

Chemical Microengineering. III. Multiphase Catalysis

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Introduction

This is the third in a CACHE News series [1,2] about a Virginia-Tech senior-elective course, entitled "chemical microengineering", that includes the study of the continuity-of-species equation for "small chemical systems". The first two articles are available as downloadable files at URLs

http://www.che.utexas.edu/cache/newsletters/fall2000_chemmicro.pdf (Fall 2000 issue) and

http://www.che.utexas.edu/cache/newsletters/spring2001_chemmicro.pdf (Spring 2001 issue).

Because of the similarities of the systems, the sections of this third article will be analogous to those for the second.

What is Multiphase Catalysis?

Multiphase catalysis is defined as a reactor technique that employs the distribution of reacting components between two or more different states -- one stationary and one mobile -- that permit the facile separation of products from the reaction state [3].

Example No. 1: Gas-Liquid Catalysis

As an example, consider gas-liquid catalysis, where a steady-state mixture of reacting components is input at the inlet of a long, hollow, stainless-steel or glass capillary column coated on the inside with a thin film of a non-volatile catalytic solution. A continuous, steady flow of gas passes through the column. After the input flow is started, a steady-state product stream appears at the exit of the column (Figure 1).

Example No. 2: Supported Liquid-Phase Catalysis (SLPC)

As a second example, consider a typical, laboratory-scale, short, hollow, stainless-steel column packed with a porous solid that is filled approximately 30% with a catalyst solution based upon a soluble, transition-metal complex. A steady-state mixture of reacting components is input to the reactor, and products are obtained at the exit. A reactant diffuses into the pores of the porous solid, dissolves in the supported liquid, and reacts, with the products evaporating into the gas phase within the pores. It is important to have a balance of both gas and liquid phases within the pores. [4,5]

Example No. 3: Heterogeneous Catalysis (Gas-Solid Adsorption Catalysis)

As with Example No. 2, consider a typical, laboratory-scale, short, hollow, stainless-steel column packed with a porous solid that contains a dispersed metal such as, for example, platinum, palladium, or rhodium,

metal oxide, metal sulfide, metal carbide, or metal nitride. A steady-state mixture of reacting components is input to the reactor, and products are obtained at the exit. A reactant diffuses into the pores of the porous solid, adsorbs on the catalyst surface, and reacts to form product, which either desorb into the gas phase within the pores. [6]

What is the Gimmick Associated with Gas-Liquid Catalysis?

The basic "gimmick" behind ideal gas-liquid catalysis is the existence of two phases -- one stationary and one mobile -- between which the reacting components of an input mixture rapidly equilibrate. In the ideal case, the equilibration of each reacting component is ideal, in the sense that there exist no mass-transfer limitations to equilibration and the quantity of each component is sufficiently small such that linear partition coefficients apply. The reacting phase is stationary.

Just like ideal partition chromatography, ideal gas-liquid catalysis can be considered to be, in effect, an example of two-dimensional thermodynamics. The three vector directions in Example No. 1 include a single, axial coordinate direction (the length of the capillary tubing; see Figure 1) and two lateral coordinate directions (one being the radial direction) over which thermodynamic equilibrium exists at every point z within the steady-state gas-liquid catalytic column.

Typical Multiphase Catalysis Apparatus: A Tubular Flow System

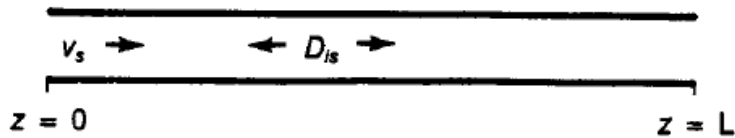


Figure 1. Steady-state reaction and convection in a tubular flow system. A mixture of components is fed continuously into the column at $z=0$ and the products appear at the exit, $z = L$.

Multiphase Catalysis as a Linear Multistate System

The teaching of the basic principles behind gas-solid and liquid-solid adsorption catalysis (typically called "heterogeneous" catalysis) has been a part of the chemical engineering curriculum for decades, specially in graduate school. However, the generality of multiphase catalysis has not been usually taught.

Consider the following linear partition coefficient between states 1 and 2 for an reacting component i ,

$$K_{i2} = \frac{C_{i2}}{C_{i1}} \tag{1}$$

which has units of concentration/concentration. The resulting conservation-of-species equation -- involving diffusion, convection, and irreversible first-order reaction along the axial coordinate direction z -- is,

$$\frac{\partial c_{is}}{\partial t} - D_{ieff} \frac{\partial^2 c_{is}}{\partial z^2} + v_{ieff} \frac{\partial c_{is}}{\partial z} + k_{ieff} c_{is} = 0 \quad (2)$$

In the absence of axial diffusion and the accumulation term, Equation (2) simplifies to,

$$v_{ieff} \frac{\partial c_{is}}{\partial z} + k_{ieff} c_{is} = 0 \quad (3)$$

For a boundary condition of

$$c_{is} (z = 0) = c_{is}^0 \quad (4)$$

at the inlet to a column reactor, the concentration of the reactant at any point, z , within the reactor becomes,

$$\frac{c_{is}}{c_{is}^0} = e^{-\frac{k_{ieff} z}{v_{ieff}}} \quad (5)$$

The next step is to decide what are the specific forms for the effective rate constant and velocity.

What is a State?

Multiphase catalysis basically is the superposition of two-dimensional thermodynamics -- a non-reactive mobile phase and a reactive, stationary phase -- upon steady-state reaction and convection in a third dimension. The purpose of the mobile phase is to provide fresh reactants and to remove products. For simplicity, the two-dimensional equilibrium and third-dimension dynamics can be characterized by a pair of states for the rate-determining, reacting component in a catalytic column (see Figure 2).

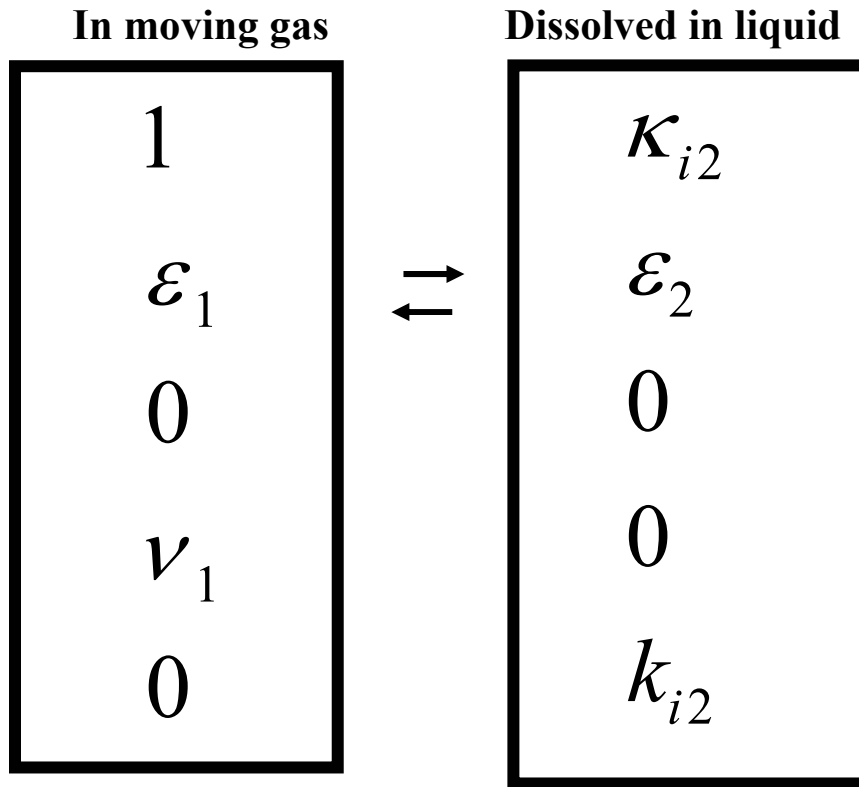


Figure 2. Box representation of the two states (for each reacting component i) in gas-liquid multiphase catalysis for a tubular column system.

In Figure 2, the subscript i represents a reacting component; the subscript numbers 1 and 2 represent the mobile and stationary phases, respectively; k is the first-order or pseudo-first-order rate constant in a phase; and v is the convective velocity of phase 1 . At the bottom of each state box, the value 0 indicates that diffusion is irrelevant to the multiphase catalysis model.

Description

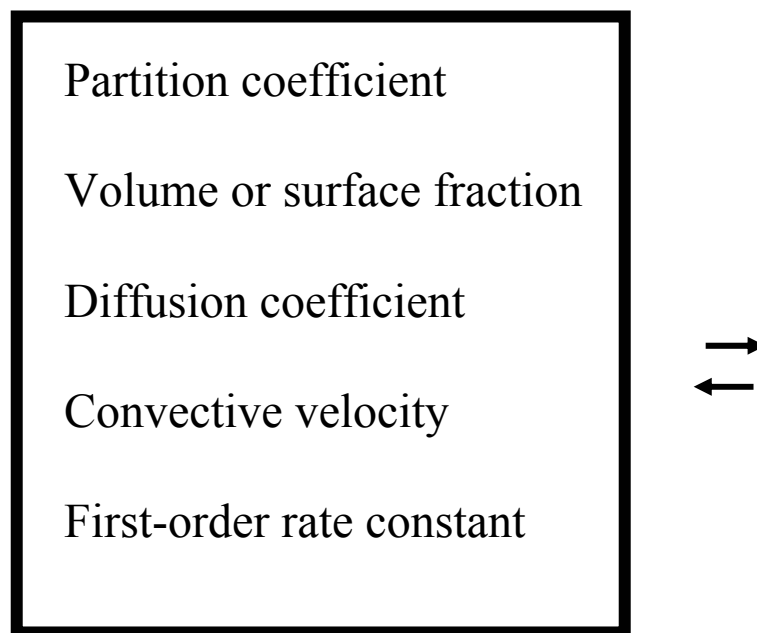


Figure 3. General box representation of a state in a linear multistate chemical system.

States in Gas-Liquid Catalysis

Figure 3 provides a general representation of a state box in any two-dimensional thermodynamic system in which reaction and mass transfer processes occur in the remaining coordinate direction. The quantity, k_{ieff} , is calculated as follows from Figure (2),

$$k_{ieff} = \frac{\varepsilon_2 K_{i2} k_{i2}}{\varepsilon_1 + \varepsilon_2 K_{i2}} \quad (6)$$

and the ratio of the effective rate constant to the effective velocity is,

$$\frac{k_{ieff}}{v_{ieff}} = \frac{\varepsilon_2 K_{i2} k_{i2}}{\varepsilon_1 v_1} \quad (7)$$

The significance of Equation (7) can be understood by the following exponential ratio in Equation (5),

$$\frac{k_{ieff} L A_{\perp}}{v_{ieff} A_{\perp}} = \frac{\varepsilon_2 K_{i2} k_{i2} A_{\perp}}{\varepsilon_1 v_1 A_{\perp}} \quad (8)$$

ε_1 and ε_2 are the volume fractions of the gas and liquid phases, respectively,

$$\varepsilon_s = \frac{\text{volume of phase } s \text{ in reactor}}{\text{total volume in reactor}} \quad (9)$$

Equation (8) therefore becomes,

$$\frac{k_{ieff} L A_{\perp}}{v_{ieff} A_{\perp}} = \frac{\epsilon_2 \kappa_{i2} k_{i2} A_{\perp}}{\epsilon_1 v_1 A_{\perp}}$$

$$= \frac{V_2 \kappa_{i2} k_{i2}}{F_1}$$

(10)

Where A_{\perp} , V_2 is the total volume of liquid in a gas-liquid catalytic column, and F_1 is the gas flow rate at reactor conditions. Based upon Equations (5) and (10), it is possible to create a plot (Figure 3), the slope of which provides the product of thermodynamic and kinetic parameters,

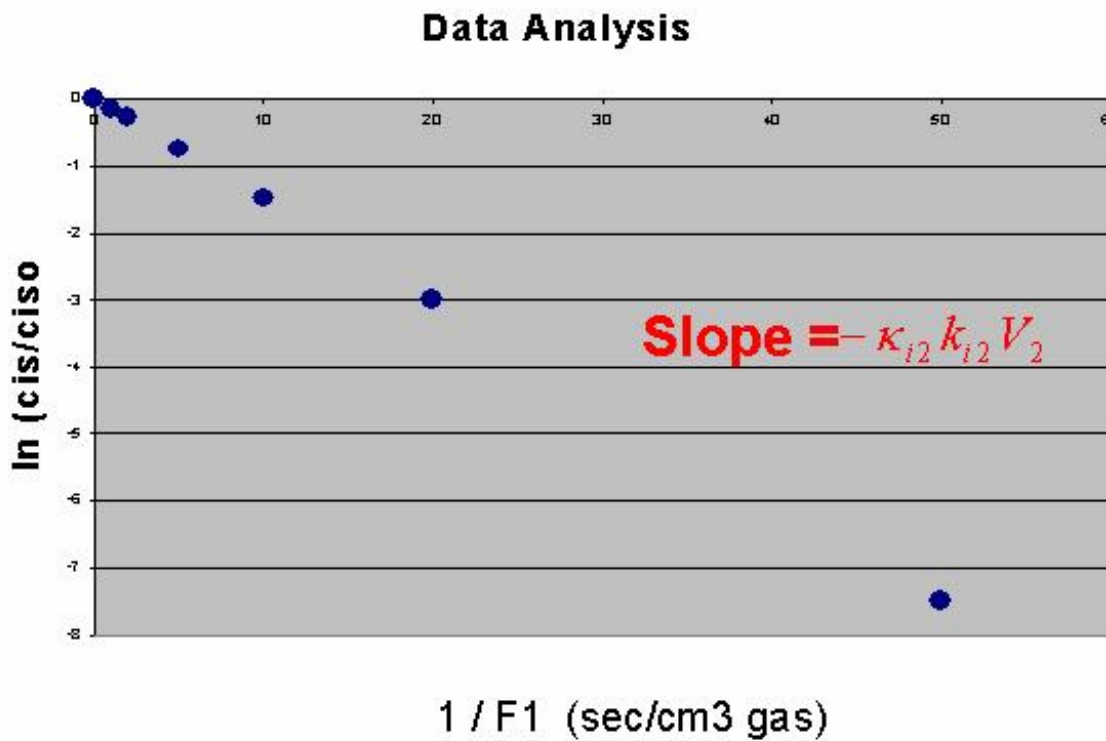


Figure 4. Plot of dimensionless conversion from a gas-liquid catalytic reactor versus the reciprocal gas flowrate at reactor conditions.

If we multiply the numerator and denominator of Equation (1) by the ratio of the volumes of phases 2 and 1, respectively, we obtain the distribution coefficient,

$$K_{i2} = \frac{c_{i2} V_2}{c_{i1} V_1} = \kappa_{i2} \frac{\varepsilon_2}{\varepsilon_1} \quad (11)$$

which has units of moles/moles.

States in Gas-Solid Adsorption Catalysis ("Heterogeneous Catalysis")

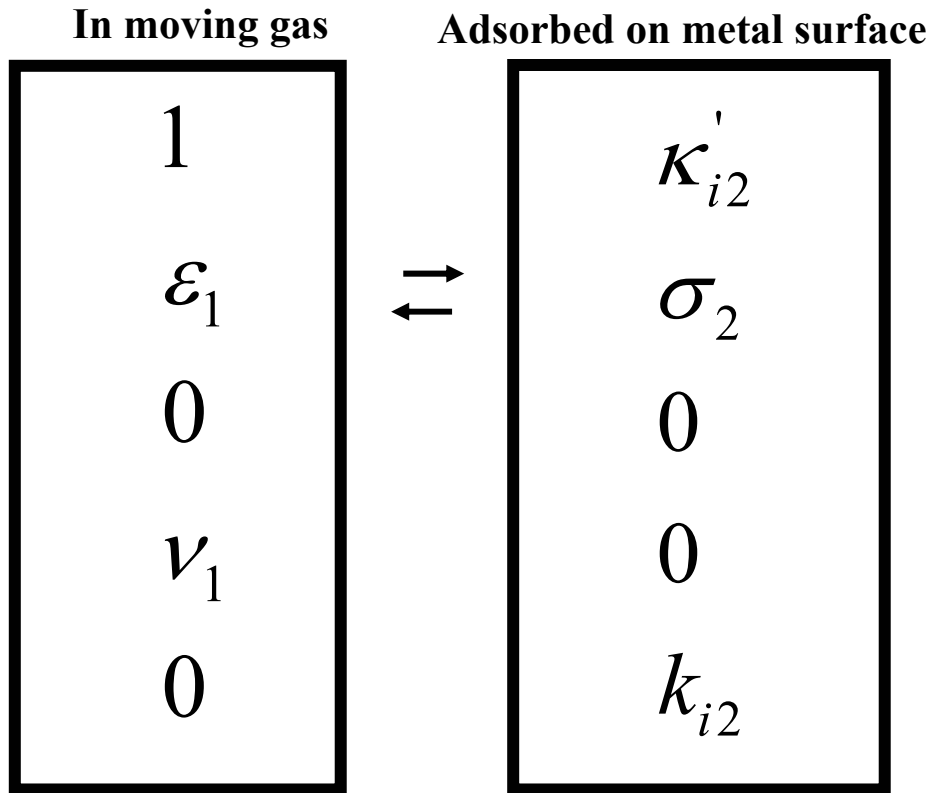


Figure 5. Box representation of the two states (for each reacting component i) in gas-solid adsorption catalysis for a packed tubular column system.

In the adsorbed state of Figure 5, σ_2 is a surface-to-volume ratio and κ'_{i2} is a surface partition coefficient, the ratio of the surface concentration of an adsorbed component divided by the concentration of the component within the gas phase. The distribution coefficient for a surface partition coefficient is,

$$K_{i2} = \frac{c'_{i2} S_2}{c_{i1} V_1} = \kappa'_{i2} \frac{\sigma_2}{\varepsilon_1} \quad (12)$$

A gas-solid adsorption catalysis system experimental plot that corresponds to Figure 4 is shown in Figure 5.

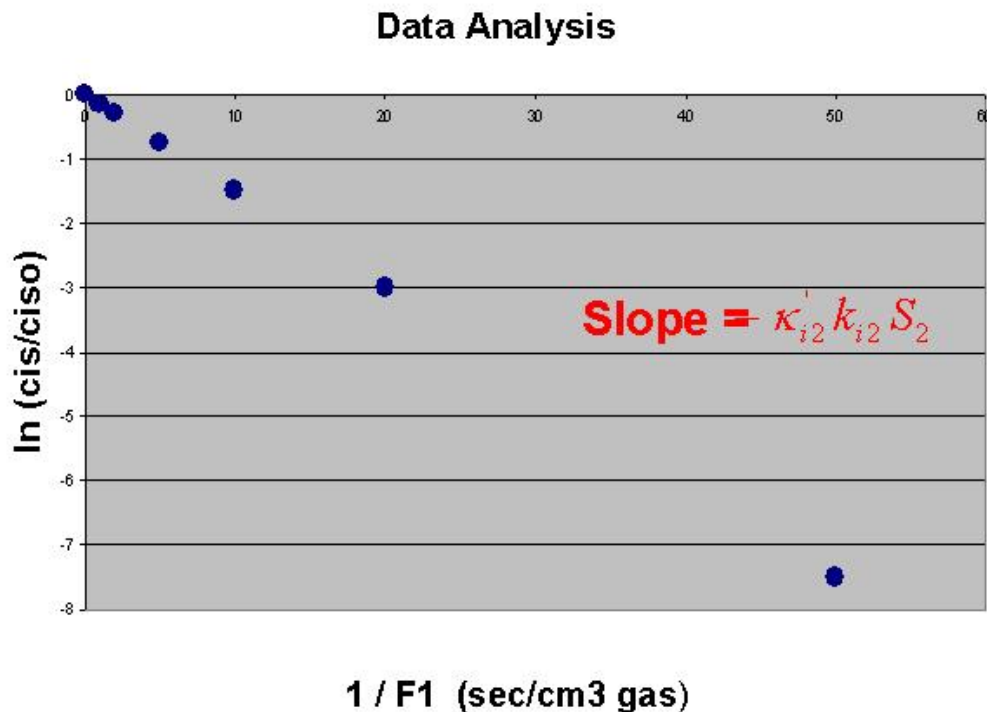


Figure 6. Plot of dimensionless conversion from a gas-solid adsorption catalytic (heterogeneous catalytic) reactor versus the reciprocal gas flowrate at reactor conditions.

In Figure 6, the slope product of the partition coefficient and the rate constant has units that seem to be cm/sec. Such units are incorrect, the correct answer being cubic centimeters gas volume divided by the product of square centimeters surface area and seconds.

Examples of Multiphase Catalysis Techniques

Table I. Standard multiphase catalysis techniques

Standard Multiphase Catalysis Technique	Mobile Phase	Stationary Phase
gas-liquid catalysis	gas	liquid contained in porous solid
gas-solid catalysis	gas	solid particles containing deposited catalyst
liquid-liquid catalysis	liquid	organic liquid contained in porous solid
solid-liquid catalysis	liquid	solid particles containing deposited catalyst
molecular-sieve catalysis	gas	molecular sieve contained deposited catalyst
ion-exchange catalysis	liquid	porous ion-exchange particles
gel-permeation catalysis	liquid	cross-linked solid particles

Table I and Table II summarize standard and non-standard multiphase catalysis techniques, respectively. Table III summarizes different categories of multiphase catalysis techniques. The techniques differ in the type of apparatus -- glass column, capillary column, stainless-steel, high-pressure column, paper, or glass

plate; whether the technique employs one or two phases; and the possible existence of superimposed chemical equilibria within a liquid phase.

Table II. Non-standard multiphase catalysis techniques

Non-Standard Catalysis Techniques
aerosol catalysis
dust catalysis
solid-liquid fiber catalysis
gas-solid fiber catalysis
flotation catalysis
oxidation-reduction catalysis
electrode catalysis
membrane catalysis

Table III. Categories of multiphase catalysis techniques

Categories of Multiphase Catalysis Techniques	Special Characteristics
High-performance techniques	apparatus consists of column under high pressure
Column techniques	apparatus consists of a cylindrical column
Paper techniques	stationary phase is paper
Thin-layer techniques	stationary phase is thin layer of porous solids
Capillary techniques	apparatus consists of a capillary column
Micro-column techniques	column is very small

Summary

Multiphase catalysis is defined as a reactor technique that employs the distribution of reacting components between two or more different states -- one stationary and one mobile -- that permit the facile separation of products from the reaction state. The reaction *state* can be a dissolved component within a phase, an adsorbed component at an interface, or a reversibly complexed (to an ion or molecule) component within a liquid phase. The apparatus can consist of a vertical glass tube; a high-pressure stainless-steel column; a long glass or stainless-steel capillary tube; paper; an electrophoresis apparatus; or a plate with a thin-layer coating of porous solid.

For an extended essay that discusses linear multistate chemical systems in general, please see reference (7). This series of CACHE News articles extends the content of this essay.

Nomenclature

Arabic letters

- c Volume concentration of reacting component, used in Equation (1)
- c' Surface concentration of reacting component, used in Equation (12)
- D Diffusion coefficient, used in Equations (2) and (3)
- k First-order or pseudo-first-order rate constant, used in Equations (2) and (3)
- K Distribution coefficient, defined by Equation (11) or (12); units of moles/moles
- t time
- v velocity, used in Equations (2) and (3)
- x x axis
- z z axis

Greek letters

- ε Volume fraction, used in Figure (2), Figure (5), and Equations (6), (9), (11), and (12)
- κ Partition coefficient, a ratio of concentrations, used in Equation (1); units of concentration/concentration
- σ Surface-to-volume fraction, used in Figure (5) and Equation (12), units of volume concentration/surface concentration

Subscripts

- eff* Effective value index, defined in Equations (2), (3), and (4)
- i* Eluting component index
- s* Environment index
- i1* Component *i* in phase or environment **1**
- i2* Component *i* in phase or environment **2**
- i3* Component *i* in phase or environment **3**
- i4* Component *i* in phase or environment **4**

Superscripts

- ' Indicates a surface state

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NOTE: Several corrections were made to this article on Tuesday, October 1, 2002. This revised file, CACHEarticle_III_06.pdf was substitute for the original article, CACHEarticle_III_05.pdf.