

A First Course on Kinetics and Reaction Engineering

Unit 39. Gas-Liquid Reactions

Overview

Unit 38 described ways to model reaction kinetics in heterogeneous catalytic systems that involve two phases. Whenever two phases are present and involved in the reactive process, interfacial concentration and temperature gradients can affect the apparent kinetics. Unit 39 offers an overview of systems where a reaction involves one component in a liquid phase and a second component in the gas phase, with the reaction taking place in the liquid phase. The approach is actually quite similar to the approach used for heterogeneous catalysts. One difference is that more than one set of dimensionless quantities are used to characterize gas-liquid systems. In one case the quantities are defined from the perspective that the occurrence of the reaction increases the apparent rate of gas absorption into the liquid while in the other, the perspective is more like heterogeneous catalysis: the gradients reduce the apparent rate of reaction.

Learning Objectives

Upon completion of this unit, you should be able to define, in words, the following terms:

- Hatta number
- Two film model
- Surface renewal model
- Liquid utilization factor
- Enhancement factor
- Gas utilization factor

Upon completion of this unit, you should be able to perform the following specific tasks and be able to recognize when they are needed and apply them correctly in the course of a more complex analysis:

- Describe the assumptions used in the formulation of the two film model for gas-liquid reactions.
- Describe the assumptions used in the formulation of the surface renewal model for gas-liquid reactions.
- Calculate liquid utilization factors and liquid enhancement factors for first order reactions with rate comparable to the diffusion rate.
- Solve simple reaction engineering problems involving gas-liquid reactions.

Information

There are a few different ways to model a gas-liquid interface for the purpose of describing the kinetics of a gas-liquid reaction. Only one kind of model will be considered in detail in this unit, and only for the situation where the diffusion and reaction rates are comparable. The purpose here is not to present a comprehensive overview, but simply to illustrate how the combined reaction and transport associated with gas-liquid reactions can be modeled. In doing so, it will be possible to illustrate two

different dimensionless quantities that can be used to account for the concentration gradients in reactor models.

The model to be considered here is called the *two film model*. The model considers a small volume somewhere within the reactor. As illustrated in Figure 39.1, the volume considered includes both phases and the interface between them. In that figure, the gas phase is colored orange and the liquid phase is colored blue. The model assumes there is a thin film or boundary layer that lies between the local bulk gas and the interface; in the figure this is colored a lighter shade of orange. The local pressure of reactant A in the bulk gas phase is equal to P_A . A concentration gradient, or equivalently, a partial pressure gradient is assumed to exist across the gas film so that the partial pressure of A at the interface is equal to P_{Ai} . The gas-liquid interface, represented by a black, vertical, solid line in the figure, is taken to be $x = 0$, with x increasing as one moves into the liquid phase in a direction perpendicular to the interface. As was assumed for the gas, the model assumes there is a second thin film or boundary layer on the liquid side of the interface. The liquid-side film is shown in light blue, and again, there is a concentration gradient across the liquid-side film. The liquid side film is assumed to extend a distance x_L into the liquid. Beyond that point lies the local bulk liquid where the composition is assumed to be uniform with respect to x . The concentration of reactant A in the liquid film right at the interface ($x = 0$) is equal to C_{Ai} and the concentration of A in the local bulk liquid is C_{Ab} .

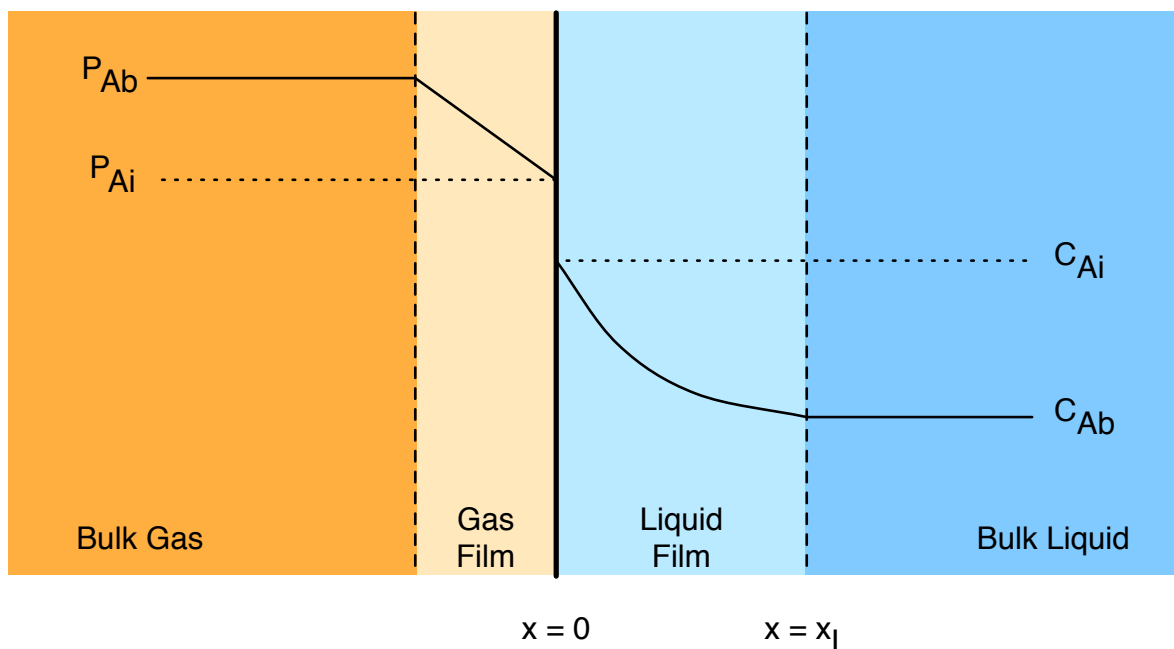


Figure 39.1. Two film representation of the local interface between a gas and a liquid.

In the development of the two film model presented here it will be assumed that within each of the films, mass transfer occurs only by diffusion. We will assume that reaction takes place between reactant A, which is supplied as one component in the gas phase and reactant B which is supplied in the liquid

phase. We will further assume that reactant B is completely nonvolatile. As a consequence, the reaction can only take place in the liquid phase between B and dissolved A; no reaction occurs in the gas phase. Exactly at the interface (i. e. at $x = 0$) it is assumed that phase equilibrium exists. Thus, assuming Henry's law can be used to describe the equilibrium between gas phase A and dissolved A, the interfacial gas phase partial pressure, P_{Ai} and the interfacial liquid phase concentration, C_{Ai} , are related according to equation (39.1) where h_A represents the Henry's law constant.

$$P_{Ai} = h_A C_{Ai} \quad (39.1)$$

There are two limiting cases of the two film model. The first is the case where the reaction is much slower than the rate of diffusion. In this limiting situation, the amount of reaction that takes place within the liquid film is negligible compared to the amount of reaction occurring in the local bulk liquid. As such, the reaction within the liquid film can be neglected and there is only diffusion taking place in each of the two films. When reaction in the films is neglected, the partial pressure gradient across the gas film and the concentration gradient across the liquid film can be related to the flux through the films using a mass transfer coefficient. This is analogous to the way fluid transport from the bulk fluid to the surface of a heterogeneous catalyst was treated in Unit 38, with the difference being the presence of two films instead of one.

The other limiting case of the two film model is where the rate of reaction is effectively instantaneous. In this case, the concentration of A in the bulk, C_{Ab} , will equal zero. In fact, there will be a plane that is parallel to the interface and located somewhere within the liquid film, i. e. between $x = 0$ and $x = L$. At this plane the concentrations of A and B will both equal zero and all reaction will take place exactly at this plane. To the right of the plane (at higher values of x) the concentration of A will equal zero and there will be a gradient in the concentration of B ($C_B = 0$ at the plane and $C_B = C_{Bb}$ at $x = L$). To the left of the plane the concentration of B will equal zero and there will be a gradient in the concentration of A ($C_A = 0$ at the plane and $C_A = C_{Ai}$ at $x = 0$). The location of the plane will be such that the flux of A from the interface is equal to the flux required by reaction stoichiometry of B from the bulk fluid.

The case to be considered here is that where the diffusion and reaction rates are comparable. In this case the concentration of A does not go to zero in the bulk liquid, but the amount of reaction taking place within the liquid film is too large to ignore. Assuming there is no change in total moles upon reaction (i. e. $A \rightarrow B$), mole balances can be written for A and B over a differentially thick slice, dx , of the liquid film. In the limit where the thickness of this slice goes to zero, the mole balances given in equations (39.2) and (39.3) result. The rates appearing in the mole balance equations are related to each other through the reaction stoichiometry (here $-r_A = r_B$).

$$D_A \frac{\partial^2 C_A}{\partial x^2} = r_A \quad (39.2)$$

$$D_B \frac{\partial^2 C_B}{\partial x^2} = r_B \quad (39.3)$$

The mole balances in equations (39.2) and (39.3) are second order differential equations, so two boundary conditions are required for each mole balance. Figure 39.1 specifies the concentration of A at the interface and in the bulk fluid, which begins at $x = x_L$, so equations (39.4) and (39.5) are used as the boundary conditions for the mole balance on A. An analogous equation can be written requiring the concentration of B in the film at $x = x_L$ to equal the bulk concentration, equation (39.6). The boundary condition at $x = 0$ is written by noting that since B is not volatile, the flux of B must equal zero at the interface, equation(39.7). The local bulk concentrations of A and B are the concentrations that would be measured experimentally, and they are the concentrations that would be used in the rate expression when writing reactor design equations for the bulk liquid in the reactor.

$$C_A(x=0) = C_{Ai} \quad (39.4)$$

$$C_A(x=x_L) = C_{Ab} \quad (39.5)$$

$$C_B(x=x_L) = C_{Bb} \quad (39.6)$$

$$N_B|_{x=0} = 0 \quad \Rightarrow \quad -D_B \left. \frac{dC_{Bf}}{dx} \right|_{x=0} = 0 \quad \Rightarrow \quad \left. \frac{dC_{Bf}}{dx} \right|_{x=0} = 0 \quad (39.7)$$

For the situation where the rate is first order in A only, the mole balances in equations (39.2) and (39.3) can be integrated analytically. In general analytical integration is only possible in a few situations; otherwise numerical solution of the mole balances on the liquid film will be necessary. Substitution of the rate expression into equation (39.2) gives equation (39.8). That equation can be solved using the boundary conditions in equations (39.4) and (39.5). The result is given in equation (39.9). The dimensionless quantity, γ , appearing in equation (39.9) is called the Hatta number and for a first order reaction in A and the planar geometry of Figure 39.1, it is defined according to equation (39.10). The film thickness, local liquid phase mass transfer coefficient and the diffusion coefficient are related according to equation (39.11), giving rise to a second definition of the Hatta number in equation (39.12). Notice the similarity between the Hatta number and the Thiele modulus from Unit 38.

$$D_A \frac{\partial^2 C_A}{\partial x^2} = kC_A \quad (39.8)$$

$$C_A = \frac{C_{Ai} \sinh \left[\gamma \left(1 - \frac{x}{x_L} \right) \right] + C_{Ab} \sinh \left(\frac{x}{x_L} \right)}{\sinh(\gamma)} \quad (39.9)$$

$$\gamma = x_L \sqrt{\frac{k}{D_A}} \quad (39.10)$$

$$k_L = \frac{D_A}{x_L} \quad (39.11)$$

$$\gamma = \frac{\sqrt{kD_A}}{k_L} \quad (39.12)$$

At steady state the rate of reaction within the liquid must just equal the flux through the gas-liquid interface. If it did not, there would be accumulation of A, and at steady state there cannot be any accumulation. The flux through the interface is given by equation (39.13); upon substitution of equation (39.9), the flux equation (39.14) results. The concentration of A at the interface appearing in equation (39.14) can be found by noting (a) the steady state flux through the gas film must equal the flux into the interface since no reaction takes place in the gas film and (b) Henry's law applies at the interface.

$$N_A = -D_A \frac{\partial C_A}{\partial x} \quad (39.13)$$

$$N_A|_{x=0} = \frac{\gamma D_A}{x_L} \frac{C_{Ai} \cosh \gamma - C_{Ab}}{\sinh \gamma} = \frac{\gamma}{\tanh \gamma} \left[1 - \frac{C_{Ab}}{C_{Ai}} \left(\frac{1}{\cosh \gamma} \right) \right] k_L C_{Ai} \quad (39.14)$$

When gas-liquid reactions are considered from the perspective of reaction engineering, the concentration gradients are seen to decrease the rate of reaction from what it could have been if no concentration gradients existed. That is, the rate of reaction in the liquid phase would larger if the concentration was equal to C_{Ai} throughout the liquid instead of dropping from C_{Ai} to C_{Ab} across the liquid film. One can define a liquid utilization factor, η_L , by analogy to the effectiveness factor for heterogeneous catalysis. The liquid utilization factor is the ratio of the actual rate of reaction (with concentration gradients present) to the rate that would result in the absence of such gradients (i. e. if $C_A = C_{Ai}$ everywhere). Mathematically this is expressed in equation (39.15), and substitution for the first flux as given above leads to equation (39.16). The quantity A_v appearing in these equations is the interfacial area per unit liquid volume.

$$\eta_L = \frac{A_v N_A|_{x=0}}{k C_{Ai}} \quad (39.15)$$

$$\eta_L = \frac{1}{\gamma Sh \tanh \gamma} \left(1 - \frac{C_{Ab}}{C_{Ai}} \frac{1}{\cosh \gamma} \right); \quad Sh = \frac{k_L}{A_v D_A} \quad (39.16)$$

Gas-liquid reactions can also be considered from the perspective of gas absorption. From this perspective, the rate at which A can be absorbed into a liquid is increased if A reacts with a solute contained in that liquid compared to the amount that would absorb in the absence of that reactive solute. Hence from the gas absorption perspective it is customary to define a liquid enhancement factor, ζ , as being equal to the actual rate of absorption (i. e. when reaction does occur) divided by the rate of

absorption that would have been observed in the absence of reaction. This can be expressed mathematically as in equation (39.17), and upon substitution of equation (39.14), the liquid enhancement factor is defined by equation (39.18).

$$\zeta = \frac{N_A}{k_L(C_{Ai} - C_{Ab})} \quad (39.17)$$

$$\zeta = \frac{\gamma}{\tanh \gamma} \left[1 - \frac{C_{Ab}}{C_{Ai}} \left(\frac{1}{\cosh \gamma} \right) \right] \quad (39.18)$$

The presentation given here is only meant to be illustrative. The equations presented for the liquid utilization factor and the liquid enhancement factor only apply for the geometry of Figure 39.1 with a reaction, $A \rightarrow B$, that is first order in A only and in the situation where the reaction and diffusion rates are comparable. Different equations result (or numerical solution is required) if any of these conditions differ. Note also that the utilization and enhancement factors have been defined here relative to the interfacial concentration, C_{Ai} . For this reason, they are sometimes referred to as liquid utilization or enhancement factors. As already noted, the interfacial concentration must be found using a gas-phase local mass transfer coefficient along with Henry's law. Alternatively, it is possible to define gas utilization and enhancement factors that are defined relative to the bulk gas phase partial pressure, P_A . Such equations will not be derived here; it can be noted that they are analogous to the global effectiveness factor that was defined for heterogeneous catalytic reactions in Unit 38.

Finally, it was noted at the start of this unit that there are other ways to model the gas-liquid interface. In the two film model considered here, the gas and fluid were assumed to be stationary so that a steady state flux into the liquid was established. An alternative approach is to assume the liquid in contact with the gas phase changes after some period of time, being replaced by fresh liquid from the bulk of the fluid. In this case, the diffusion process is not at steady state, but instead the flux into the liquid changes over time. One can then assume that the amount of time the fluid spends at the surface before being replaced is described by some age distribution function. The net flux is then found by integration over this age distribution function. This is analogous to the development of the segregated flow model for a reactor in terms of its residence time distribution. Gas-liquid reaction models formulated in this way are referred to as *surface renewal models*. A more detailed consideration of two film models and surface renewal models is typically presented in advanced textbooks or courses on kinetics and reaction engineering.