REVIEW ARTICLE

AUTHOR'S PERCEPTION ABOUT DISSOLUTION AND CRYSTALLIZATION

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ABSTRACT

Generally the concepts studied with comparisons are better understood by the readers. Author's perception here is an attempt to compare the concept of dissolution and crystallization

Key words: Dissolution, Diffusion, Diffusion Layer, Crystallization, Entropy.

DISSOLUTION

Dissolution is a process in which a substance in its solid form present in the solvent breaks into molecules forming a stagnant layer surrounding the solid solute. This layer remains closely associated with the solid. This means that regardless of how fast the bulk is stirred, the stagnant layer remains a part of the surface of the solid, moving wherever the particle moves. The thickness of this layer may get smaller as the stirring of the bulk solution increases, but it is important to recognize that the layer will always have a finite thickness however small it may get.

The molecules now diffuse through the stagnant layer to the bulk solution till a dynamic equilibrium is attained. The stagnant layer is now described as Diffusion Layer.

The driving force behind the movement of the solute molecules through the diffusion layer is the difference that exists between:

- The concentration of solute (C1) in the diffusion layer at the surface of the solid and
- The concentration on the farthest side of the diffusion layer (C2)

The greater the difference the faster is the rate of diffusion.

Dissolution can thermodynamically be stated as the process of disintegration in which solid crystal lattice, present in the solvent, breaks into molecules (molecular disintegration) and the molecules diffuse from the diffusion layer into the bulk of the system till a dynamic equilibrium is attained.

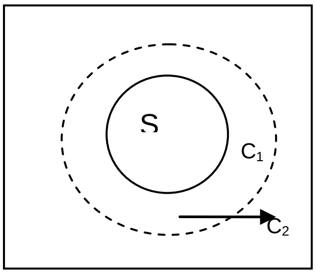

Figure 1: Dissolution of particle, showing molecular diffusion from diffusion layer to the bulk of the solution

Hence thermodynamically, dissolution is a two step process

1. Disintegration of solid crystal lattice into molecules.

2. Diffusion of molecules into the bulk of the system to attain a dynamic equilibrium.

Since the molecules of the solutes detach from the solid and move into the solution it results in an increase in entropy.

The molecules in solution like those of an ideal solution possess sufficient kinetic energy to prevent ordering or loss in entropy, hence exhibit complete randomness.

The entropy change in forming a solution can be represented as follows.

The partial molar free energy change involved in the transfer of one mole of solute from solute phase to a solution phase for an **ideal solution**[1] is written by

$$\Delta G = RT \ln X2 \qquad \textbf{(1)}$$

Where, ΔG= molar free energy change
R = molar gas constant in energy terms
T = absolute temperature (in Kelvin)
X2= mole fraction (solute)

And $\Delta G = \Delta H - T\,\Delta S$
Where, ΔH = molar latent heat
ΔS= change in entropy

When ΔH=0 (Change in differential heat of solution, when small amount of solute is added to large quantity of solution, the change in composition and heat of solution is negligible i.e. ΔH= 0)

Then, $$\Delta G = -T\Delta S \qquad \textbf{(2)}$$

From (1) & (2)

$$RT \ln X2 = -T\Delta S$$

$$\boldsymbol{\Delta S = -R \ln X2}$$

CRYSTALLIZATION

When a highly concentrated (supersaturated) solution of a substance is supercooled, clusters of molecules, called nuclei, exceeds a critical size and start growing into colloidal size crystals. These gradually increase in size in the mother liquor. The occurrence of nucleation depends upon the relative supersaturation.

If,

Css = actual supersaturated concentration before crystallization

Cs = solubility limit

Then, (Css-Cs) = supersaturation

(Css- Cs/ Cs) = relative supersaturation.

Von Weimarn recognized that the rate or velocity of nucleation (number of nuclei formed per liter per second) is proportional to the relative supersaturation $(Css\text{-}Cs/\ Cs)^2$ when the solution is supersaturated the crystallization is not necessarily favoured. For the process activation, energy for nucleation will also have to be surmounted.

The activation energy is attributed mainly to the High Interfacial Tension between the constituents and the medium.

This means that until a certain degree of supersaturation is reached the activation energy will not be overcome therefore no nuclei will be formed (at least for a certain time span)

This supersaturation concentration range where no nucleation occurs is called Metastable Zone and a conscious choice of excipients can expand this zone.

Nucleation never occurs at relative supersaturation below 3. However, this statement refers to homogenous nucleation, where the nuclei have the same chemical composition as the crystallizing phase. If the solution contains solid impurities, such as dust particles in suspension, these may act as a nuclei or center for crystallization (Heterogeneous nucleation).

Once nuclei have formed, crystallization begins. Nuclei grows by the aggregation of molecules from solution to the nuclei surface under the influence of driving force i.e. (Css- Cs). Crystallization continues until the supersaturation is relieved [ie. Until (Css ≡ Cs)] and a dynamic equilibrium is attained.

When two phases are not in equilibrium (at specific constant temperature and pressure) the total free energy of the system tends to decrease and the substance passes spontaneously from a phase of higher chemical potential to one of lower chemical potential until the potentials are equal

Crystallisation also involves two steps:

1. Diffusion of solute molecules from bulk of the solution to the nuclei liquid interface.

2. Integration of these molecules on nuclei surface into crystals

The most important application of thermodynamics is the relation between the equilibrium constant and the free energy change of homogenous crystallization, ΔG.

$\Delta G = -RT \ln K$

Here,

ΔG = Maximum change in Gibbs free energy

for formation of nuclei with a critical radius

R = Molar gas constant in energy terms

T= Absolute temperature (in Kelvin)

And

$K = J/ N0\ \upsilon$

Where,

J = number of nuclei formed per unit time or per unit volume

N0 =number of molecules of crystalline phase in unit volume

υ = Frequency of molecular transport at solid liquid interface

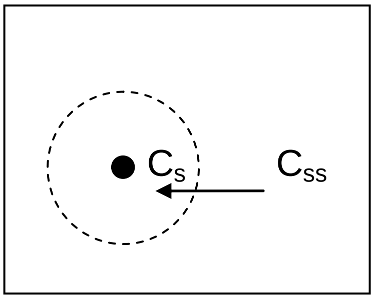

Figure 2: Formation of crystal, showing molecular diffusion from bulk of the solution to solid liquid interface.

Crystallization can thermodynamically be stated as the process of molecular integration of solute present in the solvent where the molecules diffuse from the bulk solution to the nuclei interface under the influence of supersaturation until a dynamic equilibrium is attained.

Since the molecules of solute aggregate into an ordered solid form, it results in decrease of entropy.

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