CHAPTER 1

INTRODUCTION

1.1. Introduction

Chemical reactors are at the core of most chemical production plants. While reactors usually make up only a small fraction of the total cost of the plant, the proper design of reactors are usually of vital importance for the economic success of a chemical project because this is where most of the added value is generated. Poor design of a chemical reactor can lead to product loss, leading to economic loss for the entire duration of the plant. Innovations in reactor design, on the other hand, can ensure prolonged profitability in a competitive market.

Reactor design has become increasingly important for environmental reasons as well. As emission standards have become stricter over time, it has become increasingly relevant to avoid the production of harmful side products in the reactor, to avoid expensive remediation techniques downstream.

The mathematical description of a chemical reactor consists of up to five parts:

- The **reaction kinetics**. This part describes the rate of a chemical reaction as a function of the reaction conditions (temperature, concentration, pressure, etc). This part does not describe how those conditions are established.
- The **stoichiometry**. This is a bookkeeping of the number of moles of each compound that are produced or removed by chemical reactions.
- The **material balance**. This section contains the main assumptions that are made about the mass transfer phenomena that bring the reactants in and the reaction products out of the reactor. This part calculates the concentration or partial pressure of each compound at each location in the reactor.
- The **energy balance**. This section calculates the heat flows in and out of the reactor, and calculates the temperature at each location in the reactor.
- The **momentum balance**. This section calculates the pressure at each location in the reactor.

Many reactor models contain fewer than five parts. For instance, if a preliminary calculation establishes that the pressure drop across the reactor is too small to affect its behavior, the momentum balance can be omitted. Likewise, the energy balance can be omitted if the temperature is approximately constant.

The overall objective of this book is to teach you the basics of chemical kinetics and reactor design. The text is at the undergraduate level. More advanced chemical reactor designs, for instance, involving extremely fast reactions or mass transfer problems, are beyond the scope of this text, although Chapter 10 provides some introductory information on such designs, allowing the engineer to diagnose the need for more advanced design methods.

The objective of this chapter is to provide definitions and basic equations of reaction kinetics, stoichiometry, and material and energy balances.

1.2. Reaction Rates: Definitions

In general, a **reaction rate** in a **homogeneous phase** (i.e., non-catalytic) is defined as **the number of moles reacting per unit time and per unit volume** of the phase. Reaction rates are sometimes defined as the change of a concentration per unit time. However, this is only correct in the special case of a constant volume batch reactor, as will be explained in a later section.

More specifically, consider the following homogeneous reaction:

$$aA + bB \rightarrow cC + dD \qquad \text{reaction 1} \qquad (1.1)$$

The reaction rate **of compound A in reaction 1**, $r_{A,1}$, is defined as the number of moles of A **produced** per unit time, per unit volume, as a result of reaction 1. If reaction 1 goes from left to right then $r_{A,1}$ is negative. If reaction 1 is the only reaction involving compound A, then this reaction rate is the overall reaction rate of A, r_A.

The **rate of disappearance** of A in reaction 1, $-r_{A,1}$, is the number of moles of A disappearing per unit time and per unit volume as a result of reaction 1.

Example 1.1:

500 mol ethylene gas is fed to a tank with volume 5 m^3, and irradiated with ultraviolet light for 20 seconds. Under the influence of the ultraviolet light, part of the ethylene polymerizes, and only 300 mol ethylene remains in the tank. What is the reaction rate of ethylene during the irradiation?

Solution:

The number of moles that reacted is 500 – 300 = 200 mol. This occurred over a volume of 5 m^3, during a reaction time of 20 s. Hence, the reaction rate is 200 mol/(5 m^3 × 20 s) = **2 mol m^{-3} s^{-1}**.

If the stoichiometric constants of each compound taking part in a reaction are different, then the reaction rate of each compound is different. Reaction rates are proportional to the stoichiometric constants:

$$\frac{-r_\mathrm{A}}{a} = \frac{-r_\mathrm{B}}{b} = \frac{r_\mathrm{C}}{c} = \frac{r_\mathrm{D}}{d} \tag{1.2}$$

Equation (1.2) also defines the **overall rate of reaction 1**:

$$r_1 = \frac{-r_\mathrm{A}}{a} = \frac{-r_\mathrm{B}}{b} = \frac{r_\mathrm{C}}{c} = \frac{r_\mathrm{D}}{d} \tag{1.3}$$

The disadvantage of the practice of defining reaction rates per reaction and not per reacting compound in the reaction is that the value of the reaction rate is arbitrary, as it depends on the choice of the stoichiometric constants. For instance, if we define reaction 2 as:

$$2a\mathrm{A} + 2b\mathrm{B} \rightarrow 2c\mathrm{C} + 2d\mathrm{D} \qquad \text{reaction 2} \tag{1.4}$$

then the overall rate of reaction 2 is defined as:

$$r_2 = \frac{-r_\mathrm{A}}{2a} = \frac{-r_\mathrm{B}}{2b} = \frac{r_\mathrm{C}}{2c} = \frac{r_\mathrm{D}}{2d} \tag{1.5}$$

Hence, the relationship between r_1 and r_2 is:

$$r_2 = \frac{r_1}{2} \tag{1.6}$$

in spite of the fact that chemically the two rates refer to the same reaction.

The distinction between reaction rates per compound and per reaction becomes more important when there are multiple reactions acting simultaneously. For instance, assume that the following reaction 3 occurs simultaneously with reaction 1:

$$a'\mathrm{A} + e\mathrm{E} \rightarrow f\mathrm{F} + g\mathrm{G} \qquad \text{reaction 3} \tag{1.7}$$

where a' is not necessarily the same as a. The total reaction rate of A subjected to reaction 1 and reaction 3 is:

$$r_\mathrm{A} = r_{\mathrm{A},1} + r_{\mathrm{A},2} = a r_1 + a' r_2 \tag{1.8}$$

In very complex systems, the overall reaction rate of a compound can be the sum of the contributions of hundreds of reactions. Defining reaction rates as in eq. (1.3) makes it easier to keep track of all relevant information.

The reaction rate of a **catalytic reaction** is defined as **the number of moles reacting per unit time and per unit mass of catalyst**. The same distinction between the overall rate of a reaction and the reaction rate of a compound is made in the case of catalytic reactions.

When the catalyst weight per unit volume is constant, it can be convenient to define the rate of a catalytic reaction as the number of moles reacting per unit time and per unit **volume** containing the catalyst. However, this is a purely operational definition.

A related definition is the **turnover rate** (or turnover frequency) of a catalyst. This is the number of moles reacting per unit time and per mol of active sites on the catalyst. The turnover rate has dimension time^{-1}.

Example 1.2:

A hydrogenation reactor containing 800 kg catalyst consumes 3 metric tonnes of hydrogen gas (molar mass 2 g mol^{-1}) per hour. The catalyst contains 0.05 mol active sites per kilogram catalyst. Calculate the consumption rate and the turnover rate of hydrogen gas on the catalyst.

Solution:

The reaction rate is calculated based on its definition:

$$-r_{\mathrm{H_2}} = \frac{3{,}000{,}000\,\mathrm{g} / 2\,\mathrm{g\,mol^{-1}}}{800\,\mathrm{kg} \cdot 3600\,\mathrm{s}} = \frac{1{,}500{,}000\,\mathrm{mol}}{800\,\mathrm{kg} \cdot 3600\,\mathrm{s}} = \mathbf{0.521\ mol\ kg^{-1}\ s^{-1}}$$

The turnover rate is calculated by dividing the reaction rate rate by the active site concentration on the catalyst:

$$-v_{H_2} = \frac{0.521\,\mathrm{mol\,kg^{-1}\,s^{-1}}}{0.05\,\mathrm{mol\,kg^{-1}}} = \mathbf{10.4\ s^{-1}}$$

The physical meaning of the turnover rate is immediately clear from Example 1.2. Every second, the average number of hydrogen molecules reacting per active site is 10.4.

In chemical kinetics, a distinction is made between reversible reactions and irreversible reactions. We say that a reaction is **irreversible** when it goes to completion, i.e., when the reaction does not reach equilibrium until one of the reactants has completely disappeared. This is the case if a reaction occurs in only one direction.

A reaction is **reversible** when it is the result of two opposing reactions. For instance:

aA + bB $\rightarrow$ cC + dD reaction 1 (1.1)

cC + dD $\rightarrow$ aA + bB reaction –1 (1.9)

The result is that the **net** reaction stops before any of the reactants is consumed completely. It stops when the forward reaction occurs at the same rate as the backward reaction. This corresponds with **chemical equilibrium**. The study of reversible reactions is where chemical kinetics merges with chemical thermodynamics. Of course, it is important that the kinetic theory of reversible reactions is **consistent** with the theory of chemcal thermodynamics.

Note that the words “reversible” and “irreversible” have a different meaning in chemical kinetics than in termodynamics.

A brief introduction to chemical thermodynamics is given in Appendix B.1.

1.3. The Material Balance

In its most general form, the material balance of a chemical reactor can be written as follows:

$$\text{in} - \text{out} + \text{generation} = \text{accumulation} \tag{1.10}$$

This is illustrated in Figure 1.1. In the equation, “in” refers to material (e.g., a compound A) entering the reactor through an inlet, “out” refers to material leaving the reactor through an outlet, “generation” is the production of the compound by chemical reaction, and “accumulation” is the change of the amount of compound in the reactor over time or per unit time.

In the case of a homogeneous reaction, the production term is usually the reaction rate multiplied by the volume of the system; in a heterogeneous reaction, the production is usually the reaction rate multiplied by the catalyst mass in the reactor. The accumulation is usually the concentration change multiplied by the volume of the phase containing the compound.

The material balance can apply to the entire reactor, or to a section of the reactor. The most important concern of eq. (1.10) is **consistency**: always ensure that each term in the equation refers to the same system, and has the same units. For instance, a material balance can be set up as a balance of amounts over a finite amount of time (e.g. number of moles of A), or as a balance of rates (e.g. moles of A per second).

An important simplifying case is the case of **steady state operation**. This means that the conditions in the reactor (temperature, concentration, etc.) are independent of time.

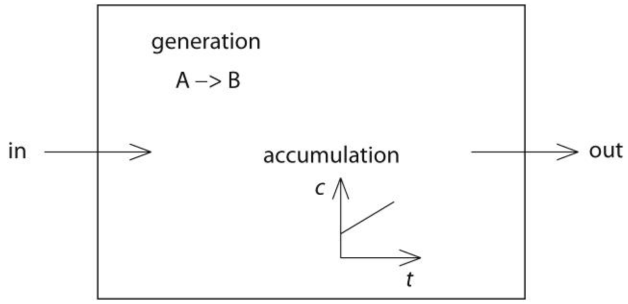

Figure 1.1. Material balance

Most continuous reactors are run in steady state. In steady state operation, eq. (1.10) can be simplified to:

$$\text{in} - \text{out} + \text{generation} = 0 \tag{1.11}$$

In this case the generation is directly related to the inflows and outflows.

Example 1.3:

A biorector with volume 10 L contains 1 mol glucose at time $t = 0$. The reactor is fed with 0.5 mol h^{-1} of glucose, in semi-batch mode (i.e., nothing leaves the reactor). After five hours the bioreactor contains 2 mol glucose. Calculate the average reaction rate of glucose in the reactor.

Solution:

Equation (1.10) is solved for the generation term:

$$\text{generation} = \text{accumulation} - \text{in} + \text{out}$$

Each of the terms will be defined as a rate:

accumulation = (2 mol – 1 mol)/5 hours = 0.2 mol h^{-1}
in = 0.5 mol h^{-1}
out = 0

Hence:

$$\text{generation} = 0.2 \text{ mol h}^{-1} - 0.5 \text{ mol h}^{-1} + 0 = -0.3 \text{ mol h}^{-1}$$

To obtain the reaction rate, the generation rate is divided by the reactor volume:

$$r = -0.3 \text{ mol h}^{-1}/10 \text{ L} = \mathbf{-0.03\ mol\ L^{-1}\ h^{-1}}$$

Material balances will be discussed in more detail in Chapters 6-8, and applied to specific types of reactors.

1.4. The Energy Balance

The energy balance is based on the first law of thermodynamics. Hence, it is useful to remember some aspects of thermodynamics here. First of all, the **internal energy** *U* of a system is a measure of all the energy contained in a system in the form of chemical and thermal energy, and interactions between the molecules of the system. This does not include external aspects of energy like potential or kinetic energy as defined with respect to the surroundings of the system. The units of *U* is J or kJ.

Internal energy depends on the temperature as follows:

$$\mathrm{d}U = C_V \,\mathrm{d}T \tag{1.12}$$

In eq. (1.12), the temperature change must be taken at constant volume, which is not always practical. Hence, the internal energy is nearly always determined in terms of the **enthalpy**. The enthalpy *H* of a system is defined as:

$$H = U + pV \tag{1.13}$$

where p is the pressure (Pa or kPa), and V is the volume of the system (m^3). Values of H of various compounds at 25 °C and 1 bar pressure are listed in tables, for instance in Appendix D.1.

The temperature dependence of the enthalpy is given by:

$$\mathrm{d}H = C_p \,\mathrm{d}T \tag{1.14}$$

The enthalpy is also dependent on the pressure. However, unless the pressure is very large, its effect is usually small, and will be ignored here. For finite temperature changes from T_1 to T_2, the enthalpy change from H_1 to H_2 is given by integrating eq. (1.14):

$$H_2 - H_1 = \int_{T_1}^{T_2} C_p \,\mathrm{d}T \tag{1.15}$$

Energy cannot be created or destroyed. Hence, there is no generation term in an energy balance. Other than that, eq. (1.10) is applicable in principle to the energy balance.

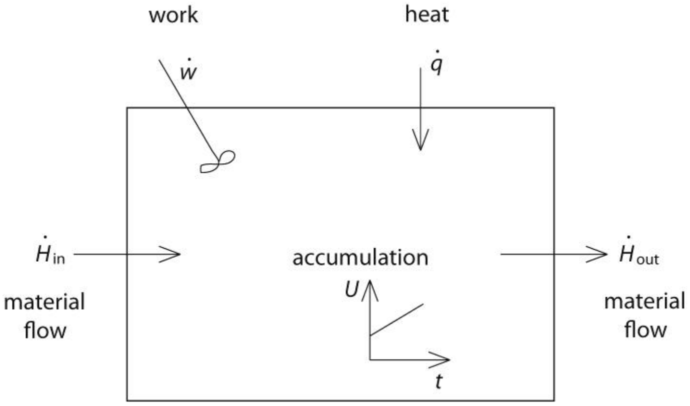

Figure 1.2. Energy balance

However, the “in” and “out” terms contain both the energy contained in the material and the work needed to push the material into or out of the reactor. Furthermore, energy can also be added to or removed from the reactor in the form of shaft work, electrical work, etc. These all need to be included in the energy balance. Based on the first law of thermodynamics, the following equation can be derived (see Appendix B.1 for a derivation):

$$\frac{\mathrm{d}U}{\mathrm{d}t} = \dot{H}_{\mathrm{in}} - \dot{H}_{\mathrm{out}} + \dot{w}_{\mathrm{s}} + \dot{q} \tag{1.16}$$

The energy balance is illustrated in Figure 1.2. In eq. (1.16) a dot over a symbol means that a flow of that property across the system boundary per unit time is indicated. Hence, all terms in eq. (1.16) have units J s^{-1} or W. U is the internal energy of the system, $\dot{H}_{\mathrm{in}}$ is the enthalpy flowing into the system with the material streams, $\dot{H}_{\mathrm{out}}$ is the enthalpy leaving the system with the material streams, $\dot{w}$ is the work added to the system (negative if the work is removed from the system), not including work exchanged in material flows. The main contribution to $\dot{w}$ in chemical reactors is usually **shaft work** $\dot{w}_{\mathrm{s}}$, but $\dot{w}$ can also include other types of work, like electrical work, or a volume change of the reactor. $\dot{q}$ is the heat added to the system. The form of eq. (1.16) actually used depends strongly on the type of reactor. For that reason, a more detailed discussion with examples is deferred to Chapters 6-8.

1.5. The Momentum Balance

The momentum balance is essentially Newton's second law applied to liquid or gas flowing through a reactor. It can take the form of the **Bernoulli equation**. For frictionless flow, the Bernoulli equation is:

$$\frac{\mathrm{d}u^2}{2} + \frac{\mathrm{d}p}{\rho} + g\mathrm{d}z = 0 \tag{1.17}$$

where u is the fluid velocity (m s^{-1}), g is the acceleration due to gravity (9.80655 m s^{-2}), and z is the height above an arbitrary reference level (m). When friction is not negligible in the system, as is often the case, then a friction term needs to be added to the Bernoulli equation. This can take the following form:

$$\frac{\mathrm{d}u^2}{2} + \frac{\mathrm{d}p}{\rho} + g\mathrm{d}z = \frac{(\mathrm{d}p)_\mathrm{f}}{\rho} \tag{1.18}$$

The height term is on the order of a few tens of m^2 s^{-2}, and is usually negligible, except in the case of gravity flow of liquids. The velocity term is usually negligible, except for some gas phase tubular reactors. Hence, in many cases the pressure terms are the only significant terms in the equation, which can then be simplified to:

$$\mathrm{d}p = (\mathrm{d}p)_\mathrm{f} \tag{1.19}$$

Practical pressure drop equations will be discussed in Chapter 8.

1.6. Some Definitions

The **conversion of a reactant A**, X_A, is the fraction of A that is reacted.

Example 1.4:

One mol oxygen is mixed with one mol hydrogen and ignited. What is the conversion of oxygen and of hydrogen after complete combustion?

Solution:

The combustion reaction is:

$2H_2 + O_2 \rightarrow 2H_2O$

Hence, the hydrogen runs out when 0.5 mol oxygen is consumed. It follows that X_{H_2} = 1 and X_{O_2} = 0.5 after complete combustion

We can see from the example that the conversion depends on the reactant considered. The reactant that runs out first is the **limiting reactant**. To identify the limiting reactant, the initial amount of each reactant is divided by its stoichiometric factor, and the reactant with the smallest number obtained is the limiting reactant. For instance, in the above example, we find a value of 1 mol/2 = 0.5 mol for H_2, and 1 mol for O_2. Hence, hydrogen is the limiting reactant.

When all reactants are limiting reactants (i.e., when all reactants run out at the same time), then the reaction is said to be run **in stoichiometric conditions**.

The **conversion of a reaction**, X, is the fraction of the limiting reactant that is reacted. The conversion of a reaction is always 1 when the reaction is completed. This is not necessarily true of the conversion of the individual reactants.

Note that conversions are normally calculated based on **amounts** of reactants, not on their concentrations. For instance, in the example above, if the reaction is carried out at constant pressure and temperature, and the produced water is allowed to condense, then the oxygen concentration in the gas phase actually increases (see next section), despite the fact that oxygen is disappearing. Instead, the volume of the system is decreasing. This shows that concentrations can give an incorrect impression of the extent of reaction, and is only an acceptable measure in the special case of constant volume.

The **yield** of a product P is the amount of P produced divided by the stoichiometric amount of P that can be produced from the limiting reactant at complete conversion and in the absence of other reactions. It is sometimes described as the conversion to P, because the yield of P equals the conversion of the limiting compound if there are no competing reactions of any kind.

The **overall selectivity** of a reaction to a reaction product P is the yield of P divided by the conversion of the limiting reactant. The overall selectivity equals 1 if there are no competing reactions of any kind.

The **point selectivity** is the rate of change of the yield of P divided by the rate of change of the conversion of the limiting reactant.

The **average residence time** of the reactor is the average time a fluid element spends in the reactor. All fluid elements do not necessarily spend the same amount of time in the reactor. If the density of the fluid is constant (and hence the volumetric flow rate), the the average residence time t_{av} is given by:

$$t_{\mathrm{av}} = \frac{V_{\mathrm{int}}}{Q} \tag{1.20}$$

where V_{int} is the internal volume of the reactor, and Q is the volumetric flow rate. When the volumetric flow rate is not constant, the average residence time is given by:

$$t_{\mathrm{av}} = \int_{V_{\mathrm{int}}} \frac{\mathrm{d}V}{Q} \tag{1.21}$$

Sometimes the internal volume of a reactor is poorly defined because it is filled with catalyst. Also, if the temperature and/or pressure is not known in the entire reactor, and the fluid is a gas, the flow rate Q is not defined throughout the reactor. In those cases it is more practical to define the **space time** τ_{st} of the reactor:

$$\tau_{\mathrm{st}} = \frac{V}{Q_{\mathrm{in}}} \tag{1.22}$$

where V is the reactor volume (contents including catalyst), and Q_{in} is the inlet volumetric flow rate. The **space velocity** SV is the inverse of the space time:

$$\mathrm{SV} = \frac{1}{\tau_{\mathrm{st}}} = \frac{Q_{\mathrm{in}}}{V} \tag{1.23}$$

Sometimes it is more convenient to define space velocity in terms of catalyst mass. In that case we talk about the **weight hourly space velocity** WHSV:

$$\mathrm{WHSV} = \frac{Q_{\mathrm{m}}}{W} \tag{1.24}$$

where Q_m is the mass flow rate of the fluid (kg h^{-1}), and W is the catalyst mass (kg)

1.7. Stoichiometric Calculations

As indicated in the previous section, the concentration is often a poor measure of the progress of a chemical reaction. However, the rate of a chemical reaction usually is dependent on the concentration, so it is important to be able to link conversion to concentration. This is the purpose of stoichiometric calculations. It will be illustrated with an example.

Example 1.5:

One mol of oxygen is mixed with one mol of hydrogen, and ignited. The conversion of the combustion is 90 %. Calculate the concentration of all compounds before and after combustion

(a) at a constant volume, with an initial pressure of 1 bar and a temperature of 100 °C.

(b) at a temperature of 100 °C and a (constant) pressure of 1 bar, assuming that all the water stays in the vapor phase.

(c) at a temperature of 0 °C and a (constant) pressure of 1 bar, assuming that all the water leaves the vapor phase.

Solution:

As before, the reaction is:

$$2H_2 + O_2 \rightarrow 2H_2O$$

Central to the calculations in all three conditions is the number of moles of each compound. They are calculated in the table below. We note that hydrogen is the limited compound, so the conversion of the reaction is the conversion of hydrogen.

Compound	Before (mol)	Change (mol)	After (mol)
H_2	1	–0.9 × 1 = –0.9	0.1
O_2	1	–0.9 × 1/2 = –0.45	0.55
H_2O	0	0.9 × 2/2 = 0.9	0.9
Total	2	–0.45	1.55
Total without H_2O	2	–1.35	0.65

In the table, the change of the number of moles of hydrogen is calculated as the conversion of hydrogen multiplied by the number of moles of hydrogen. The sign is negative, reflecting the fact that hydrogen is disappearing. Hence, a value of –0.9 × 1 mol = –0.9 mol is obtained.

The changes of the other numbers of moles are calculated based on the stoichiometric coefficients of the reaction. For each two moles of hydrogen reacting, one mole of oxygen reacts, so the change of the amount of oxygen is –0.9 mol × 1/2 = –0.45 mol. For each two moles of hydrogen reacting, two moles of water are produced, amounting to 0.9 mol. For the total number of moles, the values depend on whether water stays in the same phase, or leaves the phase.

(a) constant volume

First, the volume of the system is calculated with the ideal gas law:

$$pV = nRT$$

Hence:

$$V = nRT/p = 2\text{ mol} \times 8.314472\text{ J mol}^{-1}\text{ K}^{-1} \times 373.15\text{ K}/100{,}000\text{ Pa} = 0.06205\text{ m}^3$$

The concentration of each compound is simply the number of moles divided by the volume. Before combustion, the following values are obtained:

H_2: $c_{H_2} = 1\text{ mol}/0.06205\text{ m}^3 = 16.12\text{ mol m}^{-3}$

O_2: $c_{O_2} = 16.12\text{ mol m}^{-3}$

H_2O: $c_{H_2O} = 0\text{ mol m}^{-3}$

After combustion, the following concentrations are obtained:

H_2: $c_{H_2} = 0.1\text{ mol}/0.06205\text{ m}^3 = 1.61\text{ mol m}^{-3}$

O_2: $c_{O_2} = 0.55\text{ mol}/0.06205\text{ m}^3 = 8.86\text{ mol m}^{-3}$

H_2O: $c_{H_2O} = 0.9\text{ mol}/0.06205\text{ m}^3 = 14.50\text{ mol m}^{-3}$

(b) constant pressure, water in vapor phase

At constant pressure, the concentrations are calculated based on the total concentration and the mole fraction. The total concentration is calculated with the ideal gas law:

$c = n/V = p/RT = 100{,}000\ \mathrm{Pa}/(8.314472\ \mathrm{J\ mol^{-1}\ K^{-1}} \times 373.15\ \mathrm{K}) = 32.23\ \mathrm{mol\ m^{-3}}$.

The mole fractions are based on the numbers of moles in the stoichiometric table. Before combustion, the results are:

H_2: $x_{H_2} = 1\ \mathrm{mol}/2\ \mathrm{mol} = 0.5$
O_2: $x_{O_2} = 0.5$
H_2O: $x_{H_2O} = 0$

After combustion the total number of moles is 1.55, so the mole fractions are:

H_2: $x_{H_2} = 0.1\ \mathrm{mol}/1.55\ \mathrm{mol} = 0.0645$
O_2: $x_{O_2} = 0.55\ \mathrm{mol}/1.55\ \mathrm{mol} = 0.3548$
H_2O: $x_{H_2O} = 0.9\ \mathrm{mol}/1.55\ \mathrm{mol} = 0.5806$

The concentrations are obtained by multiplying the mole fractions by the total concentration. Before combustion, the following values are obtained:

H_2: $c_{H_2} = 0.5 \times 32.23\ \mathrm{mol\ m^{-3}} = 16.12\ \mathrm{mol\ m^{-3}}$
O_2: $c_{O_2} = 16.12\ \mathrm{mol\ m^{-3}}$
H_2O: $c_{H_2O} = 0\ \mathrm{mol\ m^{-3}}$

Not surprisingly, the results are the same as in (a). After combustion, however, the results are not the same:

H_2: $c_{H_2} = 0.0645 \times 32.23\ \mathrm{mol\ m^{-3}} = 2.08\ \mathrm{mol\ m^{-3}}$
O_2: $c_{O_2} = 0.3548 \times 32.23\ \mathrm{mol\ m^{-3}} = 11.44\ \mathrm{mol\ m^{-3}}$

H_2O: c_{H_2O} = 0.5806×32.23 mol m^{-3} = 18.72 mol m^{-3}

Because the volume of the system has decreased, the concentrations are higher than in case (a).

(c) constant pressure, water condenses

Because the water leaves the vapor phase, we use the total number of moles excluding water. First, we calculate the new total concentration based on the new temperature:

$c = n/V = p/RT$ = 100,000 Pa/(8.314472 J mol^{-1} K^{-1} × 273.15 K) = 44.03 mol m^{-3}.

The mole fractions before combustion are the same as in case (b) and will not be repeated here. Based on a total number of moles of 0.65, the mole fractions after combustion are calculated as:

H_2: x_{H_2} = 0.1 mol/0.65 mol = 0.1538
O_2: x_{O_2} = 0.55 mol/0.65 mol = 0.8462

Based on the mole fractions and a total concentration of 44.03 mol m^{-3}, the concentrations of hydrogen and oxygen before combustion are:

H_2: c_{H_2} = 0.5 × 44.03 mol m^{-3} = 22.02 mol m^{-3}
O_2: c_{O_2} = 0.8462 × 44.03 mol m^{-3} = 22.02 mol m^{-3}

After combustion, the concentrations are:

H_2: c_{H_2} = 0.1538 × 44.03 mol m^{-3} = 6.77 mol m^{-3}
O_2: c_{O_2} = 0.8462 × 44.03 mol m^{-3} = 37.26 mol m^{-3}

We find the counter-intuitive result that the oxygen concentration increases despite being reacted away.

1.8. Units and Unit Conversions in Chemical Reactor Engineering

This book uses SI (metric) units. The advantage of metric units is that they form a consistent set, which simplifies engineering calculations considerably. The disadvantage, obviously, is that metric units are not commonly used in the United States. This section provides the necessary conversions, and some rules of thumb.

The **base quantities** (or dimensions) are shown in Table 1.1, along with their SI units (Cohen et al., 2008).

Derived quantities are obtained by combining base quantities, as shown in Table 1.2.

To indicate large or small quantities, the prefixes in Table 1.3 are used.

Table 1.1. Base quantities and their units

Quantity	Unit	Comment
length	meter (m)	
mass	kilogram (kg)	
time	second (s)	
thermodynamic temperature	kelvin (K)	°K or degree kelvin is outdated
amount of substance	mole (mol)	gmol or grammolecule is outdated

Table 1.2. Derived quantities and their units

Quantity	Unit	Comment
force	newton (N = kg m s^{-2})	lowercase letter for full name,
energy	joule (J = N m)	captial letter for abbreviation
pressure	pascal (Pa = N m^{-2})	
power	watt (W = J s^{-1})	

Table 1.3. Prefixes for large or small quantities

Prefix	Abbreviation	Meaning
nano	n	10^{-9}
micro	μ	10^{-6}
milli	m	10^{-3}
kilo	k (not K)	10^{3}
mega	M	10^{6}
giga	G	10^{9}

Table 1.4. Alternative units

Alternative unit	Equivalent in SI units	Comment/Rule of thumb
1” (inch)	0.0254 m	
1’ (foot)	0.3048 m	
1 cm	0.01 m	10 cm is about 4”
1 lb	0.45359237 kg	1 kg is about 2.2 lb
1 tonne	1000 kg	metric ton
1 ton (U.S.)	907.18474 kg	1 short ton = 2000 lb
1 ton (U.K.)	1016.046909 kg	1 long ton = 2240 lb
1 psi	6894.75729...	pound per square inch
1 atm	101,325 Pa	1 atm is about 14.7 psi
1 bar	100,000 Pa	1 bar is about 14.5 psi
760 Torr	101,325 Pa	lowercase t when it is not preceded by a number
1 cal	4.184 J	The International Steam Table uses 4.1868 J

Alternative units include imperial units, and units derived from the SI system. Some relevant alternative units for chemical reaction engineering are listed in Table 1.4.

Common units for temperature are degree Celcius (“centigrade” is not an official term):

$$\theta_{\mathrm{C}} / {}^{\circ}\mathrm{C} = T / \mathrm{K} - 273.15 \tag{1.25}$$

and degree Fahrenheit:

$$\theta_{\mathrm{F}} / {}^{\circ}\mathrm{F} = 1.8\theta_{\mathrm{C}} / {}^{\circ}\mathrm{C} + 32 \tag{1.26}$$

The degree Rankine scale is the absolute temperature scale derived from the degree Fahrenheit scale:

$$\theta_{\mathrm{R}} / {}^{\circ}\mathrm{R} = \theta_{\mathrm{F}} / {}^{\circ}\mathrm{F} + 459.67 = 1.8T / \mathrm{K} \tag{1.27}$$

SI units are closely linked with the values of some physical constants. Table 1.5 shows some relevant constants.

The standard notation of the chemical sciences is determined by the International Union of Pure and Applied Chemistry (IUPAC), and compiled in the “Green Book” (Cohen et al.,

Table 1.5. Universal physical constants and conventional constants (Mohr and Taylor, 2005)

Constant	Value	Comment
c	299,792,458 m s^{-1}	speed of light
g	9.80665 m s^{-2}	by convention
k	1.3806505×10^{-23} J K^{-1}	Boltzmann constant
N_A	6.0221415×10^{-23} mol^{-1}	Avogadro constant
R	8.314472 J mol^{-1} K^{-1}	ideal gas constant (= kN_A)
h	6.6260693×10^{-34} J s	Planck constant

2008). The notation used here is based on the Green Book. Engineers, even the ones who write textbooks, often use notation that is considered outdated in the Green Book, and it is useful to be aware of such variations in notation. Examples are ΔH_r for enthalpy of reaction (official notation $\Delta_r H$), Q for heat (official notation q), and W for work (official notation w).

References

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