Crystallization

THIRD EDITION

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J. W. MULLIN

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Third Edition

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Preface to Third Edition

Twenty years have elapsed since the second edition of *Crystallization* was published, and more than thirty since the first. Over this period of time, significant advances have been made in our understanding of the basic mechanisms of crystallization. There has also been an upsurge of interest in the utilization of crystallization as a processing technique throughout a wide range of industries. It is pleasing, therefore, to note that problems of crystallizer design and operation can now be approached with some confidence.

This third edition is essentially a completely new book. Most sections have been extensively rewritten and some considerably enlarged to reflect the important developments of recent years. The subject matter has been rearranged to produce a more coherent structure. For example, all methods of crystal size characterization and measurement are brought together in Chapter 2. The measurement and prediction of solubility data are given some prominence in Chapter 3. Nucleation and crystal growth respectively are now dealt with in separate chapters, and the topics of crystal habit modification and phase transformation are given special attention. The techniques of recrystallization, precipitation, sublimation, and crystallization from melts and solutions are all treated separately, and in considerable detail. For solution crystallization, a number of different crystallizer operating modes, including batch operation, are assessed and some simple design procedures are outlined. The problems of scale-up and downstream process requirements are also addressed.

I am deeply indebted to past research students, visiting researchers and colleagues who have worked with me in the Crystallization Group at UCL over more than thirty years for their help and support in so many different ways. They are too numerous to name individually here, but much of their work is recorded and duly acknowledged in appropriate sections throughout this edition. I should like to express my sincere personal thanks to them all. I am also very grateful to those who have written to me over the years with useful suggestions for improvements to the text. Finally, and most importantly, it gives me great pleasure to acknowledge the debt I owe to my wife, Averil, who has assisted me with all three editions. Without her tremendous help in preparing the manuscript of this third edition, the task of writing it would not have been completed.

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JOHN MULLIN
University College London
1992

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Preface to First Edition

Crystallization must surely rank as the oldest unit operation, in the chemical engineering sense. Sodium chloride, for example, has been manufactured by this process since the dawn of civilization. Today there are few sections of the chemical industry that do not, at some stage, utilize crystallization as a method of production, purification or recovery of solid material. Apart from being one of the best and cheapest methods available for the production of pure solids from impure solutions, crystallization has the additional advantage of giving an end product that has many desirable properties. Uniform crystals have good flow, handling and packaging characteristics: they also have an attractive appearance, and this latter property alone can be a very important sales factor.

The industrial applications of crystallization are not necessarily confined to the production of pure solid substances. In recent years large-scale purification techniques have been developed for substances that are normally liquid at room temperature. The petroleum industry, for example, in which distillation has long held pride of place as the major processing operation, is turning its attention most keenly to low-temperature crystallization as a method for the separation of 'difficult' liquid hydrocarbon mixtures.

It is rather surprising that few books, indeed none in the English language, have been devoted to a general treatment of crystallization practice, in view of its importance and extensive industrial application. One reason for this lack of attention could easily be that crystallization is still referred to as more of an art than a science. There is undoubtedly some truth in this old adage, as anyone who has designed and subsequently operated a crystallizer will know, but it cannot be denied that nowadays there is a considerable amount of science associated with the art.

Despite the large number of advances that have been made in recent years in crystallization technology, there is still plenty of evidence of the reluctance to talk about crystallization as a process divorced from considerations of the actual substance being crystallized. To some extent this state of affairs is similar to that which existed in the field of distillation some decades ago when little attempt had been made to correlate the highly specialized techniques developed, more or less independently, for the processing of such commodities as coal tar, alcohol and petroleum products. The transformation from an 'art' to a 'science' was eventually made when it came to be recognized that the key factor which unified distillation design methods lay in the equilibrium physical properties of the working systems.

There is a growing trend today towards a unified approach to crystallization problems, but there is still some way to go before crystallization ceases to be the Cinderella of the unit operations. More data, particularly of the applied kind, should be published. In this age of prolific outputs of technical literature such a recommendation is not made lightly, but there is a real deficiency of this type of

published information. There is, at the same time, a wealth of knowledge and experience retained in the process industries, much of it empirical but none the less valuable when collected and correlated.

The object of this book is to outline the more important aspects of crystallization theory and practice, together with some closely allied topics. The book is intended to serve process chemists and engineers, and it should prove of interest to students of chemical engineering and chemical technology. While many of the techniques and operations have been described with reference to specific processes or industries, an attempt has been made to treat the subject matter in as general a manner as possible in order to emphasize the unit operational nature of crystallization. Particular attention has been paid to the newer and more recently developed processing methods, even where these have not as yet proved adaptable to the large-scale manufacture of crystals.

My thanks are due to the Editors of *Chemical Engineering Practice* for permission to include some of the material and many of the diagrams previously published by me in Volume 6 of their 12-volume series. I am indebted to Professor M. B. Donald, who first suggested that I should write on this subject, and to many of my colleagues, past and present, for helpful discussions in connection with this work. I would also like to take this opportunity of acknowledging my indebtedness to my wife for the valuable assistance and encouragement she gave me during the preparation of the manuscript.

JOHN MULLIN
London
1960

Nomenclature and units

The basic SI units of mass, length and time are the kilogram (kg), metre (m) and second (s). The basic unit of thermodynamic temperature is the kelvin (K), but temperatures and temperature differences may also be expressed in degrees Celsius (°C). The unit for the amount of substance is the mole (mol), defined as the amount of substance which contains as many elementary units as there are atoms in 0.012 kg of carbon-12. Chemical engineers, however, are tending to use the kilomole (kmol $= 10^3$ mol) as the preferred unit. The unit of electric current is the ampere (A).

Several of the derived SI units have special names:

Quantity	Name	Symbol	SI unit		Basic SI unit			
Frequency	hertz	Hz			s^{-1}			
Force	newton	N			m	kg	s^{-2}	
Pressure	pascal	Pa	N	m^{-2}	m^{-1}	kg	s^{-2}	
Energy, work; heat	joule	J	N	m	m^2	kg	s^{-2}	
Power	watt	W	J	s^{-1}	m^2	kg	s^{-3}	
Quantity of electricity	coulomb	C			s	A		
Electric potential	volt	V	W	A^{-1}	m^2	kg	s^{-3}	A^{-1}
Electric resistance	ohm	Ω	V	A^{-1}	m^2	kg	s^{-3}	A^{-2}
Conductance	siemens	S	A	V^{-1}	m^{-2}	kg^{-1}	s^3	A^2
Capacitance	farad	F	C	V^{-1}	m^{-2}	kg^{-1}	s^4	A^2
Magnetic flux	weber	Wb	V	s	m^2	kg	s^{-2}	A^{-1}
Magnetic flux density	tesla	T	Wb	m^{-2}	kg	s^{-2}	A^{-1}	
Inductance	henry	H	Wb	A^{-1}	m^2	kg	s^{-2}	A^{-2}

Up to the present moment, there is no general acceptance of the pascal for expressing pressures in the chemical industry; many workers prefer to use multiples and submultiples of the bar (1 bar $= 10^5$ Pa $= 10^5$ N m^{-2} $\approx$ 1 atmosphere). The standard atmosphere (760 mm Hg) is defined as 1.0133×10^5 Pa, i.e. 1.0133 bar.

The prefixes for unit multiples and submultiples are:

10^{-18}	atto	a		10^1	deca	da
10^{-15}	femto	f		10^2	hecto	h
10^{-12}	pico	p		10^3	kilo	k
10^{-9}	nano	n		10^6	mega	M
10^{-6}	micro	μ		10^9	giga	G
10^{-3}	milli	m		10^{12}	tera	T
10^{-2}	centi	c		10^{15}	peta	P
10^{-1}	deci	d		10^{18}	exa	E

Conversion factors for some common units used in chemical engineering are listed below. An asterisk (*) denotes an exact relationship.

Length	*1 in	:	25·4 mm
	*1 ft	:	0·304 8 m
	*1 yd	:	0·914 4 m
	1 mile	:	1·609 3 km
	*1 Å (ångstrom)	:	10^{-10} m
Time	*1 min	:	60 s
	*1 h	:	3·6 ks
	*1 day	:	86·4 ks
	1 year	:	31·5 Ms
Area	*1 in²	:	645·16 mm²
	1 ft²	:	0·092 903 m²
	1 yd²	:	0·836 13 m²
	1 acre	:	4046·9 m²
	1 hectare	:	10 000 m²
	1 mile²	:	2·590 km²
Volume	1 in³	:	16·387 cm³
	1 ft³	:	0·028 32 m³
	1 yd³	:	0·764 53 m³
	1 UK gal	:	4546·1 cm³
	1 US gal	:	3785·4 cm³
Mass	1 oz	:	28·352 g
	1 grain	:	0·064 80 g
	*1 lb	:	0453 592 37 kg
	1 cwt	:	50 802 3 kg
	1 ton	:	1016·06 kg
Force	1 pdl	:	0·138 26 N
	1 lbf	:	4·448 2 N
	1 kgf	:	9·806 7 N
	1 tonf	:	9·964 0 kN
	*1 dyn	:	10^{-5} N
Temperature difference	*1 degF (degR)	:	$\frac{5}{9}$ degC (K)
Energy (work, heat)	1 ft lbf	:	1·355 8 J
	1 ft pdl	:	0·042 14 J
	*1 cal (internat. table)	:	4·186 8 J
	1 erg	:	10^{-7} J
	1 Btu	:	1·055 06 kJ
	1 chu	:	1·899 1 kJ
	1 hp h	:	2·684 5 MJ
	*1 kW h	:	3·6 MJ
	1 therm	:	105·51 MJ
	1 thermie	:	4·185 5 MJ

Calorific value (volumetric)	1 Btu/ft^3	:	37·259 kJ m^{-3}
	1 chu/ft^3	:	67·067 kJ m^{-3}
	1 kcal/ft^3	:	147·86 kJ m^{-3}
	1 kcal/m^3	:	4·186 8 kJ m^{-3}
	1 therm/ft^3	:	3·726 0 GJ m^{-3}
Velocity	1 ft/s	:	0·304 8 m s^{-1}
	1 ft/min	:	5·080 0 mm s^{-1}
	1 ft/h	:	84·667 μm s^{-1}
	1 mile/h	:	0·447 04 m s^{-1}
Volumetric flow	1 ft^3/s	:	0·028 316 m^3 s^{-1}
	1 ft^3/h	:	7·865 8 cm^3 s^{-1}
	1 UK gal/h	:	1·262 8 cm^3 s^{-1}
	1 US gal/h	:	1·051 5 cm^3 s^{-1}
Mass flow	1 lb/h	:	0·126 00 g s^{-1}
	1 ton/h	:	0·282 24 kg s^{-1}
Mass per unit area	1 lb/in^2	:	703·07 kg m^{-2}
	1 lb/ft^2	:	4·882 4 kg m^{-2}
	1 ton/mile^2	:	392·30 kg km^{-2}
Density	1 lb/in^3	:	27·680 g cm^{-3}
	1 lb/ft^3	:	16·019 kg m^{-3}
	1 lb/UK gal	:	99·776 kg m^{-3}
	1 lb/US gal	:	119·83 kg m^{-3}
Pressure	1 lbf/in^2	:	6·894 8 kN m^{-2}
	1 tonf/in^2	:	15·444 MN m^{-2}
	1 lbf/ft^2	:	47·880 N m^{-2}
	1 kgf/m^2	:	9·806 7 N m^{-2}
	*1 standard atm	:	101·325 kN m^{-2}
	*1 at (1 kgf/cm^2)	:	98·066 5 kN m^{-2}
	*1 bar	:	10^5 N m^{-2}
	1 ft water	:	2·989 1 kN m^{-2}
	1 in water	:	249·09 N m^{-2}
	1 inHg	:	3·386 4 kN m^{-2}
	1 mmHg (1 torr)	:	133·32 N m^{-2}
Power (heat flow)	1 hp (British)	:	745·70 W
	1 hp (metric)	:	735·50 W
	1 erg/s	:	10^{-7} W
	1 ft lbf/s	:	1·355 8 W
	1 Btu/h	:	0·293 08 W
	1 Btu/s	:	1·055 1 kW
	1 chu/h	:	0·527 54 W
	1 chu/s	:	1·899 1 kW
	1 kcal/h	:	1·163 0 kW
	1 ton of refrigeration	:	3516·9 W

Moment of inertia	$1\,\text{lb ft}^2$	:	$0.042\,140\,\text{kg m}^2$
Momentum	$1\,\text{lb ft/s}$	:	$0.138\,26\,\text{kg m s}^{-1}$
Angular momentum	$1\,\text{lb ft}^2/\text{s}$	:	$0.042\,140\,\text{kg m}^2\,\text{s}^{-1}$
Viscosity, dynamic	*1 poise $(1\,\text{g/cm s})$	:	$0.1\,\text{N s m}^{-2}$ $(0.1\,\text{kg m}^{-1}\,\text{s}^{-1})$
	$1\,\text{lb/ft h}$	:	$0.413\,38\,\text{mN s m}^{-2}$
	$1\,\text{lb/ft s}$	:	$1.488\,2\,\text{N s m}^{-2}$
Viscosity, kinematic	*1 stokes $(1\,\text{cm}^2/\text{s})$	:	$10^{-4}\,\text{m}^2\,\text{s}^{-1}$
	$1\,\text{ft}^2/\text{h}$	:	$0.258\,06\,\text{cm}^2\,\text{s}^{-1}$
Surface energy (surface tension)	$1\,\text{erg/cm}^2$ $(1\,\text{dyn/cm})$	:	$10^{-3}\,\text{J m}^{-2}$ $(10^{-3}\,\text{N m}^{-1})$
Surface per unit volume	$1\,\text{ft}^2/\text{ft}^3$	:	$3.280\,8\,\text{m}^2\,\text{m}^{-3}$
Surface per unit mass	$1\,\text{ft}^2/\text{lb}$	:	$0.204\,82\,\text{m}^2\,\text{kg}^{-1}$
Mass flux density	$1\,\text{lb/h ft}^2$	:	$1.356\,2\,\text{g s}^{-1}\,\text{m}^{-2}$
Heat flux density	$1\,\text{Btu/h ft}^2$	:	$3.154\,6\,\text{W m}^{-2}$
	*1 kcal/h m^2	:	$1.163\,\text{W m}^{-2}$
Heat transfer coefficient	$1\,\text{Btu/h ft}^2\,°\text{F}$	:	$5.678\,4\,\text{W m}^{-2}\,\text{K}^{-1}$
	$1\,\text{kcal/h m}^2\,°\text{C}$	:	$1.1630\,\text{W m}^{-2}\,\text{K}^{-1}$
Specific enthalpy (latent heat, etc.)	*1 Btu/lb	:	$2.326\,\text{kJ kg}^{-1}$
Heat capacity (specific heat)	*1 Btu/lb °F	:	$4.186\,8\,\text{kJ kg}^{-1}\,\text{K}^{-1}$
Thermal conductivity	$1\,\text{Btu/h ft}\,°\text{F}$	:	$1.730\,7\,\text{W m}^{-1}\,\text{K}^{-1}$
	$1\,\text{kcal/h m}\,°\text{C}$	:	$1.163\,\text{W m}^{-1}\,\text{K}^{-1}$

The values of some common physical constants in SI units include:

Avogadro number, N_A	$6.023 \times 10^{23}\,\text{mol}^{-1}$
Boltzmann constant, k	$1.3805 \times 10^{-23}\,\text{J K}^{-1}$
Planck constant, h	$6.626 \times 10^{-34}\,\text{J s}$
Stefan–Boltzmann constant, σ	$5.6697 \times 10^{-8}\,\text{W m}^{-2}\,\text{K}^{-4}$
Standard temperature and pressure (s.t.p.)	$273.15\,\text{K}$ and $1.013 \times 10^5\,\text{N m}^{-2}$
Volume of 1 kmol of ideal gas at s.t.p.	$22.41\,\text{m}^3$
Gravitational acceleration	$9.807\,\text{m s}^{-1}$
Universal gas constant, R	$8.3143\,\text{J mol}^{-1}\,\text{K}^{-1}$
Faraday constant, F	$9.6487 \times 10^4\,\text{C mol}^{-1}$

Contents

1 *The crystalline state*

The three general states of matter – gaseous, liquid and solid – represent very different degrees of atomic or molecular mobility. In the gaseous state, the molecules are in constant, vigorous and random motion; a mass of gas takes the shape of its container, is readily compressed and exhibits a low viscosity. In the liquid state, random moelcular motion is much more restricted. The volume occupied by a liquid is limited; a liquid only takes the shape of the occupied part of its container, and its free surface is flat, except in those regions where it comes into contact with the container walls. A liquid exhibits a much higher viscosity than a gas and is less easily compressed. In the solid state, molecular motion is confined to an oscillation about a fixed position, and the rigid structure generally resists compression very strongly; in fact it will often fracture when subjected to a deforming force.

Some substances, such as wax, pitch and glass, which possess the outward appearance of being in the solid state, yield and flow under pressure, and they are sometimes regarded as highly viscous liquids. Solids may be crystalline or amorphous, and the crystalline state differs from the amorphous state in the regular arrangement of the constituent molecules, atoms or ions into some fixed and rigid pattern known as a lattice. Actually, many of the substances that were once considered to be amorphous have now been shown, by X-ray analysis, to exhibit some degree of regular molecular arrangement, but the term 'crystalline' is most frequently used to indicate a high degree of internal regularity, resulting in the development of definite external crystal faces.
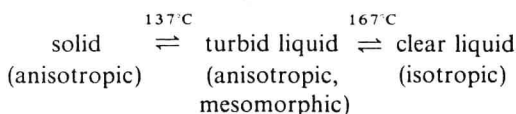
As molecular motion in a gas or liquid is free and random, the physical properties of these fluids are the same no matter in what direction they are measured. In other words, they are *isotropic*. True amorphous solids, because of the random arrangement of their constituent molecules, are also isotropic. Most crystals, however, are *anisotropic*; their mechanical, electrical, magnetic and optical properties can vary according to the direction in which they are measured. Crystals belonging to the cubic system are the exception to this rule; their highly symmetrical internal arrangement renders them optically isotropic. Anisotropy is most readily detected by refractive index measurements, and the striking phenomenon of double refraction exhibited by a clear crystal of Iceland spar (calcite) is probably the best-known example.

1.1 Liquid crystals

Before considering the type of crystal with which everyone is familiar, namely the solid crystalline body, it is worth while mentioning a state of matter which possesses the flow properties of a liquid yet exhibits some of the properties of the crystalline state.

Although liquids are usually isotropic, some 200 cases are known of substances that exhibit anisotropy in the liquid state at temperatures just above their melting point. These liquids bear the unfortunate, but popular, name 'liquid crystals': the term is inapt because the word 'crystal' implies the existence of a precise space lattice. Lattice formation is not possible in the liquid state, but some form of molecular orientation can occur with certain types of molecules under certain conditions. Accordingly, the name 'anisotropic liquid' is preferred to 'liquid crystal'. The name 'mesomorphic state' is used to indicate that anisotropic liquids are intermediate between the true liquid and crystalline solid states.

Among the better-known examples of anisotropic liquids are *p*-azoxy-phenetole, *p*-azoxyanisole, cholesteryl benzoate, ammonium oleate and sodium stearate. These substances exhibit a sharp melting point, but they melt to form a turbid liquid. On further heating, the liquid suddenly becomes clear at some fixed temperature. On cooling, the reverse processes occur at the same temperatures as before. It is in the turbid liquid stage that anisoptropy is exhibited. The changes in physical state occurring with change in temperature for the case of *p*-azoxyphenetole are:

$$\underset{\text{(anisotropic)}}{\text{solid}} \underset{137^{\circ}\text{C}}{\rightleftharpoons} \underset{\substack{\text{(anisotropic,} \\ \text{mesomorphic)}}}{\text{turbid liquid}} \underset{167^{\circ}\text{C}}{\rightleftharpoons} \underset{\text{(isotropic)}}{\text{clear liquid}}$$

The simplest representation of the phenomenon is given by Bose's swarm theory, according to which molecules orientate into a number of groups in parallel formation (*Figure 1.1*). In many respects this is rather similar to the behaviour of a large number of logs floating down a river. Substances that can exist in the mesomorphic state are usually organic compounds, often aromatic, with elongated molecules.

The mesomorphic state is conveniently divided into two main classes. The *smectic* (soap-like) state is characterized by an oily nature, and the flow of such liquids occurs by a gliding movement of thin layers over one another. Liquids in the *nematic* (thread-like) state flow like normal viscous liquids, but mobile threads can often be observed within the liquid layer. A third class, in which
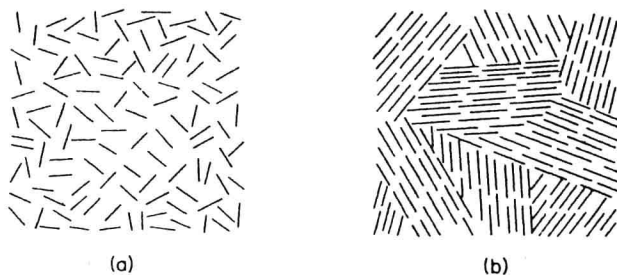

(a)   (b)

Figure 1.1. *Isotropic and anisotropic liquids. (a) Isotropic: molecules in random arrangement; (b) anisotropic: molecules aligned into swarms*

strong optical activity is exhibited, is known as the *cholesteric* state; some workers regard this state as a special case of the nematic. The name arises from the fact that cholesteryl compounds form the majority of known examples.

For further information on this subject, reference should be made to the relevant references listed in the Bibliography at the end of this chapter.

1.2 Crystalline solids

The true solid crystal comprises a rigid lattice of molecules, atoms or ions, the locations of which are characteristic of the substance. The regularity of the internal structure of this solid body results in the crystal having a characteristic shape; smooth surfaces or faces develop as a crystal grows, and the planes of these faces are parallel to atomic planes in the lattice. Very rarely, however, do any two crystals of a given substance look identical; in fact, any two given crystals often look quite different in both size and external shape. In a way this is not very surprising, as many crystals, especially the natural minerals, have grown under different conditions. Few natural crystals have grown 'free'; most have grown under some restraint resulting in stunted growth in one direction and exaggerated growth in another.

This state of affairs prevented the general classification of crystals for centuries. The first advance in the science of crystallography came in 1669 when Steno observed a unique property of all quartz crystals. He found that the angle between any two given faces on a quartz crystal was constant, irrespective of the relative sizes of these faces. This fact was confirmed later by other workers, and in 1784 Haüy proposed his Law of Constant Interfacial Angles: the angles between corresponding faces of all crystals of a given substance are constant. The crystals may vary in size, and the development of the various faces (the crystal habit) may differ considerably, but the interfacial angles do not vary; they are characteristic of the substance. It should be noted, however, that substances can often crystallize in more than one structural arrangement (polymorphism – see section 1.8) in which case Haüy's law applies only to the crystals of a given polymorph.

Interfacial angles on centimetre-sized crystals, e.g. geological specimens, may be measured with a contact goniometer, consisting of an arm pivoted on a protractor (*Figure 1.2*), but precisions greater than 0·5° are rarely possible. The reflecting goniometer (*Figure 1.3*) is a more versatile and accurate apparatus. A crystal is mounted at the centre of a graduated turntable, a beam of light from an illuminated slit being reflected from one face of the crystal. The reflection is observed in a telescope and read on the graduated scale. The turntable is then rotated until the reflection from the next face of the crystal is observed in the telescope, and a second reading is taken from the scale. The difference α between the two readings is the angle between the normals to the two faces, and the interfacial angle is therefore $(180 - \alpha)°$.

Modern techniques of X-ray crystallography enable lattice dimensions and interfacial angles to be measured with high precision on milligram samples of crystal powder specimens.