A First Course on Kinetics and Reaction Engineering
Unit 10. Heterogeneous Catalysis

Overview

This course is divided into four parts; part II is focused upon modeling the rates of chemical reactions, that is, rate expressions. Previous units have discussed the generation of a rate expression for a non-elementary reaction from the mechanism underlying the reaction. Unit 9 focused upon homogeneous reactions where the catalyst is present in the same phase as the reacting mixture. This unit examines mechanisms involving heterogeneous catalysts, focusing on the most common situation where the catalyst is a solid and the reagents are present in the surrounding fluid. After noting that the elementary reaction rate expressions involve two-dimensional surface concentrations, the fractional surface coverage is introduced and used as the composition variable in both rate expressions and the statement of the conservation of catalytic sites. The unit concludes by noting simplifications of the rate expression that may occur if one surface species occupies almost all of the active sites on the catalyst surface.

Learning Objectives

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

- active site
- adsorption
- desorption
- fractional coverage
- most abundant surface intermediate

Upon completion of this unit, you should be able to write the defining equation for the following quantities:

- surface coverage
- conservation of surface sites
- elementary surface reaction rates

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:

- generate a rate expression for a non-elementary reaction when its mechanism involves reactions on the surface of a solid catalyst, and simplify that expression so that it does not contain concentrations or partial pressures of reactive intermediates
- apply the concept of a most abundant intermediate to simplify a rate expression for a heterogeneous catalyst that has been derived from a mechanism

Information

Unit 9 considered reaction mechanisms involving homogeneous catalysts or enzymes. Many industrial processes utilize heterogeneous catalysts. Most typically the catalyst is solid while the reagents are in the fluid phase (gas or liquid). In these cases of heterogeneous catalysis, the reaction actually

takes place on the surface of the catalyst at specific locations called *active sites*. When writing a reaction that involves an active site, it is common to use some type of star to represent the site, e. g. ✳. Reactants, intermediates and products can bond to these sites in much the same way as they can form complexes with homogeneous catalysts or enzymes. In heterogeneous catalysis, the bonding of a species to the surface of the catalyst is a process referred to as *adsorption*, and the surface complexes that are generated are called *adsorbed species*. The reverse process, where a species leaves the surface and enters the fluid phase is called *desorption*.

In simple situations, it is usually safe to assume that the total surface area of the heterogeneous catalyst remains constant during the course of the reaction. It can also be safely assumed that the number (and therefore the concentration) of active sites, C_{sites}, remains constant. Note that this is a two-dimensional concentration (sites per surface area) not a three dimensional one (sites per volume). In heterogeneous catalytic kinetics, the concentration of an adsorbed species, i, (which is a reactive intermediate – it appears in the reaction mechanism, but not in the macroscopically observed overall reaction) is usually expressed in terms of the fraction of the total sites that it covers, θ_i. This quantity is then referred to as the *fractional coverage* or the surface coverage of species i. Thus, the concentration of any surface species, i_{surf}, that adsorbs on a single site is given by equation (10.1).

$$C_{i_{surf}} = C_{sites}\theta_i \qquad (10.1)$$

It won't be done here, but transition state theory can be used to derive a rate expression for an elementary surface reaction. When this is done, the concentration of sites above can be combined with the pre-exponential factor of the rate coefficient. After doing so, the resulting rate expression for an elementary surface reaction, j, is given in equation (10.2), where the C_{sites} terms associated with the coverages, θ_i, have been included the pre-exponential factors of the rate coefficients. The square brackets in equation (10.2) represent either the concentrations (per fluid volume) or partial pressures for the fluid phase species. Equation (10.2) also could be re-written in a form equivalent to equation (6.2) where the reverse rate term is replaced with an equilibrium term.

$$r_j = k_{j,f}\left(\prod_{\substack{i=\text{all}\\ \text{fluid phase}\\ \text{reactants}}}\left[i\right]^{-\nu_{i,j}}\prod_{\substack{m=\text{all}\\ \text{surface}\\ \text{reactants}}}\theta_m^{-\nu_{m,j}}\right) - k_{j,r}\left(\prod_{\substack{n=\text{all}\\ \text{fluid phase}\\ \text{products}}}\left[n\right]^{\nu_{n,j}}\prod_{\substack{l=\text{all}\\ \text{surface}\\ \text{products}}}\theta_l^{\nu_{l,j}}\right) \qquad (10.2)$$

For engineering purposes, it is not desirable to have a rate expression that contains surface coverages because they are typically unknown and difficult to measure. Therefore, the mechanistic rate expression is simplified using the Bodenstein steady-state approximation or other valid assumptions. Similar to homogeneous and enzymatic catalysis, the heterogeneous catalytic sites are conserved, and this introduces an additional constraint which can be imposed when extracting the rate expression from a postulated mechanism. In the case of heterogeneous catalysis, the conservation of catalytic sites is expressed in terms of the surface coverages as given in equation (10.3).

$$\theta_{vacant} + \sum_{\substack{i = \text{all} \\ \text{adsorbed} \\ \text{species}}} \theta_i = 1 \tag{10.3}$$

Occasionally there is one species present on the surface of the catalyst in much, much greater concentration than all other species. This species is called the *most abundant surface intermediate* or masi. If a species can be identified as a masi, the rate expression sometimes can be simplified considerably by applying equation (10.4). The means by which equation (10.4) is used to simplify a rate expression is best described by an example, and so Example 10.1 illustrates the process.

$$\theta_{masi} \gg \theta_i \qquad (i = \text{any species other than the masi}) \tag{10.4}$$

Just as the term Michaelis-Menton kinetics is used to describe the kinetics of enzyme-catalyzed reactions that follow one simple type of reaction mechanism, the term Langmuir Hinshelwood kinetics generally refers to heterogeneous catalytic reaction kinetics that can be described by a certain type of mechanistic model. In Langmuir-Hinshelwood models a surface reaction step is usually assumed to be rate-determining, and each adsorption/desorption step is assumed to be quasi-equilibrated. The surface of the catalyst is modeled as being energetically uniform, and it is assumed that there is no energetic interaction between species adsorbed on the surface. These are the same assumptions that Langmuir used in deriving his isotherm to model surface adsorption processes [1]. The derivation of a Langmuir-Hinshelwood rate expression is illustrated in Example 10.2.

There are endless possibilities with respect to which step (if any) is rate-limiting, which steps are equilibrated or irreversible, whether there is a rate-determining step, etc. As previously noted in Unit 5, Hougen and Watson [2], and later Yang and Hougen [3], showed that a very large number of these cases lead to rate expressions with the same generic form given in equation (10.5). The exact form of each term in equation (10.10) as well as the exponent n depends on the reaction stoichiometry, which species are adsorbed, and other mechanistic details. Yang and Hougen present tables from which each of the terms can be constructed for a wide variety of cases.

$$r = \frac{k\left(\text{kinetic term}\right)\left(\text{potential term}\right)}{\left(\text{adsorption term}\right)^n} \tag{10.5}$$

References Cited

[1]   Langmuir, J. Amer. Chem. Soc. 1918, **40**, 1361.

[2]   O. A. Hougen and K. M. Watson, Ind. Eng. Chem. 1943, **35**, 529.

[3]   K. H. Yang and O. A. Hougen, Chem. Eng. Prog. 1950, **46**, 146.