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Michael Steiger

Institut für Anorganische und Angewandte Chemie Universität Hamburg michael.steiger@chemie.uni-hamburg.de

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INFLUENCE OF SALTS ON THE FREEZING TEMPERATURE OF WATER: IMPLICATIONS ON FROST DAMAGE TO POROUS MATERIALS

Michael Steiger

Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Germany

Abstract

This paper provides a discussion on the influence of the presence of salts on the liquidsolid equilibrium of water in porous building materials. Based on a thermodynamic analysis of the liquid water-ice equilibrium, the influence of single salts is discussed first. The freezing point depressions of a number of salts typically found in building materials are presented in order to obtain information on the crystallization pathways at low temperatures. The properties of the NaCl–NaNO₃–H₂O system at subzero temperatures are discussed in order to assess the behavior of salt mixtures using both, solubility and temperature-water activity diagrams. From the analysis of the phase equilibria at low temperatures it is concluded that it is not useful to discuss salt and ice crystallization as two distinctly different processes. Crystallization pressure as a result of growth from supersaturated solutions is considered as the principal damage mechanism for both, salt and ice crystallization. It is shown that the pressure exerted by growing crystals may be conveniently calculated based on appropriate expressions for the supersaturation of a pore solution. Finally, a numerical example is provided, which demonstrates that high crystallization pressure, exceeding the tensile strength of most building stones, may be generated by growing crystals of ice and hydrohalite (NaCl·2H₂O) assuming only moderate supersaturations

Keywords: ice, frost damage, salts, freezing temperature, crystallization pressure

1 Introduction

The interaction of salts and salt mixtures with water in the liquid and in the gaseous state causes a number of different phase transitions including crystallization or hydration of salts. Crystal growth associated with these phase transformations is generally considered as an important cause of damage in porous materials and there is a huge number of experimental studies that provide evidence for the deleterious effects of the growth of salt crystals in stone and other building materials. Also, there is a considerable number of investigations available now, providing insight into the theoretical thermodynamic background of such phase transformation processes involving salt mixtures.

On the other hand, though it is well-known that the crystallisation of ice is an important cause of damage as well, it appears that much less is known about the influence of the presence of salt mixtures in a porous material on the phase equilibria of water, in particular on the equilibrium between liquid water and ice.

This paper presents an analysis of the thermodynamics of the ice–water equilibrium in the presence of salts. Examples are discussed illustrating the effect of the freezing point depression in single and mixed salt solutions. Temperature-humidity phase diagrams at low temperatures are presented and are used to assess the behaviour of salt mixtures at low temperatures. Finally, equations are presented allowing for the calculation of crystallization pressure of both, salt and ice crystals, based on a thermodynamic consistent expression for the degree of supersaturation of a solution.

2. Thermodynamics of freezing

Water is present in porous materials in the gaseous (vapor), liquid (solvent) or solid state (ice, hydration water). Phase transformation processes that cause damage usually include a transfer of water from one phase to another, e.g. evaporation, hydration, freezing. Hence, the equilibria of ice, liquid water and water vapor are of critical importance. At equilibrium the chemical potential of water in the vapour phase, $\mu_{w(g)}$, equals that of the liquid phase, $\mu_{w(d)}$. Assuming ideal gas behavior for water vapor, we obtain:

$$\mu_{w(l)} = \mu_{w(l)}^{\circ} + RT \ln a_w = \mu_{w(g)}^{\circ} + RT \ln \frac{P_w}{P_w^{\circ}}$$
(1)

where $\mu_{w(g)}^{\circ}$ and $\mu_{w(l)}^{\circ}$ are the standard chemical potentials of the gas and the liquid phases, respectively. *R* is the gas constant, *T* is the absolute temperature and a_w is the water activity in the liquid phase. P_w and P_w° are the water vapor pressure and the saturation vapor pressure, respectively. Considering pure water at equilibrium, we have $a_w = 1$ and $P_w = P_w^{\circ}$, hence, $\mu_{w(g)}^{\circ} = \mu_{w(l)}^{\circ}$. In the presence of a solute the water activity is decreased $a_w < 1$, hence, $P_w < P_w^{\circ}$, which is known as the vapor pressure lowering above salt solutions. At equilibrium the water activity of a salt solution equals the relative humidity above the solution.

$$a_w = \frac{P_w}{P_w^{\circ}} \tag{2}$$

For liquid water and ice at equilibrium:

$$\mu_{w(l)} = \mu_{w(l)}^{\circ} + RT \ln a_w = \mu_{w(s)}^{\circ} + RT \ln a_{w(s)}$$
(3)

where $\mu_{w(s)}^{\circ}$ and $a_{w(s)}$ are the standard chemical potential and the activity of ice, respecttively. In the case of pure ice $(a_{w(s)}=1)$

$$\mu_{w(s)}^{\circ} = \mu_{w(l)}^{\circ} + RT \ln a_w \tag{4}$$

The freezing temperature of pure water $(a_w=1)$ is 273.15 K, hence at that temperature we have $\mu_{w(s)}^{\circ} = \mu_{w(l)}^{\circ}$. In the presence of a solute $(a_w<1)$, $\mu_{l(w)}$ is decreased and in order to reestablish equilibrium the chemical potential of ice must be decreased also, which can be accomplished by decreasing the temperature. The system is in equilibrium again if the decrease of the chemical potential of ice due to the drop in temperature equals the decrease in $\mu_{l(w)}$ due to both, the drop in temperature and the addition of solute which is known as the depression of the freezing point of an aqueous solution. An expression can be derived relating the depression of the freezing point to the water activity, $a_{w,fp}$, of a solution in equilibrium with ice (Klotz & Rosenberg 1972).

$$\ln a_{w,fp} = -9.6918 \cdot 10^{-3} \Delta T - 4.955 \cdot 10^{-6} \Delta T^{2} +8.27 \cdot 10^{-8} \Delta T^{3} + 4.88 \cdot 10^{-10} \Delta T^{4} + 2.19 \cdot 10^{-12} \Delta T^{5}$$
(5)

where $\Delta T = (273.15 \text{ K} - T_{fp})$ and T_{fp} is the freezing temperature.

3 Freezing temperature of salt solutions

According to Eqs. (2) and (5) the freezing temperature of a salt solution is directly related to the relative humidity, RH. The stability field of ice in a humidity–temperature diagram is depicted in Fig. 1. Ice is the thermodynamically stable phase at low temperatures and high relative humidities (hatched area in Fig. 1).



Figure 1: Freezing point depression and saturation humidities of single salts: (1) K_2SO_4 (2) KNO_3 , (3) $MgSO_4 \cdot 7H_2O$, (4) KCl, (5) $NaNO_3$, (6) $Ca(NO_3)_2 \cdot 4H_2O$, (7) $CaCl_2 \cdot 6H_2O$.

Curve *a* represents the equilibrium between liquid water in a salt solution and ice crystals according to Eq. (5). The curve starts at 0 °C (100% RH) and decreases with temperature reaching a value of 61.7% RH at -50 °C. According to Eq. (2) the freezing temperature of a salt solution is determined by its vapor pressure lowering, i.e. its equilibrium RH which is given by the solution concentration. With increasing concentration the water activity decreases as does the freezing temperature. However, the maximum concentration at a given temperature, i.e. the minimum water activity (or RH), is limited by the solubility of the salt. Equilibrium humidities of the saturated solutions of several salts are also shown in Fig. 1 (curves 1–7). At relative humidities below these deliquescence curves the respective crystalline salts are stable, while above the deliquescence curve the solution is the stable phase. For example, at 15 °C and a relative humidity of 80% (point *A* in Fig. 1), K₂SO₄, KNO₃, MgSO₄ · 7H₂O, and KCl remain in crystalline form as their deliquescence humidities are above 80%. The remaining salts shown in Fig. 1, i.e. NaNO₃, Ca(NO₃)₂ · 4H₂O, and CaCl₂ · 6H₂O are deliquescent at 80% and 15 °C, hence, they exist as solutions.

We can conclude that in a binary salt–water system a solution can only exist at relative humidities above the saturation humidity but below the equilibrium RH curve for the ice–water equilibrium. The lowest temperature at which a solution of a salt can exist is given as the intersection of the respective deliquescence curve and the ice–water coexistence curve *a*. Due to its low solubility, the freezing point depression of potassium sulfate solutions is negligible. Also, the effects of potassium nitrate and magnesium sulfate are only moderate. Saturated solutions of potassium chloride and sodium nitrate can exist down to temperatures of -11 °C and -17 °C, respectively. The most pronounced effects are observed for calcium nitrate and chloride, their solutions can exist to temperatures of about -30 °C and -50 °C, respectively.

Considering a solution of a single salt, the precipitation of a solid may be either caused by a change in RH, or temperature, or by a change in both. The possible crystallization pathways are illustrated in Fig. 2 for sodium chloride solutions. Several different situations may be considered. For example, isothermal evaporation of water from a solution A at 10 °C (1) would cause the crystallization of halite (NaCl) at humidities below 75.5% which is the equilibrium humidity of the saturated solution A' at that temperature.



Figure 2: Freezing point depression of NaCl(aq) and saturation humidities of NaCl \cdot 2H₂O and NaCl.

Similarly, at lower temperatures a drop of the relative humidity below the saturation humidity would cause the precipitation of hydrohalite (NaCl \cdot 2H₂O) which is the stable solid at temperatures below 0.16 °C.

In order to discuss the effect of a temperature drop, we might first consider the case that temperature is decreased at constant relative humidity as illustrated by path (2a) in Fig. 2. Starting from point *B*, the solution becomes saturated at -15 °C with respect to hydrohalite. Further decreasing the temperature would, therefore, cause the precipitation of hydrohalite. Hence, the concentration of the remaining solution is decreased leading to an increase in its water activity. At lower temperatures NaCl·2H₂O is continuously precipitated until the endpoint *E* is reached at -21 °C. The solution is now saturated with respect to both, hydrohalite and ice. A further temperature decrease would cause the crystallization of both solids.

In many practical situations, a temperature decrease at constant relative humidity might not be a realistic description of the situation at an object. The second pathway that might be considered is, therefore, a decrease in temperature at constant *absolute* humidity. Then, the relative humidity moves along curve (2b) in Fig. 2. In order to maintain equilibrium, the NaCl solution would pick-up water vapor until the water activity equals the relative humidity according to Eq. (2). In effect, the solution reaches saturation with respect to ice at about -4.4 °C and 95.5% RH. Upon further temperature decrease ice crystallization starts and the resulting concentration increase in the remaining solution causes a continuous decrease of the water activity. Hence, as more ice crystallizes out, a_w moves along line *DE* until, finally, at point *E* the endpoint is reached where the solution is also saturated with hydrohalite.

The two crystallization pathways described so far represent limiting cases. In most practical situations it is expected that neither the relative nor the absolute humidity will remain constant during a change in temperature and the actual crystallization of hydrohalite and ice might follow a pathway in between. Also, it has to be noted that our discussion is based on the assumption of full equilibrium neglecting kinetic effects.

Moving to salt mixtures the situation is slightly more complicated as the water activity and, particularly, the saturation humidities of mixed solutions depend on the mixture composition. This is illustrated in Figs. 3 and 4 for a salt mixture containing NaCl and NaNO₃. The range of stable existence of a solution in this system is limited by the freezing curves to low concentrations and by the solubility isotherms to high concentrations.



Figure 3: Freezing points and solubilities in the system NaCl–NaNO₃–H₂O at –20 °C, –15 °C, –10 °C and –5 °C; solid phases are (1): NaNO₃ and (2): NaCl \cdot 2H₂O.



Figure 4: Water activities of solutions saturated with NaNO₃ and NaCl \cdot 2H₂O at -20 °C; also shown are the water activities of solutions saturated with ice at -20 °C, -15 °C, -10 °C and -5 °C.

For instance, the hatched area in Fig. 3 indicates the range of stable existence of a solution in the ternary system at -20 °C. With increasing temperature there is an increase in the solubility of NaNO₃ and NaCl · 2H₂O, hence the solution field extends to higher molalities *m* (cf. isotherms at -20 °, -15 °C, -10 ° and -5 °C). The limit to low molalities is given by the freezing temperatures which are decreasing with increasing molality as shown by the freezing curves at -5 °C, -10 °C, -15 °C and -20 °C. For the particular salt mixture shown in Fig. 3, the situation is quite simple as the freezing curves are nearly straight lines, hence, the equilibrium molalities of the mixed solutions may be easily interpolated from data of the pure salts.

Consider a solution of composition A that is cooled to -20 °C. The solution becomes saturated with ice at -10 °C. Upon further cooling, ice is precipitated resulting in a

concentration increase. Hence, the solution composition moves along line AB until arriving at the equilibrium concentration at -20 °C (point B).

Fig. 4 depicts the situation for the same system in terms of water activities. At -20 °C a solution can exist in the water activity range represented by the hatched area, i.e. at water activities (relative humidities) above the saturation humidity curve and below the ice curve $(a_w = 0.823 \text{ at } -20 \text{ °C})$. The water activities of solutions in equilibrium with ice are decreasing at low temperatures. On the other hand, as the solubilities are decreasing with decreasing temperature, the saturation humidities are increasing. In effect, as already discussed for the single salts, the stability field of a salt solution becomes continuously smaller with decreasing temperature. It is obvious, however, that saturation humidities in the mixed solutions are considerably lower than in the saturated solutions of the pure salts. Hence, the mixed solutions of about equimolar composition can exist at lower temperatures than either of the two pure salts sodium nitrate (-17 °C) and sodium chloride (-21 °C). The minimum temperature at which a solution in the NaCl–NaNO₃–H₂O system can exist is -24 °C.

4 Crystallization pressure

The pressure that can be exerted by a confined crystal growing in a porous material is given by the following equation (Steiger 2004):

$$\Delta P = \frac{RT}{V_m} \ln \frac{a}{a_{0,\infty}} - \gamma_{cl} \frac{dA}{dV}$$
(6)

where ΔP is the crystallization pressure, V_m is the molar volume of the salt, *a* is the activity of the solute in the pore solution and $a_{0,\infty}$ is the saturation activity of a large crystal of infinite size. In the case of small crystals, interfacial effects cannot be neglected and are accounted for by the second term in Eq. (6) where γ_{cl} is the interfacial tension of the crystal-liquid interface, *A* and *V* are the crystal surface and volume, respectively. For crystal sizes of about >0.2 µm the interfacial energy term may be neglected. Considering a solution of a single salt of general composition

$$M_{\nu_{\mu}}X_{\nu_{\nu}}\cdot\nu_{0}H_{2}O$$

and using an appropriate expression for the activity of a salt in a binary solution we obtain (Steiger 2004):

$$\Delta P = \frac{\nu RT}{V_m} \left(\ln \frac{m}{m_0} + \ln \frac{\gamma}{\gamma_0} + \frac{\nu_0}{\nu_M + \nu_X} \ln \frac{a_w}{a_{w,0}} \right)$$
(7)

where *m*, and γ are the molality and the activity coefficient of the solute, and a_w is the water activity. The subscript zero refers to the saturated solution of the salt.

It is shown below that the same approach can be applied to calculate the crystallization pressure of growing ice crystals. It is well known (e.g. Everett 1961, Scherer 1999) that a confined ice crystal can only exert pressure, if it is in contact with a supercooled solution as illustrated in Fig. 5. Point A refers to a supercooled solution the temperature of which is lower by ΔT_{fp} than the freezing temperature T_{fp} of that solution (point B). Hence, the solution is in a metastable state and, if it is contact with a confined ice crystal, pressure is built up. According to Eq. (5) we can express the supercooling of the solution in terms of its water activity (cf. Fig. 5). The water activity of solution A exceeds the equilibrium water activity $a_{w,fp}$ of that solution (point C) at the temperature $(T_{fp}-\Delta T_{fp})$.



Figure 5: Water activity of supercooled solution



Figure 6: Water activities of NaCl solutions at -10 °C (see text for details).

Hence, we can regard solution A as being supersaturated with respect to ice where the degree of supersaturation may be conveniently expressed as the ratio $a_w/a_{w,fp}$. Applying Eq. (6) and neglecting size effects we obtain for the crystallization pressure exerted by the ice crystal.

$$\Delta P = \frac{RT}{V_{m,ice}} \ln \frac{a_w}{a_{w,fp}} \tag{8}$$

where $V_{m,ice} = 19.65 \text{ cm}^3 \cdot \text{mol}^{-1}$ is the molar volume of ice. Hence, the same equation can be used to calculate the crystallization pressure for both, crystals of the solute and the solvent. The only difference arises from different expressions required to express the degree of supersaturation.

The water activity of an aqueous solution is related to the concentration of the solute. As an example, Fig. 6 depicts the water activities of sodium chloride solutions at -10 °C. A solution of composition A is in equilibrium with ice, hence $a_w = a_{w,fp}$. More dilute solutions are supersaturated with respect to ice. For instance, the supersaturation of solution B is given by $a_w/a_{w,fp} = 1.06$, corresponding to $\Delta T_{fp} = 6$ K. The more concentrated solution C is saturated with respect to hydrohalite, its water activity equals the saturation humidity at that temperature. Finally, solution D is supersaturated with respect to hydrohalite $(m/m_0=1.05)$. In both cases—either solution B in contact with a confined ice crystal, or, solution D in contact with a confined hydrohalite crystal—pressure will build up depending on the degree of supersaturation. In the case of hydrohalite, the pressure may be calculated from Eq. (6). Using values of the activity coefficients and the water activities from the literature (Archer 1992) this yields $\Delta P=6.5$ MPa, a value which is exceeding the tensile strength of most building stones. For the particular case depicted in Fig. 6, i.e. $a_w/a_{w,fp}=1.06$, the same crystallization pressure is calculated for a growing ice crystal.

6 Conclusions

As a result of the freezing point depression in salt solutions frost damage occurs at lower temperatures in salt contaminated objects. The maximum freezing point depression of a given salt or salt mixture is given by the water activity, i.e. the equilibrium relative humidity, of its saturated solution. There is a general tendency that the saturation humidities in complex salt mixtures are lower than in the respective binary solutions of the same salts or simple mixtures thereof. As a result, complex mixtures can exist at lower temperatures than simple mixtures or single salt solutions. Salt mixtures containing substantial amounts of calcium chloride or calcium nitrate (but not calcium sulfate) are particularly efficient in depressing the freezing temperatures and considerably reduce the risk of both, frost damage and salt damage as the range of stable existence of a salt solution is greatly expanded.

At subzero temperatures different solid phases including ice may be precipitated from a mixed salt solution as a result of a change in the ambient conditions, i.e. temperature and RH. Which solid is precipitated first, is determined by the mixture composition. Hence, the crystallization pathway is variable and it does not appear useful to treat salt crystallization and ice crystallization as two distinct processes. Also concerning the damage mechanism, there is no need, nor is it helpful to distinguish between frost damage and salt damage. In both cases, damage is caused by crystals growing from supersaturated solutions. The thermodynamic analysis reveals appropriate expressions for the degree of supersaturation in order to calculate the crystallization pressure of both, the growth of salt and of ice crystals.

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