DIFFUSION

MASS TRANSFER IN FLUID SYSTEMS

THIRD EDITION

Diffusion: Mass Transfer in Fluid Systems brings unsurpassed, engaging clarity to a complex topic. Diffusion is a key part of the undergraduate chemical engineering curriculum and at the core of understanding chemical purification and reaction engineering. This spontaneous mixing process is central to our daily lives, important in phenomena as diverse as the dispersal of pollutants to digestion in the small intestine. For students, this new edition goes to the basics of mass transfer and diffusion, illustrating the theory with worked examples and stimulating discussion questions. For professional scientists and engineers, it explores emerging topics and explains where new challenges are expected. Retaining its trademark enthusiastic style, the book's broad coverage now extends to biology and medicine.

This accessible introduction to diffusion and separation processes gives chemical and biochemical engineering students what they need to understand these important concepts.

New to this Edition

- **Diffusion:** Enhanced treatment of topics such as Brownian motion, composite materials, and barrier membranes.
- **Mass transfer:** Fundamentals supplemented by material on when theories work and why they fail.
- **Absorption:** Extensions include sections on blood oxygenators, artificial kidneys, and respiratory systems.
- **Distillation:** Split into two focused chapters on staged distillation and on differential distillation with structured packing.
- **Advanced Topics:** Including electrolyte transport, spinodal decomposition, and diffusion through cavities.
- **New Problems:** Topics are broad, supported by password-protected solutions found at www.cambridge.org/cussler.

Professor Cussler teaches chemical engineering at the University of Minnesota. His research, which centers on membrane separations, has led to over 200 papers and 4 books. A member of the National Academy of Engineering, he has received the Colburn and Lewis awards from the American Institute of Chemical Engineers, the Separations Science Award from the American Chemical Society, the Merryfield Design Award from the American Society for Engineering Education, and honorary doctorates from the Universities of Lund and Nancy.

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E. L. CUSSLER
University of Minnesota

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For Jason, Liz, Sarah, and Varick
who wonder what I do all day

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List of Symbols

a	surface area per volume
a	major axis of ellipsoid (Section 5.2)
a, a_i	constant
A	area
A	absorption factor (Chapters 13 and 14)
b	constant
b	minor axis of ellipsoid (Section 5.2)
B	bottoms (Chapters 10, 12 and 13)
B, b	boundary positions (Section 7.3)
c	total molar concentration
c_1	concentration of species 1, in either moles per volume or mass per volume
c_{CMC}	critical micelle concentration (Section 6.2)
c_{T}	total concentration (Chapter 6)
$\overline{c}_1$	concentration of species 1 averaged over time (Sections 4.3 and 17.4)
c_1'	concentration fluctuation of species 1 (Sections 4.3, 17.3, and 17.4)
$\underline{c}$	vector of concentrations (Section 7.3)
c_{1i}	concentration of species 1 at an interface i
C	capacity factor (Section 13.1)
$\tilde{C}_p$, $\hat{C}_p$	molar and specific heat capacities respectively, at constant pressure
$\tilde{C}_v$, $\hat{C}_v$	molar and specific heat capacities respectively at constant volume
d	diameter or other characteristic length
D	binary diffusion coefficient
D	distillate (Chapters 12 and 13)
D_{eff}	effective diffusion coefficient, for example, in a porous solid
D_i	binary diffusion coefficient of species i
D_0	binary diffusion coefficient corrected for activity effects
D_{ij}	multicomponent diffusion coefficient (Chapter 7)
D_{Kn}	Knudsen diffusion coefficient of a gas in a small pore
D_{m}	micelle diffusion coefficient (Section 6.2)
D^*	intradiffusion coefficient (Section 7.5)
E	dispersion coefficient
E	extraction factor (Chapter 14)
$E(t)$	residence-time distribution (Section 9.2)
f	friction coefficient for a diffusing solute (Section 5.2)
f	friction factor for fluid flow (Chapter 21)
F	packing factor (Section 10.2)
F	feed (Chapters 12 and 13)
F	Faraday's constant (Section 6.1)
$F(D)$	solution to a binary diffusion problem (Section 7.3)
$\mathbf{g}$	acceleration due to gravity

G	molar flux of gas
G''	mass flux of gas (Sections 10.2 and 13.1)
G'	molar flux of gas in stripping section (Chapters 12 and 13)
h	reduced plate height (Section 15.5)
h, h_i	heat transfer coefficients (Chapters 20 and 21)
H	partition coefficient
$\tilde{H}$, $\hat{H}$	molar and specific enthalpies (Chapters 20–21 and Chapter 7, respectively)
$\bar{H}_i$	partial specific enthalpy (Chapter 7)
HTU	height of transfer unit
$\mathbf{i}$	current density (Section 6.1)
j_v	volume flux across a membrane (Section 18.3)
$\boldsymbol{j}_{\mathrm{T}}$	total electrolyte flux (Section 6.1)
$\boldsymbol{j}_i$	diffusion flux of solute *i* relative to the volume average velocity
$\mathbf{j}_i^m$	diffusion flux of solute *i* relative to the mass average velocity
j_i^*	diffusion flux relative to the molar average velocity
$\mathbf{j}_1^{(2)}$	diffusion flux of solute (1) relative to velocity of solvent (2)
$\mathbf{j}_i^a$	diffusion flux of solute *i* relative to reference velocity *a*
$\boldsymbol{J}_{\mathrm{s}}$	entropy flux (Section 7.2)
$\boldsymbol{J}_{\mathrm{T}}$	total solute flux in different chemical forms (Section 6.2)
k	mass transfer coefficient based on a concentration driving force
k_p	mass transfer coefficient based on a partial pressure driving force (Table 8.2-2)
k_x, k_y	mass transfer coefficients based on mole fraction driving forces in liquid and gas, respectively (Table 8.2-2)
k_{B}	Boltzmann's constant
k_T	thermal conductivity (Chapters 20–21)
k^0	mass transfer coefficient at low transfer rate (Section 9.5)
k^0	mass transfer coefficient without chemical reaction (Chapter 17)
k'	capacity factor (Sections 4.4 and 15.1)
K	equilibrium constant for chemical reaction
K_{G}, K_{L}	overall mass transfer coefficients based on concentration driving force in gas or liquid, respectively
K_p	overall mass transfer coefficient based on partial pressure difference in gas
K_x, K_y	overall mass transfer coefficient based on mole fraction driving force in liquid or gas, respectively
Kn	Knudsen number (Section 6.4)
l	length, e.g., of a membrane
L	length, e.g., of a pipe
L	molar flux of liquid
L''	mass flux of liquid (Sections 10.2 and 13.1)
L'	molar flux of liquid in stripping section (Sections 12.3 and 13.3)
L_{ij}	Onsager phenomenological coefficient (Section 7.2)
L_p	solvent permeability (Section 18.3)
m	partition coefficient relating mole fractions in gas and liquid
M	mass
M	total solute (Sections 4.2 and 5.5)
$\tilde{M}_i$	molecular weight of species *i*

n	micelle aggregation number or hydration number (Section 6.2)
$\boldsymbol{n}_i$	flux of species i relative to fixed coordinates
N	number of ideal stages
$\tilde{N}$	Avogadro's number
N_i	flux of species i at an interface
N_i	number of moles of species i
NTU	number of transfer units
p	pressure
P	power
P	membrane permeability (Chapter 18)
P_{ij}	weighting factor (Section 7.3)
q	scattering vector (Section 5.6)
q	feed quality (Sections 12.3 and 13.3)
q	solute concentration per volume adsorbent (Chapter 15)
$\boldsymbol{q}$	energy flux (Chapters 7, 20, and 21)
r	radius
r, r_i	rate of chemical reaction
R	gas constant
R_{D}	reflux ratio (Chapters 12 and 13)
R_0	characteristic radius
s	distance from pipe wall (Section 9.4)
$\hat{S}$	specific entropy (Chapter 7)
$\bar{S}_i$	partial specific entropy of species i
t	time
$\mathbf{t}$	modal matrix (Section 7.3)
t_i	transference number of ion i (Section 6.1)
$t_{1/2}$	reaction half-life
T	temperature
u_i	ionic mobility (Section 6.1)
U	overall heat transfer coefficient
$\hat{U}$	specific internal energy
v_r, v_θ	velocities in the r and θ directions
v_x, v_y	velocities in the x and y directions
$\boldsymbol{v}$	mass average velocity
$\boldsymbol{v}^a$	velocity relative to reference frame a
$\boldsymbol{v}^{\mathrm{o}}$	volume average velocity
$\boldsymbol{v}'$	velocity fluctuation (Sections 4.3 and 17.4)
$\boldsymbol{v}^*$	molar average velocity
$\boldsymbol{v}_i$	velocity of species i
V	volume
$\bar{V}_i$	partial molar or specific volume of species i
V_{ij}	fraction of molecular volume (Section 5.1)
W	width
W	work (Section 20.2)
W_s	shaft work (Section 20.2)
x	mole fraction in liquid of more volatile species (Chapters 12 and 13)

x_B, x_D, x_F	mole fractions of more volatile species in bottoms, distillate and feed, respectively (Chapters 12 and 13)
x_i	mole fraction of species i, especially in a liquid or solid phase
$\mathbf{X}_i$	generalized force causing diffusion (Section 7.2)
y	mole fraction in vapor of more volatile species (Chapters 12 and 13)
y_i	mole fraction of species i in a gas
z	position
$\lvert z \rvert$	magnitude of charge (Section 6.1)
z_i	charge on species i
α	thermal diffusivity (Chapters 20 and 21)
α	thermal diffusion factor (Section 21.5)
α	flake aspect ratio (Sections 6.4 and 9.5)
α_{ij}	conversion factor (Section 7.1)
β	diaphragm cell calibration constant (Sections 2.2 and 5.5)
β	pervaporation selectivity (Section 18.4)
γ	interfacial influence (Section 6.3)
γ	surface tension (Section 6.4)
γ_i	activity coefficient of species i
δ	thickness of thin layer, especially a boundary layer
$\delta(z)$	Dirac function of z
δ_{ij}	Kronecker delta
ε	void fraction
ε	enhancement factor (Section 17.1)
ε_{ij}	interaction energy between colliding molecules (Sections 5.1 and 20.4)
ζ	combined variable
η	Murphree efficiency (Section 13.4)
η	effectiveness factor (Section 17.1)
θ	dimensionless concentration
θ	fraction of unused adsorption bed (Section 15.3)
θ	fraction of surface elements (Section 9.2)
κ_i, κ_{-i}	forward and reverse reaction rate constants respectively of reaction i
λ	length ratio (Section 6.4)
λ	heat of vaporization (Sections 12.3 and 13.3)
λ_i	equivalent ionic conductance of species i (Section 6.1)
Λ	equivalent conductance
μ	viscosity
μ_i	chemical potential of species i
μ_i	partial specific Gibbs free energy of species i, i.e., the chemical potential divided by the molecular weight (Section 7.2)
ν	kinematic viscosity
ν	stoichiometric coefficient (Sections 16.5 and 17.2)
ξ	dimensionless position
ξ	correlation length (Section 6.3)
$\prod$	osmotic pressure (Section 18.3)
ρ	total density, i.e., total mass concentration
ρ_i	mass concentration of species i
σ	rate of entropy production (Section 7.2)

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σ	standard deviation (Sections 5.5 and 15.4)
σ, σ'	reflection coefficients (Section 18.3)
σ	Soret coefficient (Section 21)
$\boldsymbol{\sigma}$	diagonal matrix of eigenvalues (Chapter 7)
σ_i	eigenvalue (Section 7.3)
σ_{ij}	collision diameter
τ	characteristic time
τ	tortuosity (Section 6.4)
τ	residence time for surface element (Section 9.2)
τ	shear stress (Chapter 21)
τ_0	shear stress at wall (Section 9.4)
ϕ	Thiele modulus (Section 17.1)
ϕ_i	volume fraction of species *i*
ψ	electrostatic potential
$\boldsymbol{\psi}$	combined concentration (Section 7.3)
ω	jump frequency (Section 5.3)
ω	regular solution parameter (Section 6.3)
ω	coefficient of solute permeability (Section 18.3)
ω_i	mass fraction of species *i*
Ω	collision integral in Chapman–Enskog theory (Section 5.1)

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Preface to the Third Edition

Like its earlier editions, this book has two purposes. First, it presents a clear description of diffusion, the mixing process caused by molecular motion. Second, it explains mass transfer, which controls the cost of processes like chemical purification and environmental control. The first of these purposes is scientific, explaining how nature works. The second purpose is more practical, basic to the engineering of chemical processes.

While diffusion was well explained in earlier editions, this edition extends and clarifies this material. For example, the Maxwell–Stefan alternative to Fick's equation is now treated in more depth. Brownian motion and its relation to diffusion are explicitly described. Diffusion in composites, an active area of research, is reviewed. These topics are an evolution of and an improvement over the material in earlier editions.

Mass transfer is much better explained here than it was earlier. I believe that mass transfer is often poorly presented because it is described only as an analogue of heat transfer. While this analogue is true mathematically, its overemphasis can obscure the simpler physical meaning of mass transfer. In particular, this edition continues to emphasize dilute mass transfer. It gives a more complete description of differential distillation than is available in other introductory sources. This description is important because differential distillation is now more common than staged distillation, normally the only form covered. This edition gives a much better description of adsorption than has been available. It provides an introduction to mass transfer applied in biology and medicine.

The result is an engineering book which is much more readable and understandable than other books covering these subjects. It provides much more physical insight than conventional books on unit operations. It explores the interactions between mass transfer and chemical reaction, which are omitted by many books on transport phenomena. The earlier editions are good, but this one is better.

The book works well as a text either for undergraduates or graduate students. For a one-semester undergraduate chemical engineering course of perhaps 45 lectures plus recitations, I cover Chapter 2, Sections 3.1 to 3.2 and 5.1 to 5.2, Chapters 8 to 10, 12 to 15, and 21. If there is time, I add Sections 16.1 to 16.3 and Sections 17.1 to 17.3. If this course aims at describing separation processes, I cover crystallization before discussing membrane separations. We have successfully taught such a course here at Minnesota for the last 10 years.

For a one semester graduate course for students from chemistry, chemical engineering, pharmacy, and food science, I plan for 45 lectures without recitations. This course covers Chapters 2 to 9 and Chapters 16 to 19. It has been a mainstay at many universities for almost 30 years.

This description of academic courses should not restrict the book's overall goal. Diffusion and mass transfer are often interesting because they are slow. Their rate controls many processes, from the separation of air to the spread of pollutants to the size of a human sperm. The study of diffusion is thus important, but it is also fun. I hope that this book catalyzes that fun for you.

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Preface to Second Edition

The purpose of this second edition is again a clear description of diffusion useful to engineers, chemists, and life scientists. Diffusion is a fascinating subject, as central to our daily lives as it is to the chemical industry. Diffusion equations describe the transport in living cells, the efficiency of distillation, and the dispersal of pollutants. Diffusion is responsible for gas absorption, for the fog formed by rain on snow, and for the dyeing of wool. Problems like these are easy to identify and fun to study.

Diffusion has the reputation of being a difficult subject, much harder than, say, fluid mechanics or solution thermodynamics. In fact, it is relatively simple. To prove this to yourself, try to explain a diffusion flux, a shear stress, and chemical potential to some friends who have little scientific training. I can easily explain a diffusion flux: It is how much diffuses per area per time. I have more trouble with a shear stress. Whether I say it is a momentum flux or the force in one direction caused by motion in a second direction, my friends look blank. I have never clearly explained chemical potentials to anyone.

However, past books on diffusion have enhanced its reputation as a difficult subject. These books fall into two distinct groups that are hard to read for different reasons. The first group is the traditional engineering text. Such texts are characterized by elaborate algebra, very complex examples, and turgid writing. Students cheerfully hate these books; moreover, they remember what they have learned as scattered topics, not an organized subject.

The second group of books consists of texts on transport processes. These books present diffusion by analogy with fluid flow and heat transfer. They are much more readable than the traditional texts, especially for the mathematically adroit. They do have two significant disadvantages. First, topics important to diffusion but not to fluid flow tend to be omitted or deemphasized. Such cases include simultaneous diffusion and chemical reaction. Second, these books usually present diffusion last, so that fluid mechanics and heat transfer must be at least superficially understood before diffusion can be learned. This approach effectively excludes students outside of engineering who have little interest in these other phenomena. Students in engineering find difficult problems emphasized because the simple ones have already been covered for heat transfer. Whether they are engineers or not, all conclude that diffusion must be difficult.

In the first edition, I tried to describe diffusion clearly and simply. I emphasized physical insight, sometimes at the loss of mathematical rigor. I discussed basic concepts in detail, without assuming prior knowledge of other phenomena. I aimed at the scope of the traditional texts and at the clarity of books on transport processes. This second edition is evidence that I was partly successful. Had I been completely successful, no second edition would be needed. Had I been unsuccessful, no second edition would be wanted.

In this second edition, I've kept the emphasis on physical insight and basic concepts, but I've expanded the book's scope. Chapters 1–7 on diffusion are largely unchanged, though some description of diffusion coefficients is abridged. Chapter 8 on mass transfer

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is expanded to even more detail, for I found many readers need more help. Chapters 9–12, a description of traditional chemical processes are new. The remaining seven chapters, a spectrum of topics, are either new or significantly revised. The result is still useful broadly, but deeper on engineering topics.

I have successfully used the book as a text for both undergraduate and graduate courses, of which most are in chemical engineering. For an undergraduate course on unit operations, I first review the mass transfer coefficients in Chapter 8, for I find that students' memory of these ideas is motley. I then cover the material in Chapters 9–12 in detail, for this is the core of the subject. I conclude with simultaneous heat and mass transfer, as discussed in Chapters 19–20. The resulting course of 50 classes is typical of many offered on this subject. On their own, undergraduates have used Chapters 2–3 and 8–9 for courses on heat and mass transfer, but this book's scope seems too narrow to be a good text for that class.

For graduate students, I give two courses in alternate years. Neither requires the other as a prerequisite. In the first graduate course, on diffusion, I cover Chapters 1–7, plus Chapter 17 (on membranes). In the second graduate course, on mass transfer, I cover Chapters 8–9, Chapters 13–16, and Chapter 20. These courses, which typically have about 35 lectures, are an enormous success, year after year. For nonengineering graduate students and for various short courses, I've usually used Chapters 2, 8, 15–16, and any other chapters specific to a given discipline. For example, for those in the drug industry, I might cover Chapters 11 and 18.

I am indebted to many who have encouraged me in this effort. My overwhelming debt is to my colleagues at the University of Minnesota. When I become disheartened, I need simply to visit another institution to be reminded of the advantages of frank discussion without infighting. My students have helped, especially Sameer Desai and Diane Clifton, who each read large parts of the final manuscript. Mistakes that remain are my fault. Teresa Bredahl typed most of the book, and Clover Galt provided valuable editorial help. Finally, my wife Betsy gives me a wonderful rich life.