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Thermodynamics and Salt Crystallization Kinetics

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1.1. Introduction

The crystallization of salts from aqueous solutions is a common, even daily event, the appearance of which does not seem to cause much difficulty. The increase in temperature or the evaporation of water are two typical causes, sometimes concurrent, which cause this phase transition, while the initial composition of the solution makes it favorable to the generation of salts.

Yet it is not trivial to accurately predict when and in what form a salt will appear in water. Also, it is not so easy to know where the salt will form, especially when the solution is moving through a network of channels and/or pores. The calcification of heating pipes, very heterogeneous and often atypical, is a good example of these complexities.

The purpose of this chapter is to look precisely at what thermodynamics, the science behind the driving forces, and kinetics, the science of transformation paths, say about these phase transitions. Far from an overview of commonly reviewed concepts, this chapter aims to highlight some subtle concepts that establish unsuspected connections between the water of the solution, the species which are dissolved therein, the pore walls enclosing it and local physicochemical conditions.

Salt Crystallization in Porous Media,
coordinated by Hannelore Derluyn and Marc Prat. © ISTE Ltd 2024.

1.2. Thermodynamic driving force

1.2.1. *Equilibrium, spontaneity, irreversibility*

Energy is always difficult to define in a strict sense, but a fairly natural understanding of this concept can be made by pointing out that energy is a product of a force by an extensive term (quantity dependent); typically the elastic energy of a spring is written as: $E = F.l$, with F being the force of the spring and l its length. The force characterizes the intensity under which the considered energy is present in the system, for example, the force of a table lamp spring is not comparable to that of a car shock absorber. The term extensive translates the extent under which the force can be expressed: here, the elongation of the spring allows a "stronger" reservoir, more "intense", to communicate elastic energy to the spring studied. Similarly, during its shortening, the spring makes energy available in proportion to the variation in its length.

According to the first law, the law of conservation of energy, two reservoirs in contact will exchange energy until their energy forces equalize, when all exchange stops. The state of equilibrium is thus the attractor of any system that is not in equilibrium: the evolution of natural systems is neither arbitrary nor random. The thermal energy goes from the hot source to the cold source, and the opposite is never observed: the energy therefore travels in the direction of decreasing temperature, the temperature here measuring the intensity, the force under which the thermal energy is present in the two reservoirs. The first law therefore makes it possible to state that the energy is conserved during the exchanges, which take place from the most intense reservoirs to the less intense reservoirs, by an exchange of extensity that decreases in the strongest reservoir and increases in the weakest reservoir. One can give as an example the flow of electric charges, electric extensity, which moves in the direction of decreasing electric voltage.

The second law adds precision to these possible developments. This law of directionality fixes the direction in which the transformations become spontaneous. This point is often misunderstood, in the sense that the first law already states that the transformations are not arbitrary, since they occur in the direction of decreasing intensity. The point that the second law clarifies is the fact that there are transformations that take place without exchanging extensive terms between two reservoirs. When a hot source heats a cold source, there is a flow of thermal extensity (entropy, immaterial extensity) from the first to the second. It is not a spontaneous transformation, the contact between the two sources must be ensured so that the extensity flows from one to the other. Spontaneity occurs when a transformation takes place without the need for an entropy source: subjected to an intensity gradient, the system begins to create entropy in proportion to this gradient, as if it were in contact with an entropy source. The immaterial aspect of entropy makes it possible to create it without contravening the law of conservation of matter, and since it is an extensity and not an energy, this creation does not contravene the first law either. The system therefore evolves spontaneously, since the necessary entropy is created on site, and irreversible because it created entropy that can no longer be destroyed. To conclude, it is therefore clear that a system subjected to an energy gradient can transform itself even in the absence of any extensive reservoir, if the creation of entropy makes it possible to establish an energy exchange chain that respects the first law.

With these rather abstract considerations having been made, now let us see how a spontaneous transformation can be quantified. For this, it is necessary to know if the creation of entropy is possible for the transformation of interest. One might assume that it suffices to measure the change in entropy in the system. The difficulty is that the entropy exchanged and the entropy created are indistinguishable, while spontaneity is only expressed by the second. The solution lies in monitoring the thermodynamic potential of the system, which is a property whose value changes in direct relation to the creation of entropy. It is easy to understand that an isothermal, isochoric system (constant T, V) can only create entropy in the same way as an isothermal, isobaric system (constant T, P); in fact, several thermodynamic properties can become a thermodynamic potential depending on the state variables of the system. In the case that concerns us with nucleation and crystal growth in an aqueous solution, the adequate thermodynamic potential is known as the free enthalpy or Gibbs free energy.

Gibbs free energy, as thermodynamic potential, is written as follows:

$$\Delta G_{T,P} = -T.\Delta S_{created} \qquad [1.1]$$

Any decrease in free enthalpy during an isothermal, isobaric transformation is therefore associated with a creation of entropy, reflecting an irreversible and spontaneous transformation. The reverse transformation is in fact impossible.

1.2.2. *Parameters controlling the driving force*

1.2.2.1. *Activity of dissolved species*

As we are interested in chemical transformations, it is appropriate to note that the free enthalpy of one mole of a chemical compound is equal to its chemical potential. However, the chemical potential makes it possible to integrate into the reasoning the characteristic terms of the composition of the system. Whatever the compound and its physical state (liquid, solid, gas, solute), its chemical potential μ is written as follows:

$$\mu = \mu^\circ + RT.\ln(a) \qquad [1.2]$$

where μ° is the chemical potential of the compound when it is in a conventional state, called the standard state; a is the thermodynamic activity of the compound; R is the ideal gas constant and T is the temperature. The activity is equal to 1 in the standard state and deviates from this value when the compound deviates from this conventional state. A standard state has at least four attributes: composition, "aggregation" state, temperature or range of temperatures, and pressure or range of pressures. The most common are written as follows:

– $a_{\text{solid/liquid}} = \gamma\, x$ for solids and liquids $\forall$ T,P, x being the mole fraction of the solid or liquid in the mixture. So $a_{\text{solid/liquid}} = 1$ for pure solids or liquids (in the stoichiometric sense, $x = 1$).

– $a_{\text{gas}} = \chi P/\chi^\circ P^\circ$ for gases $\forall$ T with $\chi^\circ = 1$ and $P^\circ = 1$ bar. The product of the fugacity coefficient and the pressure is the fugacity, denoted as f: $a = f/f^\circ$ with $f^\circ = 1$.

– $a_{\text{solute}} = \gamma\, m/\gamma^\circ m^\circ$ for solutes $\forall$ T,P with $\gamma^\circ = 1$ and $m^\circ = 1$ mol/kg. The standard state thus appears as a hypothetical situation where a solute concentrated at 1 mol·kg (rather high value) would behave like a solute in infinite dilution ($\gamma^\circ = 1$).

– A compositon term (x, P, m) is combined with the activity coefficient (γ, Xi) which enhances (γ, $\chi > 1$) or diminishes (γ, $\chi < 1$) the contribution of the composition to the chemical potential.

The case of concentrated aqueous solutions is archetypal of this notion of activity. When the solution is diluted, the solutes dissolved in water are separated from each other by large quantities of water molecules, whose properties are little affected by these few extrinsic elements. Consequently, the activity of water in the aqueous solution is negligibly different from 1, and the activities of the dissolved ions are almost identical to their concentration: the activity coefficients are a little higher or lower than 1. In this case, the mutual influence of the solutes between them is perceived in an undifferentiated way, so that a single parameter, the ionic strength denoted I, is sufficient to describe most of the associated energy disturbances. It describes the half-sum of the electric charges distributed in a rather homogeneous way throughout the solution, which is itself electrically neutral. Several empirical models, based on interaction microphysics, calculate the activity coefficients across various concentration ranges, such as the Debye–Hückel ($I \leq 0.02$) or Davies ($I \leq 0.7$) models.

At high concentrations, the distance between the dissolved solutes decreases so that the amounts of "in-between" water are small, and their mutual influences become specific. The models integrate an increasingly large number of specific interaction parameters. The most successful model is that of Pitzer, which can consider binary (two ions of opposite charge and the same charge), or even ternary (three ions, with different variants) interaction parameters for ionic strengths beyond 3.5 mol/kg. The water activity deviates significantly from 1 (see section 1.2.2.2), and the ion activity coefficients change significantly. In addition, the formation of high salinity ion pairs further complicates the situation. The main problem with the Pitzer model is having the necessary data as the interactions become numerous and increasingly specific. Nevertheless, it offers a remarkable self-consistency so that its use could be extended for systems reaching ionic strengths of 30 or 40 mol/kg (Lach et al. 2015; Lassin et al. 2015).

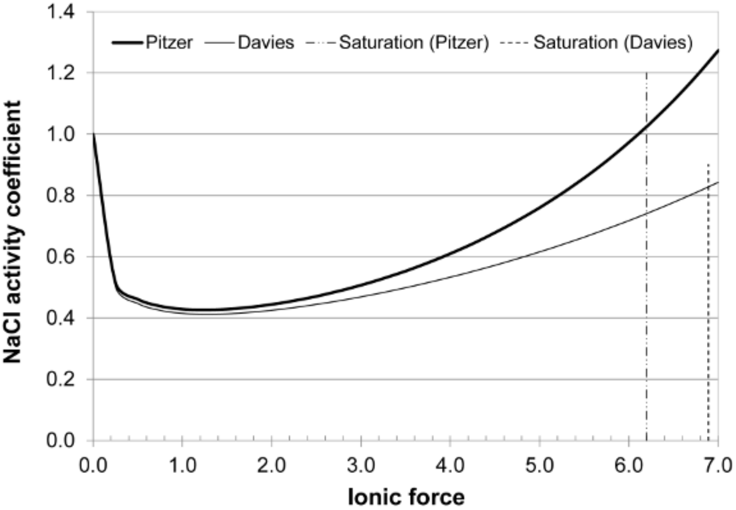


Figure 1.1. *Variation in the activity coefficient of the NaCl electrolyte according to two different models. Note that the saturation with respect to the halite depends on the model used*

For the calculation methods, the reader can refer to Steiger (2005) or Lassin et al. (2015) for an in-depth discussion of the Pitzer model, its evolution over time and modern developments. It is especially interesting to note that the activity coefficients of ions are generally less than 1 until saturation, which means that the solubility of the salts that dissociate into ions (halite, calcite, etc.) increases with the ionic strength. The presence of a minimum in the curve, which is also very typical, indicates that this effect varies greatly. In the case of NaCl, it is curious and usual to point out that at saturation, the activity coefficient is very close to 1. Another point of interest, the saturation with respect to the salt will be verified for varying ionic strengths depending on the activity coefficient model used. Here, this shows that Pitzer's model is the only one that accounts for the observations (saturation at 65 g/L), but also that a model that lowers the activity coefficients increases the solubilities. This very simple comparison illustrates the importance of these corrections when working with soluble salts.

Steiger (2005) correctly points out that extrapolating the Pitzer model beyond the saturation of the corresponding solid is not wise, because the terms involved are not conservative. He therefore proposes adjustments to explore the supersaturation of some salts.

1.2.2.2. *Water activity*

Water activity changes with the concentration and nature of dissolved species because they alter the dynamics of the intermolecular network that controls the thermodynamic properties of water. Therefore, the activity of water is a function of all the activities of the solutes, according to the following classical expression:

$$\ln a_{water} = -\phi \frac{M_{water}}{1{,}000} \nu\, m$$

where M_{water} is the molar mass of water, ϕ is the osmotic coefficient of the solute whose molality is m and which contains ν anions per mole of solute. In solutions whose ionic strength is less than 1, the water activity of any electrolyte can be estimated using that of a NaCl solution of the same concentration. For an ionic strength greater than 3, the Pitzer model in all its complexity must be used.

Besides the calculation method, the addition of solutes systematically leads to a decrease in activity with the increase in ionic strength. This indicates that water is less thermodynamically active, causing colligative properties (decrease in melting point, increase in boiling point, decrease in vapor pressure). The direct measurement of the variation in activity can be carried out by monitoring the drop in saturated vapor pressure of the solution with respect to the vapor pressure of pure water at the same temperature.

The dilution of a solvent by a solute is not the only way to vary the vapor pressure of water: a variation in the internal pressure of pure water also varies its saturated vapor pressure. This makes it possible to define the concept of osmotic pressure: it is the pressure of the free solvent (outside the water of solvation), which makes it possible to obtain the observed vapor pressure. As the activity drops, the vapor pressure is lower than that of pure water: the osmotic pressure of water in an aqueous solution is generally lower than the pressure of pure water.

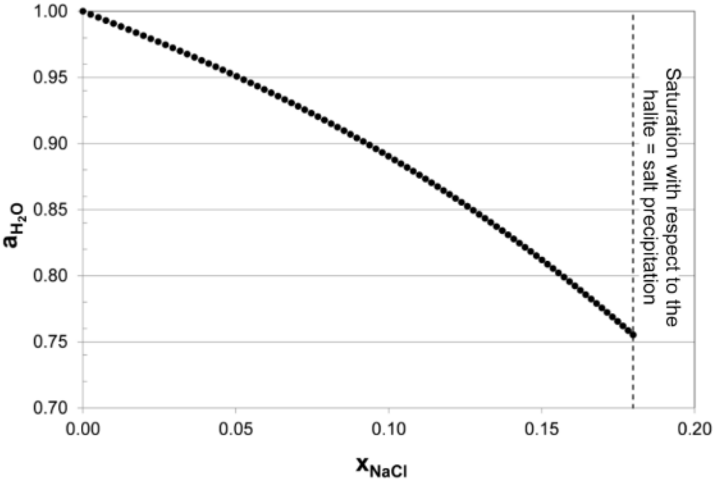


Figure 1.2. *Variation in water activity with NaCl molality until saturation with respect to the halite*

1.2.2.3. *Reaction stoichiometry*

Besides the activity of each species, it is necessary to emphasize the importance of the rule of defined proportions, which makes it possible to establish the conservation of mass during a chemical transformation (closed system):

$$\mathrm{aCation^{+} + bAnion^{-} + cH_2O = Cat_aAn_b.cH_2O} \quad [1.3]$$

Written like this, the system is assumed to move from the initial state on the left to the final state on the right. This can be verified by calculating the free enthalpy of this transformation, of course integrating the proportions of each participant:

$$\begin{aligned}\Delta_R G_{T,P} &= \mathring{\mu}_{Solid} + RT.\ln(a_{solid}) \\ &- \big[a.\mathring{\mu}_{Cation} + RT.\ln(\gamma_{cation}.C_{cation})^a + b.\mathring{\mu}_{anion} + \\ &RT.\ln(\gamma_{anion}.C_{anion})^b + c.\mathring{\mu}_{pure\,water} + RT.\ln(\gamma_{water}.x_{water})^c\big]\end{aligned} \quad [1.4]$$

Standard state chemical potentials are standard state molar free enthalpies, and their values are usually tabulated. Moreover, in most cases, the activity of solids is equal to 1 (pure solid).

Equation [1.4] easily rearranges into:

$$\Delta_R G_{T,P} = \Delta_R G^{\circ}_{T,P} + RT.\, ln\left(\frac{1}{(\gamma_{cation}\cdot c_{cation})^{a}\cdot(\gamma_{anion}\cdot c_{anion})^{b}\cdot(\gamma_{water}\cdot x_{water})^{c}}\right) \qquad [1.5]$$

The right-hand side of [1.5] highlights the ratio of the activities of the compounds that participate in the transformation, each to the exponent of its stoichiometric coefficient. This ratio is called reaction quotient, denoted as Q.

Note the importance of the stoichiometric term, especially when the salt considered involves ions of different valence, or for hydrates, since the number of water molecules is the exponent of the activity. Of course, when the ionic strength increases, the drop in water activity reduces the impact of this parameter.

1.2.2.4. *Temperature*

The temperature appears explicitly in expression [1.5] associated with the reaction quotient Q but is also less visibly involved in the calculation of the free enthalpy in the standard state. For each active species in the solution, the temperature where the transformation takes place must be considered for the calculation of its standard free enthalpy through the following expression:

$$\Delta G^{\circ}_{T,1bar} = \Delta G^{\circ}_{25^{\circ}C,1bar} - S^{\circ}_{25^{\circ}C,1bar} + \int_{298}^{T} Cp.\, dT - T.\int_{298}^{T} \frac{Cp}{T}.\, dT \qquad [1.6]$$

where *Cp* is the heat capacity of the considered species. Data are widely available in the literature (Robie et al. 1978; Woods and Garrels 1987) for many minerals and soluble salts, making it possible to calculate these corrections, which are moderate for the majority of the ranges of interest (–20°C to +50°C).

1.2.2.5. *Pressure*

Sometimes the pressure is also a parameter of evolution of the system, and initially, it is expressed and quantified like the temperature in the calculation of the standard free enthalpy. The expression for a given compound is written as:

$$\Delta G^{\circ}_{T,P} = \Delta G^{\circ}_{T,1bar} + \int_{1}^{P} V^{\circ}.\, dP \qquad [1.7]$$

Note that for all incompressible phases over the considered pressure range, the term on the right simplifies to a product of the volume times the pressure difference: $V°\cdot(P_{final} - P_{initial})$.

Within a porous system, the pressure of each cohabiting phase can vary, which is typically expressed by a curved separation surface. Two examples can be easily given, with curved liquid–air interfaces and capillarity, and curved solid–liquid interfaces compared to the natural external forms of minerals.

1.2.2.5.1. Curvature of the water–air interface

In such a situation, liquid and air are at different pressures, the concavity of the curvature sinking toward the side of the lowest pressure phase. With the liquid being purely elastic, the deformation of the surface is a function only of this elasticity, which refers to the surface tension of the liquid γ (same notation as the activity coefficients, unfortunately). The mechanical equilibrium between the two phases at different pressures is reached when the Young–Laplace equality is verified:

$$\Delta P = P_{air} - P_{liquid} = \gamma_{liquid-air}\cdot\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \frac{2\gamma}{r_{spherical\ meniscus}} \qquad [1.8]$$

where γ is the surface tension, so it should be specified which phases the interface separates. Strictly speaking, a water–water vapor interface has a different surface tension than a water–atmosphere meniscus. R_1 and R_2 are the two curvatures of the separation surface, which are equal for a spherical separation surface.

The Kelvin equation, the second law of capillarity, establishes the condition of chemical equilibrium between curved water and air at constant pressure:

$$ln\left(\frac{p}{p_s}\right) = \left[\frac{1}{RT}\int_1^P V_{water}\,.\,dP\right]_{capillary\ effect} + [\ln a_{water}]_{osmotic\ effect} \qquad [1.9]$$

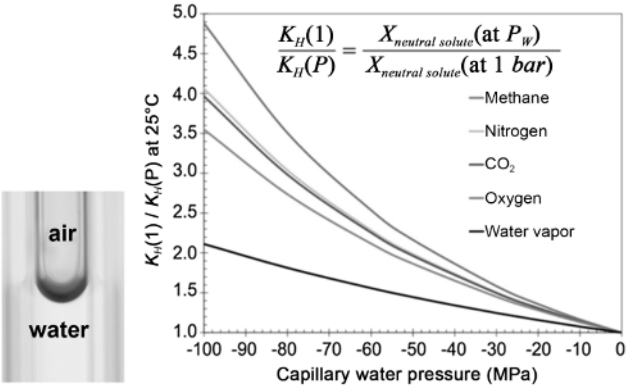
With the term *dP* being negative in the case of a concave interface toward the air, the vapor pressure of the capillary water decreases, and is added to that due to the dilution of the solvent by the solutes (see section 1.2.2.2). In terms of calculation, and to avoid counting the same effect several times, Lassin et al. (2005) recommend separating the two effects, considering the osmotic effect of salinity thanks to the water activity, while the capillary effect is integrated in the free enthalpy in the standard state. The term on the right of equation [1.9] brings out this distinction.

When a porous system saturated with water begins to dry out, the evaporation of the water and the associated loss of mass lead to the appearance of capillary menisci in the pores, the average radius of which verifies relation [1.8]. These menisci reflect the fact that the internal pressure of the water is lower than atmospheric pressure. This pressure contrast, this anisobarism of the water–air system, can be significant, and induce a capillary tension or negative pressure (r < 1.45 μm to 21°C). In particular, the chemical potential of the solution, that is, of the solvent and the solutes, is modified in proportion to this variation in internal pressure. The assumption is made that an aqueous solution constitutes a dielectric continuum so that the internal pressure in the solution has a continuous value. The pressures of water and solutes are equal, controlled by the Young–Laplace ratio (Mercury and Tardy 1997a, 1997b, 2001; Mercury et al. 2003).

As a result, it becomes easy to express the variation of free enthalpy due to the capillary effect:

$$\text{Gas} + \text{water} \leftrightarrows \text{Solute(s)} + \text{water} \qquad [1.10]$$

$$d\Delta_R G_{curvature} = \int_1^P V_{solute(s)}\, dP \qquad [1.11]$$



a) b)

Figure 1.3. *(a) Photograph of a cylindrical tube (∅ = 150 μm) and a capillary interface, concave toward the air. (b) Solubility of different gases in a solution under increasing capillary pressure. For a color version of this figure, see www.iste.co.uk/derluyn/salt.zip*

Using this formalism, we can calculate the variation in solubility of air gases in water as it becomes more capillary (Figure 1.3) (Mercury et al. 2004). A decrease in solubility is systematically predicted, via the salting-out effect, proportional to the molar mass of the gas. This thermodynamic prediction was recently confirmed by three series of independent experimental measurements (Lassin et al. 2016; Lidon et al. 2018; Hulin and Mercury 2019b).

In agreement with section 1.2.2.1, the variation in pressure of the solution imposes a correction on the activity coefficients. Lassin et al. (2005) showed that this correction increased with the ionic strength, using the model known as Ḃ (analogous to the Truesdell–Jones approach). Unfortunately, an explicit calculation at high ionic strength requires using the Pitzer model, whose calculation parameters as a function of pressure are not yet available.

Another point of interest is that the pressure value is determined by the fineness of the pore where the meniscus is placed and not according to the average radius in the porous system. Within a heterogeneous system, a meniscus trapped in a nanometric pore can put a large volume of solution under high capillary tension, because it is contained in much larger pores. (Mercury et al. 2003; Bouzid et al. 2011b; Hulin and Mercury 2019a, 2019b): it is the ink bottle effect (Figure 1.4) (Hillel 1998, p. 160).

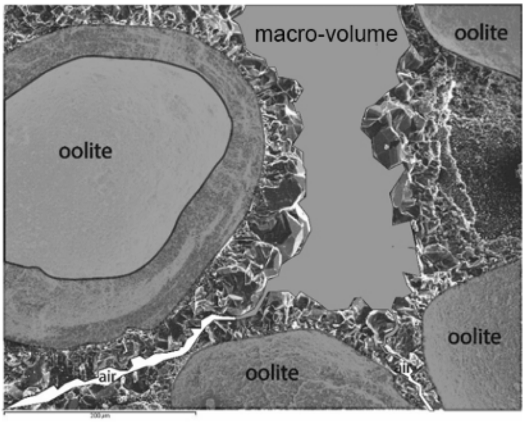


Figure 1.4. *Capillary trapping of a large amount of limited water by nanometric menisci in Young–Laplace and Kelvin equilibria, in a sedimentary rock (according to Hulin and Mercury (2019a)). For a color version of this figure, see www.iste.co.uk/derluyn/salt.zip*

1.2.2.5.2. Curvature of solid–solution interface

It is easy to write an equation of the type [1.8] for the curvature between the solid phase and the solution. We can cite the case of the Gibbs–Thompson equation, which links the variation in the melting temperature of a solid to its curvature. The

Ostwald–Freundlich equation is also widely used; it accounts for the excess solubility of small crystals compared to large crystals:

$$ln\frac{S}{S^{\circ}} = \frac{V_{solid}}{RT}.k.\frac{\gamma_{solid-solution}}{r_{solid}} \quad [1.12]$$

where S and S° represent the solubility for a solid of finite and infinite dimensions respectively, and k is a form factor. It is analogous to the Kelvin equation [1.9] and the Gibbs–Thompson equation.

In a porous medium, crystallization occurs in a finite size medium, that of the pore. If the pore is small enough, [1.12] puts a very strong constraint on the size accessible to any crystal it contains: the solubility of the mineral formed will therefore depend on the size of the host pore. Rijniers et al. (2005) produced very nice illustrations of this reality and showed that the solubility of different salts varied significantly for pores smaller than 30 nm. The experiments were carried out at water saturation, which excluded any role of the capillary pressure of the water.

Equation [1.12] also states that anybody exhibits a form of equilibrium when growth occurs without a space constraint or material limitation. This shape is defined by its surface tension γ and corresponds to a reference solubility. It can be easily obtained for any polyhedral mineral by using the Wulff construction, which obeys the following mechanical equilibrium:

$$P_{solid} - P_{solution} = 2.\frac{\gamma_n}{h_n} \quad [1.13]$$

where n is the index of any face of a Wulff crystal and h is the distance from the center of gravity to the outer surface of the face. Note that the term γ encompasses both the formation energy and the elastic contribution. The pressure increase in [1.13] therefore results from a chemical potential difference ($\Delta P = \Delta\mu/V$) and not surface tension. These distinctions are clearly discussed by Sanfeld and Steinchen (2000).

Consider a crystal growing in a medium under pressure $P_{solution}$. If one portion of the crystal grows faster than another, the radius of curvature there decreases. If γ is positive (Gibbs considers the case of negative surface tension; Gibbs 1928, p. 329), the pressure of the solid increases locally, which causes the material to flow back towards the interior of the crystal, the chemical potential increases, the growth slows down and a flat interface is obtained. This is what the Wulff construction (Figure 1.5) causes in the case of a polyhedral solid, where the surface tension is different from one face to the other. If the surface tension is constant, the mineral is spherical (spherule).

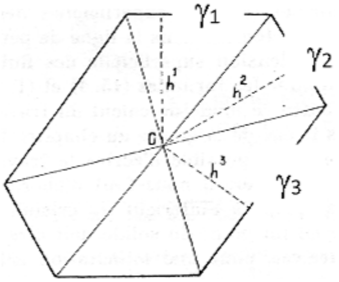


Figure 1.5. *Diagram of a crystal with the magnitudes of the Wulff construction (according to Defay and Prigogine (1951, p. 234))*

In practice, the chemical potential of solids is generally tabulated at 25°C and 1 bar: this is the chemical potential of the "natural" crystalline form under these conditions (*T,P*) of the initial solution. Any modification from this form of equilibrium reflects a change in chemical potential correlated with a change in pressure of the solid. Bouzid et al. (2011a) present an illustrative experiment with the coexistence of cubic and round NaCl, in connection with variable formation conditions.

We see by this that any modification with respect to the reference form is indicative of a thermochemical change when the observation is not taken in a too transient situation. Caution is required because the morphologies can also testify to kinetic factors. The main parameter is the diffusion of species at the interface. Typically, dendritic-like shapes that exhibit strong curvatures of solid–solution interfaces can be interpreted as resulting from high pressure gradients. However, they are also the consequence of mass deficit in certain directions of growth, when the growth rate at a tip is higher than the rate of diffusion in the solution. This term is also not purely kinetic, since the tip has a local excess of surface energy, which promotes precipitation. In the same way, the thermal effects linked to the dissipation of crystallization enthalpies can promote dendritic morphologies. Hollow crystals, called "hopper" crystals (Desarnaud et al. 2014), are also morphologies promoted by preferential growth rates, combining severe diffusional limitations with energetic factors like the presence of dislocations.

1.2.3. *Expression of the driving force*

The effects of temperature, pressure and composition can thus be dealt with in a thermodynamic way by evaluating the share of energy that each parameter brings or withdraws to the tendency of an aqueous solution to crystallize salts, and to therefore move beyond equilibrium. To consider the anisobaric effect linked to interface curvatures, it is possible to calculate the free enthalpy of each species under its own conditions, before combining them to evaluate the thermodynamic reaction potential. It should be noted that to know the directionality of the transformation, the free enthalpy is the potential to minimize, because if the system is anisobaric, the pressure relations express equilibrium conditions and they do not vary during the transformation.

To be in equilibrium ($\Delta_R G = 0$, no creation of entropy), it is necessary that the product of the activities, that is, the reaction quotient Q, is equal to $\Delta_R G°$. This is the $Q_{equilibrium}$ and this equilibrium reaction product is denoted K:

$$\Delta_R \overset{\circ}{G}_{T,P} = -RT.lnQ_{equilibrium} = -RTlnK \qquad [1.14]$$

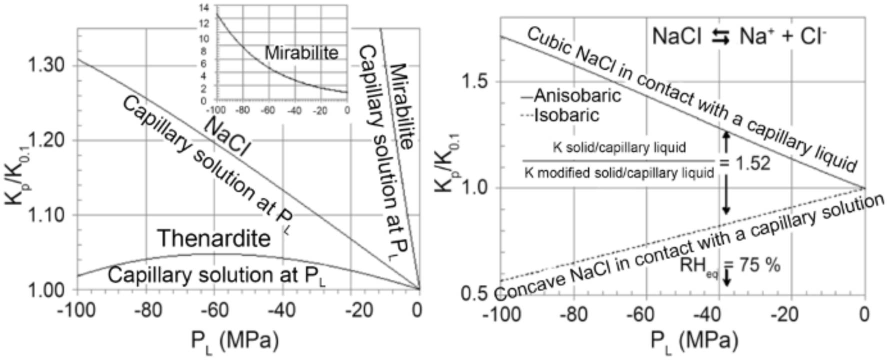
Whenever the composition of the solution does not allow it to be at equilibrium, the actual reaction quotient can be compared to the reaction quotient required for it to be at equilibrium:

$$\Delta_R G_{T,P} = -RT.lnQ_{equilibrium} + RTlnQ_{actual} = RTln\frac{Q}{K} \qquad [1.15]$$

The ratio Q/K is the focal point of this whole demonstration. It helps to understand how the composition and the physicochemical "quality" (via the activity coefficients γ) control the sense in which the reaction is spontaneous. If $Q > K$, the thermodynamic potential is negative (creation of entropy) if one moves from right to left, for a reaction such as [1.3], a solid dissolves in such a solution. Under the same conditions, if $Q < K$, spontaneity is established from left to right, and it is the salt that crystallizes.

It is very easy to see that the more the ratio of the concentrations increases, the more the term Q is supposed to grow. However, the evolution of the ratio also depends on the value taken by the activity coefficients. If γ decreases, the proportion of this solute, which is active in the transformation, decreases. On the contrary, when γ increases, the solute is more thermodynamically active, that is, the interactions in solution increase its reactivity at constant composition. The temperature is considered the same throughout the whole system but affects each species according to their own sensitivity. The pressure can vary through interfaces characteristic of interfacial equilibria, as indicated above. To illustrate this effect, and certainly the least frequently studied, we can compare the behavior of mirabilite and thenardite, the decahydrate and anhydrous forms of sodium sulfate: the hydrated form is much more strongly impacted than the anhydrous form by the variation in pressure of the solution (Figure 1.6(a)). We can also look at the change in solubility of NaCl, if its external form is independent (anisobaric case) or dependent (isobaric case) of the pressure of the liquid (Figure 1.6(b)). Bouzid et al. (2011a) presented an experiment confirming that halite bears a different shape depending on the formation conditions.

The degrees of freedom of a system not saturated with water, with capillary interfaces, are greater than those of a saturated system. Water–air menisci give occluded water supersolubility with respect to gases and solids. Capillary water can also trigger precipitation of nominally undersaturated solids, provided they change their external shape. These effects are greater when the mineral is hydrated. We can thus see that the external forms and the degrees of hydration are good markers of the formation conditions.



a) b)

Figure 1.6. *(a) Effect of solid (ambient pressure) – solution (capillary pressure) anisobarism for three different solids (according to Hulin and Mercury (2019a)). (b) Solubility of the halite in isobaric and anisobaric situations (according to Bouzid et al. (2011a))*

1.3. Stability, metastability, and instability

Thermodynamics can predict the state of equilibrium by calculating the minimum value of the thermodynamic potential that the system can reach by creating entropy. This assumes that nothing prevents this transformation from taking place, once the created entropy is made available. However, in many cases, the transformation must expend additional energy to start the transformation, which is called the activation energy E_a. To illustrate this point in the situation that interests us, the first crystal that is made is generally small, and therefore has a higher surface/volume ratio (S/V) than a big crystal. However, the surfaces of a solid have an additional energy term, called surface energy, which is added to the energy density of the compound. In this sense, the higher the *S/V* ratio, the more energy the production of the corresponding crystal requires. Some additional energy must therefore be given to a solution to make the first crystal and all its interfaces. This is typically the situation described by [1.12], which greatly exceeds the case of intrapore growth in fine pores.

Whether it is a problem of the existing solid surface or not, we immediately see that the presence of pre-existing pore walls or particles in suspension drastically changes the situation with respect to this triggering element. The problem becomes a little more subtle with the energy compatibility between the crystal structure of the existing surface compared to that of the crystal to nucleate and grow. For this, the surface tension is the relevant parameter. We can thus define a homogeneous nucleation, which only depends on the interfacial energy of the nucleus, the supersaturation (i.e. the frequency of "favorable collisions") and the temperature. If we consider a heterogeneous nucleation, the interfacial energy is expressed differently to consider the role of the mediating substrate (Stumm 1992):

homogeneous case: $\Delta G_{SURF} = \gamma_{NL}.A$

heterogeneous case: $\Delta \mathrm{G}_{\mathrm{SURF}} = \gamma_{\mathrm{NL}}.\mathrm{A}_{\mathrm{NL}} + (\gamma_{\mathrm{NS}} - \gamma_{\mathrm{SL}}).\mathrm{A}_{\mathrm{NS}}$

where *N* is the nucleus, *L* is the liquid, *S* is the substrate and *A* is the surface area.

Heterogeneous nucleation is generally accompanied by a lowering of the energy barrier because, most often, $\gamma_{NS} < \gamma_{SL}$. The borderline case is epitaxial growth, when the host surface of the substrate corresponds very well, even perfectly, to the crystal to be formed ($\gamma_{NS} \rightarrow 0$ and $\gamma_{SL} \rightarrow \gamma_{NL}$).

The characteristic equation usually written is that of the classical nucleation theory, which gives the rate of nucleation *J* in a volume for 1 mole:

$$J = J_0.exp\frac{-W*}{RT} = J_0.\exp\frac{-k.\gamma_{NL}^3.V^2}{R^3T^3\left(ln{}^{Q}/_{K}\right)^2} \qquad [1.16]$$

with J_0 is the pre-exponential factor, $W*$ is the activation energy of a spherical germ with a finite interface *V* is the molar volume of the nucleus (the other factors have already been mentioned).

These developments provide a good understanding of the thermodynamic reasoning for metastable states. The higher the energy barrier, the longer the activation time, that is, the time required for a fluctuation to provide sufficient energy to overcome it. This time is a function of the kinetics of formation of germs in the system, which is the product of a frequency factor and the density of matter. When the activation energy is surpassed, the system becomes unstable, and nothing keeps it from converging to the equilibrium point. Once nucleation has been activated, the initial solution sees many germs appear, then each begins to grow according to the laws of crystal growth, which obey the principle of energy minimization (see Wulff crystal). Depending on the amount of mass available locally and the growth rate relative to the diffusion rate of the species in the solution, the external forms will be automorphic or not.

In our case, the energy barrier is provided by the critical chemical supersaturation that triggers crystallization. When the excess chemical energy, associated with fluctuations, usually of the thermal type, becomes commensurate with the energy barrier at any point in the system, nucleation is activated, and the phase transition becomes spontaneous and takes place instantaneously: it can no longer be stopped until it has reached equilibrium concentration. Equation [1.16] indicates that the greater the interfacial tension of a solid and its volume, the higher the critical supersaturation will be. Note that this purely thermodynamic term does not consider the rate at which the supersaturation changes. However, it is a parameter that is well known experimentally, with the supercooling rate for example. The rate of change generates supersaturation gradients in the solution, but also compositional gradients around the seeds, due to diffusion. Crystallization is a process that must be studied locally.

A final aspect that can be reported is the occurrence of metastable phases that form first, before the stable phase: disordered dolomite before ordered dolomite (Navrotsky 1999), amorphous calcium carbonate, then vaterite or aragonite before calcite (Lassin et al. 2018), heptahydrate before sodium sulfate decahydrate (Steiger and Asmussen 2008), etc. In fact, the phase that forms first is the one that nucleates the most easily and not the one that is the most stable (Navrotsky 2004). Kinetic and thermodynamic arguments support this “rule”.

1.4. Kinetics of phase transformations

Thermodynamics is a science of initial and final states but does not consider the path taken to get from one to the other. Therefore, it is an effective science to predict the transformation that should occur, but it cannot say if the transformation occurs, let alone when, even taking into account the activation energy. Chemical kinetics thus usefully completes this.

1.4.1. *Characteristic equation*

The rate of the phase transition is a function of the supersaturation reached and depends on the diffusion of the species which "feed" this supersaturation and on the total volume of solution, but also on other more strictly kinetic terms. It is usual to write a global kinetic law (Palandri and Kharaka 2004) that groups the active parameters over the time required for a chemical system to reach equilibrium:

$$R = k_0 . A' \, exp\left(-\frac{E_a}{RT}\right) . \frac{A^{\circ}}{V}\left(\frac{m}{m^{\circ}}\right)^{n} . \prod_i a_i^{n_i} . \left(1-\left(\frac{Q}{K}\right)^{e_1}\right)^{e_2} \qquad [1.17]$$

where k_0 is the intrinsic kinetic constant in mol/(sec.m^2) ; *A'* is a pre-exponential factor and E_a is the activation activation; *A°* is the surface area initially offered for transformation; *V* is the volume of the active solution; *m/m°* is the lost mass correction; n, n_i, e_1, e_2 are empirical exponents; Πa_i encompasses all the possible effects related to the composition.

The intrinsic constant is the reaction time per unit area. Measured in the laboratory under conditions far from equilibrium, it gives the upper rate limit. The Arrhenius term that follows corrects this rate for the effect of temperature. *A'* and E_a are generally considered independent of temperature and are measured experimentally. The known values of activation energies for typical solids vary from a few tens to a few hundreds of kJ/mol. An $E_a \leq 20$ kJ/mol means that the reaction time will be rather limited by the diffusion of the transformation partner species. An $E_a \geq 80$ kJ/mol will indicate a need for bond breaking in the transformation, which will limit reaction time.

The next parameter *A°/V* is crucial when studying a dissolution, and the notion of reactive surface is still much debated and under study. In the case of crystallization, its role is much less important except in the case of epitaxial growth (from a substrate identical to the nucleus, homoepitaxy, or different, heteroepitaxy). On the other hand, the mass ratio at time *t* of the initial mass makes it possible to correct the reactive surface area of the mass lost during a dissolution.

The activity product of the ions indicated in [1.17] makes it possible to integrate the role of inhibitors or catalysts, or even the role of pH, on the reaction rate. Obviously, kinetics deals with transformation mechanisms so that the speed of movement of these species with respect to the reaction site where they occur (formation of the activated complex, sorption, etc.) is also a parameter that will contribute to the weight of this parameter.

The last term expresses the deviation from thermodynamic equilibrium with respect to the reaction studied, weighted by empirical exponents for reasons that will not be detailed here. Note that this is a local *Q/K* ratio, at the very place where the reaction advances, lowering itself by consuming the supersaturation. This is why it is important to measure the local concentration in the domains where the phase transition takes place, and to be able to characterize the diffusive and/or advective fluxes, which move the dissolved mass toward/from this local domain.

1.4.2. *Chemistry-transport coupling*

This chapter has so far focused on a closed system, whose composition changes with evaporation (for example) and whose (over)saturation increases with water loss. However, real systems are of course open, combining phenomena of advection, diffusion and dispersion. Advection occurs even in the unsaturated zone, under the effect of capillary pressure gradients, which bring mass back to the most strongly bound water–air menisci. These are effects that play a significant role in CO_2 storage and can contribute to decreasing the injectivity in the nearby carbon sink (André et al. 2014; Ott et al. 2014). Fickian diffusion combined with tortuosity diffusion is the first barrier to crystal growth. Note that in the case of concentrated solutions, the Fickian diffusion lacks generality because it is strictly applicable only in an infinitely dilute solution with uncharged species. Electrochemical migration makes it possible to study the role of charged species, by including different diffusion coefficients for each species while preserving the electroneutrality of the solution (Steefel 2008). However, this effect has been little studied and is very rarely considered. The second limit of the Fickian approach is encountered when working with concentrated solutions, which is the case with soluble salts. The driving force of the movement is no longer the concentration gradient alone, but the chemical potential gradient, which brings up terms of activity coefficients. As a result, the concentration term, which increases near the interfaces, can be reduced or even reversed by the activity coefficient term, so that counter-concentration diffusions can be considered (Steefel 2008).

The chemistry-transport coupling integrating the kinetic aspects could be the subject of a specific chapter. The use of dimensionless terms is particularly useful for looking at the relative importance of dynamic processes and accounting for reaction fronts. These studies also make it possible to specify the exact regime of the crystallization studied, and its exact control regarding the circumstances: control by transport or reaction, or even mixed control. For a complex process, the limiting step is obviously the slowest one. In fact, without coupling, it becomes very difficult to qualify the time constraints, usable mass and impacted space. It is also impossible to scale reaction rates in a heterogeneous porous medium by ignoring these couplings. Finally, dissipative structures (reactive fingers, Liesegang rings and oscillating reactions, chemomechanical replacements, etc.) most often result from initial conditions far away from equilibrium with very large driving forces and available masses. They cannot be understood without an approach coupling reaction and transport, but also involving thermal and mechanical stress fields.

1.5. Conclusion

This brief overview aims to establish the conceptual landscape within which crystallization phenomena can be interpreted, understood and quantified within porous media. One of the main obstacles in this field is the consistency of two rather disjoint approaches, with fluid mechanics, dominated by a vectorial vision linked to force (intensity and direction), with respect to thermodynamics, dominated by a scalar and energetic vision, whose directionality is ensured by the maximum entropy (second law). The thermodynamics of irreversible processes, especially in its linear approximation, makes it possible to linearly link the flow to its driving gradient (typically the chemical potential) with phenomenological coefficients, measurable quantities characteristic of the coupling.

Inside the reactive compartment itself, the combination of thermodynamic and kinetic terms must consider subtle co-influences and feedbacks, which are not always very easy to separate. Typically, the surface tension of the solid, or interfacial tension, is the key parameter both in the reaction energetics, but also in the paths followed. It is a local term, which can therefore be discretized within a complex process, while also capable of being scaled up.

These proposed frameworks offer interesting benchmarks for the construction of coupled thermokinetic models, which make it possible to follow the composition of driving forces and flows, on scales of time and space favorable to this mechanistic approach. We cannot say that a unified theory is already defined to comprehend the discrete scale of the pore. Further work will be required to scale up and integrate these approaches on a continuous scale.

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