

## A course in . . .

# MASS TRANSFER WITH CHEMICAL REACTION

W. J. DECOURSEY

University of Saskatchewan

Saskatoon, Saskatchewan, Canada S7N 0W0

**I**NDUSTRIAL USE OF absorption and stripping in cases where simultaneous homogeneous chemical reaction has an appreciable effect on the rate of mass transfer goes back at least fifty years to the introduction of ethanolamine solutions to absorb hydrogen sulfide and carbon dioxide from gases. Theoretical development in this area goes back about the same length of time to the pioneering studies of Hatta [1, 2]. However, as in many other areas, industrial development had to run ahead of theory; design was based on empirical studies and scale-up. The first reference books devoted entirely to mass transfer with chemical reaction appeared in 1967 [3] and 1970 [4].

I began to teach a graduate course in mass transfer in 1964. The content of that course has been modified considerably in the intervening years. It always contained some mass transfer with chemical reaction, but the content in that area increased appreciably after the book by Danckwerts [4] was published. In recent years, mass transfer with chemical reaction has become the dominant section of the course.



**W. J. DeCoursey** received his bachelor's degree from the University of Alberta and his PhD from Imperial College, University of London, England, both in chemical engineering. After five years with Sherritt Gordon Mines Limited in Alberta, he spent a year in graduate study at the Massachusetts Institute of Technology. He has taught chemical engineering at the University of Saskatchewan since 1961.

. . . industrial development had to run ahead of theory; design was based on empirical studies and scale-up. The first reference books devoted entirely to mass transfer with chemical reaction appeared in 1967 and 1970.

### COURSE CONTENT

The main topics included in the present course and the approximate distribution of time are shown in Table 1.

**1. Mathematical Models of Mass Transfer** • This topic deals with some basic principles. We consider diffusion equations, diffusivities, and diffusion of electrolytes. This consideration results in differential equations of various degrees of complexity based on various assumptions. Next comes mathematical development of the most important models of convective mass transfer: the film model of Whitman and Lewis, the penetration model of Higbie, and the surface renewal model of Danckwerts. The relation of the Danckwerts model, with its exponential distribution function, to the Laplace transform is discussed. We examine the available experimental evidence regarding the relative accuracy of predictions from the three basic models of convective mass transfer.

**2. Enhancement of Mass Transfer Rates by Homogeneous Chemical Reaction** • We begin this topic with a simplified form of the diffusion equation with chemical reaction

$$D_A (\partial^2 [A] / \partial x^2) - (\partial [A] / \partial t) - r_A = 0 \quad (1)$$

and a simplified form of Fick's Law

$$N_A = - D_A (\partial [A] / \partial x) \quad (2)$$

These equations are used in subsequent development. The rate of diffusion of component A at the interface between liquid and gas is related to the mass transfer coefficient for A according to the various models. The enhancement factor, E, is defined as the ratio of the time-mean flux of A at the interface with

© Copyright ChE Division ASEE 1987

**TABLE 1**  
**Course Content**

TOPIC	APPROX. NO. OF LECTURE HOURS
A. Mathematical Models of mass transfer	5
B. Enhancement of mass transfer rates	18
C. Gas-liquid systems with chemical reaction	6
D. Industrial examples	3
E. Students' presentations	3

reaction to the time-mean flux of A at the interface without reaction but with the same driving force and the same hydrodynamic conditions. This reduces to the ratio of mass transfer coefficients with and without chemical reaction.

In cases where the enhancement factor is appreciably more than one, several studies [5, 6, 7, 8] have shown that in normal industrial equipment, the chemical reaction rate must be large enough so that the composition in the bulk of the liquid is very close to equilibrium. If the reaction is irreversible, that means that concentration of component A from the gas phase is effectively zero in the bulk of the liquid. This simplifies one of the boundary conditions to Eq. (1).

Hatta's analysis is still applicable to the simplest cases, absorption with instantaneous irreversible reaction and absorption with first-order irreversible reaction, both according to the film model. Although combination of Eq. (1) for first-order reaction with the film model, Higbie model, and Danckwerts model respectively gives expressions for the enhancement factor which are widely different in mathematical form, it is quite remarkable how closely the results agree numerically when they are put in terms of Brian's general parameter M [9] or the equivalent

**TABLE 2**  
**Effect of Increasing Reaction Rate**

For mass transfer with second-order reaction,  
 $A + zB \rightarrow \text{products}$

Reaction Rate	$[B]_i$	Reaction zone	Enhancement Factor
Slow	$[B]_o$	negligible	$\sim 1$
Pseudo-1st-order	$[B]_o$	broad region	$E_{1st}$
Intermediate	$<[B]_o, >0$	region	$> E_{1st}, < E_a$
Instantaneous	0	plane	$E_a$

Hatta number. The asymptotes for large or small values of M by the various models are identical, and predictions of first-order enhancement factors from the three models agree within 8.1% of the largest prediction, which comes from the Danckwerts model. Such agreement is extraordinary when the different assumptions of the three models are considered.

Second-order reactions of the type

$$r_A = k[A][B] \quad (3)$$

simplify to pseudo-first-order reactions when the depletion of component B (from the liquid phase) becomes negligible at the interface with the gas phase. This corresponds to a comparatively slow reaction, or a small value of the Hatta number. On the other hand, the asymptotic limit for a second-order reaction at high reaction rate is an instantaneous reaction. Thus it is reasonable that expressions for the enhancement factor for second-order irreversible reactions should

**The principal mathematical difficulty in obtaining an expression for the enhancement factor for second-order reactions is that the rate expression makes the differential equation non-linear. In fact, there is a non-linear differential equation for each chemical species.**

reduce to expressions applicable to pseudo-first-order reactions at small values of the Hatta number and to expressions applicable to instantaneous reactions at large Hatta numbers. A chart for comparison is shown in Table 2.

The principal mathematical difficulty in obtaining an expression for the enhancement factor for second-order reactions is that the rate expression makes the differential equation non-linear. In fact, there is a non-linear differential equation for each chemical species. Van Krevelen and Hoftijzer [10] found an approximate solution for the irreversible case and the film model by two modifications. First they combined the differential equations for species A (from the gas) and B (from the liquid) to eliminate the non-linear rate term, and then integrated to obtain a bridging expression relating the concentration of component B in the liquid bulk and at the interface. Then, realizing that the reaction rate closest to the interface has the largest effect on the enhancement factor, they took the concentration of B in the reaction term as equal to its interfacial concentration independent of distance from the interface. This gave a linear differential equation which could be solved by standard methods. The approach of van Krevelen and Hoftijzer has been applied also to enhancement factors by the Danckwerts

model, both for irreversible [11] and reversible [12] second-order reactions.

Other sub-topics discussed under enhancement include extension to other kinetic forms and relations for reversible reactions. Desorption with reaction is found to be similar to absorption with reaction, but with some important differences [13]. Liquid extraction with chemical reaction is also similar. Non-isothermal enhancement factors are important in cases where temperatures vary appreciably between the bulk of the liquid and the interface. The Marangoni effect gives extra enhancement in some cases. Scale-up from laboratory or pilot-plant experiments is an important area in practice.

### 3. Gas-Liquid Systems with Chemical Reaction •

The ideas of total molarity and degree of saturation, as introduced by Astarita and Savage [13, 15], are discussed and applied to chemical equilibrium. These concepts are applied also in developing an operating line equation suitable for systems involving chemical reaction. Design relations for a packed column are derived, and an example design problem is discussed.

**4. Industrial Examples •** The chemistry of a few important cases, such as reactions of carbonates or ethanolamines with hydrogen sulfide or carbon dioxide, is discussed briefly.

### ASSIGNMENTS

As you might expect, the course includes frequent problem assignments to illustrate the theory and its applications. A longer assignment toward the end of the course involves design of a packed column for a particular separation. Some results for mass transfer coefficients without reaction and for interfacial areas, calculated from the equation of Onda *et. al.* [16], are given to the students to reduce the amount of time they must spend on the problem.

A term paper is an important part of the course. It is intended to bring students into contact with recent literature and to promote a critical attitude toward the literature. It is to be a critical review of a recent paper, pointing out weaknesses in a chosen paper from the literature, clarifying its application, or extending its scope. Each student submits a written term paper and presents it orally to the class.

### REFERENCE BOOKS

The main references used in this course are shown in Table 3. Cussler [17] has produced an excellent book on topics related to diffusion. The present course uses

**TABLE 3**  
**Main Reference Books**

- A. **Mathematical models of mass transfer:** Cussler [17]; Bird, Stewart, Lightfoot [18]
- B. **Enhancement of mass transfer rates:** Danckwerts [4]
- C. **Gas-liquid systems with chemical:** Astarita, Savage, Bisio [15]
- D. **Industrial examples:** Astarita, Savage, Bisio [15]

only a small part of the material in this book. Some topics from the standard reference by Bird, Stewart, and Lightfoot [18] are used.

Teachers and researchers are divided on the best approach to the theory of enhancement factors. Some prefer the approach of Astarita [3, 15], while others prefer the approach of Danckwerts [4]. Personally, I find Danckwerts more direct and logical.

The book by Astarita, Savage, and Bisio [15] is the only one which introduces the ideas of total molarity and degree of saturation. However, I find some inconsistencies in this book, and its lack of many references in my opinion makes it not very useful for a graduate course.

For recent developments students must be referred to the original articles in the literature.

### CONCLUSION

Although many mass transfer devices involving homogeneous chemical reaction are still designed on a strictly empirical basis, often with large factors of safety to allow for areas of ignorance, the theory has advanced now to the point where it is of considerable use in practice. Edwards [10] has pointed out some of the applicable material. Thus there is a need for graduate courses in this area.

### NOMENCLATURE

[A], [B]	Concentrations of chemical species
$D_A$	Diffusivity of component A
E	Enhancement factor
$E_{1st}$	Enhancement factor for first-order reaction
$E_a$	Enhancement factor for instantaneous reaction
Ha	Hatta number, $\sqrt{M}$
k	Second-order chemical rate constant
$k_L^*$	Mass transfer coefficient without reaction
M	$D_A k [B]_o / (k_L^*)^2$
$N_A$	Flux of component A
$r_A$	Reaction rate of A per unit volume of solution



## CHEMICAL ENGINEERING DIVISION ACTIVITIES

### TWENTY-FIFTH ANNUAL LECTURESHIP AWARD TO JAMES J. CHRISTENSEN

The 1987 ASEE Chemical Engineering Division Lecturer is James J. Christensen of Brigham Young University. The purpose of this award lecture is to recognize and encourage outstanding achievement in an important field of fundamental chemical engineering theory or practice. The 3M Company provides the financial support for this annual award.

Bestowed annually upon a distinguished engineering educator who delivers the annual lecture of the Chemical Engineering Division, the award consists of \$1,000 and an engraved certificate. These were presented to James Christensen at a banquet on August 12, 1987, at the Summer School at Southeastern Massachusetts University. The award is made on an annual basis, with nominations being received through February 1, 1988. Your nominations for the 1988 lectureship are invited. They should be sent to Donald K. Anderson, Michigan State University, East Lansing, MI 48824-1226.

**EDITORS NOTE ADDED IN PROOF:** CEE has learned that Professor Christensen died suddenly at his home on September 5, 1987. We mourn his loss.

### NEW EXECUTIVE COMMITTEE OFFICERS

The Chemical Engineering Division officers for 1987-88 are: Chairman, **John Sears** (Montana State University);

t Time  
x Distance from the interface  
overbar Time-mean value

### REFERENCES

1. Hatta, S., *Technol. Repts. Tohoku Imp. University*, **8**, 1 (1928-9), as reported in ref. 4.
2. Hatta, S., *Technol. Repts. Tohoku Imp. University*, **10**, 119 (1932), as reported in ref. 4.
3. Astarita, G., *Mass Transfer with Chemical Reaction*, Elsevier, Amsterdam, 1967.
4. Danckwerts, P. V., *Gas-Liquid Reactions*, McGraw-Hill, New York, 1970.
5. Peaceman, D. W., Sc.D. thesis, Mass. Inst. Technol., Cambridge, Mass., 1951, as reported in ref. 9.
6. Danckwerts, P. V., ref. 4, page 162.
7. Huang, D. T.-J., J. J. Carberry, and A. Varma, *AIChE J.*, **26**, 832 (1980).
8. White, D., L. E. Johns, paper no. 123a, AIChE Annual Meeting, Miami Beach, November 1986.

Past Chairman, **Phillip C. Wankat** (Purdue University); Chairman Elect, **James E. Stice** (University of Texas); Secretary-Treasurer, **William E. Beckwith** (Clemson University); Directors, **Gary Poehlein** (Georgia Institute of Technology), **Conrad Burris** (Manhattan College), **Richard M. Felder** (North Carolina State University), and **Lewis Derzansky** (Union Carbide).

### AWARD WINNERS

A number of chemical engineering professors were recognized for their outstanding achievements. The George Westinghouse Award was presented to **John H. Seinfeld** (California Institute of Technology) to acknowledge his commitment to excellence in education and his many contributions to the improvement of teaching methods for engineering students.

**C. Stewart Slater** (Manhattan College) and **A. K. M. Uddin** (Trinity University) received the Zone I and Zone III (respectively) New Engineering Educator Excellence Awards. The awards are presented to non-tenured educators in the first six years of their appointment in recognition of superior performance in teaching and research.

**Louis Theodore** (Manhattan College) was honored with an AT&T Foundations Award, presented to outstanding teachers of engineering students, and the grade of ASEE Fellow Member was conferred on **James E. Stice** (University of Texas) in recognition of his many important contributions in the field of engineering education.

### CORCORAN AWARD TO R. BYRON BIRD

**R. Byron Bird** (University of Wisconsin) was the recipient of the second annual Corcoran Award, presented in recognition of the most outstanding paper published in *Chemical Engineering Education* in 1986. His paper, "Hougen's Principles," appeared in the fall 1986 issue of *CEE*.

9. Brian, P. L. T., J. F. Hurley, and E. H. Hasseltine, *AIChE J.*, **7**, 226 (1961).
10. Van Krevelen, D. W., P. J. Hoftijzer, *Rec. Trav. Chim.*, **67**, 563 (1948).
11. DeCoursey, W. J., *Chem. Eng. Sci.*, **29**, 1867 (1974).
12. DeCoursey, W. J., *Chem. Eng. Sci.*, **37**, 1483 (1982).
13. Astarita, G., D. W. Savage, *Chem Eng. Sci.*, **35**, 659, 1755 (1980).
14. Joshi, S. V., G. Astarita, D. W. Savage, *AIChE Symp. Ser.*, #202, **77**, 63 (1981).
15. Astarita, G., D. W. Savage, A. Bisio, *Gas Treating with Chemical Solvents*, Wiley, New York (1983).
16. Onda, K., H. Takeuchi, Y. Okumoto, *J. Chem. Eng. Japan*, **1**, 56 (1968).
17. Cussler, E. L., *Diffusion: Mass Transfer in Fluid Systems*, Cambridge U.P., Cambridge, 1984.
18. Bird, R. B., W. E. Stewart, E. N. Lightfoot, *Transport Phenomena*, Wiley, New York, 1960.
19. Edwards, W. M., in R. H. Perry, D. Green, (ed.), *Perry's Chemical Engineers' Handbook*, section 14, McGraw-Hill, New York, 1984. □