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Thermodynamics: Enthalpy

Big Idea: Spontaneity

A spontaneous change is a change that occurs without outside intervention. All spontaneous changes lead to equilibrium.

Identify each change below as *spontaneous* or *nonspontaneous* based on the information given.

- 1. A piece of hot metal is placed in a beaker of cold water. Heat is transferred from the hot metal to the cooler water until thermal equilibrium is reached.
- 2. A gas diffuses throughout a room.
- 3. A sample of hydrogen peroxide decomposes in the presence of a catalyst.
- 4. A handful of calcium carbonate is placed in a small amount of water. A tiny fraction of the sample dissolves until equilibrium is reached.
- 5. Sodium bicarbonate decomposes when heated.

Big Idea: Enthalpy

Enthalpy, *H*, is the heat content of a substance. In experiments at constant pressure, the enthalpy change, ΔH , is the difference between the final and initial enthalpy content. Negative values of ΔH imply that heat is transferred from the system to the surroundings (heat is released); exothermic processes/reactions have negative values of ΔH . Positive values of ΔH imply that heat is transferred from the system (heat is absorbed); endothermic processes/reactions have positive values of ΔH .

Identify the sign of ΔH for each process/reaction below.

- 6. An ionic compound is placed in water, and you notice that upon dissolution, the cup feels cold.
- 7. Water decomposes into hydrogen and oxygen gas only if an outside source of energy is present.
- 8. An ionic compound is placed in water, and you notice that upon dissolution, the cup feels warm.
- 9. A spontaneous chemical reaction is accompanied by the release of light and heat.

Big Idea: Enthalpy Changes for Chemical Reactions

Enthalpy changes for chemical reactions can be measured in the laboratory using a calorimeter. The amount of heat absorbed or released is dependent on the type of reaction, the amounts of compounds, and the state of the compounds. The ΔH values for reactions that are the reverse of each are the same magnitude (same number) but with opposite signs.

Calculate the ΔH associated with each of the following reactions.

- 10. The formation of one mole of water vapor from one mole of hydrogen gas and half a mole of oxygen gas releases 241.8 kJ of energy. How much energy would be released in the formation of two moles of water vapor?
- 11. The formation of one mole of liquid water from one mole of hydrogen gas and half a mole of oxygen gas releases 285.8 kJ of energy. Why is more energy released when liquid water is formed than when water vapor is formed? Hint: consider the energy absorbed/released when water vapor condenses!

- 12. Solid sucrose, $C_{12}H_{22}O_{11}$, is oxidized in air to gaseous CO_2 and liquid H_2O . The oxidation of one mole of solid sucrose releases 5645 kJ of energy.
 - a. Write a balanced equation for the oxidation of one mole of solid sucrose according to the given information.
 - b. Write the ΔH term (ΔH =) for this reaction, including the correct sign.
 - c. What is the enthalpy change for the oxidation of 5.00 g (1 teaspoon) of sugar?

Big Idea: Hess's Law

Measuring the ΔH of a reaction is not always possible in the laboratory, so a calculation based on Hess's law is used. Hess's law states that if a reaction is the sum of two or more other reactions, ΔH for the overall process is the sum of the ΔH values of those reactions.

For questions 13 and 14, show that equation 1 and 2 sum to equation 3 by crossing out all species that appear on *both* sides of the arrow. Then calculate the unknown ΔH .

13.

Equation 1:	$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$	$\Delta H_1 = ?$
Equation 2:	$\underline{CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)}$	$\Delta H_2 = -283.0 \text{ kJ}$
Equation 3:	$C(s) + O_2(g) \longrightarrow CO_2(g)$	$\Delta H_3 = -393.5 \text{ kJ}$

14.

Equation 1:	$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(\ell)$	$\Delta H_1 = -285.8 \text{ kJ}$
Equation 2:	$H_20(\ell) \longrightarrow H_20(g)$	$\Delta H_2 = ?$
Equation 3:	$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g)$	$\Delta H_{ m 3}=-$ 241.8 kJ

15. Show how equations 1-3 sum to produce the equation below. You may have to flip a reaction and/or multiply an entire reaction by a coefficient!

 $C(s) + 2 H_2(g) \longrightarrow CH_4(g)$

- Equation 1: $C(s) + O_2(g) \longrightarrow CO_2(g)$ Equation 2: $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)$ Equation 3: $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)$
- 16. Now use the ΔH values for each reaction to determine the unknown ΔH value. Whatever you did to the equation above (flip, multiply through by a coefficient, etc.) MUST be reflected in the ΔH value, too.

 $C(s) + 2 H_2(g) \longrightarrow CH_4(g) \qquad \Delta H = ?$

Equation 1:	$C(s) + O_2(g) \longrightarrow CO_2(g)$	$\Delta H_1 = -393.5 \text{ k}$
Equation 2:	$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(\ell)$	$\Delta H_2 = -285.8 \text{ km}$
Equation 3:	$CH_4(g) + 2 O_2(g) \longrightarrow CO_2(g) + 2 H_2O(\ell)$	$\Delta H_3 = -890.3 \text{ kJ}$

17. Use Hess's law to calculate the enthalpy change for the formation of carbon disulfide (liquid) from solid carbon and solid sulfur.

$C(s) + O_2(g) \longrightarrow CO_2(g)$	$\Delta H = -393.5 \text{ kJ}$
$S(s) + O_2(g) \longrightarrow SO_2(g)$	$\Delta H = -296.8 \text{ kJ}$
$CS_2(\ell) + 3 O_2(g) \longrightarrow CO_2(g) + 2 SO_2(g)$	$\Delta H = -1103.9 \text{ kJ}$
$C(s) + 2 S(s) \longrightarrow CS_2(\ell)$	$\Delta H = ?$

Big Idea: Standard Molar Enthalpies of Formation

The formation of one mole of a compound from its elements has an associated enthalpy change: the standard molar enthalpy of formation, $\Delta H_{\rm f}^{\circ}$. The degree symbol indicates that the elements were in their standard states, meaning that at 1 atm and a specified temperature (usually 298 K), the elements were in their most stable physical form. Note that the standard enthalpy formation for an element in its standard state is zero.

- 18. Most standard molar enthalpies of formation are negative. What does this imply about the energy of formation of a compound? Is it an exothermic or endothermic process?
- 19. Consider HF(g) and HI(g).
 - a. Write the equation for the formation of each compound from its elements at 1 atm and 298 K.
 - b. The $\Delta H_{\rm f}^{\circ}$ for HF is -273.3 kJ/mol, while the $\Delta H_{\rm f}^{\circ}$ for HI is 26.5 kJ/mol. i. Which formation is more exothermic?
 - ii. Which formation results in a compound that has the lowest potential energy?
 - iii. Which compound is more stable?

Big Idea: Enthalpy Change for a Reaction

To calculate the enthalpy change for a reaction under standard conditions, use the following equation:

$$\Delta H_{rxn}^{\circ} = \Sigma [\Delta H_{f}^{\circ}(products)] - \Sigma [\Delta H_{f}^{\circ}(reactants)]$$

Remember that Σ is the capital Greak letter sigma, and it means "sum." So, to find the overall ΔH° of a reaction, sum the $\Delta H_{f^{\circ}}$ of the products and subtract from that the sum of the $\Delta H_{f^{\circ}}$ of the reactants. Make sure to multiply every $\Delta H_{f^{\circ}}$ by the number of moles of that compound in the equation!

20. Find the ΔH_{rxn}° for the following reaction using the ΔH_{f}° provided.

 $CO_2(g)$

$CaCO_3(s) \longrightarrow CaO(s)$	+ $CO_2(g)$ $\Delta H^o_{rxn} = ?$
Compound	ΔH_f° (kJ/mol)
CaCO ₃ (s)	-1207.6
CaO(s)	- 635.1

- 393.5

21. Nitroglycerin is a powerful explosive that forms four different gases when detonated:

 $2 C_3 H_5(NO_3)_3(\ell) \longrightarrow 3 N_2(g) + \frac{1}{2} O_2(g) + 6 CO_2(g) + 5 H_2O(g)$

Calculate the enthalpy change for the reaction. The enthalpy of formation of nitroglycerin, $\Delta H_{\rm f}^{\circ}$, is -364 kJ/mol. Use the table provided to find the other $\Delta H_{\rm f}^{\circ}$ values.

Big Idea: Using ΔH_{rxn}° to Determine If a Reaction is Reactant- or Product-Favored

Most product-favored reactions have negative values of ΔH_{rxn}° . There are some exceptions, which we'll discuss later, but this is a good generalization for now.

Calculate ΔH_{rxn}° for each of the following reactions and decide whether the reaction may be product- or reactant-favored.

22.2HBr(g) \rightarrow H₂(g) + Br₂(g)

23. C(diamond) \rightarrow C(graphite)