Heinrich Strathmann

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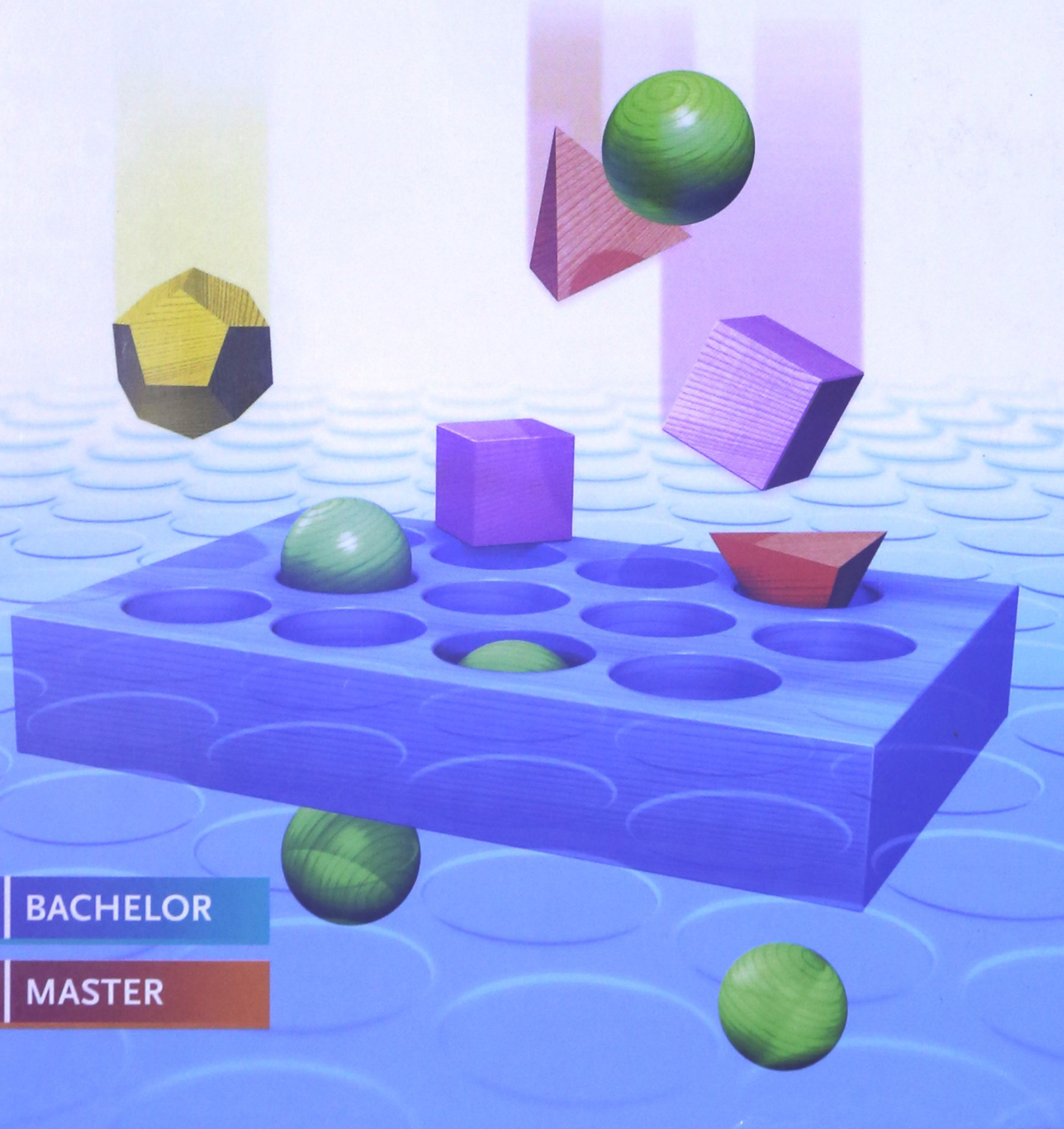
Introduction to Membrane Science and Technology



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WILEY-VCH Verlag GmbH & Co. KGaA

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Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

Typesetting Laserwords Private Limited, Chennai, India
Printing and Binding Fabulous Printers Pte Ltd
Cover Design Formgeber, Eppelheim

Printed in Singapore
Printed on acid-free paper

ISBN: 978-3-527-32451-4

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Preface

During the second half of the twentieth century the interest in synthetic membranes and membrane processes increased dramatically. A large number of membranes with highly selective mass transport properties became available. Today, membranes are used in a multitude of applications, and a membrane-based industry serves a fast-growing market with annual sales of many billion US $. The increasing importance of membranes is also reflected in an increasing number of scientific publications describing the present state of membrane technology as well as recent developments and potential future applications. Membranes and membrane processes are also described in great detail in a number of excellent reference books. However, most of these books only focus on certain aspects of membranes, depending on the special interest of the authors, so that membrane literature is rather fragmented, and it is difficult to gain a reasonably complete overview of the basic functions of membranes and their preparation and application. In spite of the growing need for scientists and engineers in industry and research organizations with a basic knowledge in membrane technology, very few universities offer adequate courses on membrane science.

The objective of this book is to provide a short but reasonably comprehensive introduction to membrane science and technology suitable for graduate students and persons with engineering or natural science background to gain a basic understanding of membranes, their function and application without studying a large number of different reference books.

The first chapter gives a short summary of membranes and membrane processes that are available today, and the main areas of their applications. In the second chapter definitions of terms used in describing membrane structures and their function are given. The basic thermodynamic and physiochemical relations used to discuss mass transport in membranes and membrane processes in various applications are briefly reviewed. The third chapter describes the preparation and characterization of membranes. The various materials and techniques used today in laboratory and industrial scale membrane production, such as extruding and sintering polymer or ceramic powders or template leaching, track etching, etc. are discussed. Because of the technical and commercial relevance of polymer membranes prepared by phase inversion this technique is discussed in more detail. Furthermore, methods for characterizing membranes in terms of their structure and transport properties are discussed. In the fourth chapter the basic principle of various membrane processes is described. Widely used state-of-the-art processes such as reverse osmosis, ultrafiltration, electrodialysis, gas separation, etc. are treated in detail. Processes that are not yet commercially available but of interest for future applications, such as capacitive deionization, osmotic distillation or the various forms of catalytic membrane reactors, are described only briefly in their basic principle. In the fifth chapter commercially available membrane modules and their application are described and the problems of concentration polarization and membrane fouling are discussed. In the last chapter the design and operation of membrane processes in selected applications is treated. The discussion concentrates on commercially available processes. Some basic relationships suitable for a rough estimation of membrane process costs are given.

The book contains an appendix with questions and simple exercises for students to test their knowledge in membrane technology. A second appendix contains tables of constants and mechanical and physical relations and other data such as osmotic and activity coefficients, ion and molecular radii, etc. These data have been extracted from standard reference or text books such as J. H. Perry *Chemical Engineering Handbook*, or P.W. Atkins, *Physical Chemistry*. The nomenclature and units used in the book are based on the metric system as used in the book of P.W. Atkins and recommended by IUPAC. Units commonly used in the US engineering literature are related to standard m/kg/s units in Table 6 of Appendix B.

Some of the readers of this book might be disappointed that very recent developments and new applications of membranes are not discussed. However, even a rudimentary treatment of these topics is beyond the scope of this book which concentrates on fundamental aspects of membrane technology only. Therefore, literature references are limited to publications that are essential for a better understanding of certain membrane properties.

It is difficult to give credit to all the individuals who have contributed to the preparation of this book. Instead of a long list of names I would like to express my sincere thanks to my colleagues and PhD students of the Membrane Technology Group of the University of Twente and of the Institute of Process Engineering of the University of Stuttgart, and friends in other universities and industrial enterprises who gave their valuable suggestions and discussions.

Tübingen, June 2011 *Heiner Strathmann*

Symbols

Tables of symbols used in the text, showing in which Chapter they appear.

Roman Symbols

a	radius	(m)	2, 3, 4
A	component	(–)	4
A, a	constant	($m^{2.5}$ $mol^{-0.5}$)	2, 5, 6
A, a	activity	(mol m^{-3})	2, 3, 4, 6
A, a_s	surface area	(m^2)	2, 3, 4, 6
a_h	hydrodynamic radius	(m)	3
B	component	(–)	4
B, b	constant	(Pa^{-1})	2, 4, 5, 6
C	concentration	(mol m^{-3})	2, 3, 4, 6
C_s	solute concentration	(mol m^{-3})	5
$\overline{C}$	average concentration	(mol m^{-3})	4
C_i^v	concentration in viscous flow stream	(mol m^{-3})	4
ΔC_s	concentration difference between diluate and concentrate	(mol m^{-3})	6
C	capacitance	(A s m^{-2})	3
C	electrical charge	(A s)	2
C	component	(–)	4
C_p	adiabatic heat capacity	(J K^{-1} mol^{-1})	4, 6
d	distance	(m)	3, 4
d	diameter	(m)	2
d_{gas}	diameter of a gas molecule	(m)	4
d_h	hydraulic diameter	(m)	3, 5
d	stirrer length	(m)	5
D_c	diameter of filtration cell	(m)	5
D	diffusive permeability	(m)	6
D	diffusion coefficient	(m^2 s^{-1})	2, 3, 4, 5
$\overline{D}$	average diffusion coefficient	(m^2 s^{-1})	2, 4
D_k	Knudsen diffusion coefficient	(m^2 s^{-1})	2, 4
$Đ_i$	Stefan–Maxwell (thermodynamic) diffusion coefficient	(m^2 s^{-1})	2
e	elementary charge	(1602 × 10^{-19} C)	2, 4
E	evaporation energy	(J)	3, 4

E	Young's modulus	(kg m^{-1} s^{-2})	3
E	electric field	(V m^{-1})	2
E	energy	(J)	2, 4
E	enrichment factor	(–)	5
E, E_{ex}	energy	(A V s)	4, 6
E_c	concentration factor	(–)	6
E_d	dialysis efficiency	(–)	6
E_{el}	electrical energy	(A V s)	4
E_o	intrinsic enrichment factor	(–)	5
E_p	pumping energy	(A V s)	6
F	Faraday constant	96 485 (A s eq^{-1})	2, 3, 4, 5, 6
F	force	(N)	2
f	friction factor	(N s m^{-1} mol^{-1})	2
g	acceleration due to gravity	(9.806 m s^{-2})	3
g	osmotic coefficient	(–)	2, 4, 5
G	Gibbs free energy	(J)	2, 3, 4, 6
ΔG_m	Gibbs free energy of mixing	(J)	3
G_{11}	cluster integral	(m^3 mol^{-1})	3
H	enthalpy	(J)	2, 3, 4, 6
h	height	(m)	3, 5
h_p	hydrodynamic permeability	(–)	2
h_p^m	hydraulic membrane permeability	(m^3 s^{-1} Pa^{-1})	6
I	current	(A)	2, 3, 4, 6
i	current density	(A m^{-2})	3, 4, 5, 6
i_{lim}	limiting current density	(A m^{-2})	4, 5, 6
j	imaginary unit	(–)	3
J	ionic strength	(mol m^{-3})	2
J	flux	(mol m^{-2} s^{-1}, m s^{-1})	2, 3, 4, 6
J_s	solute flux	(mol m^{-2} s^{-1})	5
$J_{s,\,con}$	convective solute flux	(mol m^{-2} s^{-1})	5
$J_{s,\,diff}$	diffusive solute flux	(mol m^{-2} s^{-1})	5
J_v	volume flux	(mol m^{-2} s^{-1})	5
J_{Em}	heat transport through a membrane	(J m^{-2} s^{-1})	4
J_{Ec}	heat transport by convection	(J m^{-2} s^{-1})	4
J_{Ed}	heat transport by diffusion	(J m^{-2} s^{-1})	4
K	force	(N)	2
K, k	constant	(–)	4,6
k	Boltzmann constant	(J mol^{-1} K^{-1})	2, 3, 4
k^*	constant relating bulk solution to permeate	(m s^{-1})	5
k^*	rate constant	(mol m^{-1} s^{-1})	6
k_o	equilibrium constant	(–)	5
K	dissociation constant	(–)	2
k_d	water dissociation rate constant	(m^2 s^{-1})	4
k_g	constant referring to gel layer	(–)	5
k_{con}	concentration polarization constant	(–)	6
k_i^H, k_h	Henry constant	(mol m^{-3} Pa)	2,4
k	distribution coefficient	(–)	2, 4
k	coefficient (various)	(–)	6

K, K_i, k_s	mass transfer coefficient	$(m\ s^{-1})$	5, 6
k_q	heat transfer coefficient	$(J\ m\ s^{-1}\ K^{-1})$	2, 4
K_w	water dissociation product	$(mol^2\ l^{-2})$	2, 4
l	length, thickness	(m)	2, 3, 4, 6
L	length	(m)	3, 4, 5, 6
L	phenomenological coefficient	$(mol^2\ N^{-1}\ m^{-2}\ s^{-1})$	2, 4
L_p	permeability coefficient	$(m^2\ s^{-1}\ Pa^{-1})$	2, 3, 4
L_p, L_D	diagonal coefficient	$(m^2\ s^{-1}\ Pa^{-1})$	4
$L_pD\ L_{Dp}$	cross coefficient	$(m^2\ s^{-1}\ Pa^{-1})$	4
L_t	time lag	(s)	3
L_v	hydraulic permeability	$(m^2\ s\ kg^{-1})$	4
L_w	permeability of water	$(mol^2\ s\ kg^{-1}\ m^{-2})$	4
m	mobility	$(m\ s^{-1})$	2, 4
m	mass	(kg)	2, 4
M	molar mass	$(kg\ mol^{-1})$	2, 4
M	molecular weight	$(kg\ mol^{-1})$	2, 3, 5
M_n	number average molecular weight	$(kg\ mol^{-1})$	3
M_w	weight average molecular weight	$(kg\ mol^{-1})$	3
n	number	(–)	2, 3, 4, 6
n_f	number of jumps	(–)	2
n_v	number of empty space	(–)	2
N	flux (total)	$(mol\ m^{-2}\ s^{-1})$	2, 6
N	number of chains	(–)	3
N	number of cell pairs	(–)	6
N_{Re}	Reynolds number	(–)	5
N_{Sc}	Schmidt number	(–)	5
N_{Sh}	Sherwood number	(–)	5
p	pressure, vapor pressure	(Pa)	2, 3, 4, 5, 6
p_{eff}	effective pressure	(Pa)	6
p_i	partial pressure	$(Pa\ mol^{-1})$	2, 4
p_{loss}	pressure loss	(Pa)	6
p_o	staturation pressure	(Pa)	4
p_{os}	osmotic pressure	(Pa)	6
P	permeability	$(mol\ m^{-2}\ s^{-1}\ Pa^{-1})$	3, 4, 6
P	permeability coefficient	$(mol\ m^{-1}\ s^{-1}\ J^{-1})$	2
P	power	(A V)	6
q	heat	(J)	2, 4
Q	charge	(C)	2
Q	volume flux (flow rate)	$(m^3\ s^{-1})$	2
Q_i^t	accumulate mol flux during time t	$(mol\ m^{-2})$	3
r	area resistance	$(\Omega\ m^2)$	3, 4, 6
r	distance	(m)	2
r, r_p	pore radius	(m)	2, 3, 4, 6
r_D	Debye length	(m)	2
r_g	radius of gyration	(m)	3
r_t	radius of a tube	(m)	5
r_k	Kelvin radius	(m)	3
r_m	hydrodynamic area resistance	$(kg\ m^{-2}\ s^{-1})$	5

R	resistance	(−)	6
R	Ohmic resistance	(Ω m^2)	3
R	electrical resistance	(Ω)	2, 4, 6
R	mechanical resistance	(m^{-1})	6
R	rejection, retention	(−)	2, 3, 4, 5, 6
R_{obs}	observed rejection	(−)	6
R_{true}	true rejection	(−)	6
R	gas constant	(J mol^{-1} K^{-1})	2, 3, 4, 5, 6
R	phenomenological coefficient	(kg s^{-1})	2
s	molecular drift speed	(m mol s^{-1})	2
S	permselectivity	(−)	2, 4
$S_{i/k}$	selectivity	(−)	4, 6
$S^D_{j,k}$	diffusion selectivity	(−)	4, 6
$S^P_{j,k}$	permeation selectivity	(−)	4, 6
$S^k_{j,k}$	sorption selectivity	(−)	4, 6
S	entropy	(J K^{-1})	2, 3, 4
S_i	partial molar entropy	(J K^{-1} mol^{-1})	2, 4
S	conductance	(Ω^{-1})	2
t	time	(s)	3, 4, 5, 6
T	transport number	(−)	2, 3, 4, 5, 6
T	temperature	(K)	2, 3, 4, 5, 6
T_c	critical point temperature	(K)	3
T_g	glass transition temperature	(K)	3
T_m	melting temperature	(K)	3
u	ion mobility	(m$^{2\ s-1\ V-1}$)	2, 4
u	velocity	(m s^{-1})	2, 4, 5, 6
u_{th}	thermal velocity	(m s^{-1})	2, 4
U	electrical potential	(V)	3
U	internal energy	(J)	2
U	electrical voltage	(V)	4
U_{re}	reversible voltage, electromotive force	(V)	4
U_{th}	theoretical voltage	(V)	4
V	volume	(m^3)	2, 3, 4, 5, 6
V	total molar fraction	(−)	3
V_i	partial molar volume	(m^3 mol^{-1})	2, 4
V_m	molar volume	(m^3 mol^{-1})	3
V_w	rinse water volume in diafiltration	(m^3)	6
w	work	(J)	2
w	width	(m)	6
w	mass fraction	(−)	6
w_t	swelling	(−)	3
W	weight	(kg)	3
W	channel width	(m)	5
x	directional coordinate	(m)	2, 4, 5, 6
X	mole fraction	(−)	2, 3, 6
X	driving force	(Nm mol^{-1})	2, 4
X	cell length	(m)	6

X_{pro}	process path length	(m)	6
y	directional coordinate	(m)	5
Y	cell width	(m)	6
z	charge number	(eq mol^{-1})	2, 4, 6
z	directional coordinate	(m)	2, 4, 5, 6
Z	impedance	(Ω)	3
Z_b	boundary layer thickness	(m)	5
Z_{lay}	gel layer thickness	(m)	5
Z_M	membrane thickness	(m)	6
Z_o	barrier layer thickness	(m)	3
Z_{eff}	diffusion path length	(m)	3
Δp	Partial pressure difference	(−)	3
$\Delta x/\Delta z$	Membrane thickness	(−)	2, 3, 4

Greek symbols

α	dissociation degree	(−)	2, 4
α	separation factor	(−)	2, 4, 6
β	enrichment factor	(−)	4, 6
γ	activity coefficient	(m^3 mol^{-1})	2, 4
δ	fraction solute loss	(−)	6
δ	solubility parameter	($J^{0.5}$ $V^{-0.5}$)	3
Δ	difference	(−)	2, 3, 4, 5, 6
Δ	recovery rate	(−)	5, 6
ε	surface porosity	(−)	3
ε	permittivity	($C^2 J^{-1} m^{-1}$)	2
ε	porosity	(−)	2, 4, 6
ε	stress	(−)	3
ξ	current use	(−)	4, 6
η	dynamic viscosity	(kg m^{-1} s^{-1})	2, 3, 4, 6
η_{ther}	thermodynamic efficiency	(−)	4
η_{tot}	total current efficiency	(−)	4
η_w	efficiency loss due to water transport	(−)	4
η_{el}	electrochemical efficiency	(−)	4
η_F	Faraday current efficiency	(−)	4
θ	stage cut	(−)	6
κ	specific conductivity	(Ω^{-1} m^{-1})	2, 6
λ	distance	(m)	4
λ_{eq}	equivalent conductivity	(m^2 Ω^{-1} eq^{-1})	6
λ_{vap}	heat of evaporation	J mol^{-1}	4
λ_i	ion conductivity	(m^2 Ω^{-1} mol^{-1})	4
λ	jump length/mean free path length	(m)	2, 4
Λ	electrolyte conductivity	(m^2 Ω^{-1} mol^{-1})	2, 4
μ	chemical potential	(J mol^{-1})	2, 3, 4
$\tilde{\mu}$	electrochemical potential	(J mol^{-1})	2, 4
ν	kinematic viscosity	(m^2 s^{-1})	5
ν	stoichiometric coefficient	(−)	2, 4, 5
π	constant	(−)	4, 6

π	osmotic pressure	(Pa, N m^{-2})	2, 4, 5, 6
ρ	density	(kg m^{-3})	3, 4, 5
ρ	space charge	(C)	2
ρ	specific resistance	(Ω m)	2, 3, 6
ρ_{lay}	specific gel layer resistance	(N s^{-1})	5
σ	surface tension	(N m^{-1})	3, 4
σ	entropy production	(J K^{-1} s^{-1})	4
σ	reflection coefficient	(mol N^{-1} s^{-1})	4
σ	stress	(kg m^{-1} s^{-2})	3
τ	time	(s)	2
τ	tortuosity factor	(–)	2, 3, 4
τ	shear stress tensor	(N m^{-2})	5
ϕ	contact angle	(–)	3, 4
ϕ	volume fraction	(–)	3, 4, 6
Φ	pressure ratio	(–)	5, 6
φ	phase shift angle	(°)	3
φ	fugacity coefficient	(–)	4
φ	electrical potential, overpotential	(V)	2, 4, 6
φ^{diff}	diffusion potential	(V)	4
φ^{Don}	Donnan potential	(V)	2, 4, 6
Ψ	dissipation function	(N m s^{-1})	2, 4
Ψ	membrane permselectivity	(–)	2, 3, 4
ω	circular velocity	(s^{-1})	3, 5
ω	mass fraction	(–)	2
ω	permeability	(mol m^{-1} Pa^{-1})	2

Subscripts

0 (zero)	vacuum	2
∞	infinite value	3
a	acceleration	2
A	component	2, 4, 6
A, a	anion	2, 4, 6
appl	applied	6
aq	aqueous	4
B	component	2, 4, 6
b	bulk solution	4
c	cation	2, 4, 6
c	cake layer	6
cell	dialysis cell	3, 4
cir	electric circuit	4
co	co-ion	2, 3, 4
con	convection	5
con	concentration polarization	6
cou	counter-ion	2, 3, 4
des	desalination	6
Diff	diffusion	3, 5

Don	Donnan potential	2, 3, 4, 6
e	electric charge	2, 4
eff	effective, efficiency	6
eq	equivalent, thermodynamic equilibrium potential	2, 4
F	referring to electro-osmosis	3
f	free volume	3
f	friction	2
f	feed	2, 3, 4, 5
fix	fixed ion	2, 4
fus	fusion	3
g	glass transition	3
gas	gas	2, 4
i	component i	2, 3, 4, 5, 6
i	internal	4
im	imaginary	3
in	inlet	4
irrev	irreversible	2
j	jump	2
j	component	2, 3, 4, 6
k	component	2, 4, 6
l(ell)	solvent	2
lim	limiting	6
log mean	logarithmic mean value	6
m	membrane	3, 4
m	molar quantity	3
max	maximum	3
mem	membrane	4
min	minimum	3
mol	molar	2
n	number	2, 3
n	component	2, 4
o	standard state	2, 4
op	operating	4
or	organic	4
os	osmotic pressure	6
out	outlet	4
ox	oxidation	4
p	pore	3, 4, 6
p	polymer	3
p	product	4
p	permeate	2, 3, 4
p	pressure	2, 3, 4
p	permeate	5
p_e	pump efficiency	6
pr	practical	6
pre	pressure loss	6
q	heat	2, 4
real	real	3

rec	energy recovery	6
red	reduction	4
ret	retentate	6
rev	reversible	2, 6
s	solution	3, 4, 6
s	surface	2, 4
s	solute, electrolyte, salt	2, 4, 5, 6
s	separation process	6
Size	refers to size	4
sp	strictly permselective	3
spe	specific	6
T	temperature	2, 4
th	thermodynamic	2, 4
tot	total	6
total	total	2, 4
v	volume	3, 4, 6
w	weight	3
w	mass	6
W, *w*	water, solvent	3, 4

Superscripts

$\_$	average number	2, 3, 4, 6
$+$	positive charge	4
$-$	negative charge	4
am	anion-exchange membrane	2, 4, 6
appl	applied	4
B	binodal	3
b	bulk solution	4, 5, 6
b	constant	4
bf	bulk solution of feed	5
Bl	blood	6
bp	bulk solution of permeate	6
c	concentrate	4, 6
cm	cation-exchange membrane	2, 4, 6
d	diluate	4, 6
d	diffusion	4
d	dialysate	6
diff	diffusion	5
Don	Donnan	4
eff	effective	4
evap	evaporation	6
ex	excess	4
f	feed	2, 4, 5, 6
f	Fickian diffusion	4
fw	feed side membrane surface	5
g	gas	4
g	gel layer	5

h	Henry	2, 4
in	inlet	6
K	Knudsen diffusion	4
L	Langmuir sorption	2, 4
l (ell)	liquid	4
l (ell)	solvent	2
lay	layer	5
m	membrane	2, 3, 4, 5, 6
mig	migration	2, 4, 5
n	exponential factor	5
°	standard state, reference state	2, 3, 4, 5, 6
o (oh)	pure solvent	2
out	outlet	6
p	permeate	2, 4, 5, 6
perm	permeation	6
pw	permeate side membrane surface	5
r	retentate	6
S	spinodal	3
s	solution	2, 3, 4, 5
s	surface diffusion	4
s	stripping solution	4
S	pore surface	4
t	time	4, 6
w	membrane surface	5
x	directional coordinate	5
z	directional coordinate	5

Contents