CHAPTER 2

Environmental Chemistry

2.1 INTRODUCTION

Almost every pollution problem that we face has a chemical basis. Even the most qualitative descriptions of such problems as the greenhouse effect, ozone depletion, toxic wastes, groundwater contamination, air pollution, and acid rain, to mention a few, require at least a rudimentary understanding of some basic chemical concepts. And, of course, an environmental engineer who must design an emission control system or a waste treatment plant must be well grounded in chemical principles and the techniques of chemical engineering. In this brief chapter, the topics have been selected with the goal of providing only the essential chemical principles required to understand the nature of the pollution problems that we face and the engineering approaches to their solutions.

2.2 STOICHIOMETRY

When a chemical reaction is written down, it provides both qualitative and quantitative information. Qualitatively, we can see what chemicals are interacting to produce what end products. Quantitatively, the principle of conservation of mass can be applied to give information about how much of each compound is involved to produce the
results shown. The balancing of equations so that the same number of each kind of atom appears on each side of the equation and the subsequent calculations, which can be used to determine amounts of each compound involved, is known as stoichiometry. The first step is to balance the equation. For example, suppose we want to investigate the combustion of methane (CH₄), the principal component of natural gas and a major greenhouse gas. Methane combines with oxygen to produce carbon dioxide and water, as the following reaction suggests:

\[ \text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]

The equation is not balanced. One atom of carbon appears on each side, which is fine, but there are four atoms of hydrogen on the left and only two on the right, and there are only two atoms of oxygen on the left while there are three on the right. We might try to double the water molecules on the right to balance the hydrogen on each side, but then there would be an imbalance of oxygen with two on the left and four on the right. So try doubling the oxygen on the left. This sort of trial-and-error approach to balancing simple reactions usually converges quickly. In this instance the following is a balanced equation with the same number of C, H, and O atoms on each side of the arrow:

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]

This balanced chemical equation can be read as follows: One molecule of methane reacts with two molecules of oxygen to produce one molecule of carbon dioxide and two molecules of water. It is of more use, however, to be able to describe this reaction in terms of the mass of each substance (that is, how many grams of oxygen are required to react with how many grams of methane, and so on). To do so requires that we know something about the mass of individual atoms and molecules.

The atomic weight of an atom is the mass of the atom measured in atomic mass units (amu), where one amu is defined to be exactly one-twelfth the mass of a carbon atom having six protons and six neutrons in its nucleus. While this might suggest that if we look up the atomic weight of carbon we would expect to find it to be exactly 12 amu, that is not the case. All carbon atoms do have six protons, but they do not all have six neutrons, so they do not all have the same atomic weight. Atoms having the same number of protons but differing numbers of neutrons are called isotopes. What is reported in tables of atomic weights, such as Table 2.1, is the average based on the relative abundance of different isotopes found in nature. Also shown in Table 2.1 is the atomic number, which is the number of protons in the nucleus. All isotopes of a given element have the same atomic number.

The molecular weight of a molecule is simply the sum of the atomic weights of all of the constituent atoms. If we divide the mass of a substance by its molecular weight, the result is the mass expressed in moles (mol). Usually the mass is expressed in grams, in which case the moles are g-moles; in like fashion, if the mass is expressed in pounds, the result would be lb-moles. In this text, all moles will be assumed to be g-moles. One g-mole contains \(6.02 \times 10^{23}\) molecules (Avogadro’s number), while one lb-mole is made up of \(2.7 \times 10^{26}\) molecules.

\[ \text{Moles} = \frac{\text{Mass}}{\text{Molecular weight}} \]
We already know that there are 44 grams per mole of CO\textsubscript{2}, so we do not need to recalculate that. Two moles of butane (2 mol \times 58 g/mol = 116 g) yields 8 moles of carbon dioxide (8 mol \times 44 g/mol = 352 g CO\textsubscript{2}), so we can set up the following proportion:

\[
\frac{116 \text{ g C}_4\text{H}_{10}}{100 \text{ g C}_4\text{H}_{10}} = \frac{352 \text{ g CO}_2}{X \text{ g CO}_2}
\]

To express the preceding methane reaction in grams, we need first to find the number of grams per mole for each substance. Using Table 2.1, we find that the atomic weight of C is 12, H is 1, and O is 16. Notice that these values have been rounded slightly, which is common engineering practice. Thus, the molecular weights, and hence the number of grams per mole, are:

- CH\textsubscript{4} = 12 + 4 \times 1 = 16 g/mol
- O\textsubscript{2} = 2 \times 16 = 32 g/mol
- CO\textsubscript{2} = 12 + 2 \times 16 = 44 g/mol
- H\textsubscript{2}O = 2 \times 1 + 16 = 18 g/mol

Summarizing these various ways to express the oxidation of methane, we can say:

- 1 molecule of methane + 2 molecules of oxygen \rightarrow 1 molecule of carbon dioxide + 2 molecules of water
- 1 mol of methane + 2 mol of oxygen \rightarrow 1 mol of carbon dioxide + 2 mol of water
- 16 g of methane + 64 g of oxygen \rightarrow 44 g of carbon dioxide + 36 g of water

Notice that mass is conserved in the last expression; that is, there are 80 grams on the left and 80 grams on the right.

**EXAMPLE 2.1 Combustion of Butane**

What mass of carbon dioxide would be produced if 100 g of butane (C\textsubscript{4}H\textsubscript{10}) is completely oxidized to carbon dioxide and water?

**Solution** First write down the reaction:

\[
\text{C}_4\text{H}_{10} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]

and then balance it

\[
2 \text{C}_4\text{H}_{10} + 13 \text{O}_2 \rightarrow 8 \text{CO}_2 + 10 \text{H}_2\text{O}
\]

Find the grams per mole for butane:

\[
\text{C}_4\text{H}_{10} = 4 \times 12 + 10 \times 1 = 58 \text{ g/mol}
\]

We already know that there are 44 grams per mole of CO\textsubscript{2}, so we do not need to recalculate that. Two moles of butane (2 mol \times 58 g/mol = 116 g) yields 8 moles of carbon dioxide (8 mol \times 44 g/mol = 352 g CO\textsubscript{2}). So we can set up the following proportion:

\[
\frac{116 \text{ g C}_4\text{H}_{10}}{352 \text{ g CO}_2} = \frac{X \text{ g C}_4\text{H}_{10}}{100 \text{ g C}_4\text{H}_{10}}
\]

Thus,

\[X = \frac{100 \times 352}{116} = 303 \text{ g of CO}_2 \text{ produced.}\]

Many environmental problems involve concentrations of substances dissolved in water. In Chapter 1 we introduced two common sets of units, mg/L and ppm. However, it is also useful to express concentrations in terms of molarity, which is simply the number of moles of substance per liter of solution. A 1 molar (1 M) solution has 1 mol of substance dissolved into enough water to make the mixture have a volume of 1 L. Molarity is related to mg/L concentrations by the following:

\[
\text{mg/L} = \text{Molarity (mol/L)} \times \text{Molecular weight (g/mol)} \times 10^3 \text{ (mg/g)}. \quad (2.3)
\]

The following example illustrates the use of molarity and at the same time introduces another important concept having to do with the amount of oxygen required to oxidize a given substance.

**EXAMPLE 2.2 Theoretical Oxygen Demand**

Consider a 1.67 \times 10^{-3} M glucose solution (C\textsubscript{6}H\textsubscript{12}O\textsubscript{6}) that is completely oxidized to CO\textsubscript{2} and H\textsubscript{2}O. Find the amount of oxygen required to complete the reaction.

**Solution** To find the oxygen required to oxidize this glucose completely, we first write a balanced equation, determine molecular weights, and find the mass of each constituent in the reaction:

\[
\text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{O}_2 \rightarrow 6 \text{CO}_2 + 6 \text{H}_2\text{O}
\]

Thus it takes 192 g of oxygen to oxidize 180 g of glucose. From (2.3), the concentration of glucose is

\[
\text{mg/L} = 1.67 \times 10^{-3} \text{ mol/L} \times 180 \text{ g/mol} \times 10^3 \text{ mg/g} = 300 \text{ mg/L}
\]

so the oxygen requirement would be

\[
300 \text{ mg/L glucose} \times \frac{192 \text{ g O}_2}{180 \text{ g glucose}} = 320 \text{ mg/L O}_2.
\]
If the chemical composition of a substance is known, then the amount of oxygen required to oxidize it to carbon dioxide and water can be calculated using stoichiometry, as was done in the preceding example. That oxygen requirement is known as the theoretical oxygen demand. If that oxidation is carried out by bacteria using the substance for food, then the amount of oxygen required is known as the biochemical oxygen demand, or BOD. The BOD will be somewhat less than the theoretical oxygen since some of the original carbon is incorporated into bacterial cell tissue rather than being oxidized to carbon dioxide. Oxygen demand is an important measure of the likely impact that wastes will have on a receiving body of water, and much more will be said about it in Chapter 5.

The convenience of using moles to describe amounts of substances also helps when calculating atmospheric concentrations of pollutants. It was Avogadro’s hypothesis, made back in 1811, that equal volumes of all gases, at a specified temperature and pressure, contain equal numbers of molecules. In fact, since 1 mol of any substance has Avogadro’s number of molecules, it follows that 1 mol of gas, at a specified temperature and volume, will occupy a predictable volume. At standard temperature and pressure (STP), corresponding to 0°C and 1 atm (760 mm of mercury, 101.3 kPa), 1 g-mole of an ideal gas occupies 22.4 L, or 0.0224 m³, and contains 6.02 × 10²³ molecules. This fact was used in Chapter 1 to derive relationships between concentrations expressed in µg/m³ and ppm (by volume).

Let us demonstrate the usefulness of Avogadro’s hypothesis for gases by applying it to a very modern concern: that is, the rate at which we are pouring carbon dioxide into the atmosphere as we burn up our fossil fuels.

**Example 2.3 Carbon Emissions from Natural Gas**

Worldwide combustion of methane CH₄ (natural gas) provides about 8.2 × 10¹⁴ kJ of energy per year. If methane has an energy content of 39 × 10³ kJ/m³ (at STP) what mass of CO₂ is emitted into the atmosphere each year? Also, express that emission rate as metric tons of carbon (not CO₂) per year. A metric ton, which is 1000 kg, is usually written as tonnes to distinguish it from the 2000-lb American, or short, tons.

**Solution**

We first need to express that consumption rate in moles. Converting kilojoules of energy into moles of methane is straightforward:

\[ \text{moles CH}_4 = \frac{8.2 \times 10^{14} \text{kJ/yr}}{39 \times 10^3 \text{kJ/m}^3} \times \frac{1}{22.4 \times 10^{-3} \text{m}^3/\text{mol}} = 9.4 \times 10^{13} \text{mol/yr} \]

- We know from the balanced chemical reaction given in (2.1) that each mole of CH₄ yields one mole of CO₂, so there will be 9.4 × 10¹³ mol of CO₂ emitted. Since the molecular weight of CO₂ is 44, the mass of CO₂ emitted is

\[ \text{Mass CO}_2 = 9.4 \times 10^{13} \text{mol/yr} \times 44 \text{g/mol} = 4.1 \times 10^{15} \text{g/yr} \]

To express these emissions as tonnes of C per year, we must convert grams to tonnes and then sort out the fraction of CO₂ that is carbon. The fraction of CO₂ that is C is simply the ratio of the atomic weight of carbon (12) to the molecular weight of carbon dioxide (44):

\[ \text{C emissions} = \frac{4.1 \times 10^{15} \text{g CO}_2/\text{yr} \times \frac{1 \text{kg}}{1000 \text{g}} \times \frac{1 \text{t}}{1000 \text{kg}} \times \frac{12 \text{g C}}{44 \text{g CO}_2}} = 1.1 \times 10^{13} \text{tonnes/yr} = 1.1 \text{gigatonne/yr} = 1.1 \text{Gt/yr} \]

The 1.1 × 10¹³ tonnes of carbon found in the preceding example is about 20 percent of the total, worldwide carbon emissions entering the atmosphere each year when fossil fuels (coal, oil, natural gas) are burned. As will be described in Chapter 8, the main worry about these emissions is their potential to increase the earth’s greenhouse effect.

### 2.3 ENTHALPY IN CHEMICAL SYSTEMS

Just as we used conservation of mass to balance chemical equations, we can use the conservation of energy to learn something about heat absorbed or released during chemical reactions. Since energy must be conserved, we should be able to track it from beginning to end. The first law of thermodynamics lets us say that the energy in the reactants on the left side of the equation, plus any heat added to the system, should equal the energy contained in the reaction products on the right side plus any work done during the reaction.

\[ U_1 + Q = U_2 + W \]  \hspace{1cm} (2.4)

where

- \( U_1 = \) Internal energy of the chemical system at the beginning
- \( U_2 = \) Internal energy at the end
- \( Q = \) heat absorbed during the reaction
- \( W = \) work done by the system during the reaction

While there are many forms of work that could be included in (2.4), our concern will be only with work that occurs when a system changes volume under constant pressure, which is typical of chemical reactions. Any possibility of electrical, magnetic, gravitational, or other forms work will be ignored. To analyze this work done by expansion, consider the cylinder in Figure 2.1, containing a volume of gas \( V \) exerting a constant pressure \( P \) against a piston with area \( A \). The force exerted by the gas on the piston is \( F = PA \). If the piston moves a distance \( d \), then, since work is force × distance, we can write

\[ W = Fd = PAd = (PV_f - PV_i) \]  \hspace{1cm} (2.5)

Substituting (2.5) into (2.4) and rearranging terms gives

\[ (U_2 + PV_f) - (U_1 + PV_i) = Q \]  \hspace{1cm} (2.6)

![Figure 2.1](image-url)

**Figure 2.1** Work done when a substance expands at constant pressure is \( PAV \).
As described in Chapter 1, the enthalpy, $H$, of a system is
\[ H = U + PV \] (2.7)
then
\[ H_2 - H_1 = \Delta H = Q \] (2.8)

That is, the change in enthalpy during a constant pressure reaction is equal to the heat absorbed by the system. When $\Delta H$ is positive, heat is absorbed and the reaction is said to be endothermic. When $\Delta H$ is negative, heat is liberated and the reaction is called exothermic. The change in enthalpy, $H_2 - H_1$, is called the heat of reaction.

As is usually the case for discussions about energy, it is changes in energy, or in this case enthalpy, that are of interest. For example, we can talk about the potential energy of an object as being its weight times its height above some reference elevation. Our choice of reference elevation does not matter as long as we are only interested in the change in potential energy as an object is raised against gravity from one height to another. Similarly, since changes in enthalpy during a chemical reaction are of interest, it does not really matter what reference conditions are chosen. Tabulated values of enthalpy are usually based on 1 atm of pressure and 25°C (298 K), in which case they are designated with the notation
\[ H^\circ_{298} = \text{Standard enthalpy} = \text{Enthalpy at } 1\text{ atm and } 298\text{ K} \] (2.9)

It is also assumed that the reference condition for pure elements is the stable state of the substance at 1 atm and 25°C. For example, the stable state of oxygen at 1 atm and 25°C is gaseous O\textsubscript{2}, so the standard enthalpy for O\textsubscript{2} (g), where (g) just means it is in the gaseous state, is defined to be zero. Similarly, mercury under those conditions is a liquid, so the standard enthalpy for Hg (l) is zero, where (l) means the liquid state. A table of standard enthalpies for a number of substances is presented in Table 2.2. More extensive lists can be found in chemical handbooks as well as more advanced environmental engineering texts.

The sum of the enthalpies of the reaction products minus the sum of the enthalpies of the reactants is called the heat of reaction. When it is negative, heat is liberated during the reaction; when it is positive, heat is absorbed. Since standard enthalpies are expressed as energy per mole, we must first balance the chemical reaction and then for each species multiply the number of moles by the standard enthalpy to get its total enthalpy.

**EXAMPLE 2.4** Gross Heat of Combustion for Methane

Find the heat of reaction when methane $\text{CH}_4$ is oxidized to $\text{CO}_2$ and liquid $\text{H}_2\text{O}$.

**Solution**

The reaction is written below, and beneath it are enthalpies taken from Table 2.2.

\[
\text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(l)
\]

\[
(-74.9) + 2 \times (-393.5) = 2 \times (-285.8)
\]

Notice that we have used the enthalpy of liquid water for this calculation. The heat of reaction is the difference between the total enthalpy of the reaction products and the reactants:

\[
[(-393.5) + 2 \times (-285.8)] - [(-74.9) + 2 \times (0)] = -890.2 \text{ kJ/mol of CH}_4
\]

Since the heat of reaction is negative, heat is released during combustion (i.e., the reaction is exothermic).

When a fuel is burned, some of the energy released ends up as latent heat in the water vapor produced. Usually that water vapor, along with the latent heat it contains, exits the stack along with all the other combustion gases, and its heating value is, in essence, lost. That leads to two different values of what is called the heat of combustion. The higher heating value (HHV) includes the heat released when water condenses in the liquid form, as was the case in Example 2.4. The HHV is also known as the gross heat of combustion. In the United States, the heat content of fossil fuels is usually expressed as this gross amount. The lower heating value (LHV), or net heat of combustion, is based on the heat of reaction when water is assumed to remain in the vapor state. Most fuel-efficient, modern furnaces used for space-heating buildings achieve the highest efficiencies (above 90 percent) by causing the combustion gases to cool enough to condense the water vapor before it leaves the stack. Not unexpectedly, these are called condensing furnaces. We will encounter these HHV and LHV concepts again in Chapter 9 when incineration of solid waste is described.

**EXAMPLE 2.5** The Net Heat of Combustion

Find the net heat of combustion when methane is burned.