PRECIPITATION

BASIC PRINCIPLES AND

INDUSTRIAL APPLICATIONS

O SÖHNEL • J GARSIDE



Precipitation

Basic principles and industrial applications

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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
$A_{ m F}$	filtration area
$A_{\mathbf{s}}$	surface area of crystals present in unit volume
$B_{\mathbf{N}}$	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
$\Delta c = (c - c_{\rm eq})$	concentration difference
$c_{\rm r}$	actual concentration of solute
$\dot{\Delta c}_{r}$	actual supersaturation defined by eq. (4.44b)
$c_{\mathbf{v}}$	solid phase volume fraction
cv	coefficient of variation
$C_{\mathbf{S}}$	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°	apparent diffusion coefficient defined by eq. (3.82)
$D_{\mathbf{k}}$	number of molecules attaching to a critical nucleus
	per unit time
$D_{\rm s}$	surface diffusion coefficient
E, \overline{E}	effectiveness of an admixture at respective concen-
_	tration, eqs (4.132) and (4.135)
f_{-}	surface stress
f(c)	monotonic function of concentration
f(r)	function of crystal size

C(G)	
f(S)	function of supersaturation
$f(\varepsilon_{av})$	filter cake porosity function
$f(\mathbf{\Theta})$	correction factor for heterogeneous nucleation de-
E/G)	fined 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
$g_{\mathtt{P}}$	kinetic order of polynuclear growth
$g_{\mathbf{s}}$	kinetic order of screw-dislocation growth
g(n)	function of nucleation order defined by eq. (6.23)
G	mass
$G_{\mathbf{S}}$	shear rate
G_{F}	mass of dry solid in a filter cake
ΔG	change of Gibbs energy
$\Delta G_{ m D}^{ eq}$	activation energy of diffusion
$\frac{h}{L}$	Planck constant
\bar{h}	hydration number
$h_{ m F}$	height of filter cake
h_{T}	heat-transfer coefficient
h(n)	function of nucleation order defined by eq. (6.24)
$h(n)$ H_1^0 $H_2^0(s)$	solvent molar enthalpy
$H_2^{\circ}(s)$	molar enthalpy of solid crystallizing substance
${ar H}_{2, m eq}$	partial molar enthalpy of crystallizing substance in
rī.	saturated solution
$ar{H}$ $ar{H}^{\infty}$	partial molar enthalpy
	partial molar enthalpy at infinite dilution
$\Delta H_{\rm c}$	crystallization enthalpy
$\Delta H_{\rm r}$	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 $g=1$
$I_{\rm D}$	diffusion chronomal defined by eq. (4.93)
I _g	polynuclear chronomal defined by eq. (4.100)
$j = dn_i/dt$	molar deposition rate
k	nucleation rate
k_a, k_o, k_v	Boltzmann constant
$\kappa_a, \kappa_o, \kappa_v$	shape factors of area, perimeter and volume, re-
L.	spectively
$k_{\mathbf{d}}$	diffusion mass transport coefficient
$k_{\rm F}$	proportionality constant in eq. (6.10)
k_{g}, k_{g}' k_{n}, k_{n}'	growth kinetic constant (eq. (3.130))
κ_n, κ_n	kinetic nucleation constant (eq. (3.23))

k_{T}	thermal conductivity
	adsorption equilibrium constant
$K_{\rm ad}$	constant in eq. (6.34)
$K_{\rm c}$	
$K_{\rm D}$	constant defined by eq. (4.92)
$K_{ m diss}$	thermodynamic dissociation constant (eq. (3.159))
K_{F}	constant in filtration expression eq. (6.4)
$K_{\mathbf{g}}$	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)
$K_{\rm s}^{\rm P}$	analytical ionic product (eq. (4.50))
$K_{\rm sp}^{\rm s}$	thermodynamic solubility product (eq. (2.65))
$K_{\rm I}$	rate constant of integration of molecules
K_{II}	rate constant for integration of ions
L L	length; diameter of mixed vessel
	concentration expressed in molalities
m M	molecular mass
	kinetic order of nucleation
n	
n_i	number of moles of ith component
n(r)	population density, i.e. distribution function repre-
	senting 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
$N_{\mathbf{A}}$	Avogadro number
N_{1}	number of separate molecules present in unit
-	volume
$Nu = h_{\rm T}d/k_{\rm T}$	Nusselt number
p_i	concentration of ith component expressed in mass
F 1	per cent
P	pressure; perimeter
ΔP	filtration pressure drop
$P_{\rm r}$	production rate
•	specific performance of a filter
q_{F}	
$q_{\rm r}$	specific performance of a reactor
Q	defined by eq. (2.30)
r	radius
$r_{ m C}$	cut size of crystals
$r_{ m d}$	dominant crystal size corresponding to the mode of
	the distribution
$r_{ m F}$	specific volume filtration resistance
\dot{r}	average crystal growth rate
$\dot{r}_{_{ m I}}$	growth rate controlled by integration
·	

$\dot{r}_{\mathrm{C}},\dot{r}_{\mathrm{CD}},\dot{r}_{\mathrm{D}},\dot{r}_{\mathrm{M}},\dot{r}_{\mathrm{P}},\dot{r}_{\mathrm{S}}$	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))
$r_{ m vis}$	minimum radius at which crystal becomes visible
$R_{,}$	gas constant; draw-off ratio (eq. (6.103))
$R_{\rm m}$	filter cloth resistance
$R_{\rm r}$	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
$ar{s}$ S	geometric standard deviation defined by eq. (4.146)
	supersaturation ratio
S _r Sc .	actual supersaturation defined by eq. (4.44a)
$Sh = k_{\rm d}d/D$	Schmidt number defined by eq. (3.98) Sherwood number
$t = \kappa_{\rm d} u/D$	time
$t_{\rm c}$	capillary suction time; batch time
$t_{\mathbf{C}}$	average circulation time of a fluid element (eq.
•C	(4.166))
$t_{ m F}$	filtration time
$t_{\mathbf{g}}$	time for critical nucleus to grow to visible size
$t_{\mathbf{i}}$	time necessary for the critical nucleus to be formed
t_{ind}	induction period
t_{M}	characteristic time for the mixing process (eq.
,	(4.167))
$t_{\mathbf{n}}$	mean time of critical nucleus formation
$t_{ m tr}$	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; par-
**	ameter 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
$\stackrel{\dot{v}}{V}$	growth step velocity
$V_{ m F}$	volume of filtrate
$V_{\rm m}$	volume of filtrate molar volume
′ m	moiar volume

$\overset{V}{\cdot}_{ m r}$	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 ith component
W(x)	cumulative mass distribution function
x	mole fraction; dimensionless crystal size $(=r/\dot{r}t_z)$
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
$lpha_{ m F}$	specific mass filtration resistance
$\bar{\alpha}, \bar{\alpha}_1$	collision effectiveness factor for perikinetic and
7-1	orthokinetic agglomeration, respectively
β	geometric factor defined by eq. (3.15)
β'	geometric factor defined by eq. (3.114)
γ	activity coefficient
	stoichiometric mean activity coefficient
νί	mean activity coefficient of a free ion
γ _± γ' _± γ ^s	surface energy (intensive surface energy parameter)
γ_{13}^{s}	interfacial tension between crystal and surrounding
/13	phase
Γ	gamma function
δ	thickness of diffusion layer around the crystal
Δ	difference
ε	entropy factor defined by eq. (3.104); energy dissi-
	pation rate
$arepsilon_{\mathbf{a}\mathbf{v}}$	average porosity of filter cake, eq. (6.3)
ζ	probability that a molecule arriving on crystal
7	surface will be incorporated into the lattice; zeta
	potential
η	viscosity
$\eta_{\mathbf{D}}$	crowding factor defined by eq. (3.86)
Θ	wetting angle; fraction of surface covered by admix-
_	ture
heta	time; temperature in °C
κ	number of molecules of crystalline water per mol-
	ecule of compound in solid state; conductivity
K	defined by eq. (4.138)
$\lambda_{\mathbf{K}}$	Kolmogoroff velocity microscale
	mean-free path of building unit on crystal surface
$rac{\lambda_{s}}{\lambda^{0}}$	limiting ionic mobility
**	mineing forme modificy

 μ chemical potential

 μ^0 standard chemical potential

 $v = v_{+} + v_{-}$ number of ions into which a molecule dissociates frequency of molecular jumps in adsorption layer

 \bar{v}_i stoichiometric coefficient of reaction

 ξ activity coefficient ratio; probability of attaching a

molecule to a nucleus

 ρ density

 $\sigma = S - 1$ relative supersaturation

 $\sigma_{\rm h}$ edge free energy specific surface work

 τ time

φ molal osmotic coefficient defined by eq. (2.36)

 ϕ affinity defined by eq. (2.80)

 $\phi_{\rm v}^{\rm o}$ partial molar volume of the dissolved substance at

infinite dilution

χ number of molecules arriving at a unit surface per

unit time

 $\psi_{\rm D}$ diffusion effectiveness factor (eq. (3.151b))

 ψ_1 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 ith componentimp admixtureinf inflection

m expressed in molalities

max maximum 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

r	quantity related to two-dimensional nucleus
*	quantity related to critical nucleus
	derivative with respect to time (d/dt)
••	second derivative with respect to time (d^2/dt^2)
o	quantity in a standard state
-	average quantity

Miscellaneous

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

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Appendix 2 Surface energy of solids

substances

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Appendix 4 Experimental precipitation studies

Appendix 3 Solubility products of sparingly soluble inorganic

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 $10\,\mu\text{m}$.

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