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Crystallization

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Cover :

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Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

©2013 Wiley-VCH Verlag GmbH & Co. KGaA,
Boschstr. 12, 69469 Weinheim, Germany

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Print ISBN: 978-3-527-32762-1

ePDF ISBN: 978-3-527-65035-4

ePub ISBN: 978-3-527-65034-7

mobi ISBN: 978-3-527-65033-0

oBook ISBN: 978-3-527-65032-3

Cover Design Simone Benjamin, McLeese Lake,
Canada

Typesetting Thomson Digital, Noida, India

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1

Crystallization: Introduction*Wolfgang Beckmann*

The beauty of crystals can be found in both the naturally appearing minerals such as diamonds or quartzite crystals and the industrial products such as sugar crystals. Crystals that are bound by flat faces intersecting at well-defined angles are characteristic of the substance and give the crop a reproducible appearance. This regular appearance is due to the long-range order of the building blocks of the crystal, be it either atoms or molecules. For example, in sodium chloride, the sodium and chlorine atoms are arranged in a cubic lattice (Figure 1.1). This arrangement maximizes the attractive interactions between the building blocks and thus minimizes the energetic state. The long-range order of its building blocks makes the crystalline state distinct from the gaseous and liquid as well as the amorphous solid state. The long-range order is also the root cause of a number of well-defined properties of the crystals, so these properties can be tailored through the crystallization process.

A further consequence of the well-defined arrangement of the building blocks is the outer shape of the crystals; crystals are limited by flat faces that intersect under well-defined angles determined by the lattice. This can be easily observed for the large crystals of rock sugar (Figure 1.2). For a given substance, ordering is a characteristic. Consequently, the faces and their angles are characteristics of a given substance. All crystals grown under similar conditions will exhibit the same faces and partitioning of the faces.

Though the lattice is characteristic of a given substance, a large number of substances can crystallize following more than one ordering motive, leading to polymorphism. Carbon, for example, can crystallize in two different lattices, as diamond and as graphite. In diamond, the carbon atoms are arranged in two face-centered cubic lattices; in graphite, the carbon atoms are arranged in layers in which the atoms have a hexagonal symmetry (Figure 1.3). With respect to energy and stability, graphite is more stable than diamond at room temperature and ambient pressure, though the barrier for transformation is extremely high.

A further equally important consequence of packing is the well-known purification during crystallization; only molecules of one type are incorporated, while most other molecules are rejected by the growing interface. This is for geometric as well as



Figure 1.1 Arrangement of the sodium and chlorine atoms in the simple cubic lattice of sodium chloride.



Figure 1.2 Crystals of rock sugar with large well-developed flat faces, which intersect under certain angles characteristic of the substance; note that the apparent roughness of the faces arises not from the crystallization process, but from the downstream processes like washing.

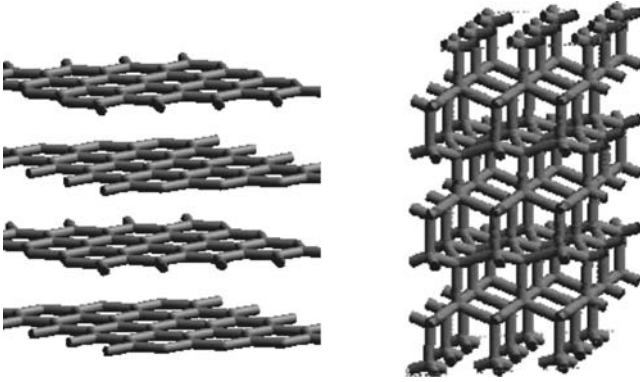


Figure 1.3 Carbon crystallizing in two different modifications – as graphite and as diamond – having different lattice arrangements.

for energetic reasons as it is energetically favorable to incorporate a proper building block instead of an impurity molecule.

Crystallization belongs to the oldest unit operations known to mankind. Namely, the crystallization of salts can be found through the ages. Early civilizations in coastal areas used large open ponds, salines, to crystallize out the salt, which could then be easily handled, stored, transported, traded, and finally used (Figure 1.4). Salines around the seaport of Ostia are said to have facilitated the development of Roma and the Roman Empire.

However, salt obtained by evaporation of seawater had a number of drawbacks; the purity was limited, mainly due to the high content of inclusions of mother liquor that entrained impurities. Hence, industrial techniques have developed over the time for the industrial crystallization of salt, resulting in the modern continuous vacuum crystallization apparatus.

Today, crystalline products can be found in every aspect of life. Relevant product properties are determined by crystal properties and thus tailored via crystallization. Three examples are shown in Figure 1.5. Sucrose, sugar, is extracted from



Figure 1.4 Solar ponds in Venezuela (courtesy of Günter Hofmann).



Figure 1.5 Sugar, table salt, and chocolate as examples of everyday life products, where the properties of the crystalline state determine product properties and where the crystallization is tailored to meet this demand.

plants and crystallized to meet a certain particle size distribution, typically in the range of 700–800 μm , to be free of fines, which allows a free-flowing product that does not agglomerate. Finally, the process arrives at purities of $>99.5\%$ in an essentially single-step process of a seeded batch crystallization. Table salt also is required to be free flowing and not to agglomerate even in the high relative humidity environment of a kitchen. Here, additives can be employed during the crystallization, which is usually continuously operated evaporation crystallization. Finally, one of the main components of chocolate, cocoa fat has to be crystallized in a certain crystal modification or polymorph to achieve the special mouth taste of chocolate. This modification is unstable at room temperature and achieved via melt crystallization, where the crystals of the desired modification are generated and grown via a temperature program. In addition, additives can be used to stabilize the required modification. The unstable modification of the fatty acid ester can recrystallize to a more stable one, resulting in undesired changes in the appearance of the product.

In a number of cases, mother liquor is the desired product of the crystallization process. The crystallization of ice from aqueous solutions can be used for freeze concentration of aqueous solutions. One example of everyday life is orange

Table 1.1 Examples for the annual production of crystalline products in various fields.

Product	Produced in	Production (t/a)
Sodium chloride	2001 in the EU	38 350 000
Sugar	2001 in the EU	15 000 000
Caprolactam	2002 worldwide	3 500 000
Ascorbic acid	2009 worldwide	110 000
Acetylsalicylic acid	2008 worldwide	35 000

juice that can be freeze concentrated at low temperatures gently and in an energy-efficient way. The concentration of waste from effluent waters is another application.

The application of crystallization in industry ranges from the isolation of the few milligrams of a substance newly synthesized in the laboratory – where a well-defined melting point is used to both achieve and prove a decent purity of the crop and as an identity check – to a mass crystallization carried out in very diverse industries; some products are listed with their annual production volume in Table 1.1.

The equipment used in the industrial crystallization varies widely, from multi-purpose batch vessels in the life science industry to highly sophisticated dedicated equipment used for some large volume products.

In the following chapters, the basic concepts of the modern understanding of crystallization will be discussed, such as the internal structure of the crystals and their growth mechanisms or the phase diagrams. Attention will be directed to the purification by crystallization and to effects of polymorphism. Next, the basic methods to carry out a crystallization, from both the solution and the melt, are discussed. Finally, the concepts of mass crystallization in continuously operated crystallizers will be shown.

2

Mechanisms of Crystallization*Wolfgang Beckmann*

One of the most important features of crystals is the long-range order of their building blocks and symmetry of their arrangement. This arrangement maximizes the interaction between the building blocks, stabilizing the crystal. Most macroscopic properties of crystals, such as their shape or the purification during crystallization, are a direct consequence of this arrangement. Thus, the discussion of the mechanisms of crystallizations has first to deal with the symmetry and long-range order in crystals. In the second part, the nucleation and growth mechanisms of crystals are discussed. In both cases, a supersaturated mother phase or a deviation from saturation is necessary. The dependence of the processes on supersaturation and other parameters has to be discussed. The discussion of crystal nucleation has two goals: first, to determine the mechanisms and thus also the prerequisites for nucleation; second, to derive expressions for the dependence on supersaturation.

2.1

Crystal Lattice

2.1.1

Arrangement of Building Blocks and Symmetries

Crystallization is a phase transformation for which the free enthalpy $\Delta_{\text{tr}}G$ has to be negative (Equation 2.1). The crystal will be stabilized by minimizing the enthalpy term $\Delta_{\text{tr}}H$, which is determined by the interaction of the building blocks. Interactive forces might either be van der Waals or electrostatic forces. In molecular crystals, hydrogen bonding also plays an important role.

The van der Waals forces do have a relatively short-range order, a typical potential is given by $\Phi = (A/r^{12}) - (B/r^6)$, where r is the distance between the interaction bodies. The potential is shown in Figure 2.1. The interaction potential of electrostatic forces decreases via $\Phi = C/r$.

$$\Delta_{\text{tr}}G = \Delta_{\text{tr}}H - T\Delta_{\text{tr}}S. \quad (2.1)$$