

9.4: Enthalpy and Chemical Reactions

Learning Objectives

- Define *enthalpy*.
- Properly express the enthalpy change of chemical reactions.
- Explain how enthalpy changes are measured experimentally.

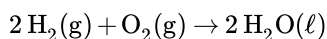
Now that we have shown how energy, work, and heat are related, we are ready to consider energy changes in chemical reactions. A fundamental concept is that *every chemical reaction occurs with a concurrent change in energy*. Now we need to learn how to properly express these energy changes.

Our study of gases in Chapter 6, and our definition of work in Section 7.3, indicate that conditions like pressure, volume, and temperature affect the energy content of a system. What we need is a definition of energy that holds when some of these conditions are specified (somewhat similar to our definition of standard temperature and pressure in our study of gases). We define the **enthalpy change** (ΔH) as the heat of a process when pressure is held constant:

$$\Delta H \equiv q \text{ at constant pressure}$$

The letter H stands for "enthalpy," a kind of energy, while the Δ implies a change in the quantity. We will always be interested in the change in H , rather than the absolute value of H itself.

When a chemical reaction occurs, there is a characteristic change in enthalpy. The enthalpy change for a reaction is typically written after a balanced chemical equation and on the same line. For example, when two moles of hydrogen react with one mole of oxygen to make two moles of water, the characteristic enthalpy change is 570 kJ. We write the equation as



with $\Delta H = -570 \text{ kJ}$

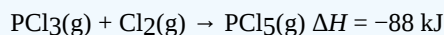
A chemical equation that includes an enthalpy change is called a **thermochemical equation**. A thermochemical equation is assumed to refer to the equation in molar quantities, which means it must be interpreted in terms of moles, not individual molecules.

✓ Example 9.4.1

Write the thermochemical equation for the reaction of $\text{PCl}_3(\text{g})$ with $\text{Cl}_2(\text{g})$ to make $\text{PCl}_5(\text{g})$, which has an enthalpy change of -88 kJ .

Solution

The thermochemical equation is



? Exercise 9.4.1

Write the thermochemical equation for the reaction of $\text{N}_2(\text{g})$ with $\text{O}_2(\text{g})$ to make $2\text{NO}(\text{g})$, which has an enthalpy change of 181 kJ .

Answer



You may have noticed that the ΔH for a chemical reaction may be positive or negative. The number is assumed to be positive if it has no sign; a $+$ sign can be added explicitly to avoid confusion. A chemical reaction that has a positive ΔH is said to be **endothermic**, while a chemical reaction that has a negative ΔH is said to be **exothermic**.

What does it mean if the ΔH of a process is positive? It means that the system in which the chemical reaction is occurring is gaining energy. If one considers the energy of a system as being represented as a height on a vertical energy plot, the enthalpy

change that accompanies the reaction can be diagrammed as in part (a) of Figure 9.4.1 Reaction Energy: the energy of the reactants has some energy, and the system increases its energy as it goes to products. The products are higher on the vertical scale than the reactants. Endothermic, then, implies that the system *gains*, or absorbs, energy.

An opposite situation exists for an exothermic process, as shown in part (b) of Figure 9.4.1 - Reaction Energy. If the enthalpy change of a reaction is negative, the system is losing energy, so the products have less energy than the reactants, and the products are lower on the vertical energy scale than the reactants are. Exothermic, then, implies that the system *loses*, or gives off, energy.

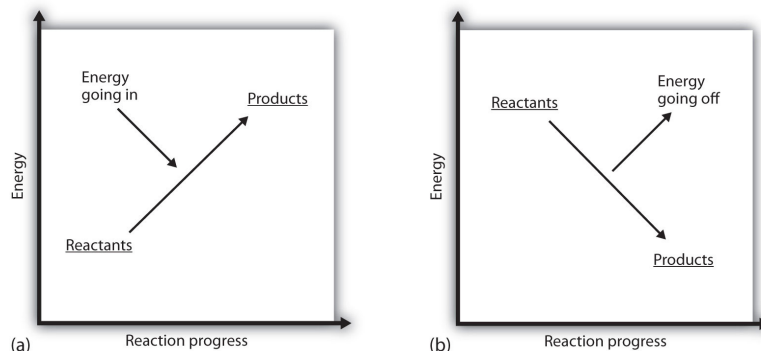
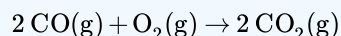


Figure 9.4.1 Reaction Energy (a) In an endothermic reaction, the energy of the system increases (i.e., moves higher on the vertical scale of energy). (b) In an exothermic reaction, the energy of the system decreases (i.e., moves lower on the vertical scale of energy).

✓ Example 9.4.2

Consider this thermochemical equation.



with $\Delta H = -565 \text{ kJ}$

Is it exothermic or endothermic? How much energy is given off or absorbed?

Solution

By definition, a chemical reaction that has a negative ΔH is exothermic, meaning that this much energy—in this case, 565 kJ—is given off by the reaction.

? Exercise 9.4.2

Consider this thermochemical equation.



Is it exothermic or endothermic? How much energy is given off or absorbed?

Answer

Endothermic; 42 kJ are absorbed.

How are ΔH values measured experimentally? Actually, ΔH is not measured; q is measured. But the measurements are performed under conditions of constant pressure, so ΔH is equal to the q measured.

Experimentally, q is measured by taking advantage of the equation

$$q = mc\Delta T$$

We pre-measure the mass of the chemicals in a system. Then we let the chemical reaction occur and measure the change in temperature (ΔT) of the system. If we know the specific heat of the materials in the system (typically we do), we can calculate q . That value of q is numerically equal to the ΔH of the process, which we can scale up to a molar scale. The container in which the system resides is typically insulated, so any energy change goes into changing the temperature of the system, rather than being

leaked from the system. The container is referred to as a **calorimeter**, and the process of measuring changes in enthalpy is called **calorimetry**.

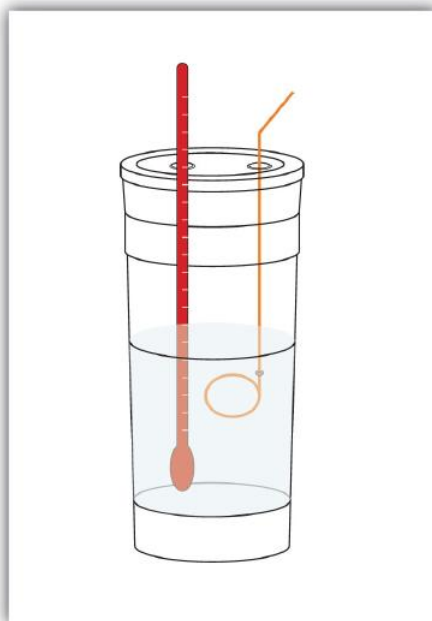
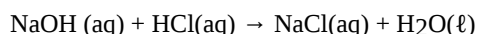


Figure 9.4.2 Calorimeters. A simple calorimeter can be constructed from some nested foam coffee cups, a cover, a thermometer, and a stirrer.

For example, suppose 4.0 g of NaOH, or 0.10 mol of NaOH, are dissolved to make 100.0 mL of aqueous solution; while 3.65 g of HCl, or 0.10 mol of HCl, are dissolved to make another 100.0 mL of aqueous solution. The two solutions are mixed in an insulated calorimeter, a thermometer is inserted, and the calorimeter is covered (See Figure 9.4.2 - Calorimeters for an example setup). The thermometer measures the temperature change as the following chemical reaction occurs:



An observer notes that the temperature increases from 22.4°C to 29.1°C. Assuming that the heat capacities and densities of the solutions are the same as those of pure water, we now have the information we need to determine the enthalpy change of the chemical reaction. The total amount of solution is 200.0 mL, and with a density of 1.00 g/mL, we thus have 200.0 g of solution. Using the equation for q , we substitute for our experimental measurements and the specific heat of water (in Table 9.4.1 of Section 7.3).

$$q = (200.0 \text{ g})(4.184 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}})(6.7 ^\circ\text{C})$$

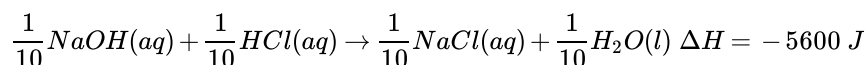
Solving for q , we get

$$q = 5600 \text{ J} \equiv \Delta H \text{ for the reaction}$$

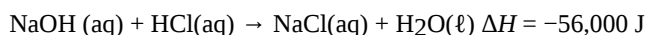
The heat q is equal to the ΔH for the reaction because the chemical reaction occurs at constant pressure. However, the reaction is giving off this amount of energy, so the actual sign on ΔH is negative:

$$\Delta H = -5,600 \text{ J for the reaction}$$

Thus, we have the following thermochemical equation for the chemical reaction that occurred in the calorimeter:



The 1/10 coefficients are present to remind us that we started with one-tenth of a mole of each reactant, so we make one-tenth of a mole of each product. Typically, however, we report thermochemical equations in terms of moles, not one-tenth of a mole. To scale up to molar quantities, we must multiply the coefficients by 10. However, when we do this, we get 10 times as much energy. Thus, we have



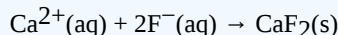
The ΔH can be converted into kJ units, so our final thermochemical equation is



We have just taken our experimental data from calorimetry and determined the enthalpy change of a chemical reaction. Similar measurements on other chemical reactions can determine the ΔH values of any chemical reaction you want to study.

✓ Example 9.4.3

A 100 mL solution of 0.25 mol of $\text{Ca}^{2+}(\text{aq})$ was mixed with 0.50 mol of $\text{F}^{-}(\text{aq})$ ions, and CaF_2 was precipitated:



The temperature of the solution increased by 10.5°C . What was the enthalpy change for the chemical reaction? What was the enthalpy change for the production of 1 mol of CaF_2 ? Assume that the solution has the same density and specific heat as water.

Solution

Because we are given ΔT directly, we can determine the heat of the reaction, which is equal to ΔH :

$$q = (100 \text{ g}) \left(4.184 \frac{\text{J}}{\text{g} \cdot ^{\circ}\text{C}} \right) (10.5 ^{\circ}\text{C})$$

Solving for q , we get

$$q = 4,400 \text{ J}$$

Therefore, $\Delta H = -4,400 \text{ J}$.

According to the stoichiometry of the reaction, exactly 0.25 mol of CaF_2 will form, so this quantity of heat is for 0.25 mol. For 1 mol of CaF_2 , we need to scale up the heat by a factor of four:

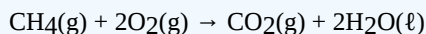
$$q = 4,400 \text{ J} \times 4 = 17,600 \text{ J for 1 mol CaF}_2$$

On a molar basis, the change in enthalpy is

$$\Delta H = -17,600 \text{ J} = -17.6 \text{ kJ}$$

? Exercise 9.4.3

In a calorimeter at constant pressure, 0.10 mol of $\text{CH}_4(\text{g})$ and 0.20 mol of $\text{O}_2(\text{g})$ are reacted.



The reaction warms 750.0 g of H_2O by 28.4°C . What is ΔH for the reaction on a molar scale?

Answer

-891 kJ

Key Takeaways

- Every chemical reaction occurs with a concurrent change in energy.
- The change in enthalpy equals heat at constant pressure.
- Enthalpy changes can be expressed by using thermochemical equations.
- Enthalpy changes are measured by using calorimetry.

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