 \text{ kJ/mol}} \text{ endothermic.} \end{aligned}$$

e. Entropy

- The randomness or disorder of a system is the **entropy (S)** of that system.
- Only *changes* in entropy are used in this course. We only use "ΔS" in this course.
- When a reaction has a positive ΔS, that entropy change is a **favorable** condition.
 - Entropy is just one of the variables involved when predicting whether or not a reaction will occur, but reactions which increase entropy are more likely to occur than ones in which the entropy decreases, all things being equal.
 - Entropy increases - and therefore the sign of ΔS is positive - when the system becomes more disordered.
 - Some examples of increasing entropy:
 - the system becomes more disordered when the reaction causes an increase in the number of particles, such as occurs during a decomposition reaction
 - the system becomes more disordered when matter changes phase from a more orderly phase of matter to a less orderly phase of matter during the course of the reaction, such as occurs during an explosion that produces gases from a solid or liquid starting material
- When a reaction has a negative ΔS, that entropy change is an **unfavorable** condition.
 - Entropy is just one of the variables involved when predicting whether or not a reaction will occur, but reactions which decrease entropy are less likely to occur than ones in which the entropy increases, all things being

equal.

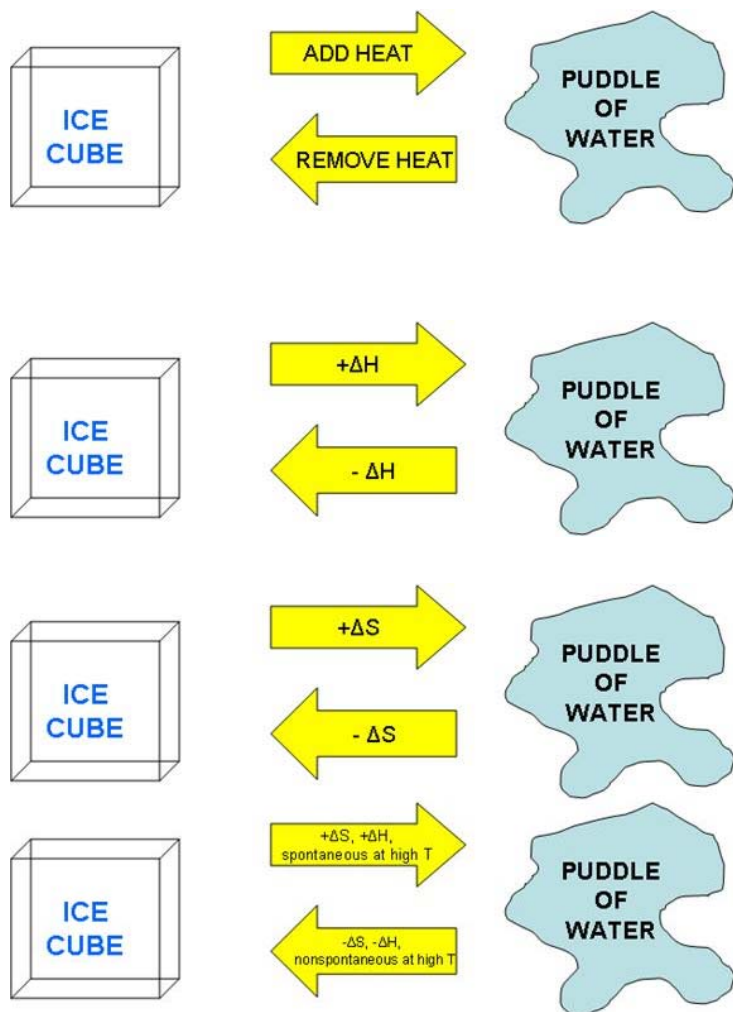
- Entropy decreases - and therefore the sign of ΔS is negative - when the system becomes more orderly (that is, more organized and *less* disordered).
 - Some examples of decreasing entropy
 - the system becomes more ordered (*less* disorganized) when the reaction causes an decrease in the number of particles. During a synthesis (a.k.a. combination) reaction, there is a decrease in the number of particles.
 - the system becomes more ordered (*less* disorganized) when matter changes phase from a disorderly phase of matter to a more orderly phase of matter during the course of the reaction. For instance, a reaction that creates a liquid or a solid from a gas would create a more orderly form of matter from a more disorderly form of matter.

- Units of ΔS: J/(K•mol)
- Qualitative example problems
- Quantitative example problems
- Gibbs free energy and reaction spontaneity
 - The **spontaneity** of a chemical reaction is the possibility of the reaction occurring or not without the aid of outside energy.
 - If a reaction occurs without a net input of energy, it is called "**spontaneous**." This type of reaction actually releases ("gives off") useful energy.
 - If a reaction requires energy in order to occur, it is called "**nonspontaneous**." This type of reaction takes in energy when it occurs.
 - Depiction of spontaneity with a reaction energy diagram
 - Gibbs free energy** is the energy that is "free" to do work. "Free" *does not* mean "costs nothing;" rather, it means "available," as in "Are you *free* tonight at around 8:00?"
 - It is impossible to measure directly. Only *changes* in Gibbs free energy are used in this course. We only use "ΔG" in this course.
 - Units of Gibbs free energy: most often kJ/mol.
 - Important formula: **ΔG = ΔH - TΔS**
 - This formula shows that ΔG depends on the enthalpy (ΔH) and the entropy (ΔS)
 - Remember, when ΔH is negative that is a favorable condition, whereas a positive ΔH is unfavorable.
 - Remember, when ΔS is positive that is a favorable condition, whereas a negative ΔS is unfavorable.
 - T must be in Kelvins
 - When the sign of ΔG for some reaction is **negative**, the reaction is **spontaneous**.
 - When the sign of ΔG for some reaction is **positive**, the reaction is **nonspontaneous**.
 - Helpful table summarizing favorability and spontaneity

END RESULT	Sign of ΔH	Sign of ΔS	Overall Sign of ΔG
Spontaneous	- (favorable)	+ (favorable)	-
Depends on T	- (favorable)	- (unfavorable)	?
Depends on T	+ (unfavorable)	+ (favorable)	?

Nonspontaneous	+ (unfavorable)	- (unfavorable)	+
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5. Helpful example that summarizes whether or not a temperature-dependent reaction is spontaneous



g. Example problems

- Qualitative prediction of a reaction's enthalpic *favorability*
- Qualitative prediction of a reaction's entropic *favorability*
- Qualitative prediction of reaction *spontaneity*
- Quantitative prediction of reaction spontaneity