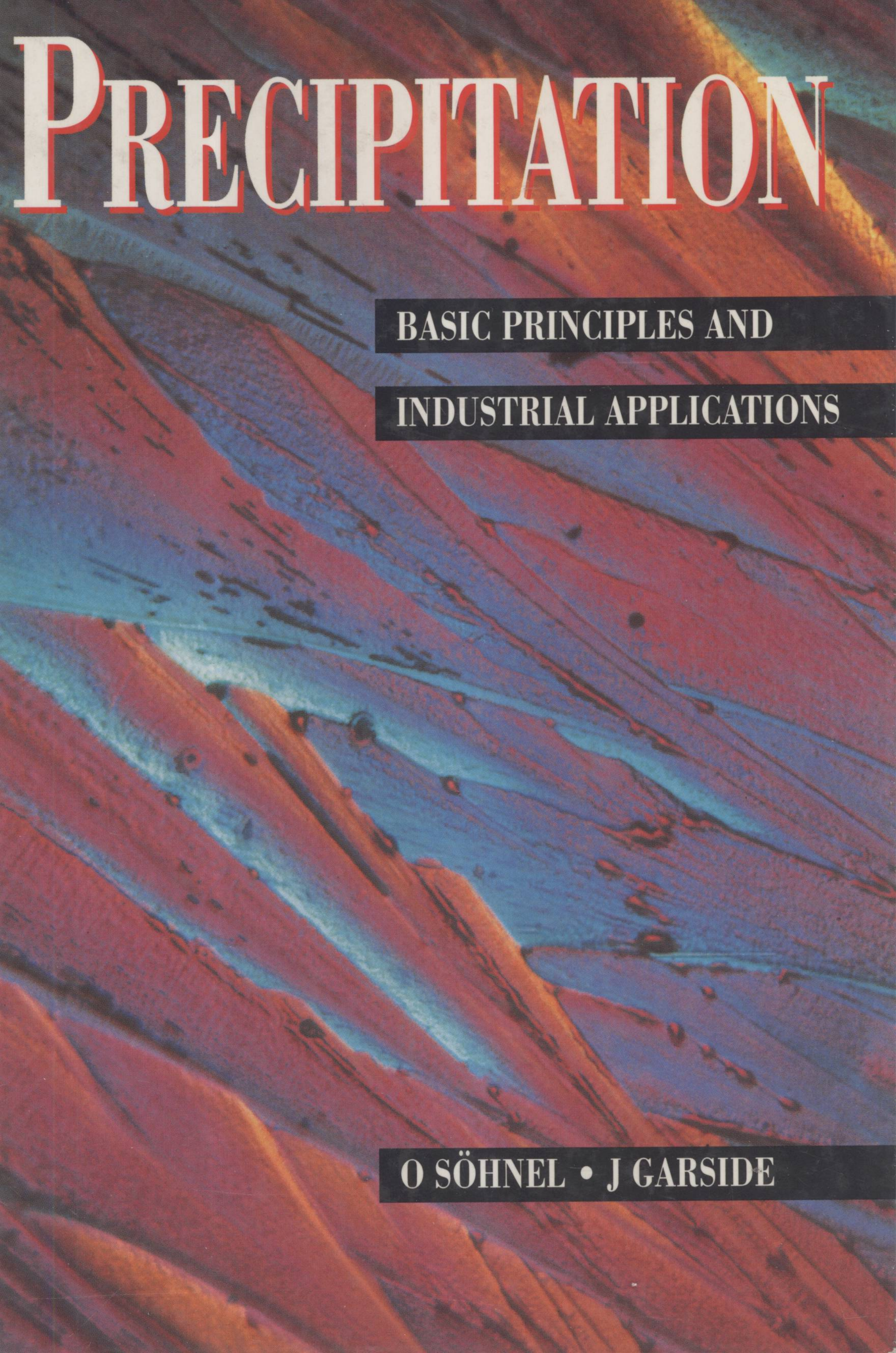
PRECIPITATION



BASIC PRINCIPLES AND INDUSTRIAL APPLICATIONS

O SÖHNEL • J GARSIDE

Precipitation

Basic principles and industrial applications

Otakar Söhnel
Department of Inorganic Processes,
Institute of Chemical Technology, University of Pardubice
Pardubice, Czechoslovakia

and

John Garside
Department of Chemical Engineering,
University of Manchester Institute of Science and Technology (UMIST)
Manchester, UK

BUTTERWORTH
HEINEMANN

Butterworth-Heinemann Ltd
Linacre House, Jordan Hill, Oxford OX2 8DP

PART OF REED INTERNATIONAL BOOKS

OXFORD LONDON BOSTON
MUNICH NEW DELHI SINGAPORE SYDNEY
TOKYO TORONTO WELLINGTON

First published 1992

British Library Cataloguing in Publication Data
Söhnel, Otakar
Precipitation: Basic Principles and Industrial Applications
I. Title II. Garside, John
660

ISBN 0 7506 1107 3

Library of Congress Cataloguing in Publication Data
Söhnel, Otakar.
Precipitation: basic principles and industrial applications / Otakar Söhnel and John Garside
p. cm.
Includes bibliographical references and index.
ISBN 0 7506 1107 3
1. Precipitation (Chemistry) I. Garside, John. II. Title.
QD547.S63 1992
541.3′422–dc20 92-22007
CIP

Typeset by Vision Typesetting, Manchester
Printed in Great Britain by Redwood Press Limited, Melksham, Wiltshire

Precipitation

Basic principles and industrial applications

Preface

Crystallization is one of the oldest chemical engineering operations to have been exploited commercially. It has been argued that the first pure chemical produced artificially was alum manufactured by crystallization; the Egyptians were certainly using alum produced in this way before 1500 BC. As a scientific discipline, however, crystallization came into being during the late 18th century when Lowitz studied the behaviour of supersaturated solutions. Since that time great strides have been made in understanding the scientific basis of crystallization and in developing the technologies to exploit its many advantages as a purification and separation technique in the chemical and process industries.

The crystallization of sparingly soluble substances, that is, crystallization by precipitation, or simply 'precipitation', is rather poorly understood when compared with the crystallization of more soluble materials. Precipitation is difficult to study because it generally involves the simultaneous and rapid occurrence of nucleation and growth as well as the presence of secondary processes such as ageing and agglomeration. These are difficult to separate and investigate independently and the scientific problems involved in their understanding are challenging.

Precipitation is of considerable and growing industrial importance; it also has many applications in medicine, biology and analytical chemistry. Despite this importance and the many efforts directed towards its understanding, precipitation still remains a largely underdeveloped field, its practical application relying to a considerable extent on experience while the underlying theoretical basis is often founded on little more than educated guesses. This situation is reflected in the small number of books available on precipitation. Only two specific texts have been produced and these were both published in the 1960s – the splendid book by A. E. Nielsen (*Kinetics of Precipitation*, Pergamon, 1964) and the rather more specialized text by A. G. Walton (*The Formation and Properties of Precipitates*, Interscience, 1967). Although a considerable volume of theoretical and experimental work has accumulated since that time, it is scattered throughout the periodical literature and little attempt has so far been made to build a uniform and coherent picture of the overall process of precipitation. We have here attempted to address this situation by collecting together theoretical and experimental material concerning precipitation. The focus is primarily on aqueous solutions. The overall picture is still far from complete but we hope the present volume will contribute to the evolution of a unified approach.

Despite considerable variety in the methods of precipitation, perhaps creating the impression that completely different mechanisms are involved, the basic kinetic processes taking place are similar in all precipitations. There is little difference in the process by which a solid is formed from a solution if the solvent is water, an organic solvent or concentrated sulphuric acid; further growth of the solid is governed by basic theoretical principles regardless of the chemical nature of the solid. We have therefore considered the features common to all precipitation processes rather than individual cases. In particular, we have placed considerable emphasis on developing a rigorous theoretical background to the kinetics of precipitation as well as attempting to show how this might be applied to industrial operations.

One particular difficulty in writing this book has been the choice of symbols for the many quantities involved in the derivations and equations that it has been necessary to include. Information has been drawn from many different sources so that it has not been possible to use one conventional and existing set of symbols. As far as possible, we have based our notation on that recommended by the European Federation of Chemical Engineering (EFCE) Working Party on Crystallization ('Recommended Symbols for Industrial Crystallisation', J. W. Mullin, *The Chemical Engineer*, July/August 1974, p. 458) although we have had to make many modifications and additions to this.

Finally, it is a pleasure to acknowledge our debt to innumerable friends and colleagues with whom we have worked. Particular thanks are due to John Mullin for his support and advice over the many years of our association with him at University College London, to Jaroslav Nývlt of the Czechoslovak Academy of Sciences who has done so much to develop the study of crystallization throughout Europe, and to our many research colleagues and students who have forced us to ask many of the questions, and indeed have provided most of the answers, that form the basis of this book. We also thank the Science and Engineering Research Council and the British Council for the provision of various grants that have enabled our collaboration to develop over many years. Most importantly we thank our wives, Helena and Pat, for their rare support, patience and tolerance of our hobby, crystallization.

Otakar Söhnel
John Garside

Notation

Symbols that appear infrequently or only in one specific section are not included in this tabulation.

a	activity; surface area per ion
$a_{\pm}$	mean ionic activity
A	surface area
A_F	filtration area
A_s	surface area of crystals present in unit volume
B_N	system constant defined by eq. (6.80)
B_S	parameter of BCF growth rate expression (eq. (3.134))
c	concentration expressed in molarities; exponent of secondary nucleation (eq. (6.75))
c'	concentration of solute at a crystal surface
$\Delta c = (c - c_{eq})$	concentration difference
c_r	actual concentration of solute
Δc_r	actual supersaturation defined by eq. (4.44b)
c_v	solid phase volume fraction
cv	coefficient of variation
C_S	parameter of BCF growth rate expression (eq. (3.134))
CSI	separation intensity (eq. (6.108))
d	diameter; interplanar distance in a crystal lattice
d_p	surface-average diameter of a particle
D	diffusion coefficient
D^o	apparent diffusion coefficient defined by eq. (3.82)
D_k	number of molecules attaching to a critical nucleus per unit time
D_s	surface diffusion coefficient
E, $\bar{E}$	effectiveness of an admixture at respective concentration, eqs (4.132) and (4.135)
f	surface stress
$f(c)$	monotonic function of concentration
$f(r)$	function of crystal size

$f(S)$	function of supersaturation
$f(\varepsilon_{av})$	filter cake porosity function
$f(\Theta)$	correction factor for heterogeneous nucleation defined by eq. (3.28)
$F(S)$	function of supersaturation defined by eqs (3.125) to (3.129)
g	kinetic order of crystal growth
g_M	kinetic order of mononuclear growth
g_P	kinetic order of polynuclear growth
g_S	kinetic order of screw-dislocation growth
$g(n)$	function of nucleation order defined by eq. (6.23)
G	mass
G_S	shear rate
G_F	mass of dry solid in a filter cake
ΔG	change of Gibbs energy
$\Delta G_D^{\neq}$	activation energy of diffusion
h	Planck constant
$\bar{h}$	hydration number
h_F	height of filter cake
h_T	heat-transfer coefficient
$h(n)$	function of nucleation order defined by eq. (6.24)
H_1^0	solvent molar enthalpy
$H_2^0(s)$	molar enthalpy of solid crystallizing substance
$\bar{H}_{2,eq}$	partial molar enthalpy of crystallizing substance in saturated solution
$\bar{H}$	partial molar enthalpy
$\bar{H}^{\infty}$	partial molar enthalpy at infinite dilution
ΔH_c	crystallization enthalpy
ΔH_r	reaction enthalpy
$i=n/g$	relative kinetic order
i_c	parameter of eq. (6.36)
I	ionic strength of solution defined by eq. (2.47)
I_1	polynuclear chronomal for $g=1$
I_D	diffusion chronomal defined by eq. (4.93)
I_g	polynuclear chronomal defined by eq. (4.100)
$j=dn_i/dt$	molar deposition rate
J	nucleation rate
k	Boltzmann constant
k_a, k_o, k_v	shape factors of area, perimeter and volume, respectively
k_d	diffusion mass transport coefficient
k_F	proportionality constant in eq. (6.10)
k_g, k_g'	growth kinetic constant (eq. (3.130))
k_n, k_n'	kinetic nucleation constant (eq. (3.23))

k_T	thermal conductivity
K_{ad}	adsorption equilibrium constant
K_c	constant in eq. (6.34)
K_D	constant defined by eq. (4.92)
K_{diss}	thermodynamic dissociation constant (eq. (3.159))
K_F	constant in filtration expression eq. (6.4)
K_g	constant defined by eq. (4.99)
K_{ip}	equilibrium constant of ion pair formation (eq. (4.124))
K_p	defined by eqs (3.123) or (3.124)
K_s	analytical ionic product (eq. (4.50))
K_{sp}	thermodynamic solubility product (eq. (2.65))
K_I	rate constant of integration of molecules
K_{II}	rate constant for integration of ions
L	length; diameter of mixed vessel
m	concentration expressed in molalities
M	molecular mass
n	kinetic order of nucleation
n_i	number of moles of *i*th component
$n(r)$	population density, i.e. distribution function representing the number of particles as a function of size per unit volume of solid-free liquid
$n'(r)$	particle size distribution frequency function
N	number of atoms or molecules; number of crystals in a unit volume of solid-free liquid
N_A	Avogadro number
N_1	number of separate molecules present in unit volume
$Nu = h_T d/k_T$	Nusselt number
p_i	concentration of *i*th component expressed in mass per cent
P	pressure; perimeter
ΔP	filtration pressure drop
P_r	production rate
q_F	specific performance of a filter
q_r	specific performance of a reactor
Q	defined by eq. (2.30)
r	radius
r_C	cut size of crystals
r_d	dominant crystal size corresponding to the mode of the distribution
r_F	specific volume filtration resistance
$\dot{r}$	average crystal growth rate
$\dot{r}_I$	growth rate controlled by integration

$\dot{r}_C, \dot{r}_{CD}, \dot{r}_D, \dot{r}_M, \dot{r}_P, \dot{r}_S$	growth rate controlled by convection, convection and diffusion, diffusion, mononuclear, polynuclear and screw-dislocation mechanism, respectively
$\bar{r}_{i+1,j}$	weighted average size (eq. (4.42))
r_{vis}	minimum radius at which crystal becomes visible
R	gas constant; draw-off ratio (eq. (6.103))
R_m	filter cloth resistance
R_r	stirrer speed
Re	Reynolds number defined by eq. (3.97)
s	specific surface area defined by eq. (6.2)
s_{eff}	specific surface area of solid effective for filtration
$\bar{s}$	geometric standard deviation defined by eq. (4.146)
S	supersaturation ratio
S_r	actual supersaturation defined by eq. (4.44a)
Sc	Schmidt number defined by eq. (3.98)
$Sh = k_d d/D$	Sherwood number
t	time
t_c	capillary suction time; batch time
t_C	average circulation time of a fluid element (eq. (4.166))
t_F	filtration time
t_g	time for critical nucleus to grow to visible size
t_i	time necessary for the critical nucleus to be formed
t_{ind}	induction period
t_M	characteristic time for the mixing process (eq. (4.167))
t_n	mean time of critical nucleus formation
t_{tr}	transient period
t_z	mean residence time
$t_{0.5}$	half-life of system
t_1	characteristic time of precipitation defined by eq. (4.10)
T	absolute temperature
ΔT_{max}	maximum achievable undercooling
u	parameter in eq. (6.37)
U	relative velocity between crystal and solution; parameter of eqs (4.69) to (4.75)
U_o	superficial liquid velocity through a porous bed
v	molecular volume
v_g	linear face growth rate
$\dot{v}$	growth step velocity
V	volume
V_F	volume of filtrate
V_m	molar volume

V_r	effective volume of reactor
$\dot{V}_1$	suspension discharge rate from reactor
w	mass fraction
$w(x)$	differential mass fraction distribution
w_i	mass fraction of *i*th component
$W(x)$	cumulative mass distribution function
x	mole fraction; dimensionless crystal size ($=\mathrm{r}/\dot{\mathrm{r}}\mathrm{t_z}$)
y	parameter defined by eq. (4.49)
y_s	concentration of solid in a suspension
$\dot{y}_s$	specific production rate of reactor
z	ionic charge
α	extent of reaction
α'	degree of dissociation
α_F	specific mass filtration resistance
$\bar{\alpha},\bar{\alpha}_1$	collision effectiveness factor for perikinetic and orthokinetic agglomeration, respectively
β	geometric factor defined by eq. (3.15)
β'	geometric factor defined by eq. (3.114)
γ	activity coefficient
$\gamma_\pm$	stoichiometric mean activity coefficient
$\gamma'_\pm$	mean activity coefficient of a free ion
γ^s	surface energy (intensive surface energy parameter)
γ^s_{13}	interfacial tension between crystal and surrounding phase
Γ	gamma function
δ	thickness of diffusion layer around the crystal
Δ	difference
ε	entropy factor defined by eq. (3.104); energy dissipation rate
ε_{av}	average porosity of filter cake, eq. (6.3)
ζ	probability that a molecule arriving on crystal surface will be incorporated into the lattice; zeta potential
η	viscosity
η_D	crowding factor defined by eq. (3.86)
Θ	wetting angle; fraction of surface covered by admixture
θ	time; temperature in °C
κ	number of molecules of crystalline water per molecule of compound in solid state; conductivity
K	defined by eq. (4.138)
λ_K	Kolmogoroff velocity microscale
λ_s	mean-free path of building unit on crystal surface
λ^0	limiting ionic mobility

μ	chemical potential
μ^0	standard chemical potential
$\nu = \nu_+ + \nu_-$	number of ions into which a molecule dissociates
ν_{in}	frequency of molecular jumps in adsorption layer
$\bar{\nu}_i$	stoichiometric coefficient of reaction
ξ	activity coefficient ratio; probability of attaching a molecule to a nucleus
ρ	density
$\sigma = S - 1$	relative supersaturation
σ_h	edge free energy
σ_p	specific surface work
τ	time
φ	molal osmotic coefficient defined by eq. (2.36)
ϕ	affinity defined by eq. (2.80)
ϕ_v^o	partial molar volume of the dissolved substance at infinite dilution
χ	number of molecules arriving at a unit surface per unit time
ψ_D	diffusion effectiveness factor (eq. (3.151b))
ψ_I	surface integration effectiveness factor (eq. (3.151a))
Ω	pre-exponential factor in nucleation rate expression

Subscripts

a	expressed in activities
A	anhydrous
c	expressed in molarities
crit	critical
eq	value at equilibrium
f	final; liquid
het	heterogeneous
hom	homogeneous
H	hydrate
i	*i*th component
imp	admixture
inf	inflection
m	expressed in molalities
max	maximum
min	minimum
N	quantity related to a nucleus formed by *N* particles
prim	primary
rel	relative
s	solid
sec	secondary
susp	suspension

tot	total
w	water
x	expressed in mole fractions
o	initial
1	solvent
+	cation
−	anion
∞	at infinity

Superscripts

$'$	quantity related to two-dimensional nucleus
*	quantity related to critical nucleus
$\dot{}$	derivative with respect to time (d/dt)
$\ddot{}$	second derivative with respect to time (d^2/dt^2)
o	quantity in a standard state
$\bar{}$	average quantity

Miscellaneous

(N)	for number N
(r)	for particle of radius r
(0)	value at time $t = 0$
(t)	value at time t
(∞)	at infinity or in equilibrium
[ ]	molar concentrations
Π	product
pA	$-\log[A]$
Σ	summation

Contents

Chapter 1

Introduction

The definition of 'precipitation' as opposed to the more general term 'crystallization' has always caused difficulty. Indeed, it is probably impossible to produce a precise definition of precipitation, at least in part because there is no clear dividing line between the two phenomena. It is perhaps best to think of precipitation as embodying fast crystallization. The rapidity of the precipitation process is a consequence of the high supersaturation at which it takes place.

A number of consequences flow from this definition, most of which give rise to other characteristics of precipitation. First, it is usually relatively insoluble materials that lead to precipitated products since the low solubility of such materials allows the development of high supersaturations. Second, the high supersaturations at which nucleation takes place ensures that primary nucleation rates are usually very high; nucleation therefore plays a major role in the precipitation processes. The third consequence, and following directly from these characteristically high nucleation rates, is that a large number of crystals are produced; this limits the average size to which the crystals can grow. As a result, the particle concentration is usually very high, typically between about 10^{11} and 10^{16} particles cm^{-3}, and the crystal size is usually relatively small, perhaps between 0.1 and 10 μm.

Fourth, if the precipitated crystals are sufficiently small a number of secondary processes such as ripening, ageing, agglomeration and coagulation may occur and these can cause major changes in the precipitate size distribution; the development of colloidal systems may also be important. The fifth important feature is that the supersaturation necessary for precipitation frequently results from a chemical reaction; indeed, precipitation is sometimes referred to as reactive crystallization. The chemical reactions may involve two liquids, a liquid and a solid or a liquid and a gas. Many such reactions are fast and so the role of mixing is frequently important in precipitation processes. Finally, precipitations are usually carried out at constant temperature and do not usually rely on cooling to produce supersaturation.

Precipitation processes are of great importance in the chemical and process industries. Many of these processes are long-established; for example, the Solvay process which involves the precipitation of sodium bicarbonate was invented in 1863 (Forbes and Dijksterhuis, 1963) and is still widely used