

J.W. MULLIN

CRYSTALLIZATION

FOURTH EDITION

结晶学 第4版

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Crystallization

Fourth Edition

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Crystallization Fourth Edition

J. W. Mullin

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Preface to Fourth Edition

This fourth edition of *Crystallization* has been substantially rewritten and up-dated. The 1961 first edition, written primarily for chemical engineers and industrial chemists, was illustrated with practical examples from a range of process industries, coupled with basic introductions to the scientific principles on which the unit operation of crystallization depends. It was also intended to be useful to students of chemical engineering and chemical technology. The aims and objectives of the book have remained intact in all subsequent editions, although the subject matter has been considerably expanded each time to take into account technological developments and to reflect current research trends into the fundamentals of crystallization mechanisms.

The continuing upsurge in interest in the utilization of crystallization as a processing technique covers an increasing variety of industrial applications, not only in the long-established fields of bulk inorganic and organic chemical production, but also in the rapidly expanding areas of fine and specialty chemicals and pharmaceuticals. These developments have created an enormous publication explosion over the past few decades, in a very wide range of journals, and justify the large number of specialist symposia that continue to be held world-wide on the subject of crystallization.

Particular attention is drawn in this edition to such topical subjects as the isolation of polymorphs and resolution of enantiomeric systems, the potential for crystallizing from supercritical fluids, the use of molecular modelling in the search for tailored habit modifiers and the mechanisms of the effect of added impurities on the crystal growth process, the use of computer-aided fluid dynamic modelling as a means of achieving a better understanding of mixing processes, the separate and distinct roles of both batch and continuous crystallization processing, and the importance of potential downstream processing problems and methods for their identification from laboratory investigations. Great care has been taken in selecting suitable literature references for the individual sections to give a reliable guide to further reading.

Once again I want to record my indebtedness to past research students, visiting researchers and colleagues in the Crystallization Group at University College London over many years, for their help and support in so many 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 all those who have spoken or written to me over the years with useful suggestions for corrections or 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 four editions of

Crystallization. Without her tremendous help in preparing the manuscripts, my task of writing would not have been completed.

JOHN MULLIN
University College London
2001

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 ($^{\circ}\text{C}$). 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 ($\text{kmol} = 10^3 \text{ mol}$) as the preferred unit. The unit of electric current is the ampere (A).

Several of the derived SI units have special names:

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

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 ($1 \text{ bar} = 10^5 \text{ Pa} = 10^5 \text{ N m}^{-2} \approx 1 \text{ atmosphere}$). The standard atmosphere (760 mm Hg) is defined as $1.0133 \times 10^5 \text{ Pa}$, 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	: 0.3048 m
	*1 yd	: 0.9144 m
	1 mile	: 1.6093 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 in ²	: 645.16 mm ²
	1 ft ²	: 0.092903 m ²
	1 yd ²	: 0.83613 m ²
	1 acre	: 4046.9 m ²
	1 hectare	: 10 000 m ²
	1 mile ²	: 2.590 km ²
Volume	1 in ³	: 16.387 cm ³
	1 ft ³	: 0.02832 m ³
	1 yd ³	: 0.76453 m ³
	1 UK gal	: 4546.1 cm ³
	1 US gal	: 3785.4 cm ³
Mass	1 oz	: 28.352 g
	1 grain	: 0.06480 g
	*1 lb	: 0.45359237 kg
	1 cwt	: 50.8023 kg
	1 ton	: 1016.06 kg
Force	1 pdl	: 0.13826 N
	1 lbf	: 4.4482 N
	1 kgf	: 9.8067 N
	1 tonf	: 9.9640 kN
	*1 dyn	: 10^{-5} N
Temperature difference	*1 degF (degR)	: $\frac{5}{9}$ degC (K)
Energy (work, heat)	1 ft lbf	: 1.3558 J
	1 ft pdl	: 0.04214 J
	*1 cal (internat. table)	: 4.1868 J
	1 erg	: 10^{-7} J
	1 Btu	: 1.05506 kJ
	1 chu	: 1.8991 kJ
	1 hp h	: 2.6845 MJ
	*1 kW h	: 3.6 MJ
	1 therm	: 105.51 MJ
	1 thermie	: 4.1855 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	: 4.1868 kJ m ⁻³
	1 therm/ft ³	: 3.7260 GJ m ⁻³
Velocity	1 ft/s	: 0.3048 m s ⁻¹
	1 ft/min	: 5.0800 mm s ⁻¹
	1 ft/h	: 84.667 μm s ⁻¹
	1 mile/h	: 0.44704 m s ⁻¹
Volumetric flow	1 ft ³ /s	: 0.028316 m ³ s ⁻¹
	1 ft ³ /h	: 7.8658 cm ³ s ⁻¹
	1 UK gal/h	: 1.2628 cm ³ s ⁻¹
	1 US gal/h	: 1.0515 cm ³ s ⁻¹
Mass flow	1 lb/h	: 0.12600 g s ⁻¹
	1 ton/h	: 0.28224 kg s ⁻¹
Mass per unit area	1 lb/in ²	: 703.07 kg m ⁻²
	1 lb/ft ²	: 4.8824 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	: 6.8948 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	: 9.8067 N m ⁻²
	*1 standard atm	: 101.325 kN m ⁻²
	*1 at (1 kgf/cm ²)	: 98.0665 kN m ⁻²
	*1 bar	: 10 ⁵ N m ⁻²
	1 ft water	: 2.9891 kN m ⁻²
	1 in water	: 249.09 N m ⁻²
	1 inHg	: 3.3864 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	: 1.3558 W
	1 Btu/h	: 0.29308 W
	1 Btu/s	: 1.0551 kW
	1 chu/h	: 0.52754 W
	1 chu/s	: 1.8991 kW
	1 kcal/h	: 1.1630 kW
	1 ton of refrigeration	: 3516.9 W

Moment of inertia	1 lb ft ²	: 0.042140 kg m ²
Momentum	1 lb ft/s	: 0.13826 kg m s ⁻¹
Angular momentum	1 lb ft ² /s	: 0.042140 kg m ² s ⁻¹
Viscosity, dynamic	*1 poise (1 g/cm s)	: 0.1 N s m ⁻² (0.1 kg m ⁻¹ s ⁻¹)
	1 lb/ft h	: 0.41338 mN s m ⁻²
	1 lb/ft s	: 1.4882 N s m ⁻²
Viscosity, kinematic	*1 stokes (1 cm ² /s)	: 10 ⁻⁴ m ² s ⁻¹
	1 ft ² /h	: 0.25806 cm ² s ⁻¹
Surface energy (surface tension)	1 erg/cm ² (1 dyn/cm)	: 10 ⁻³ J m ⁻² (10 ⁻³ N m ⁻¹)
Surface per unit volume	1 ft ² /ft ³	: 3.2808 m ² m ⁻³
Surface per unit mass	1 ft ² /lb	: 0.20482 m ² kg ⁻¹
Mass flux density	1 lb/h ft ²	: 1.3562 g s ⁻¹ m ⁻²
Heat flux density	1 Btu/h ft ²	: 3.1546 W m ⁻²
	*1 kcal/h m ²	: 1.163 W m ⁻²
Heat transfer coefficient	1 Btu/h ft ² °F	: 5.6784 W m ⁻² K ⁻¹
	1 kcal/h m ² °C	: 1.1630 W m ⁻² K ⁻¹
Specific enthalpy (latent heat, etc.)	*1 Btu/lb	: 2.326 kJ kg ⁻¹
Heat capacity (specific heat)	*1 Btu/lb°F	: 4.1868 kJ kg ⁻¹ K ⁻¹
Thermal conductivity	1 Btu/h ft°F	: 1.7307 W m ⁻¹ K ⁻¹
	1 kcal/h m°C	: 1.163 W m ⁻¹ 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	$6.626 \times 10^{-34} \text{ Js}$
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 K and $1.013 \times 10^5 \text{ N m}^{-2}$
Volume of 1 kmol of ideal gas at s.t.p.	22.41 m ³
Gravitational acceleration	9.807 m s ⁻²
Universal gas constant, R	8.3143 J mol ⁻¹ K ⁻¹
Faraday constant, F	$9.6487 \times 10^4 \text{ C mol}^{-1}$

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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 molecular 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.

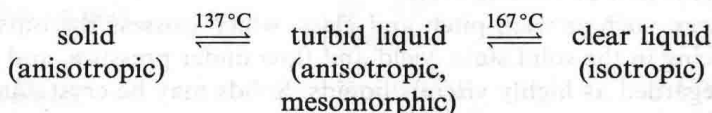
As molecular motion in a gas or liquid is free and random, the physical properties of these fluids are the same no matter in what direction they are measured. In other words, they are *isotropic*. True amorphous solids, because of the random arrangement of their constituent molecules, are also isotropic. 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*-azoxyphenetole, *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 anisotropy is exhibited. The changes in physical state occurring with change in temperature for the case of *p*-azoxyphenetole are:



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

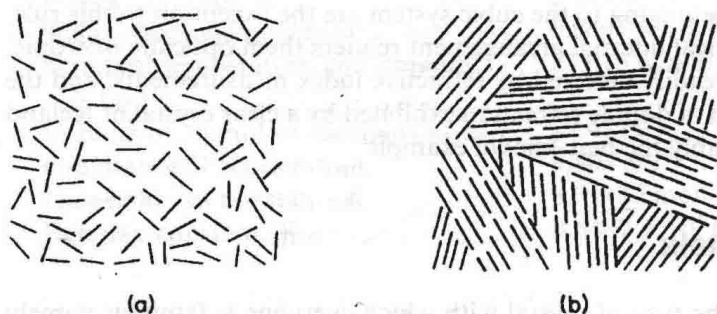


Figure 1.1. Isotropic and anisotropic liquids. (a) Isotropic: molecules in random arrangement; (b) anisotropic: molecules aligned into swarms