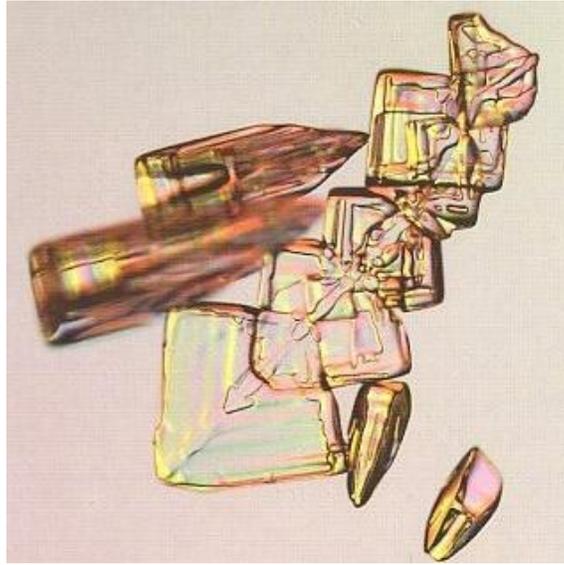


Crystallization



Arrowhead snowflakes. © Patricia Rasmussen

Crystallization is a typical example of the first-order phase transition attended with a change of the aggregative state of substance. Crystallization leads to formation of solid phase in solutions, melts, and gases. The driving force of crystallization process is supersaturation, i.e., an excess of the actual concentration of the substance getting crystallized over its equilibrium concentration under given conditions. This is a very simple yet very important definition. From the definition it follows that lack of supersaturation would stop the crystallization process.

The thermodynamic state of a system determines its entropy (structure). Since the structure of a solution undergoes changes in the course of crystallization, we can vary the kinetics of the crystallization process by changing the entropy. In other words, alternation of the values of the factors that define the system's entropy, such as temperature, pressure, soluble impurities, and electric or magnetic field intensity, can result in changing kinetics of crystallization. If a salt has different crystallographic modifications, by changing the structure of the initial solution it is possible to make it predominantly crystallize in one of said modification forms.

Crystallization process

The crystallization process is governed by the same laws as the process of condensation, which is formation of liquid phase drops from gaseous phase, but crystallization is complicated by the presence of solvent. Crystallization consists of two stages: formation of crystal nuclei and their subsequent growth to visible dimensions. Rate of crystallization is, in general, limited by the rate of nucleation. On foreign, in relation to the substance getting crystallized, inclusions, such as dust particles, the surfaces of process equipment, the walls of blood vessels, electrically charged particles, etc., the rate of nucleation is 1000 to 100,000 times higher than in the body of the liquid proper. As early as 1912, G. Wilson invented an apparatus for making visible the tracks of ionizing particles. Supersaturation steam was condensed, when the charged particles moved in it. This discovery earned G. Wilson the Nobel Prize.

In describing the crystallization process, the basic concepts are solubility and the solubility product. Solubility is defined as the amount of substance that can get dissolved in a given amount of liquid under fixed thermodynamic conditions. It naturally follows from the definition that a change in the thermodynamic state of the system would result in a change in solubility, which implies that solubility is not constant. Changes in temperature, pressure, chemical potential of the dissolved salts, intensity of electrical or magnetic field etc., that is, the values of the factors defining the structure (entropy) of the solution, would affect the solubility of a given salt and, consequently, the process of its crystallization. Most salts are characterized by the so-called direct solubility-to-temperature relationship, that is, by growth of solubility with growth of the solution temperature.

Electrolytic dissociation

S. Arrhenius's theory of electrolytic dissociation formulated in 1887 gives rise to the concept of the solubility product. If a solution consists of ions their origin, i.e., the material at dissolution of which they were formed, plays no significant role. It turns out, however, that the product of ion concentrations at which crystallization of a particular substance starts, called the solubility product, is, as well as solubility itself, a constant value under fixed thermodynamic conditions.

Another outcome of the electrolytic dissociation theory as applied to the crystallization process is the assertion that in a solution consisting of any combination of ions, the first salt to crystallize would be the salt having the lowest solubility product value (solubility value) at given thermodynamic conditions.

Crystallization on surfaces

The first heterogeneous nucleation theory was elaborated by Volmer in 1939. He explained why a crystalline nucleus forms on a foreign to the crystallizing substance surface of some hard impurity much more readily than it does at a chance collision between molecules of the substance within the body of supersaturated steam or solution. Detailed investigations of the process of crystallization on a foreign surface, or substrate, resulted in appearance and rapid development of such a powerful industry as electronics, which is impossible without crystallizing, on a substrate, semiconductor crystals with pre-designed properties.

Long-term studies have demonstrated that in the role of a nucleation center, there can appear any energy-inhomogeneous object, such as an electrically charged particle, a free radical, crystal surface as an object having free surface energy, or structural defects of a crystal surface. However, not every energy-inhomogeneous object and not every surface can initiate nucleation equally well.

In 1935, the physicist Royer formulated the principle of structural-geometric similarity on the basis of long-term study of the crystallization process on crystalline surfaces. The principle, in essence, implies that a heterogeneous surface can serve as a matrix forming a crystal of a salt getting crystallized. It occurs when configurations of an elementary cell of the crystal of the surface material and the substance crystallized on the surface coincide, and parameters of their lattices differ by not more than 20%. It is natural that supersaturation remains to be the key factor in the case. The higher is the supersaturation, the greater can be the difference in the parameters of crystal lattices at which crystallization of a salt on the surface starts.

The absolute value of crystallographic misfit is used as a criterion of seeding activity of a surface (substrate):

$$\delta = |\mathbf{a}_s - \mathbf{a}_c|/\mathbf{a}_c = |\mathbf{a}_s/\mathbf{a}_c - \mathbf{1}|,$$

where: \mathbf{a}_s is the value of parameter \mathbf{a} of the crystal lattice of the substrate; \mathbf{a}_c is the value of parameter \mathbf{a} of the crystal lattice of the substance getting crystallized.

The less is the crystallographic misfit, the more intensively does the surface initiate nucleation of the substance getting crystallized, and the lower is the supersaturation at which that occurs. For instance, a glauber salt solution saturated at 32.3° would crystallize under supercooling of $D = 17^\circ$. However, provided borax crystals have been introduced to the solution, crystallization would start even at a $D = 2 \pm 1^\circ$ supercooling. Crystallographic misfit of glauber salt and borax makes $d = 0,015$. It was established that when crystallizing surfaces from aqueous solutions, relative supersaturation, at which crystallization on the substrate surface starts, grows linearly with growing crystallographic misfit value.

References and further reading

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