

# Chemical Microengineering. IV. The Conservation-of-Species Equation for a Linear Multistate Chemical System

By\*

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## Introduction

This article provides the theoretical basis for the conservation-of-species equation for a *linear, multistate, chemical system*. The derivation dates back to the first "chemical microengineering" senior-elective course, which was taught at Virginia Tech starting in 1973 [1].

## Heterogeneous Systems: The Concept of a *State*

Most chemical systems in practical situations are heterogeneous systems. Even the classic, homogeneous, batch reactor in organic chemistry -- the three-necked round-bottom flask -- is a heterogeneous system in principle. In addition to the stirred liquid, there are several phases and interfaces, namely, the glass walls, the surface of the stirrer, and the gas above the liquid. Only under the assumption of no equilibration or reaction on the walls and in the gas does the assumption of homogeneity become valid for the system.

Some sort of bookkeeping is required to keep track of the different solutes "I" in/on the different phases and interfaces of a heterogeneous system. We have anticipated this need by defining a phase/interface environment subscript, "S", and by using it consistently in our conservation-of-species equations, even when only a single phase "S" present. Thus, the concentration of solute "I" in environment "S" is written as  $c_{is}$ .

We call the combination of solute "I" in environment [example, a phase or interface] "S" a *state* (**NOTE:** 29 years ago, we called such a combination a *partition state* [1,2,3,4]). The *state* nomenclature simplifies the discussion of simultaneous reaction, diffusion, and convection in heterogeneous systems in which rapid equilibration of solute "I" occurs among the phases/interfaces "S". The reader is referred to References [3] and [4] for a discussion of the thermodynamic significance of the concept of a *state*. The customary statement of phase equilibrium [3], "*If two phases are in equilibrium, all components capable of passing from one to the other must have the same chemical potential in the two phases,*" can be broadened, through the use of the concept of a *state*, to incorporate both physical (i.e., phase/interface) and chemical equilibria: "*If two states are in equilibrium, a component capable of passing from one to the other must have the same chemical potential in the two states.*" This is an important

generalization, because it permits us to write the *conservation-of-species* (also called the *continuity-of-species*) equation for a class of heterogeneous chemical systems in a manner that is independent of the types of equilibria that occur.

It should be emphasized a final time that the concept of a *state* has both bookkeeping and thermodynamic significance. In this article, it is the bookkeeping function that is most useful. If a solute "I" can be identified by physical or chemical means, and if it is present in/at different phases/interfaces "S", then each combination "IS" represents a different *state* for the solute. In terms of the *conservation-of-species* equation, the dynamic behavior of each *state* can be characterized in terms of a diffusion coefficient, convective velocity, pseudo-first-order rate constant, distribution coefficient for the state, and volume fraction or surface-to volume ratio for the environment "S" in which the *state* exists.

## The Conservation-of-Species Equation for a State

The conservation-of-species law for a chemical system consisting of a specified region of space  $\mathbf{V}$  that is bounded by a closed surface  $\mathbf{S}$  and that contains one or more components can be stated as follows:

*The time rate of change of mass of each component I in a multicomponent mixture is equal to the net rate at which the mass of component I is produced by chemical reactions less the net rate of mass efflux of component I from the region of space  $\mathbf{V}$  through the closed surface  $\mathbf{S}$ .*

The conservation-of-species law for a single state IS can be restated in the following manner:

$$\left[ \begin{array}{l} \text{net rate of accumulation} \\ \text{of state IS in } \mathbf{V} \end{array} \right] = \left[ \begin{array}{l} \text{net rate of chemical} \\ \text{production of state IS in } \mathbf{V} \end{array} \right] - \left[ \begin{array}{l} \text{net rate of mass input/output} \\ \text{of state IS through } \mathbf{S} \end{array} \right]$$

which leads immediately to a classic shell balance, as given on page 555 of Bird, Stewart and Lightfoot (BSL) [5].

In Cartesian coordinates, the shell balance derivation applies to a volume element,  $\Delta x \Delta y \Delta z$ , through which a multicomponent mixture is both flowing and reacting. BSL wrote the following rates of change, input, and output in a single dimension, which we shall change to the z-direction instead of the x-direction. One additional difference: we shall write the shell balance in terms of state IS.

Time rate of change of mass of state IS in volume element  $\Delta x \Delta y \Delta z$

$$\frac{\partial r_{is}}{\partial t} \Delta x \Delta y \Delta z \quad (1)$$

input of state IS across face of z

$$n_{ISZ} \Big|_z \Delta x \Delta y \quad (2)$$

output of state IS across face at z +  $\Delta z$

$$n_{ISZ} \Big|_{z+\Delta z} \Delta x \Delta y \quad (3)$$

rate of production of state IS by chemical reaction

$$r_{is} \Delta x \Delta y \Delta z \quad (4)$$

Our derivation here differs from BSL when we consider the input/output of IS across the faces in the x and y directions. We do not apply a similar procedure as BSL to the x and y directions, divide through by  $\Delta x \Delta y \Delta z$ , and let the size of the volume element decrease to zero to get

$$\frac{\partial \mathbf{r}_{is}}{\partial t} + \left( \frac{\partial n_{isX}}{\partial x} + \frac{\partial n_{isY}}{\partial y} + \frac{\partial n_{isZ}}{\partial z} \right) = r_{is} \quad (5)$$

Instead,

- (a) we sum the shell-balance terms for component I over all of its linear states  $IS = i1, i2, i3, \dots$ ;
- (b) we assume that there is no mass flux for the sum in both the x and y directions;
- (c) we assume that a separate reaction is associated with component I in each of its linear states;
- (d) we let the size of the volume element decrease to zero; and
- (e) we obtain a simplified equation that contains a mass flux only in the z direction.

$$\sum_{s=1}^n \left[ \frac{\partial \mathbf{r}_{is}}{\partial t} + \frac{\partial n_{isZ}}{\partial z} - r_{is} \right] = 0 \quad (6)$$

In Equations (1) through (6),

$n_{isX}$  = mass flux of component I in state IS in the X coordinate direction

$n_{isY}$  = mass flux of component I in state IS in the Y coordinate direction

$n_{isZ}$  = mass flux of component I in state IS in the Z coordinate direction

$v_i$  = mass average velocity of component I in the multi-component mixture

$t$  = time

$x$  = x coordinate direction

$y$  = y coordinate direction

$z$  = z coordinate direction

$r_{is}$  = mass density of component I in state IS in the multi-component mixture

Equation (6) requires an expression for the total mass flux of component I in the multi-component mixture [1],

$$n_{isZ} = - \mathbf{r} D_{is}^m \frac{\partial w_{is}}{\partial z} + \mathbf{r}_{is} \mathbf{v}_s \quad (7)$$

where

$D_{is}^m$  = the diffusivity of component I in state IS in the multi-component mixture

$\mathbf{v}_s$  = mass average velocity of environment S in the multi-component mixture

$r_{is}$  = mass density of component I in state IS in the multi-component mixture

$\mathbf{r}$  = mass density of the multi-component mixture

$w_{is}$  = mass fraction of component I in state IS in the multi-component mixture

We substitute Equation (7) into Equation (6) and make the assumption of constant  $\mathbf{r}$  and constant  $D_{is}^m$  to obtain,

$$\sum_{s=1}^n \left[ \frac{\partial r_{is}}{\partial t} - \frac{\partial \left[ \mathbf{r} D_{is}^m \frac{\partial w_{is}}{\partial z} + \mathbf{r}_{is} \mathbf{v}_s \right]}{\partial z} - r_{is} \right] = 0 \quad (8)$$

and then convert to molar concentrations to yield,

$$\sum_{s=1}^n \left[ \frac{\partial c_{is}}{\partial t} - \frac{\partial \left[ D_{is}^m \frac{\partial c_{is}}{\partial z} + c_{is} v_s \right]}{\partial z} - R_{is} \right] = 0 \quad (9)$$

In the derivation of Equation (9), it should be noted that,

$$c_{is} = \frac{r_{is}}{M_i} \quad (10)$$

$$R_{is} = \frac{r_{is}}{M_i} \quad (11)$$

where  $M_i$  is the molecular weight of component I.

We now integrate the summation in Equation (9) over the entire volume  $V$  of the system,

$$\sum_{s=1}^n \iiint_V \left[ \frac{\partial c_{is}}{\partial t} - \frac{\partial \left[ D_{is}^m \frac{\partial c_{is}}{\partial z} + c_{is} v_s \right]}{\partial z} - R_{is} \right] dV = 0 \quad (12)$$

Equation (12) simplifies to,

$$\sum_{s=1}^n \iiint_V \left[ \frac{\partial c_{is}}{\partial t} - D_{is} \frac{\partial^2 c_{is}}{\partial z^2} + v_s \frac{\partial c_{is}}{\partial z} - R_{is} \right] dV = 0 \quad (13)$$

where we have assumed that the diffusion coefficient of component I in state IS within the multi-component mixture is a constant and have dropped the superscript  $m$ . The differential volume  $dV$  can be written as a differential volume element,

$$dV = A_{\perp} dz \quad (14)$$

where

$A_{\perp}$  = cross-sectional area transverse (perpendicular) to the Cartesian-coordinate axis  $z$

The differential volume  $dV_s$  of the phase that contains state IS also can be written as a cylindrical, differential volume element,

$$dV_s = A_{\perp s} dz \quad (15)$$

where

$A_{\perp s}$  = cross-sectional transverse (perpendicular) area of the phase that contains state IS

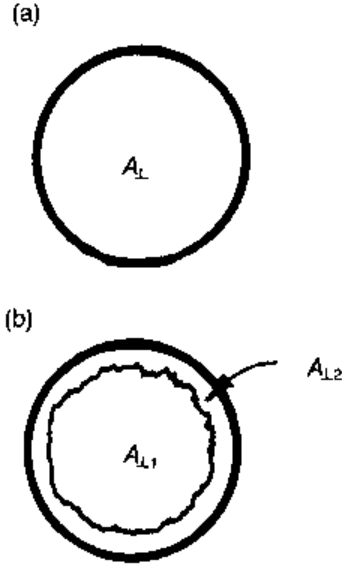
Equation (15) applied to Equation (13) therefore yields,

$$\int_z \sum_{s=1}^n A_{\perp s} \left( \frac{\partial c_{is}}{\partial t} - D_{is} \frac{\partial^2 c_{is}}{\partial z^2} + v_s \frac{\partial c_{is}}{\partial z} - R_{is} \right) dz = 0 \quad (16)$$

Since this equation applies to any smaller differential length  $dz$ , we can eliminate the single integral and obtain the following one-dimensional partial differential equation,

$$\sum_{s=1}^m A_{\perp s} \left( \frac{\partial c_{is}}{\partial t} - D_{is} \frac{\partial^2 c_{is}}{\partial z^2} + v_s \frac{\partial c_{is}}{\partial z} - R_{is} \right) = 0 \quad (17)$$

that contains a summation for component I over all of its states IS. The quantity  $A_{\perp}$  is the total cross-sectional area of the chemical system, and the quantity  $A_{\perp s}$ , is the total cross-sectional area of a given phase “S” (Figure 1).



**Figure 1.** Cross-sectional areas in (a) a single-phase, and (b) a two-phase chemical system. It is assumed that such areas remain constant throughout the entire length of the cylindrical-geometry system.

The next step is the assumption of a linear relationship between the concentration of solute “I” in state “IS” and its concentration in a carefully-chosen reference state “ISREF”. The constant that characterizes this relationship is known in the chemical literature as a *partition coefficient*,

$$\mathbf{k}_{is} = \frac{c_{is}}{c_{isref}} \quad (18)$$

A change in concentration in one of the states instantaneously influences the concentrations in all other states according to the partition coefficient relationship, Equation (18). The result of applying Equations (18) and (19), which is a rate expression for a pseudo-first-order or first-order reaction,

$$R_{is} = -k_{is} c_{is} \quad (19)$$

to Equation (17) is Equation (20),

$$\frac{\partial c_{isref}}{\partial t} - \frac{\partial^2 c_{isref}}{\partial z^2} \frac{\sum_{s=1}^n A_{\perp s} \mathbf{k}_{is} D_{is}}{\sum_{s=1}^n A_{\perp s} \mathbf{k}_{is}} + \frac{\partial c_{isref}}{\partial z} \frac{\sum_{s=1}^n A_{\perp s} \mathbf{k}_{is} v_s}{\sum_{s=1}^n A_{\perp s} \mathbf{k}_{is}} + c_{isref} \frac{\sum_{s=1}^n A_{\perp s} \mathbf{k}_{is} k_{is}}{\sum_{s=1}^n A_{\perp s} \mathbf{k}_{is}} = 0 \quad (20)$$

which can be simplified to Equation (21),

$$\frac{\partial c_{isref}}{\partial t} - D_{ieff} \frac{\partial^2 c_{isref}}{\partial z^2} + v_{ieff} \frac{\partial c_{isref}}{\partial z} + k_{ieff} c_{isref} = 0 \quad (21)$$

accumulation
multistate diffusion
multistate convection
multistate pseudo-first-order reaction

The physical significance of the constant “effective” parameters  $D_{ieff}$ ,  $v_{ieff}$ ,  $k_{ieff}$  will be discussed in a subsequent section. Since any state can be selected as the reference state for component I, ISREF, the “ref” can be dropped everywhere in Equation (21), as shown in Equation (22).

$$\frac{\partial c_{is}}{\partial t} - D_{ieff} \frac{\partial^2 c_{is}}{\partial z^2} + v_{ieff} \frac{\partial c_{is}}{\partial z} + k_{ieff} c_{is} = 0 \quad (22)$$

accumulation
multistate diffusion
multistate convection
multistate reaction

A chemical system that satisfies the above assumptions and the steps associated with this derivation, is called a *linear multistate chemical system* [1]. Ideal thermodynamic systems exhibit no spatial concentration gradients in any of *three coordinate directions*. Our linear, multistate, chemical-system approach relaxes such a restriction to only *two coordinate directions* (the two transverse coordinate directions x and y), with the third coordinate direction z exhibiting dynamic processes that are not at thermodynamic equilibrium.

## What do the “Effective” Parameters Mean?

According to Equations (20) and (21), the three “effective” parameters are defined as follows,

$$D_{ieff} = \frac{\sum_{s=1}^n A_{\perp s} k_{is} D_{is}}{\sum_{s=1}^n A_{\perp s} k_{is}} \quad (23)$$



$$V_{ieff} = \frac{\sum_{s=1}^n A_{\perp s} k_{is} v_s}{\sum_{s=1}^n A_{\perp s} k_{is}} \quad (24)$$

$$k_{ieff} = \frac{\sum_{s=1}^n A_{\perp s} k_{is} k_{is}}{\sum_{s=1}^n A_{\perp s} k_{is}} \quad (25)$$

These “effective” parameter equations can be simplified. The simplification process given in this paper is as follows:

- (a) Point out that Equations (23) through (25) can apply to both *physical* and *chemical equilibria*.
- (b) Define the *partition coefficient* for both a volume state and a surface state.
- (c) Define the *distribution coefficient* for both a volume state and a surface state.
- (d) Define the *volume fraction* and also the *surface-to-volume ratio*.
- (e) Define a dimensionless parameter, the *segregation fraction*.
- (f) Rewrite Equations (23) through (25) in terms of *segregation fractions*.
- (g) Provide an example of the ratio,  $k_{ieff} / v_{ieff}$ , for a *supported-liquid-phase catalyst pellet* in a packed tubular reactor.
- (h) Provide several reasons why Equation (22), and Equations (23) through (25), are useful to students.

## Physical and Chemical Equilibria

Several definitions are in order [1]:

**reaction** -- Taken in its broadest sense, any change in the internal constitution of a system. Such a change may be in the physical state of the components or it may be the result of chemical transformations among the molecules in the system.

**physical reaction** -- A reaction in which the change is in the physical state of the components.

**chemical reaction** -- A reaction in which the change is a chemical transformation among the molecules. When applied to chemical systems, the term equilibrium has in the past been used in two ways: to denote the condition of equilibrium, in which the chemical affinity of each reaction is equal to zero [6] and to collectively denote physical or chemical reactions whose affinities are equal to zero (for example, when the terms “phase equilibria” or “chemical equilibria” are used in textbooks and articles). We shall follow the second of these meanings and use the following definitions [2]:

**chemical equilibrium** -- A chemical reaction in which the chemical affinity is equal to zero.

**physical equilibrium** -- A physical reaction in which the chemical affinity is equal to zero.

Thus we use the term physical equilibria instead of phase equilibria, a term frequently found in the chemistry and chemical engineering literature.

## Partition Coefficient

Once the concept of a state has been defined, the distinction between the concepts of *partition* coefficient and *distribution* coefficient can be given without difficulty:

*partition coefficient* -- The ratio of the concentrations of a solute “I” in two of its states.

*distribution coefficient* -- The ratio of the amounts of a solute “I” in two of its states.

The partition coefficient is defined as Equation (27),

$$k_{is} = \frac{c_{is}}{c_{isref}} \quad \text{or} \quad k'_{is} = \frac{c'_{is}}{c_{isref}} \quad (26)$$

A prime is used for both the concentration  $c'_{is}$  and the partition coefficient  $k'_{is}$  if the state “IS” is a surface state. In such a case, the surface concentration has units of mol/area, and the corresponding partition coefficient has units of volume/area.

Why is it necessary to define a reference state? Consider the following example. In a heterogeneous system of three states (IS = I1, I2, and I3), there are two independent partition coefficients for a species “I” that equilibrates between the states. Being a ratio of concentrations, the partition coefficient must have the concentration of one of these five states in the denominator. In order to simplify computations, this same concentration should be in the denominator

for all four states. We call the state whose concentration is in the denominator the *reference state* and use the notation ISREF to characterize it. Thus, for ISREF = i1, the two independent partition coefficients in a five-state system are,

$$\mathbf{k}_{i2} = \frac{c_{i2}}{c_{i1}} \quad (27)$$

$$\mathbf{k}_{i3} = \frac{c_{i3}}{c_{i1}}$$

In linear systems, each partition coefficient is constant. The concentration of component I in environment S can have units of either mol/vol (for a volumetric state) or mol/area (for a surface state). To repeat, a surface concentration has a prime associated with it, as in  $c'_{is}$ . In order to calculate the amount  $n_{is}$  of solute I in a given state IS, one must multiply the concentration by either a volume  $V_s$ , or an interfacial area  $S_s$ :

$$n_{is} = c_{is} V_s \quad (28)$$

$$n_{is} = c'_{is} S_s \quad (29)$$

Unlike the distribution coefficient, which is dimensionless, the partition coefficient has dimensions of either volume/volume or else volume/area. Different phases are like apples and oranges -- their volume units must be retained when units for symbols are given. As in any good bookkeeping system, retention of the units of the phases under consideration provides an important reminder that the total amount of each phase will be required during the course of the calculation.

In this chapter, the symbol for a partition coefficient is the Greek letter kappa,  $\mathbf{k}$ , plus a suitable state subscript. A better symbol than kappa is desirable to represent partition coefficients because of the potential confusion among the symbols for partition coefficient, distribution coefficient, and rate constant, ( $\mathbf{k}, K, k$ ), respectively) Kappa is retained here because of its prior use in the literature [1], [2], [3].

## Distribution Coefficient

In a system at thermodynamic equilibrium, the *distribution coefficient* is defined mathematically as the ratio of the number of moles of solute "I" in state "IS" to the number of moles of solute "I" in a reference state, which we have designated as ISREF:

$$K_{is} = \frac{n_{is}}{n_{isref}} \quad (30)$$

Note that  $K_{is}$  is a dimensionless quantity. The selection of the reference state is arbitrary and generally follows customs established in the literature. The distribution coefficient can also be written as the product of a partition coefficient,  $k_{is}$ , and either a volume fraction  $e_s$  or a surface-to-volume ratio  $s_s$ ,

$$K_{is} = k_{is} \frac{e_s}{e_{sref}} \quad (31)$$

$$K_{is} = k_{is} \frac{s_s}{e_{sref}} \quad (32)$$

These additional physical parameters will now be discussed.

## Volume Fraction and Surface-to-Volume Ratio

Chemistry and biochemistry textbooks do not treat heterogeneous systems as frequently as do chemical engineering textbooks. As a result, chemistry and biochemistry students fail to gain an appreciation for two very important quantities in heterogeneous systems, namely, the volume fraction and the surface-to-volume ratio. Definitions are in order:

*volume fraction* -- The ratio of the volume of phase S to the total volume of the chemical system.

*surface-to-volume ratio* -- The ratio of the surface area between two phases to the total volume of the chemical system.

Neither quantity is dimensionless because volume units associated with different phases do not cancel. The manner in which the volume fraction appears in the derivation of the conservation-of-species equation for a linear multistate chemical system is as a ratio of cross-sectional areas of the chemical system [Figure (1)], which are assumed to be uniform as a function of the axial spatial variable  $z$ .

$$e_s = \frac{A_{\perp s}}{A_{\perp}} \quad (33)$$

Two other, standard definitions for the volume fraction and the surface-to-volume ratio are [1]:

$$\mathbf{e}_s = \frac{V_s}{V} \quad (34)$$

$$\mathbf{e}_s = \frac{S_s}{V} \quad (35)$$

Note that a volume is the product of a cross-sectional area times a length (for example, the total length  $L$  of the system):

$$V = A_{\perp} L \quad (36)$$

$$V_s = A_{\perp s} L \quad (37)$$

A surface-to-volume ratio is an important quantity because it significantly influences the total rate of mass transfer (mol/s) between two phases, or between a phase and an interface (as would occur with a heterogeneous catalyst). The higher the surface-to-volume ratio, the greater the mass transfer rate. Two examples where high ratios are important are in the human lungs and in porous heterogeneous catalysts.

## Segregation Fraction

The diffusion coefficient, and velocity have already been explained in previous sections of this chapter. A new and useful dimensionless quantity is the *segregation fraction*  $Y_{is}$  of solute "I" in state "IS" [2].

In a system at thermodynamic equilibrium,  $Y_{is}$  is defined mathematically as

$$Y_{is} = \frac{n_{is}}{n_i^0} \quad (38)$$

where  $n_{is}$  is the number of moles of solute "I" in state "IS", and  $n_i^0$  is the total number of moles of "I" in the system. For a linear system with linear distribution coefficients, the segregation fraction is determined according to the equation,

$$Y_{is} = \frac{K_{is}}{\sum_{s=1}^n K_{is}} \quad (39)$$

where  $K_{is}$  is a distribution coefficient, also a dimensionless quantity. Equation (48) also applies to two-dimensional linear multistate chemical systems, and provides an alternative method for computing  $Y_{is}$  ;

### Effective Diffusion Coefficient, Velocity, and First-Order Rate Constant

The effective diffusion coefficient, velocity, and rate constant are defined by the following three equations, all of which have the same basic form and represent weighted averages of the diffusion coefficient, velocity, and rate constant of solute “I” in all of its equilibrating states.

$$D_{ieff} = \sum_{s=1}^n Y_{is} D_{is} \quad (40)$$

$$v_{ieff} = \sum_{s=1}^n Y_{is} v_{is} \quad (41)$$

$$k_{ieff} = \sum_{s=1}^n Y_{is} k_{is} \quad (42)$$

In these equations,

$D_{is}$  = diffusion coefficient of solute I in state IS (length squared /time)

$v_s$  = mass-average velocity of state IS (length/time)

$k_{is}$  = first-order rate constant of solute I in state IS (1/time)

$Y_{is}$  = fraction of solute I in state IS (dimensionless)

$C_{is}$  = concentration of solute I in state IS (mol/volume)

$Z$  = axial coordinate direction (length)

### Example: Supported-Liquid-Phase Catalyst (SLPC) Pellet in a Packed Tubular Reactor

Consider a supported liquid-phase catalyst, which was discussed in Part III of this series of articles [7]. The quantity,  $k_{ieff}$ , is calculated as follows,

$$k_{ieff} = \frac{e_2 k_{i2} k_{i2}}{e_1 + e_2 k_{i2}} \quad (43)$$

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

$$\frac{k_{ieff}}{v_{ieff}} = \frac{e_2 k_{i2} k_{i2}}{e_1 n_1} \quad (44)$$

The significance of Equation (44) can be understood by the following exponential ratio in Equation (45), which is the concentration of the reactant at any point,  $z$ , within the reactor discussed in part III of this series [7],

$$\frac{C_{is}}{C_{is}^0} = e^{-\frac{k_{ieff} z}{v_{ieff}}}$$

(45)

If we multiply the numerator and denominator in the exponential of Equation (46) by the total cross-sectional area of the reactor (see Figure 1), we obtain Equation (46),

$$\begin{aligned} \frac{k_{ieff} L A_{\perp}}{v_{ieff} A_{\perp}} &= \frac{\mathbf{e}_2 \mathbf{k}_{i2} k_{i2} A_{\perp}}{\mathbf{e}_1 \mathbf{n}_1 A_{\perp}} \\ &= \frac{V_2 \mathbf{k}_{i2} k_{i2}}{F_1} \end{aligned}$$

(46)

where  $V_2$  is the total volume of liquid in a gas-liquid catalytic column, and  $F_1$  is the gas flow rate at reactor conditions.  $\mathbf{e}_1$  and  $\mathbf{e}_2$  are the volume fractions of the gas and liquid phases, respectively,

$$\mathbf{e}_s = \frac{\text{volume of phase } s \text{ in reactor}}{\text{total volume in reactor}}$$

(47)



## Why is Equation (22) Useful to Students?

Historically, Equation (22) was useful to the author because it helped answer questions in the categories of mass transfer and reactors encountered during a brief, industrial research career at Monsanto and Exxon Research & Engineering. Typical questions included:

- For a first-order rate constant in heterogeneous catalysis, why are the units of the rate constant in cm/sec rather than in inverse seconds?
- What is the basic gimmick for why elution chromatography is able to separate a mixture of molecules into separated peaks?
- In the use of gas-liquid chromatography to separate a mixture of low-MW olefins, why does ethylene glycol as a stationary phase fail to separate the olefins whereas as the dissolution of silver nitrate in the ethylene glycol succeed in separating them?
- How does one interpret experimental data for a tubular, catalytic reactor packed with supported liquid-phase catalyst particles?
- How does one interpret experimental data for a tubular, catalytic reactor packed with heterogeneous catalyst particles?
- What is the principle behind carrier diffusion through a membrane?
- How does one gracefully and logically incorporate volume fractions into conservation-of-species equations?
- What is the gimmick associated with steady-state, countercurrent separation processes?
- How does one interpret experimental data for capillary gas-liquid chromatography to obtain absolute or relative thermodynamic properties?

## Summary

We have defined the concept of a state to facilitate discussions of “heterogeneous” chemical systems in which two-dimensional physical and chemical equilibria are superimposed on one-dimensional dynamic processes such as diffusion, convection, and reaction. The result is a simple and powerful equation, Equation (34), that can be used to teach the basic principles of chromatography; continuous, countercurrent separation processes; heterogeneous fixed-bed reactors; multiphase catalysis; phase-transfer catalysis; facilitated diffusion; and other chemical processes that rely upon the conservation-of-species equation. We have reduced the theoretical treatment of multistate chemical systems to (a) solution of the homogeneous one-dimensional conservation-of-species equation, and (b) bookkeeping associated with the many states in which a solute “I” can participate. We have made no fundamental distinction between physical and chemical equilibria in defining the concept of a state.

A related publication, which may be out of print, is “Continuity of Species in Physical and Chemical Processes” [8].

## Acknowledgement

The author gratefully acknowledges Professor Emeritus Richard Rice, who provided the following commentary: “*I really disliked immensely the Gauss-Ostragradiskii (henceforth denoted as GO) method of doing material balances. It ALWAYS confused students.*” In the author’s opinion, the world is a better place now that the GO theorem has been expunged from the last drafts of this manuscript.

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