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An Introduction to Barrier Interference

With 40 Figures and 9 Tables

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Preface

When a fluid mixture (liquid, vapor, gas) is forced to traverse a permeable partition, such as a membrane or septum, its components are likely to move at different speed. The ensuing spread in rate and composition is a *barrier separation* effect. Unlike equilibrium separations, which depend on the thermodynamic condition of the fluid mixtures alone, barrier separations additionally are subject to specific interactions of the mixture components with the barrier. While the thermodynamics of fluid mixtures is predictable and open to adjustment, *barrier interference* adds another dimension to the repertoire of separation effects. Exploiting barrier interference is the challenge of membrane separation science and technology. This book is about the principles behind.

As *membrane processes*, barrier separations independently have acquired their peculiar identities and colorful diversity, each fondling its own tradition, each adhering to its own terminology (down to defying SI units), each earning different public attention and support. By way of illustration: Gas leakage through everything inflatable has been observed since the time the elemental gases were identified; gaseous diffusion of UF_6 through a microporous barrier, for better or worse, gave access to nuclear energy; osmotic phenomena, originally of academic interest to botanists, were engineered into providing "fresh water from the sea" by reverse osmosis; electromembrane processes, again of academic origin, now offer the vision of a clean mobility based on fuel cells; hemodialysis, starting from little known beginnings among pharmacologists, may well be viewed as the most benevolent of membrane processes; evaporation across a suitable barrier breaks azeotropes and tends to favor the higher boiling species, aqueous aromas being a case in point; microfiltration got its start at stabilizing wine through removal of microorganisms, foreshadowing the use of membranes in biotechnology.

Attempting to formally – let alone retrospectively – unify all this would be a disservice to grown variety. Yet, ignoring the fundamental kinship limits information exchange, as frequently it has in the past, and, for no good reason, burdens information dissemination as in teaching. The feature in common, and ordering principle, is the formal structure of mass transfer in barrier separation, being construed of a *driving force* (intrinsic to the fluid mixtures to be separated) and a *permeability* (summarily describing the interaction of the mixture components with the barrier). The plan of this book, accordingly, is to present the relevant thermodynamic features of fluid mixtures in contact with semipermeable barrieres, then to apply this information in deriving the working principles and design requirements of individual membrane separation processes. The membranes, by this approach, are introduced by way of the mass transport and selectivity demands which they are to meet, with due reference to the separation effects which they inspire.

The approach is made specific by examining the information needed, (a) to interpret a membrane effect (hindsight), or (b) to design a membrane separation process (foresight). In practical terms, three independent sources of information are available.

- The thermodynamic condition of the fluid mixtures to be separated, both upstream and downstream of the barrier to identify gradients. Constituting the driving force for mass transfer, this information translates into the operating conditions of the respective membrane separation process.
- The barrier (membrane) itself, its chemical nature and physical characteristic. This information comes from material science, foremost from polymer science, with additional emphasis on the art of creating thin films and microporous structures.
- The permeability of the barrier (membrane), which effectively introduces a barrier selectivity differing from equilibrium selectivity. A conglomerate of many influences, membrane permeability acquires meaning only in the context of specific applications. Independent information on polymer permeability comes from sorption and diffusion studies ("small molecule meets big molecule") originally designed to elucidate polymer structure.

This is not a compilation of expert knowledge, nor a universe of citations. Rather, an attempt is made to survey, in systematic order, the terms and concepts by which barrier separations operate, and through which practical membrane separation processes are designed.

If there is to be a motto: *The only meaningful perspective is that of context.*

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Symbols and Abbreviations

Symbols

a_i	activity of *i*	[*concentration*]
bp.	boiling point	[°C]
c	concentration (generic)	[*various units*]
c_i	mass concentration	[kg/m^3]; [mol/m^3]
D	diffusion coefficient	[m^2/s]
d	diameter; pore diameter	[m]; [µm]
E	recovery (*Entnahme*)	[%]
G	Gibbs free energy	[J/mol]
g	acceleration of gravity	[9.81 m/s^2]
gfd	gallons per square foot & day	[*flux*]
J	mass flux (flow density)	[kg/s m^2]; [mol/s m^2]
J_p	permeance	[kg/s m^2 bar]
J_v	volume flux (practical)	[L/h m^2]
J (Joule)	energy; work (Nm)	[Ws]; [kWh]
k	mass transfer coefficient	[m/s]
L	permeability (*Leitfähigkeit*)	[*various units*]
L_p	hydraulic permeability	[*various units*]
m	molality of solute	[mol/kg]
n	number of mols	[–]
P	total pressure	[Pa]; [bar]
p	pressure	[Pa]; [bar]
p_i	partial pressure of *i*	[Pa]; [bar]
$p_i°$	pure component vapor pressure	[Pa]; [bar]
ppm	parts per million	[mg/L]
psi	pounds per square inch	[*pressure*]
Q	flow rate	[L/h]
R	gas constant	[8.314 J/mol K]
R (x100)	retention; rejection	[0–1] or (%)
S	sorption coefficient	[*various units*]

T	temperature	[°C]
T_g	glass transition temperature	[°C]
V	volume	[m^3]; [L]; [mL]
$\overline{V_i}$	partial molar volume	[m^3/mol]
W (Watt)	power (rate of work)	[J/s]
w_i	weight fraction of *i*	[kg/kg]
x_i	mol fraction of *i* (feed)	[mol/mol]
y_i	mol fraction of *i* (permeate)	[mol/mol]
z	distance coordinate	[m]
z	membrane thickness	[μm]

Greek

α_{ij}	separation factor	[–]
β_i	enrichment factor	[–]
γ_i	activity coefficient	[–]
δ	thickness of polarization layer	[μm]
δ	solubility parameter	[$(cal/cm^3)^{0.5}$]
ε	porosity (surface or volume)	[–]
η	viscosity	[kg/s m]
μ_i	chemical potential of *i*	[J/mol]
π	osmotic pressure	[bar]
ρ	mass density	[kg/m^3]
σ	reflection coefficient	[–]
τ	tortuosity factor	[–]

Indices

i, j	components *i*, *j*
1, 2	components *1* = solvent; *2* = solute
'	feed; feed side
"	permeate; permeate side
°	standard or reference state
b	bulk (well mixed feed)
liq	liquid
m (as index)	membrane; membrane phase
org	organic

p (as index)	permeate
v (as index)	volume
vap	vapor
w	wall (interface)
w	water

Abbreviations

ABE	acetone-butanol-ethanol
CA	cellulose acetate (generic)
CED	cohesive energy density
ED	electrodialysis
HD	hemodialysis
HF	hollow fiber
IX	ion exchange
MBR	membrane bioreactor
MD	membrane distillation
MF	microfiltration
MW	molecular weight
NF	nanofiltration
NOM	natural organic matter
PA	polyamide (generic)
PRO	pressure retarded osmosis
PV	pervaporation
RO	reverse osmosis
SDI	silt density index
SLM	supported liquid membrane
SW	seawater; spiral wound
TDS	total dissolved solids
UF	ultrafiltration
VLE	vapor-liquid equilibrium
VOC	volatile organic compound

Polymer notation

See Appendix D.