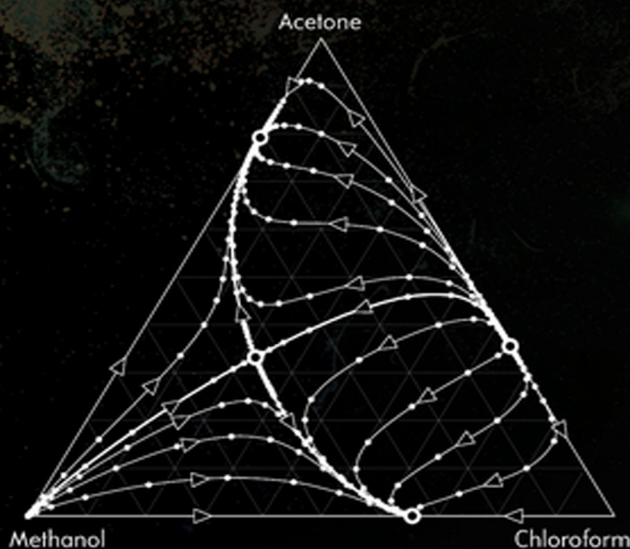


SECOND EDITION

DISTILLATION

PRINCIPLES AND PRACTICE



JOHANN STICHLMAIR | HARALD KLEIN
SEBASTIAN REHFELDT

DISTILLATION

DISTILLATION

Principles and Practice

Second Edition

Prof. Dr.-Ing. JOHANN STICHLMAIR

Prof. Dr.-Ing. HARALD KLEIN

Dr.-Ing. SEBASTIAN REHFELDT

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Contents

Preface	<i>xi</i>
Nomenclature	<i>xiii</i>
1 Introduction	1
1.1 Principle of Distillation Separation	1
1.2 Historical	3
2 Vapor–Liquid Equilibrium	7
2.1 Basic Thermodynamic Correlations	7
2.1.1 Measures of Concentration	7
2.1.2 Equations of State (EOS)	8
2.1.3 Molar Mixing and Partial Molar State Variables	12
2.1.4 Saturation Vapor Pressure and Boiling Temperature of Pure Components	13
2.1.5 Fundamental Equation and the Chemical Potential	14
2.1.6 Gibbs–Duhem Equation and Gibbs–Helmholtz Equation	17
2.2 Calculation of Vapor–Liquid Equilibrium in Mixtures	18
2.2.1 Basic Equilibrium Conditions	18
2.2.2 Gibbs Phase Rule	19
2.2.3 Correlations for the Chemical Potential	20
2.2.4 Calculating Activity Coefficients with the Molar Excess Free Energy	23
2.2.5 Thermodynamic Consistency Check of Molar Excess Free Energy and Activity Coefficients	28
2.2.6 Iso-fugacity Condition	30
2.2.7 Fugacity of the Liquid Phase	30
2.2.8 Fugacity of the Vapor Phase	31
2.2.9 Vapor–Liquid Equilibrium Using an Equation of State	32
2.2.10 Fugacity of Pure Liquid as Standard Fugacity: Raoult's Law	47
2.2.11 Fugacity of Infinitely Diluted Component as Standard Fugacity: Henry's Law	48
2.2.12 Correlations Describing the Molar Excess Free Energy and Activity Coefficients	49

2.2.13	Using Experimental Data of Binary Mixtures for Correlations Describing the Molar Excess Free Energy and Activity Coefficients	55
2.2.14	Vapor–Liquid Equilibrium Ratio of Mixtures	59
2.2.15	Relative Volatility of Mixtures	59
2.2.16	Boiling Condition of Liquid Mixtures	61
2.2.17	Condensation (Dew Point) Condition of Vapor Mixtures	62
2.3	Binary Mixtures and Phase Diagrams	81
2.3.1	Boiling Curve Correlation	81
2.3.2	Condensation (Dew Point) Curve Correlation	83
2.3.3	(p, x, y)-Diagram	84
2.3.4	(T, x, y)-Diagram	84
2.3.5	McCabe–Thiele Diagram	86
2.3.6	Boiling and Condensation Behavior of Binary Mixtures	86
2.3.7	General Aspects of Azeotropic Mixtures	90
2.3.8	Limiting Cases of Binary Mixtures	104
2.4	Ternary Mixtures	114
2.4.1	Boiling and Condensation Conditions of Ternary Mixtures	114
2.4.2	Triangular Diagrams	116
2.4.3	Boiling Surfaces	116
2.4.4	Condensation Surfaces	122
2.4.5	Derivation of Distillation Lines	123
2.4.6	Examples for Distillation Lines	128
3	Single-Stage Distillation and Condensation	137
3.1	Continuous Closed Distillation and Condensation	137
3.1.1	Closed Distillation of Binary Mixtures	137
3.1.2	Closed Distillation of Multicomponent Mixtures	140
3.2	Batchwise Open Distillation and Open Condensation	152
3.2.1	Binary Mixtures	152
3.2.2	Ternary Mixtures	157
3.2.3	Multicomponent Mixtures	167
3.3	Semi-continuous Single-Stage Distillation	169
3.3.1	Semi-continuous Single-Stage Distillation of Binary Mixtures	169
4	Multistage Continuous Distillation (Rectification)	173
4.1	Principles	173
4.1.1	Equilibrium-Stage Concept	176
4.1.2	Transfer-Unit Concept	177
4.1.3	Comparison of Equilibrium-Stage and Transfer-Unit Concepts	180
4.2	Multistage Distillation of Binary Mixtures	181
4.2.1	Calculations Based on Material Balances	182

4.2.2	Calculation Based on Material and Enthalpy Balances	189
4.2.3	Distillation of Binary Mixtures at Total Reflux and Reboil	192
4.2.4	Distillation of Binary Mixtures at Minimum Reflux and Reboil	198
4.2.5	Energy Requirement for Distillation of Binary Mixtures	204
4.3	Multistage Distillation of Ternary Mixtures	206
4.3.1	Calculations Based on Material Balances	208
4.3.2	Distillation of Ternary Mixtures at Total Reflux and Reboil	215
4.3.3	Distillation of Ternary Mixtures at Minimum Reflux and Reboil	224
4.3.4	Energy Requirement of Ternary Distillation	248
4.4	Multistage Distillation of Multicomponent Mixtures	255
4.4.1	Rigorous Column Simulation	256
5	Reactive Distillation, Catalytic Distillation	283
5.1	Fundamentals	284
5.1.1	Chemical Equilibrium	284
5.1.2	Stoichiometric Lines	284
5.1.3	Non-reactive and Reactive Distillation Lines	287
5.1.4	Reactive Azeotropes	289
5.2	Topology of Reactive Distillation Lines	293
5.2.1	Reactions in Ternary Systems	293
5.2.2	Reactions in Ternary Systems with Inert Components	295
5.2.3	Reactions with Side Products	297
5.2.4	Reactions in Quaternary Systems	298
5.3	Topology of Reactive Distillation Processes	298
5.3.1	Single Product Reactions	300
5.3.2	Decomposition Reactions	302
5.3.3	Side Reactions	306
5.4	Arrangement of Catalysts in Columns	307
5.4.1	Homogeneous Catalyst	307
5.4.2	Heterogeneous Catalyst	308
6	Multistage Batch Distillation	313
6.1	Batch Distillation of Binary Mixtures	314
6.1.1	Operation with Constant Reflux	315
6.1.2	Operation with Constant Distillate Composition	318
6.1.3	Operation with Minimum Energy Input	323
6.1.4	Comparison of Energy Requirement for Different Modes of Distillation	327
6.2	Batch Distillation of Ternary Mixtures	327
6.2.1	Zeotropic Mixtures	328
6.2.2	Azeotropic Mixtures	332

6.3	Batch Distillation of Multicomponent Mixtures	336
6.4	Influence of Column Liquid Hold-up on Batch Distillation	337
6.5	Processes for Separating Zeotropic Mixtures by Batch Distillation	340
6.5.1	Total Slop Cut Recycling	340
6.5.2	Binary Distillation of the Accumulated Slop Cuts	340
6.5.3	Recycling of the Slop Cuts at the Appropriate Time	341
6.5.4	Cyclic Operation	341
6.6	Processes for Separating Azeotropic Mixtures by Batch Distillation	341
6.6.1	Processes in One Distillation Field	342
6.6.2	Processes in Two Distillation Fields	343
6.6.3	Process Simplifications	348
6.6.4	Hybrid Processes	348
7	Energy Economization in Distillation	357
7.1	Energy Requirement of Single Columns	358
7.1.1	Reduction of Energy Requirement	358
7.1.2	Reduction of Exergy Losses	359
7.2	Optimal Separation Sequences of Ternary Distillation	363
7.2.1	Process and Energy Requirement of the α -Path	363
7.2.2	Process and Energy Requirement of the c -Path	365
7.2.3	Process and Energy Requirement of the Preferred α/c -Path	366
7.3	Modifications of the Basic Processes	368
7.3.1	Material (Direct) Coupling of Columns	368
7.3.2	Processes with Side Columns	370
7.3.3	Thermal (Indirect) Coupling of Columns	386
7.4	Design of Heat Exchanger Networks	391
7.4.1	Optimum Heat Exchanger Networks	392
7.4.2	Modifying the Optimum Heat Exchanger Network	397
7.4.3	Dual Flow Heat Exchanger Networks	401
7.4.4	Process Modifications	401
8	Industrial Distillation Processes	407
8.1	Constraints for Industrial Distillation Processes	407
8.1.1	Feasible Temperatures	407
8.1.2	Feasible Pressures	409
8.1.3	Feasible Dimensions of Columns	410
8.2	Fractionation of Binary Mixtures	412
8.2.1	Recycling of Diluted Sulfuric Acid	412
8.2.2	Ammonia Recovery from Wastewater	414
8.2.3	Hydrogen Chloride Recovery from Inert Gases	416

8.2.4	Linde Process for Air Separation	418
8.2.5	Process Water Purification	421
8.2.6	Steam Distillation	425
8.3	Fractionation of Multicomponent Zeotropic Mixtures	429
8.3.1	Separation Paths	429
8.3.2	Processes with Side Columns	431
8.4	Fractionation of Heterogeneous Azeotropic Mixtures	435
8.5	Fractionation of Azeotropic Mixtures by Pressure Swing Processes	436
8.6	Fractionation of Azeotropic Mixtures by Addition of an Entrainer	439
8.6.1	Processes for Systems Without Distillation Boundary	440
8.6.2	Processes for Systems with Distillation Boundary	444
8.6.3	Hybrid Processes	455
8.7	Industrial Processes of Reactive Distillation	469
8.7.1	Synthesis of MTBE	469
8.7.2	Synthesis of Mono-ethylene Glycol	471
8.7.3	Synthesis of TAME	473
8.7.4	Synthesis of Methyl Acetate	474
9	Design of Mass Transfer Equipment	481
9.1	Types of Design	482
9.1.1	Tray Columns	482
9.1.2	Packed Columns	484
9.1.3	Criteria for Use of Tray or Packed Columns	486
9.2	Design of Tray Columns	487
9.2.1	Design Parameters of Tray Columns	487
9.2.2	Operating Region of Tray Columns	489
9.2.3	Two-Phase Flow on Trays	497
9.2.4	Mass Transfer in the Two-Phase Layer on Column Trays	518
9.3	Design of Packed Columns	533
9.3.1	Design Parameters of Packed Columns	534
9.3.2	Operating Region of Packed Columns	545
9.3.3	Two-Phase Flow in Packed Columns	549
9.3.4	Mass Transfer in Packed Columns	568
9.A	Appendix: Pressure Drop in Packed Beds	587
10	Control of Distillation Processes	601
10.1	Control Loops	602
10.1.1	Single Control Loop	602
10.1.2	Ratio Control Loop	604
10.1.3	Disturbance Feedforward Control Loop	604

10.1.4	Cascade Control Loop	605
10.2	Single Control Tasks for Distillation Columns	605
10.2.1	Liquid Level Control	605
10.2.2	Split Stream Control	606
10.2.3	Pressure Control	611
10.2.4	Product Concentration Control	613
10.3	Basic Control Configurations of Distillation Columns	613
10.3.1	Basic Control Systems Without Composition Control	617
10.3.2	One-Point Composition Control Configurations	623
10.3.3	Two-Point Composition Control Configurations	626
10.4	Application Ranges of the Basic Control Configurations	629
10.4.1	Impact of Split Parameters According to Split Rule 2	629
10.4.2	Sharp Separations of Ideal Mixtures with Constant Relative Volatility at Minimum Reflux and Boilup Ratio	639
10.4.3	Extended Application Ranges of the Basic Control Configurations	643
10.5	Examples for Control Configurations of Distillation Processes	646
10.5.1	Azeotropic Distillation Process by Pressure Change	646
10.5.2	Distillation Process for Air Separation	647
10.5.3	Distillation Process with a Main and a Side Column	649
10.5.4	Azeotropic Distillation Process by Using an Entrainer	650
10.6	Control Configurations for Batch Distillation Processes	651
	Index	655

Preface

Distillation is the most important and the most effective technology for the fractionation of multicomponent mixtures. Fields of application are all branches of the process industry, for instance, petroleum refineries, chemical industries, and food industries. The often very tall distillation towers dominate the view of many chemical sites. According to its great importance, distillation is a highly developed technology.

The fundamental mechanism of distillation is the mass transfer between a gaseous and a liquid phase. The driving force for this interfacial mass transfer is the difference between the actual and the equilibrium concentration of the phases.

The book consists of 10 chapters. Chapter 1 deals with the basic principle of distillation and with some historical aspects of the art.

Chapter 2 concentrates on the thermodynamics of vapor–liquid equilibrium, since a good knowledge of vapor–liquid equilibrium is an indispensable prerequisite for the design of distillation processes. As compared to many other textbooks, the mixtures are not limited to two components, but ternary mixtures along with their boiling surfaces and triangular diagrams are considered.

The Chapters 3 – 6 deal with the thermodynamics of single-stage distillation (Chapter 3) and multi-stage distillation (Chapter 4), which is often called rectification, reactive distillation (Chapter 5), and batch distillation (Chapter 6). Special attention is given as described above to ternary mixtures, since they represent a more general case than binary mixtures most textbooks on distillation focus on.

In Chapter 7 the energy requirement of distillation processes is discussed. This chapter demonstrates how the large energy requirement of distillation processes can be drastically reduced by internal column coupling and intelligent process modifications.

Important examples of industrial distillation processes are presented in Chapter 8. Here, special attention is given to processes for the fractionation of azeotropic mixtures.

The design of distillation columns is treated in Chapter 9 with focus on tray columns and packed columns. Finally, the control of distillation columns is the objective of Chapter 10 where the concept of split stream control is applied.

The prime intention of this textbook is to let the reader develop a deep understanding of the art of distillation. Many fully worked out examples demonstrate the easy applicability of the theoretical findings. These examples are arranged in boxes to

facilitate the readability of the text.

Of course, not only the authors are involved in the completion of such a comprehensive book. At this point we would like to thank everyone who contributed to the success of this project: Felicitas Engel, M.Sc., Philipp Fritsch, M.Sc., Patrick Haider, M.Sc., Florian Hanusch, M.Sc., Robert Kender, M.Sc., Thomas Kleiner, M.Sc., Maximilian Neumann, M.Sc., Dr.-Ing. Anna Reif, Marc Xia, M.Sc., Alexander Eder, B.Sc., Florian Kaufmann, M.Sc., and Jan Oettig, B.Sc., as well as the valuable expertise of Dr.-Ing. Volker Engel. Many thanks also to Stephan Korell for his helpful advice on the $\text{\LaTeX}$ implementation.

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Harald Klein,
Sebastian Rehfeldt

Munich, February 2020

Nomenclature

Latin Symbols

a	low boiler	—
a	specific surface area	m^2/m^3
a_{eff}	specific effective interfacial area	m^2/m^3
a/v^2	cohesion pressure van der Waals equation	Pa
a	coefficient cubic equation of state of mixture	$\text{J} \cdot \text{m}^3/\text{kmol}^2$
a_{ii}	coefficient cubic equation of state of pure component i	$\text{J} \cdot \text{m}^3/\text{kmol}^2$
a_{ij}	cross coefficient cubic equation of state of component i and j	$\text{J} \cdot \text{m}^3/\text{kmol}^2$
a_i	activity of component i	—
A	area	m^2
A_i	Antoine or Wagner parameter of component i	—
A_{ij}	binary parameter Margules and van Laar equation of component i and j	—
b	high boiler (binary mixture) or intermediate boiler (ternary mixture)	—
b	constant	—
b	co-volume van der Waals equation	m^3
b	coefficient cubic equation of state of mixture	m^3/kmol
b_i	coefficient cubic equation of state of pure component i	m^3/kmol
B	mole amount of bottom product	kmol
B	width of packing channel base	m
$\dot{B}$	bottom flow rate	kmol/s
B	virial coefficient of mixture	m^3/kmol

B_i	Antoine or Wagner parameter of component i	—
B_{ii}	virial coefficient of pure component i	m^3/kmol
B_{ij}	cross virial coefficient of component i and j	m^3/kmol
c	high boiler (ternary mixture) or intermediate boiler (quaternary mixture)	—
c	specific or molar heat capacity	$\text{J}/(\text{kg} \cdot \text{K})$ $\text{J}/(\text{kmol} \cdot \text{K})$
c, C	constant	—
C	second mixture virial coefficient of mixture	m^6/kmol^2
C_i	Antoine or Wagner parameter of component i	—
C_G	capacity factor	m/s
C_h	empiric packing factor	—
d	high boiler quaternary mixture	—
d	diameter, distance	m
D	diameter	m
D	diffusion coefficient	m^2/s
D	mole amount of overhead product (distillate)	kmol
$\dot{D}$	overhead (distillate) flow rate	kmol/s
D_E	dispersion coefficient (eddy diffusion coefficient)	m^2/s
D_i	Wagner parameter of component i	—
e	entrainer	—
E_{OG}	overall gas-side point efficiency	—
E_{OGM}	overall gas-side tray efficiency	—
E	exergy	J
f	friction factor	—
f_i	fugacity of component i	Pa
f_i^0	standard fugacity of component i	Pa
F	F -factor (gas load)	$\text{Pa}^{0.5}$
F	mole amount of feed	kmol
$\dot{F}$	feed flow rate	kmol/s
F_i	surface area fraction/mole fraction UNIQUAC equation of component i	—
g	gravitational acceleration $g = 9.81 \text{ m}/\text{s}^2$	m/s^2
g	molar Gibbs free energy	J/kmol
g_i	gas flow rate of component i	kmol/s
g_i	partial molar Gibbs free energy of component i	J/kmol

Δg	molar mixing Gibbs free energy	J/kmol
g^E	molar excess free energy	J/kmol
g_i^E	partial molar excess free energy of component i	J/kmol
Δg_{ij}	binary parameter NRTL equation of component i and j	—
G	mole amount of vapor	kmol
$\dot{G}$	gas/vapor flow rate	kmol/s
G	Gibbs free energy	J
G^E	excess free energy	J
G_{ij}	binary parameter NRTL equation of component i and j	—
h	specific or molar enthalpy	J/kg
		J/kmol
h_i	partial molar enthalpy of component i	J/kmol
Δh	molar mixing enthalpy	J/kmol
h	height	m
h_{dyn}	dynamic hold-up	m ³ /m ³
h_{dyn0}	dynamic hold-up below loading point	m ³ /m ³
h_f	froth height	m
h_L	clear liquid height	m
h_L	liquid hold-up	m ³ /m ³
h_p	height of pressure drop	m
h_{stat}	static hold-up	m ³ /m ³
h_w	weir height	m
H	enthalpy	J
$\dot{H}$	enthalpy flow rate	W
H	tray spacing or packing height	m
H_{ij}	Henry coefficient of component i in component j	Pa
HL	molar hold-up of liquid	kmol
$HETP$	height equivalent to one theoretical plate	m
HTU	height of a transfer unit	m
J	stripping factor	—
k	numbers of components in mixture	—
k	mass transfer coefficient	kmol/(m ² · s)
k_{ij}	binary parameter cubic equation of state of component i and j	—

K_i	vapor–liquid equilibrium ratio of component i	–
K_R	reaction equilibrium constant	–
l	(path) length	m
l_i	liquid flow rate of component i	kmol/s
L	amount of liquid	kmol
$\dot{L}$	liquid flow rate	kmol/s
L_p	wetted perimeter	m
m	slope of equilibrium curve	–
m	exponent	–
M	mass	kg
M	mole amount of mixture in the middle vessel	kmol
$\hat{M}$	molecular weight	kg/kmol
$\dot{M}$	mixture flow rate	kmol/s
n	number of equilibrium stages	–
n	exponent	–
N	mole amount	kmol
$\dot{N}$	molar flow rate	kmol/s
NTU	number of transfer units	–
p	pitch	m
p	pressure	Pa
p_i	partial pressure of component i	Pa
p_i^0	saturation vapor pressure of pure component i	Pa
p^+	reference pressure	Pa
Ph	number of phases	–
Poy_i	Poynting correction of component i	–
q_i	relative van der Waals surface UNIQUAC equation of component i	–
q_F	caloric factor (thermal state) of the feed	–
Q	heat	J
Q	dimensionless concentration change	–
$\dot{Q}$	heat flow	W
r_i	relative van der Waals volume UNIQUAC equation of component i	–
r	molar latent heat of vaporization	J/kmol
$\hat{R}$	ideal gas constant $\hat{R} = 8314 \text{ J}/(\text{kmol} \cdot \text{K})$	J/(kmol · K)
$\dot{R}$	reactor effluent flow rate	kmol/s
R_G	external reboil (boilup) ratio	–

R_L	external reflux ratio	—
s	molar entropy	J/(kmol · K)
s	plate thickness	m
S	length of packing channel side	m
$\dot{S}$	molar flow rate after decanter, side product	kmol/s
S	entropy	J/K
S	correction factor (Example 2.2)	—
t	time	s
T	temperature	K
T_i^0	boiling temperature of pure component i	K
u	superficial velocity	m/s
Δu_{ij}	binary parameter UNIQUAC equation of component i and j	—
U	internal energy	J
v	molar volume	m ³ /kmol
v_i	partial molar volume of component i	m ³ /kmol
Δv	molar mixing volume	m ³ /kmol
V	volume	m ³
$\dot{V}$	volumetric flow rate	m ³ /s
V_i	volume fraction/mole fraction UNIQUAC equation of component i	—
w_i	mass (weight) fraction of component i	—
w_{iG}	mass fraction of component i in gas phase	kg/kg
w_{iL}	mass fraction of component i in liquid phase	kg/kg
W	work	J
x_i	mole fraction liquid phase of component i	—
$\tilde{x}_i$	transformed mole fraction complete chemical reaction of component i	—
X	function	—
X_i	transformed concentration of component i in reactive systems	—
y_i	mole fraction vapor phase of component i	—
$\tilde{y}_i$	estimated mole fraction vapor phase of component i (Example 2.3)	—
z	number of interacting molecules UNIQUAC equation	—

z	number of particles or channels	—
z	locus, dimensionless tray length	—
z_i	mole fraction two-phase mixture of component i	—
Z	compressibility factor	—
Z_f	number of independent state variables (degrees of freedom)	—

Greek Symbols

α	discharge coefficient	—
$\alpha_i(T)$	temperature function cubic equation of component i	—
α_{ij}	non-randomness factor NRTL equation of component i and j	—
α_{ij}	relative volatility (separation factor) of component i and j	—
β	mass transfer coefficient	m/s
γ_L	liquid-phase distribution	—
Δ	difference	
Δp	pressure drop	Pa
$\Delta \rho$	density difference	kg/m ³
ΔS_{g^E}	sum of squares for g^E	J ² /kmol ²
$\Delta \lambda_{ij}$	binary parameter Wilson equation of component i and j	—
ε	porosity, voidage, relative content	—
ζ	drag coefficient, orifice coefficient	—
ζ_E	friction factor in Ergun equation	—
η	dynamic viscosity	Pa · s
ϑ	contact angle	°
π	pole on the enthalpy–concentration diagram	J/mol
π	circle constant $\pi = 3.14159$	—
Λ_{ij}	binary parameter Wilson equation of component i and j	—
μ_i	chemical potential of component i	J/kmol
ρ	density	kg/m ³
σ	surface tension	kg/s ²

τ	contact time	s
τ_L	liquid residence time in the two-phase layer	s
φ	relative free area of a tray	—
φ_i	fugacity coefficient of component i	—
ϕ_j	correction factor of component i	—
Φ	Underwood parameter	—
Φ_{fl}	flooding factor	—
γ_i	activity coefficient of component i	—
γ_i^∞	activity coefficient at infinite dilution of component i	—
ν_i	stoichiometric coefficient of component i	—
ω_i	acentric factor of component i	—
τ_{ij}	binary parameter NRTL and UNIQUAC equation of component i and j	—

Subscripts

a	low boiler
ac	active
$azeo$	azeotrope
b	high boiler (binary mixture) or intermediate boiler (ternary mixture)
B	bottom product
c	high boiler (ternary mixture) or intermediate boiler (quaternary mixture)
c	critical state variable
c	column
c	continuous phase
cap	bubble cap
cl	clearance under downcomer
cr	critical
C	condenser, cooling
d	high boiler quaternary mixture
d	dispersed phase
d	downcomer
d	dry
D	overhead product (distillate)
e	end

e	entrainer
eq	equivalent
E	entrainment
Exp	experimental value
f	froth
fl	flooding
F	feed
Fr	Froude number
G	gas
h	hole
h	hydraulic
H	heating
irr	irrigated
j	stage number
k	number of components
lam	laminar
L	liquid
m	intermediate
m	mean
max	maximum
min	minimum
n	number of plates or steps
n	nominal
o	openings
o	overflow
OG	overall gas phase
OL	overall liquid phase
p	particle
P	pinch point
r	residual
r	reduced state variable (related to critical state variable)
R	reboiler
s	packing section
s	particle swarm
S	solid
SP	side pinch

t	plate/tray
$turb$	turbulent
T	transition point
vc	vena contracta
v	valve
w	weir
α	start
ω	end
0	orifice, single particle
∞	infinity

Superscripts

0	pure component
<i>azeo</i>	azeotrope
C	combinatorial part UNIQUAC equation
E	excess state variable
id	ideal gas
$id0$	pure ideal gas
n	iteration step or step on distillation line
<i>new</i>	new estimate (Example 2.3)
R	residual part UNIQUAC equation
'	liquid phase
"	vapor phase
$\wedge$	molar
*	equilibrium state
/	modified

Abbreviations

A-1	absorber
C-1	column
E-1	heat exchanger, extractor
R-1	reactor
S-1	decanter

Dimensionless Numbers

$$Bo = \frac{\varrho \cdot g}{\sigma \cdot a^2}$$

Bond number

$$Fr = \frac{u^2}{g \cdot d}$$

Froude number

$$Pe = \frac{l^2}{D \cdot \tau}$$

Peclet number

$$Re = \frac{\varrho \cdot u \cdot d}{\eta}$$

Reynolds number

$$Sc = \frac{\eta}{\varrho \cdot D}$$

Schmidt number

$$We = \frac{u^2 \cdot \varrho \cdot d}{\sigma}$$

Weber number

1

Introduction

Distillation is a widely used method for separating liquid mixtures into their components. It is the workhorse for separation in the petroleum, petrochemical, chemical, and related industries. The consensus is that it will continue to dominate these industries in the future, too.

1.1 Principle of Distillation Separation

Distillation utilizes a very simple separation principle: an intimate contact is created between the starting mixture and a second phase in order to enhance an effective mass transfer between these two phases. The thermodynamic conditions are chosen so that primarily the component to be separated from the feed mixture enters the second phase. The phases are subsequently separated into two single phases with different compositions.

Three steps are always involved in the implementation of this separation principle; see Figure 1.1:

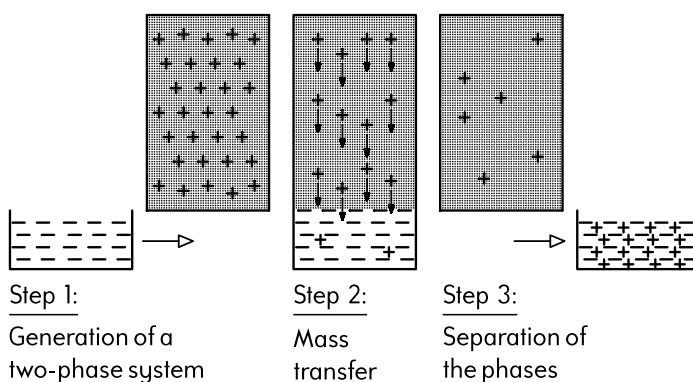


Figure 1.1 General principle of fractionation in thermal separation technology. The essential mechanism is the mass transfer between two phases.

- Generation of a two-phase system
- Mass transfer across the interface
- Separation of the phases

Many separation techniques utilize this very effective separation principle. Absorption, desorption, evaporation, condensation, and distillation involve a gaseous and a liquid phase. Solvent extraction uses two liquid phases. Separation techniques that utilize a fluid phase and a solid phase include adsorption, crystallization, drying, and leaching. In most of these separation processes, the necessary two-phase system is generated by adding an auxiliary phase to the feed mixture. The substances to be separated collect in diluted form in the auxiliary agent. In distillation, however, the second phase is created by partial vaporization of the liquid feed. Hence, the use of an auxiliary substance (often called a mass separating agent), which requires costly recovery, is avoided, and the components to be separated are recovered as relatively pure substances. Indeed, distillation requires only energy in the form of heat, which can subsequently be easily removed from the system. This is an important advantage of distillation.

In practice, distillation requires intimate contacting of vapor and liquid under such conditions that the desired components of the liquid enter the vapor phase. Governing these conditions is the vapor–liquid equilibrium. Many activities on the art of distillation are devoted to find out how closely the vapor–liquid equilibrium can be approached. In any case, it is necessary to separate the liquid and vapor phases afterward.

The vapor and liquid are brought into intimate contact by countercurrent or cross-current flow, and mass exchange occurs because the two phases are not in thermodynamic equilibrium. The phases produced during distillation are formed by evaporation and condensation of the initial mixture. The separation process can be controlled only by the heat supply.

The basis for planning distillation processes is the knowledge of the vapor–liquid equilibrium. As stated earlier, the separation depends primarily on the concentration of the individual substances in the vapor and liquid phases. In this book, principles of vapor–liquid equilibrium are discussed in Chapter 2, with special attention given to the equilibrium of ternary and multicomponent mixtures. Thermodynamic analysis of distillation and rectification is essential to establish the optimal conditions for mass transfer. The decisive factor is the driving force for mass transfer, i.e. the difference between the actual concentrations of the substances and their equilibrium concentrations. Operating conditions have to ensure that this difference is sufficiently large. Appropriate relationships and methods for determining mass transfer are described in Chapters 3 – 6. Examples of industrially important separation processes and energy requirement are discussed in Chapters 7 and 8, respectively. Since separation is achieved by bringing the two phases into intimate contact, in practice, the problems created by multiphase flow and mass transfer between phases must be confronted. The state of the art of multiphase flow is presently rather poor. Two-phase and multiphase flow is an underdeveloped field of fluid mechanics. As a result, just empirical approaches are presently available for practical equipment design, as described in

Chapter 9. Chapter 10 deals with the control of single distillation columns and of distillation processes.

1.2 Historical

Although several authors (e.g. KRELL 1958) support the view that the art of distillation has been well known to ancient Greece, this opinion has never been proven by historians. Ancient philosophers have been, however, very close by the correct understanding of the principles of distillation, for instance, at the mere philosophical debate on the circulation of water in nature. Aristoteles (384-322 BCE) writes in his *Meteorologia*: "... several authors support a similar view on the origin of rivers. The water elevated by the sun and as rain condensed humidity collects ...". In the same book, he writes later on: "That evaporated sea water is drinkable and, after condensation, does not become sea water again, that can we state from experience." However, no practical applications of these theoretical considerations have been reported, and no device for performing the process of distillation is described in ancient literature. Ancient Egypt and ancient China as well had probably no knowledge of the art of distillation. FORBES 1970 agrees with several other authors (e.g. UNDERWOOD 1935) in the opinion that the art of distillation has been invented and pioneered in use in Alexandria, Egypt, in the first century CE.

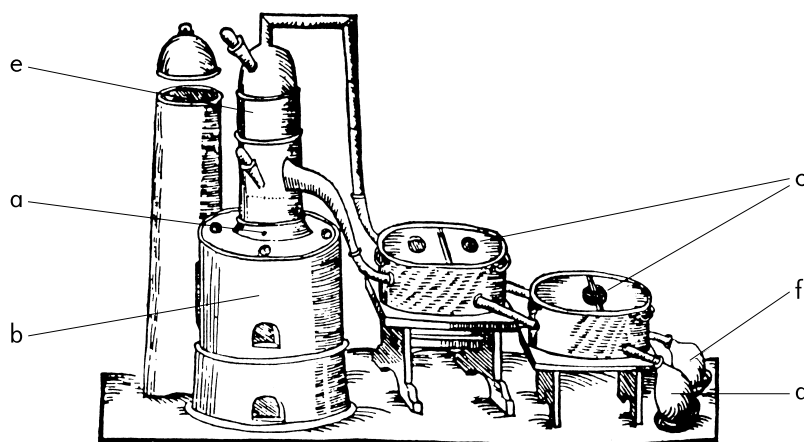


Figure 1.2 Distillation and rectification equipment taken from *The Alchemy of Andreas Libavius* [LIBAVIUS 1964]: (a) boiler, (b) oven, (c) coolers, (d) receiver, (e) headpiece, and (f) receiver.

In the following centuries the knowledge of distillation spread widely and was used around the eleventh century for the first time in northern Italy to produce alcoholic beverages. The development of distillation equipment has been influenced tremendously by this special field of application. An interesting distillation equipment, de-

scribed in the book *The Alchemy of Andreas Libavius*, published in 1597, is illustrated in Figure 1.2 [LIBAVIUS 1964]; it was used for the batch distillation of alcohol.

Heat is supplied to the liquid contents of the boiler (a), built into the oven (b), and the vapor formed was allowed to condense in two coolers (c). Cooling water was changed periodically. The only visible process was the dripping of the condensate into the receiver (d). This separation technique was named after the Latin word *destillare*, which means "dripping or trickling down". Even in early times, it was well known that a higher alcohol content could be reached by using a second distillation step. In the apparatus shown in Figure 1.2, two distillations could be carried out simultaneously. Condensate from the first distillation is returned to the headpiece (e), the so-called *rectificatorium*, which is heated with vapor rising from the boiler. The vapor produced in the headpiece is condensed in the two coolers (c). A liquid with a higher alcohol content is then collected in a second receiver (f). The term *rectification* is derived from this process, which, especially in Europe, is used to describe multistage distillation. The Latin words *recte facere* mean "to rectify or improve". Indeed, up to this day, term *rectification* refers to a process by which a further concentration change is achieved after the first evaporation step.

From such devices distillation columns have been finally developed during the following centuries. Many authors (e.g. UNDERWOOD 1935; FORBES 1970) agree in giving the credit of invention to the Frenchman Cellier-Blumenthal [CELLIER-BLUMENTHAL 1818]. Interesting are the circumstances that enhanced the development of improved distillation devices.

In 1807 Napoleon organized a blockade against England, which answered by a blockade against the European continent. In consequence, goods from the oversea colonies no longer reached Europe, which resulted in shortages of sugarcane, among many other goods. It was well known that sugar can be produced from beets grown in Europe as well [ULLMANN 1969]. However, the brown sugar from beets was much less attractive to the noblemen than the white sugar from canes. Napoleon opened a competition for producing white sugar from beets by setting a very high prize. A favorable process was extraction of sugar from the beets by alcohol instead of water – a process proposed again in recent years [ULLMANN 1969]. The alcohol was recycled within this process. However, after longer periods of operation time, the alcohol needed purification since some water accumulated in the alcohol. Cellier-Blumenthal developed the first distillation column (a tray column) for this process.

In the nineteenth and twentieth centuries, the art of distillation developed rapidly prompted by the oil and petrochemical industry [DEIBELE 1992] and by the chemical and pharmaceutical industry [FAIR 1984]. The present importance of distillation is documented by the fact that approximately 40000 distillation columns are under operation in the United States [HUMPHREY AND SEIBERT 1992]. These columns consume about 3 % of the total energy requirement of the United States [GMEHLING ET AL. 1994].

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