

Chapter 5

Equilibrium vs Rate Considerations

INTRODUCTION

There are two important factors that need to be taken into consideration when analyzing mass transfer operations: equilibrium and rate. Although these two subjects have been segmented and treated separately below, both need to be considered together when analyzing a mass transfer device.

Because of the importance of equilibrium and rate, both receive treatment in the next two chapters. However, the question often asked is: Which is the more important of the two when discussing mass transfer operations? This is best answered by noting that most—but not all—mass transfer calculations assume equilibrium conditions to apply. A correction factor or an efficiency term is then included to adjust/upgrade the result/prediction to actual (as opposed to equilibrium) conditions in order to accurately describe the phenomena in question. As one would expect, the correction factor or efficiency is usually based on experimental data, past experience, similar designs, or just simply good engineering judgement. Although this method of analysis has been maligned by many theoreticians and academicians, the approach has merit and has been routinely used by practicing engineers.⁽¹⁾ This pragmatic approach is primarily employed in this text/reference book.

EQUILIBRIUM

A state of equilibrium exists when the forward and reverse rates of a process are equal. From a macroscopic point of view, there is no change with time. Equilibrium represents a limiting value for the practicing engineer as demonstrated in the following example.

Whenever a substance distributes itself between two other materials, the system will attempt to approach equilibrium. Thus, if NH_3 gas in air is brought into contact with water at 60°F , the NH_3 will begin and continue to dissolve in the water until

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its concentration in the water has reached a maximum value at that temperature. This condition represents equilibrium, and no further solution of the NH_3 will occur unless this equilibrium is disturbed. Alternatively, if water containing NH_3 is brought into contact with air containing no NH_3 , the NH_3 will escape from the water and pass into the gas phase until the value of the concentrations in the two phases has reached the equilibrium value. This particular scenario will be revisited in Chapter 10, a chapter which is concerned with absorption and stripping.

If one wishes to remove NH_3 from an air mixture by using water, it is obvious that equilibrium can set a limit on the maximum amount of NH_3 that can be removed from the air to the water. It can also set the lower limit on the amount of water necessary for a particular degree of NH_3 removal. Therefore, equilibrium is a vital factor in the design and operation of these type of mass transfer systems. In the situation described above, equilibrium is fortunately simple to represent, and will find application in absorption as well as other systems. Occasionally, the relationships are complicated. Specific cases of importance will be discussed in Chapters 6 and 10.

RATE

The companion to *equilibrium* in mass transfer operations is *rate*. The transfer of a substance from one phase to another obviously requires time. The rate of transfer is proportional to the surface of contact between the phases, the resistance to the transfer, and the driving force present for mass transfer. This phenomena is described in Equations (5.1) and (5.2). Employing the macroscopic approach, a transfer process, whether it be mass, energy, or momentum, can be simply described as shown below:

$$\text{Rate of Transfer} = \frac{(\text{Driving Force})(\text{Area Available for Transfer})}{(\text{Resistance to Transfer})} \quad (5.1)$$

For mass transfer, the equation becomes

$$\begin{aligned} &\text{Rate of Mass Transfer} \\ &= \frac{(\text{Concentration Driving Force})(\text{Area Available for Mass Transfer})}{(\text{Resistance to Mass Transfer})} \end{aligned} \quad (5.2)$$

Other things being equal, Equations (5.1) and (5.2) indicate that the rate of transfer can be increased by:

- 1 increasing the area,
- 2 increasing the driving force, and
- 3 decreasing the resistance.

These three factors are almost always considered in the design of mass transfer equipment. As one might intuitively expect, any increase in the transfer rate leads to a more compact mass transfer device that is generally more economical. A more detailed presentation on rate considerations is provided in Chapter 7.

Consider again the comments provided earlier in the section on equilibrium concerning the NH_3 -air- H_2O system. No mention was made of the rate of transfer of NH_3 at that time. But in line with Equation (5.2), during the initial stages of the transfer process, the NH_3 concentration in the air is high while its concentration in water is low (or even zero). This produces a high concentration difference driving force that leads to a high NH_3 transfer rate. However, later in the transfer process, the NH_3 concentrations in both phases tend to “equilibrate”, leading to a lower concentration difference driving force, and a lower transfer rate. When the system ultimately reaches/achieves equilibrium, the driving force becomes zero and the rate of transfer also becomes zero.

With all mass transfer processes, the *true* driving force for mass transfer is the chemical potential of the substance to be transferred. Just as temperature acts as a *thermal potential* for heat transfer, every substance has a chemical (or “mass”) potential which “drives” it from one phase into another. A state of equilibrium is only achieved in a non-reacting system when the temperature, pressure, and chemical potential of every species is equal in all phases. While the study of chemical potential is best left to a thermodynamicist, the subject of mass transfer tends to use *concentration* as a substitute for representing the chemical potential.

Obviously, the rate as well as equilibrium play a role in the transfer process. Both effects need to be considered in designing, predicting performance, and operating mass transfer equipment. Which is more important? It depends. Normally, equilibrium information is required. Moreover, if the rate of transfer is extremely high, rate considerations can in some instances be neglected.

CHEMICAL REACTIONS

With regard to chemical reactions, there are two important questions that are of concern to the engineer:

- 1 how *far* will the reaction go?
- 2 how *fast* will the reaction go?

Chemical thermodynamics provides the answer to the first question; however, it tells us nothing about the second. Reaction rates fall within the domain of chemical kinetics and will not be treated in this text.⁽¹⁾

To illustrate the difference and importance of both of the above questions on an engineering analysis of a chemical reaction, consider the following process.^(2,3) Substance A, which costs 1 cent/ton, can be converted to B, which is worth \$1 million/lb, by the reaction $A \leftrightarrow B$. Chemical thermodynamics will provide information on the maximum amount of B that can be formed. If 99.99% of A can be converted to B, the reaction would then appear to be economically feasible, from a *thermodynamic* point of view. However, a *rate* or *kinetic* analysis might indicate that the reaction is so slow that, for all practical purposes, its rate is vanishingly small. For example, it might take 10^6 years to obtain a $10^{-6}\%$ conversion of A. The reaction is then economically unfeasible. Thus, it can be seen that both equilibrium and rate/kinetic effects

must be considered in an overall engineering analysis of a chemical reaction. The same principle applies to gaseous mass transfer separation, e.g., absorption.⁽⁴⁾

Equilibrium and rate are both important factors to be considered in the design and prediction of performance of equipment employed for chemical reactions. The rate at which a reaction proceeds will depend on the departure from equilibrium, with the rate at which equilibrium is established essentially dependent on a host of factors. As can be expected, this rate process would cease upon the attainment of equilibrium.

If one is conducting a chemical reaction in which reactants go to products, the products will be formed at a rate governed in part by the concentration of the reactants and reaction conditions such as the temperature and pressure. Eventually, as the reactants form products and the products react to form reactants, the *net* rate of reaction must equal zero. At this point, equilibrium will have been achieved.

ILLUSTRATIVE EXAMPLE 5.1

As part of his investigation, Detective Theodore paid a visit to the office of his missing bookmaker—the location where the bookmaker was last seen. In examining the premises, he notices a half-empty 5 inch tall coffee mug on the missing bookmaker's desk. Based on his experience and the stain left in the mug, Detective Theodore estimated that the coffee mug was initially full to 0.5 inches from the brim at the time of the bookmaker's disappearance and that the bookmaker had been missing for approximately two weeks. Qualitatively explain how this brilliant sleuth reached this conclusion.

SOLUTION: Detective Theodore instinctively realized that the time it took for the coffee in the mug to evaporate would reflect how long the bookmaker had been missing. In mass transfer terms, this case reduced to the evaporation of a single component, i.e., essentially pure water into a stagnant gas (air) at room temperature and 1 atm of pressure. After combining principles to be discussed later in this book, this extraordinary detective was able to calculate the time when his bookmaker disappeared. ■

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