

Introduction to Chemical Engineering for Lecture 6: Nucleation

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1. Nucleation

1.1. Introduction

When a mixture of two or more components is brought out of equilibrium by a change in a state variable (eg. temperature, pressure), new phases will form. The amounts and compositions of each new phase are given by the equilibrium at the new temperature or pressure. This has been covered in the previous lectures. In this lecture, we will consider the process of creation of the new phase.

The process of formation of a new phase is called nucleation. Some examples of nucleation include the formation of:

- liquid droplets from a vapor (eg. cloud condensation, flash distillation)
- gaseous bubbles from a liquid (eg. boiling of a liquid; CO₂ in soft drinks, flash distillation)
- solid particles from a liquid (eg. crystallization of a sugar from water)

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In this part of the lecture, we will discuss nucleation applied to crystallization. The concepts are, however, the same for other applications. Crystallization is an important process in the chemical, food and pharmaceutical industries.

Before we consider nucleation itself, we will discuss the solubility of a generic substance as an example, and its dependence on temperature. This helps to understand how a crystallization process can be designed.

1.2. Crystallization processes

The solubility of a substance in a solvent is the maximum amount of the substance which can be dissolved per unit volume of the solvent. The units of concentration can vary, possibilities include mol/L, g/mol, and g/g_{solvent}.

Example

The solubility of sodium chloride (NaCl, table salt) is 360 g/kg water at 25°C. If 350 g of NaCl is added to 1 kg of water, all of it will dissolve. If another 50 g of NaCl is added, 10 g more will dissolve and 40 g will remain in the solid state. Thus, the final concentration of NaCl in water is 360 g/kg, corresponding to the solubility, and there are 40 g of solid present.

In a crystallization process, the starting point is a clear solution, ie. a solution which has a concentration lower than the solubility (Point A, Fig. 1). Then, the solution is cooled. At some temperature, the solution reaches the solubility (Point B, Fig. 1). Upon further cooling, the solubility decreases further, while the concentration in solution remains constant. Thus the solution moves further from equilibrium and becomes supersaturated. In other words, the concentration in solution is higher than the solubility. Therefore, there is a driving force for the system to create a new phase by nucleation and return to an equilibrium state. Nucleation is an activated process, thus it does not take place immediately when the solubility curve is passed, but only when the

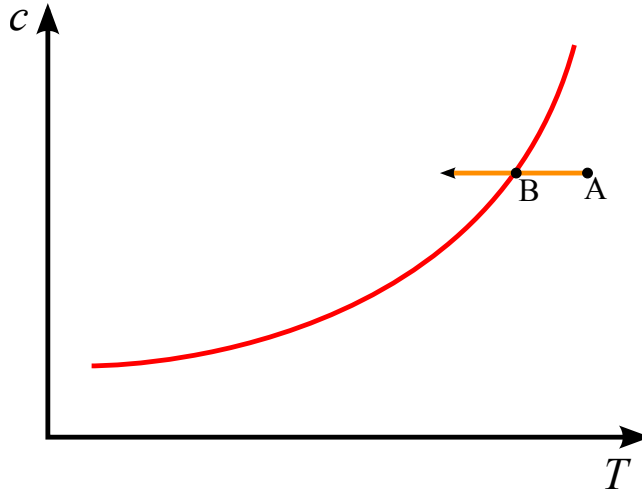


Figure 1: Schematic solubility curve showing the solubility as a function of temperature.

temperature has decreased further (this difference can be a few degrees, or as much as 10–20°C). The reasons for this will be discussed later on.

A change in temperature is not the only way to create supersaturation. Another possibility is to evaporate the solvent, which leads to an increase in the concentration, and thus to supersaturation.

1.3. Solubility calculation

The solubility can often be described using the Schröder-Van Laar equation, which can be derived in a few steps. Since at the solubility the solid phase is in equilibrium with the liquid phase, we can write an isofugacity condition for the dissolved substance. This can not be written for the solvent, since there is no solid solvent.

$$f_i^S(T, P) = f_i^L(T, P, x_i) \quad (1)$$

$$f_i^S(T, P) = f_i^L(T, P) x_i \gamma_i(T, P, x_i) \quad (2)$$

where f_i^S and f_i^L are the fugacities of the pure components in the solid and liquid phases, respectively, x_i is the concentration of substance i in the liquid phase at equilibrium, ie. the solubility. The activity coefficient γ_i represents the solution properties. For simplicity, we ignore the pressure dependence from here on. In general, crystallization processes are carried out at constant, ambient pressure.

At the melting temperature T_i^m , we can write the equilibrium condition ($dG = 0$, $G = H - TS$; see equation 67 in the first part of the lecture script)

$$\Delta\mu_i^m(T_i^m) = \Delta h_i^m - T_i^m \Delta S_i^m = 0 \quad (3)$$

$$\frac{\Delta h_i^m}{T_i^m} = \Delta S_i^m \quad (4)$$

where Δh_i^m is the melting enthalpy and ΔS_i^m is the melting entropy of the substance i . We will use Eq. 4 later on.

The above equation is valid at the melting point of the substance. Since crystallization processes are normally carried out at lower temperatures, around room temperature, we need to find expressions for the fugacity of the liquid and solid phase at lower temperatures. We do this by writing the ratio of the fugacities as differences in chemical potentials:

$$RT \ln \left(\frac{f_i^L(T)}{f_i^S(T)} \right) = \mu_i^L(T) - \mu_i^S(T) \quad (5)$$

$$RT \ln \left(\frac{f_i^L(T)}{f_i^S(T)} \right) = [h_i^L(T) - h_i^S(T)] - T [S_i^L(T) - S_i^S(T)] \quad (6)$$

Since these enthalpies and entropies are not easily accessible, we expand Eq. 6

as

$$RT \ln \left(\frac{f_i^L(T)}{f_i^S(T)} \right) = \underbrace{h_i^L(T) - h_i^L(T_i^m)}_{c_{p,i}^L(T-T_i^m)} + \underbrace{h_i^L(T_i^m) - h_i^S(T_i^m)}_{\Delta h_i^m} + \underbrace{h_i^S(T_i^m) - h_i^S(T)}_{c_{p,i}^S(T_i^m-T)} \\ - T \left[S_i^L(T) - S_i^L(T_i^m) + \underbrace{S_i^L(T_i^m) - S_i^S(T_i^m)}_{\Delta S_i^m} + S_i^S(T_i^m) - S_i^S(T) \right]$$

We can simplify the above equation by realizing that the enthalpy changes due to a temperature change, ie. the heat capacities, are much smaller than the enthalpy of melting (they also have opposite signs, thus their sum is definitely negligible). For the entropy, a similar assumption applies, ie.:

$$c_{p,i}^L(T - T_i^m) + c_{p,i}^S(T_i^m - T) \approx 0, \quad [S_i^L(T) - S_i^L(T_i^m)] + [S_i^S(T_i^m) - S_i^S(T)] \approx 0 \quad (7)$$

With these assumptions, and using Eq. 4, Eq. 6 becomes:

$$RT \ln \left(\frac{f_i^L(T)}{f_i^S(T)} \right) = \Delta h_i^m - T \Delta S_i^m = \Delta h_i^m - T \frac{\Delta h_i^m}{T_i^m} = \Delta h_i^m \left(1 - \frac{T}{T_i^m} \right) \quad (8)$$

Together with Eq. 2, Eq. 8 gives the Schröder-Van Laar equation:

$$RT \ln \frac{1}{x_i \gamma_i} = \frac{\Delta h_i^m}{T_i^m} (T_i^m - T) \quad (9)$$

which estimates the solubility of a substance based on its melting enthalpy and the melting temperature.

1.4. Free energy of nucleation

The creation of a new phase is often described as a step-wise process: molecules combine into clusters, which then grow into nuclei, and eventually form a new, macroscopic phase. This process is illustrated in Figure 2. Each step is re-

versible, in other words molecules can detach from a cluster after they have attached.

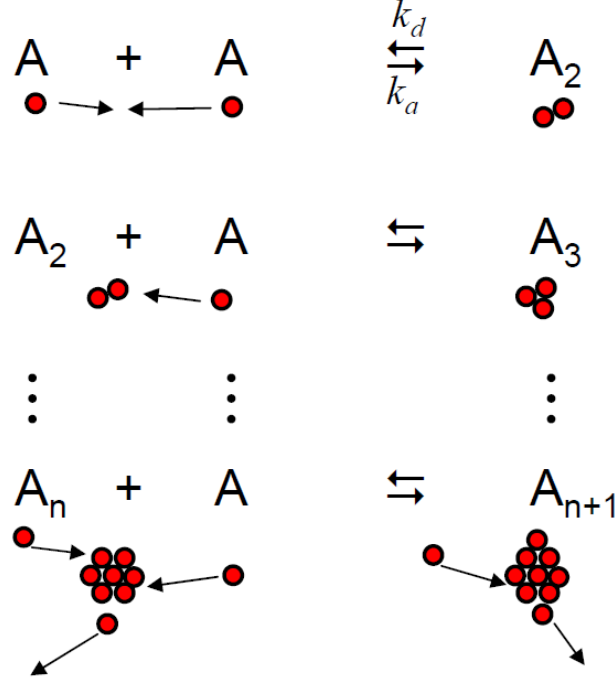


Figure 2: Reaction scheme for homogenous nucleation

This process takes place because it is energetically favorable to create a new particle¹ volume. However, at the same time a new surface for the particle is created. This is energetically unfavorable due to the interfacial tension between the particle surface and the bulk (solvent).

The change in free energy of the formation of a cluster containing n molecules (n_B in the bulk plus n_A on the surface, having free energies g_i^A or g_i^B) from the same n molecules in solution (with free energy g_i^L) is

$$\Delta G = n_B g_i^B + n_A g_i^A - n g_i^L \quad (10)$$

¹This could also be a droplet, eg. in the case of water condensing in air.

which can be expanded to

$$\Delta G = n_B g_i^B + n_A g_i^B - n_A g_i^B + n_A g_i^A - n g_i^L \quad (11)$$

$$\Delta G = n (g_i^B - g_i^L) + n_A (g_i^A - g_i^B) \quad (12)$$

This can be expressed as

$$\Delta G = n \Delta g_i^{L \rightarrow S} + a \gamma \quad (13)$$

where $\Delta g_i^{L \rightarrow S}$ is a function of the supersaturation (ratio of the concentration x_i to the solubility x_i^*), a is the surface area and γ is known as the surface tension.

The supersaturation is used as the equilibrium constant

$$\Delta g_i^{L \rightarrow S} = kT \ln \frac{x_i^*}{x_i} = -kT \ln \frac{x_i}{x_i^*} = -kT \ln S < 0 \quad (14)$$

$$\gamma = \frac{n_A}{a} (g_i^A - g_i^B) > 0 \quad (15)$$

We now consider a nucleus with a generic shape. In order to write the above equations as a function of the cluster size L instead of the number of molecules in the cluster. The volume of a cluster is given by the product of the number of molecules in the cluster and the molecular volume v_0 (i.e. the volume of one molecule), and must be the same as the volume of the nucleus. The volume and the surface area of the nucleus can be expressed in terms of the product of a characteristic length L and the shape factors k_V and k_a :

$$n v_0 = V = k_V L^3 \rightarrow n = \frac{k_V L^3}{v_0} \left(\text{for spheres } k_V = \frac{\pi}{6} \right) \quad (16)$$

$$a = k_a L^2 \left(\text{for spheres } k_a = \pi \right) \quad (17)$$

With these equations, Eq. 13 becomes

$$\Delta G = \underbrace{-\frac{k_V}{v_0} L^3 kT \ln S}_{\Delta G_V} + \underbrace{k_a \gamma L^2}_{\Delta G_A} \quad (18)$$

which makes it clear that ΔG consists of two contributions, one from the surface (ΔG_A) and one from the volume (ΔG_V). These two contributions as well as their sum are shown in Figure 3.

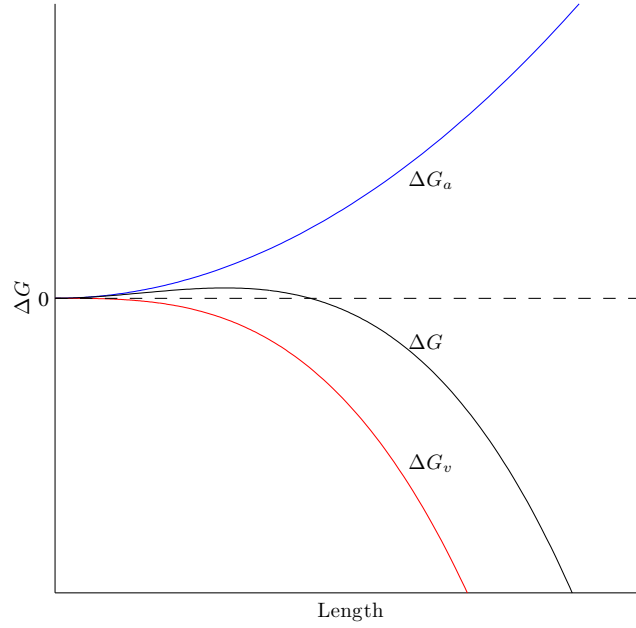


Figure 3: Behaviour of ΔG_A , ΔG_V and ΔG as a function of the cluster size L

Along the curve $\Delta G(L)$, clusters will either grow or shrink (dissolve). The preferred direction is towards smaller values of ΔG , ie. small clusters tend to shrink (they are unstable) while large clusters tend to grow (stable clusters). There is no rigorous definition of when a cluster becomes a crystal, but normally (at least in the context of nucleation) it is assumed that clusters becomes crystals when they are stable, ie. when they reach the maximum of the ΔG curve.

This maximum occurs at the critical size, L_c . Crystals or clusters at this size are in equilibrium with the surrounding solution. However, this equilibrium is unstable. The value of the critical size can be found using the condition

$$\left. \frac{d\Delta G}{dL} \right|_{L_c} = 0 \quad (19)$$

which results in the following expression for L_c :

$$L_c = \frac{2\gamma k_a v_0}{3k_v kT \ln S} \quad (20)$$

for a spherical crystal. Note that this expression changes if the crystals/clusters have a different shape! The maximum of ΔG is thus

$$\Delta G(L_c) = \frac{4\gamma^3 k_a^3 v_0^2}{27k_v^2 (kT)^2 \ln^2 S} \quad (21)$$

Thus, as S increases, the critical size and the energy barrier become smaller. It is to be expected that the rate of crystal formation increases with S !

1.5. Rate of nucleation

In order to obtain a rate expression for nucleation, we first define a nuclei as a crystal at the critical size. We then consider the equilibrium between n_c molecules of type A in solution and a cluster made up of the same n_c molecules:



This is the overall reaction for the chain of reactions shown in Figure 2. At the equilibrium of this reaction, we have the concentrations x_i for the molecules of

A and x_c for the clusters A_{n_c} . Thus, the equilibrium constant is given by

$$K_n = \frac{x_c}{x_i^{n_c}} = \exp\left(-\frac{\Delta G(L_c)}{kT}\right) \quad (23)$$

This equation can be rearranged to give the concentration of clusters as:

$$x_c = x_i^{n_c} \exp\left(-\frac{\Delta G(L_c)}{kT}\right) \quad (24)$$

$$x_c = x_i^{n_c} \exp\left(-\frac{4\gamma^3 k_a^3 v_0^2}{27k_V^2 (kT)^3 \ln^2 S}\right) \quad (25)$$

The rate of nucleation J is then given by a rate constant times this cluster concentration:

$$J = k_J x_c = k_J x_i^{n_c} \exp\left(-\frac{4\gamma^3 k_a^3 v_0^2}{27k_V^2 (kT)^3 \ln^2 S}\right) \quad (26)$$

Eq. 26 is plotted in Figure 4(a). Notice that the value of J is small even for values of $S > 1$, up to a certain threshold value, where J increases strongly. This is the reason nucleation does not start as soon as supersaturation is created. For low values of the supersaturation, the nucleation rate is negligible since not enough clusters reach the critical size. Only once the supersaturation is high enough do nuclei appear. The supersaturation which is required in order for nucleation to occur is referred to as the metastable zone limit, and is indicated qualitatively in Figure 4(b). Between the solubility curve and the metastable zone limit (ie. in the metastable zone) nucleation does not occur. It is important to note that the metastable zone width is not a fixed quantity, but depends on many factors such as the rate of generation of supersaturation, the volume of the crystallizer and the presence of solid impurities, eg. dust.

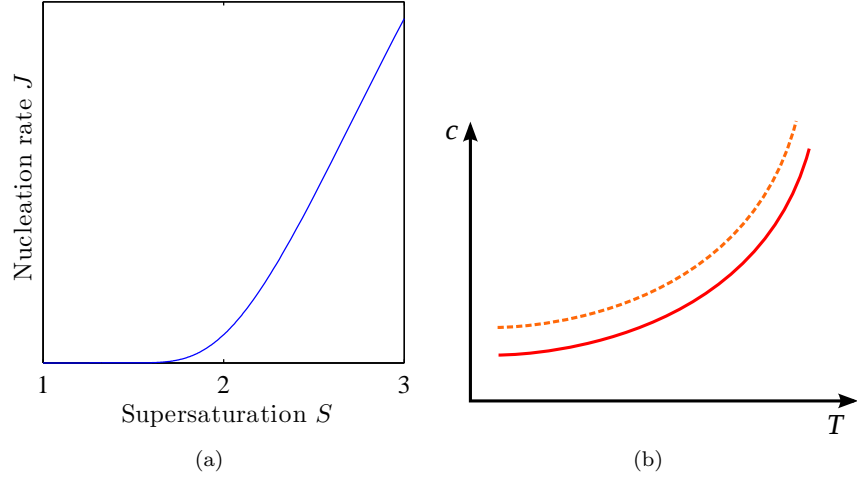


Figure 4: (a) Nucleation rate J as a function of the supersaturation S , according to Eq. 26. (b) Solubility curve (red) and metastable zone limit (dashed, orange)

Note. The equations above can also be written with the universal gas constant R instead of the Boltzmann constant k , using the relationship

$$R = kN_A \quad (27)$$

where N_A is the Avogadro constant, $N_A = 6.023 \cdot 10^{23} \text{ mol}^{-1}$. The molecular volume can then be replaced with the molar volume, using

$$V_m = v_0 N_A \quad (28)$$