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A Critical Study on Crystallization Process

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Abstract* – *Crystallization is the procedure of creation of solid crystals triggering from a solution, melt or more rarely deposited directly from a gas. Crystallization is also a chemical solid–liquid division technique, in which transmission of a solute from the fluid solution to a clean solid crystalline stage occurs. In chemical engineering crystallization occurs in a crystallizer. Crystallization is therefore a feature of triggering, obtained through a discrepancy of the solubility environment of the solute in the solvent, as compared to precipitation due to chemical reaction.

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INTRODUCTION

The crystallization process comprises of two main actions, nucleation and crystal growth. Nucleation is the process where the solute molecules detached in the solvent start to congregate into clusters, on the nanometer scale that turn out to be stable under the current operating conditions. This stable cluster comprises the nucleus. However, when the clusters are unstable, they suspend. Therefore, the clusters need to reach a critical size in order to become stable nuclei. Such significant size is observed by the working environment i.e. temperature, super-saturation, etc. It is at the phase of nucleation that the atoms organize in a definite and interrupted manner that defines the crystal structure. Crystal structure is a particular phrase that refers to the comparative arrangement of the atoms, not the macroscopic characteristics of the crystal (size and shape), although those are a consequence of the internal crystal structure.

The crystal growth is the succeeding development of the nuclei that succeed in getting the critical cluster size. Super-saturation is the powerful energy of the crystallization, hence the rate of nucleation and development is determined by the existing super-saturation in the solution. Depending upon the environment, either nucleation or growth may be leading over the other and as a consequence, crystals with dissimilar sizes and shapes are obtained (control of crystal size and shape constitutes one of the main challenges in industrial manufacturing, such as for pharmaceuticals). Once the super-saturation is worn out, the solid–liquid system achieves equilibrium and the crystallization is complete, unless the working circumstances are customized from equilibrium so as to supersaturate the solution again.

Polymorphism is the process in which compounds crystallize with dissimilar crystal structures. Each polymorph is in fact a singular thermodynamic solid state and crystal polymorphs of the same compound show dissimilar physical characteristics such as dissolution rate, shape (angles between facets and facet growth rates), melting point, etc. Hence, polymorphism has importance in industrial manufacture of crystalline goods.

ARTIFICIAL METHODS

For crystallization, the solution has to hold more solute molecules or ions dissolved than it would hold under the equilibrium. This can be performed by different methodologies, with (1) solution cooling, (2) accumulation of a second solvent to decrease the solubility of the solute (3) chemical reaction and (4) change in pH being the most common methods used in industrial practice. Other techniques, such as solvent evaporation, can also be used. The spherical crystallization has some benefits (flow-ability and bioavailability) for the formation of pharmaceutical drugs.

PURIFICATION

Crystallization differentiates a product from a liquid feed-stream, often in tremendously pure form, by cooling the feed-stream or accumulating precipitants which subordinate the solubility of the preferred product so that it forms crystals.

Perfectly shaped crystals are anticipated to be pure because each particle must fit completely into the network as it leaves the solution. Impurities would usually not vigorous as well in the pattern, and thus remain in solution preferentially. Hence, molecular identification is the law of purification in crystallization. However, there are examples when impurities integrate into the lattice, hence, reducing the intensity of purity of the absolute crystal product.

Also, in a number of cases, the solvent may integrate into the lattice forming a solvate. Additionally, the solvent may be intented within the crystal produced and this event is known as "inclusion".

THERMODYNAMIC VIEW

The character of a crystallization procedure is performed by both thermodynamic and kinetic factors, which can make it highly inconsistent and hard to organize. Factors such as impurity intensity, mixing regime, vessel design and cooling profile can have a main effect on the size, number and shape of crystals formed.

When a molecule is heated by an external source, at some temperature, the complex structural design of the crystal breaks to that of a liquid. Thermodynamics mention that melting takes place because the entropy, S, gain in system by spatial randomization of the molecules has conquer the enthalpy, H, loss due to breaking the crystal packing forces:

$$T(S_{liquid} - S_{solid}) > H_{liquid} - H_{solid}$$

$$G_{liquid} < G_{solid}$$

This regulation suffers no exceptions when the temperature is increasing. By the similar indication, on cooling the melt, at the very similar temperature the bell should ring again, and molecules should click back into the very same crystalline form. The entropy reduce due to the ordering of molecules within the system is overcompensated by the thermal randomization of the surroundings, due to the release of the heat of fusion; the entropy of the universe raises.

But liquids that perform in this mode on cooling are the exception rather than the rule; in spite of the second principle of thermodynamics, crystallization usually takes place at lower temperatures (super-cooling). This can only signifies that a crystal is more easily shattered than it is produced. Similarly, it is typically much easier to dissolve an ideal crystal in a solvent than to develop again a good crystal from the resulting solution. The nucleation and growth of a crystal are under kinetic, rather than thermodynamic, control.

CRYSTALIZATION DYNAMICS

A crystal is produced after a precise pattern, or structure, dictated by forces acting at the molecular level. As a result, during its configuration process, the crystal is in an situation where the solute concentration achieves a definite critical value, before varying status. Solid formation, impossible below the solubility threshold at the given temperature and pressure conditions, may then occur at a concentration superior than the theoretical solubility level. The distinction between the real value of the solute concentration at the crystallization limit and the fixed solubility threshold is called super-saturation and is a primary aspect in crystallization dynamics. Super-saturation is the dynamic force for both the preliminary nucleation step and the following crystal growth, both of which could not take place in saturated or under saturated conditions.

MAIN CRYSTALLIZATION PROCESSES

The main factors influencing solubility are, as we saw above:

- Concentration
- Temperature

So we may identify two main families of crystallization processes:

- Cooling crystallization
- Evaporative crystallization

This division is not really clear-cut, since hybrid systems exist, where cooling is performed through evaporation, thus obtaining at the same time a concentration of the solution.

COOLING CRYSTALLIZATION

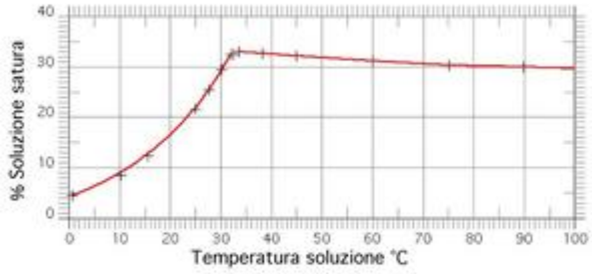
Most chemical compounds, dissolved in most solvents, show the so-called direct solubility that is, the solubility threshold increases with temperature.

So, whenever the conditions are in favor, crystal creation results from basically cooling the solution. Here cooling is a relative term: austenite crystals in a steel form well above 1000 °C. An example of this crystallization process is the production of Glauber's salt, a crystalline form of sodium sulfate. In the diagram, where equilibrium temperature is on the x-axis and equilibrium concentration (as mass percent of solute in saturated solution) in y-axis, it is clear that sulfate solubility quickly decreases below 32.5 °C. Assuming a saturated solution at 30 °C, by cooling it to 0 °C, the precipitation of a mass of sulfate occurs corresponding to the change in solubility from 29% (equilibrium value at 30 °C) to approximately 4.5% (at 0 °C) – actually a larger crystal mass is precipitated, since sulfate entrains hydration water, and this has the side effect of increasing the final concentration.

There are of course limitation in the use of cooling crystallization:

- Many solutes precipitate in hydrate form at low temperatures: in the previous example this is acceptable, and even useful, but it may be detrimental when, for example, the mass of water of hydration to reach a stable hydrate crystallization form is more than the available water: a single block of hydrate solute will be formed – this occurs in the case of calcium chloride);

- Maximum super saturation will take place in the coldest points. These may be the heat exchanger tubes which are sensitive to scaling, and heat exchange may be greatly reduced or discontinued;
- A decrease in temperature usually implies an increase of the viscosity of a solution. Too high a viscosity may give hydraulic problems, and the laminar flow thus created may affect the crystallization dynamics.
- It is of course not applicable to compounds having *reverse* solubility, a term to indicate that solubility increases with temperature decrease (an example occurs with sodium sulfate where solubility is reversed above 32.5 °C).



EVAPORATIVE CRYSTALLIZATION

Another alternative is to obtain, at a roughly stable temperature, the precipitation of the crystals by raising the solute concentration above the solubility threshold. To get this, the solute/solvent mass ratio is amplified using the technique of evaporation. This process is of course insensitive to change in temperature.

All considerations on control of crystallization parameters are the same as for the cooling models.

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