

Salts in Porous Materials: Thermodynamics of Phase Transitions, Modeling and Preventive Conservation

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Abstract

The thermodynamics of phase equilibria of salts in porous materials is discussed including all relevant phase transition reactions such as crystallization–dissolution, hydration–dehydration, and the freeze–thaw equilibrium of water. The treatment of binary systems, i.e. only one salt and water, yields binary phase diagrams that provide all information required for preventive conservation by environmental control. In the case of salt mixtures, a model approach is more appropriate to predict phase equilibria and safe ranges of environmental conditions. The properties of thermodynamic models are reviewed and several examples for the crystallization behaviour of mixed salt systems are provided. Finally, possible applications of thermodynamic models and their potential limits are discussed.

Keywords: Salts, crystallization, moisture, thermodynamic modeling, preventive conservation

Salze in porösen Materialien: Thermodynamische Analyse von Phasenübergängen, Modellierung und passive Konservierung

Zusammenfassung

Die Thermodynamik der relevanten Phasenübergänge von Salzen in porösen Materialien wird vorgestellt. Betrachtet werden Kristallisation und Lösung sowie Hydratation und Dehydratation von Salzen sowie das Gleichgewicht zwischen flüssigem Wasser und Eis. Die Behandlung binärer Systeme, also Mischungen von nur einem Salz mit Wasser, führen zu einfachen Phasendiagrammen, die zur Vorhersage geeigneter klimatischer Bedingungen für die passive Konservierung herangezogen werden können. Bei Vorliegen von Salzgemischen ist es erforderlich, thermodynamische Modelle zur Berechnung von Phasengleichgewichten und die Vorhersage des Kristallisationsverhaltens zu verwenden. Die Eigenschaften solcher Modelle werden kurz vorgestellt und zur beispielhaften Berechnung des Kristallisationsverhaltens einiger gemischter Salzsysteme verwendet. Schließlich werden die Anwendungsmöglichkeiten und Grenzen thermodynamischer Modelle diskutiert.

Stichwörter: Salze, Kristallisation, Feuchte, thermodynamische Modellierung, passive Konservierung

1 Introduction

Salt damage of porous materials is the result of crystal growth in the pore space of such materials. There are various phase changes involving crystal growth in building materials including the crystallization from supersaturated solutions, the change of the state of hydration, and chemical reactions resulting in the growth of new minerals at the expense of previously deposited phases. Similarly, the freezing of water from supercooled salt solutions results in the growth of ice crystals in a porous material. In all of these processes one or more constituents of the liquid phase, i.e. a salt solution, are subject to a transformation into a solid phase. Chemical thermodynamics is the scientific discipline establishing criteria for the feasibility and spontaneity of a given physical or chemical transformation.

Equilibrium is an important concept in chemical thermodynamics. A state of equilibrium is a state of rest in the sense that no change of macroscopic properties is observed. A system that has not reached a state of equilibrium is changing continuously toward such a state. Hence, phase transformations in porous materials only occur if the system of salt solution, solid phases and ambient environment does not represent an equilibrium state. Obviously, the concept of equilibrium is of fundamental importance in conservation. If an object is kept in an equilibrium state, no damage occurs. Such an approach of preventive conservation requires the exact knowledge of the environmental conditions either preventing or accelerating salt damage.

It has been shown by Arnold and Zehnder [1] that the dynamics of salt damage in porous materials is largely determined by the interaction of the salts present in the pore space and the surrounding atmosphere, i.e. temperature and relative humidity. This paper will briefly review the basic thermodynamics required to understand the relevant phase equilibria in porous materials and the influence of room climate. Also, the use of chemical equilibrium models to calculate phase equilibria and to predict appropriate environmental conditions for salt-contaminated objects is outlined.

2 Thermodynamics of Phase Equilibria Relevant to Salt Damage of Porous Materials

The most important equilibria affecting the behaviour of salts in a porous material are depicted in

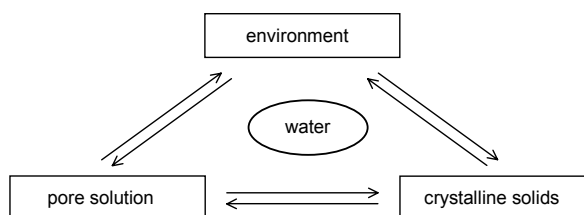


Figure 1: Phase equilibria in porous materials.

Fig. 1. Water in the gaseous (water vapour), liquid (solvent), or solid state (ice, hydration water) is involved in all of the relevant equilibria including evaporation and condensation, hydration, deliquescence and crystallization. From a thermodynamic point of view these equilibria are affected by the variables temperature, pressure and composition. For our purposes the influence of pressure can be neglected, assuming that the systems under study are under ambient pressure the minor fluctuations of which do not significantly influence the equilibria. Note, however, that pressure effects are important for the thermodynamic treatment of the basic mechanism of salt damage, i.e. the generation of stress by growing crystals [2].

There is a strong influence of temperature on the relevant phase equilibria. In the temperature range of interest from about $-40\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$, a number of relevant phase transitions occur. Temperature not only affects the formation of ice, but also the stability of various crystalline salts and their hydrates.

The chemical composition of the gas, liquid, and solid phases is of particular importance in the thermodynamics of phase equilibria. In the present context, the only important composition variable in the gas phase is the partial pressure of water vapour, p_w , which is usually expressed relative to the saturation water vapour pressure, p_0 , at a given temperature, i.e. as the relative humidity, RH .

$$RH = p_w / p_0 \quad (1)$$

The composition of the solid phases in the salt systems of interest is particularly simple. As the various salt minerals do not form solid solutions, each solid can be thermodynamically treated as an individual phase, which is either present or not. Hence, there is no variable composition of the solid phases. In contrast, the composition of the liquid phase present in the pore space of a material strongly affects the phase behaviour. Molality, i.e. the number of moles of a species dissolved in 1 kg of water, is widely used in thermodynamics and is an

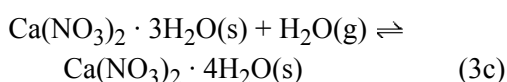
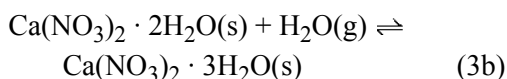
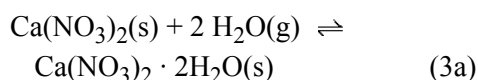
appropriate measure of the composition of electrolyte solutions.

The first equilibrium that has to be considered, is the equilibrium between liquid water in the salt solution and water vapour in the gas phase. At equilibrium, the activity of water, a_w , in a salt solution equals the relative humidity of the surrounding atmosphere.

$$a_w = p_w/p_0 \quad (2)$$

Any deviation from the equilibrium causes either evaporation of water from the solution (if $a_w > p_w/p_0$), or condensation of water vapour (if $a_w < p_w/p_0$). The water activity depends on the composition and concentration of a salt solution and can be experimentally determined by measuring the equilibrium humidity above a salt solution of given composition and the latter's concentration. The water activities of solutions of several salts are shown in Fig. 2. The equilibrium humidity decreases with increasing molality of the solutions. In other words, decreasing the relative humidity above a very dilute salt solution causes the evaporation of water and the solution becomes more and more concentrated.

There are different ways of interaction between water vapour and crystalline phases. A number of salts exist in anhydrous and various hydrated forms, in which water molecules are part of the crystal lattice of the salt mineral. The most prominent example of that type of equilibrium is the hydration-dehydration equilibrium of anhydrous sodium sulfate (thenardite) and the decahydrate (mirabilite). Most salts found in building materials form different hydrates. From a thermodynamic point of view the equilibrium is controlled by the relative humidity. If the RH increases above a critical value, the anhydrous or lower hydrated form of a salt picks up moisture from the air forming a higher hydrated state. For example, in the case of calcium nitrate several such transitions exist. At 20 °C, the critical RH values for the formation of the di-, tri-, and tetra-hydrates are 8.3%, 12.4%, and 20.5%, respectively. The corresponding phase equilibria are the following:



The tetrahydrate, nitrocalcite, is the highest hydrated form of calcium nitrate. If this salt is subjected to a slowly increasing relative humidity a point will be reached – the deliquescence or saturation humidity – where the solid picks up water vapour forming a saturated solution. At the deliquescence humidity, RH_{del} , three phases are in equilibrium, the saturated solution, the solid salt mineral and water vapour in the ambient air. As the relative humidity is further increased the solid phase dissolves completely and the solution becomes more dilute according to the equilibrium humidities illustrated in Fig. 2. The moisture uptake above the deliquescence humidity can be directly calculated from the curves in Fig. 2 yielding the hygroscopic moisture uptake depicted in Fig. 3.

The deliquescence humidity of $\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$ at 20 °C equals 53.1%. At humidities above the deliquescence humidity only two phases coexist, water vapour and the salt solution. At humidities below the deliquescence humidity, a solution is not stable and the vapour phase coexists with a solid phase only. All phase transformations included in Fig. 3 depend on temperature. A complete phase diagram of the system $\text{Ca(NO}_3)_2\text{-H}_2\text{O}$ is depicted in Fig. 4. Solid lines represent deliquescence humidities, i.e. the equilibrium conditions for the coexistence of the various solid phases and a saturated solution. Dashed lines are coexistence curves of two solid phases, i.e. the hydration–dehydration equilibria. A solution is not stable at very low temperatures. Hence, below –28.5 °C the stable phases are ice and $\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$. At temperatures between –28.5 °C and 0 °C, two equilibria have to be considered. A solution can be either in equilibrium with ice (line a) or with $\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (line b). The latter curve represents the deliquescence or saturation humidities of the tetrahydrate which is stable from –28.5 °C to 42.7 °C.

Line a in Fig. 4 describes the well-known phenomenon of freezing point depression in aqueous solutions. Thermodynamically, the freezing point of water is given as the equilibrium between the liquid and the solid phase:

$$\mu_s = \mu_l \quad (4)$$

where μ_s and μ_l are the chemical potentials of liquid water and ice, respectively. The chemical potential of the solid phase (ice) depends only on temperature, whereas μ_l depends on both, temperature and the concentration of an added solute, hence:

$$\mu_l = \mu_l^\circ + RT \ln a_w \quad (5)$$

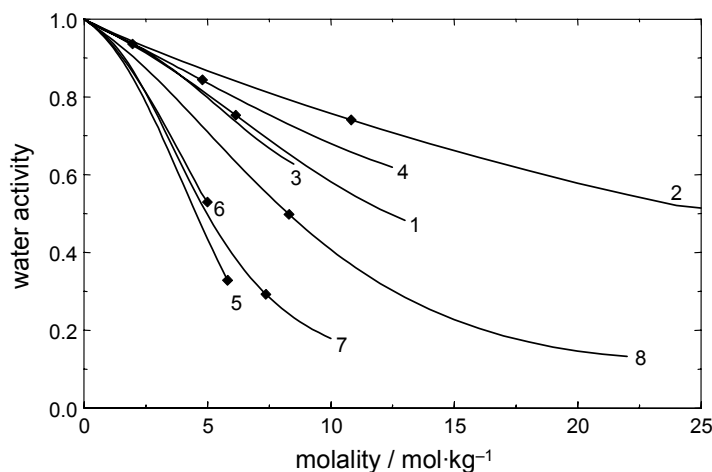


Figure 2: Water activities of solutions of some salts at 25 °C: (1) NaCl, (2) NaNO₃, (3) Na₂SO₄, (4) KCl, (5) MgCl₂, (6) Mg(NO₃)₂, (7) CaCl₂, (8) Ca(NO₃)₂; symbols mark the respective saturated solutions.

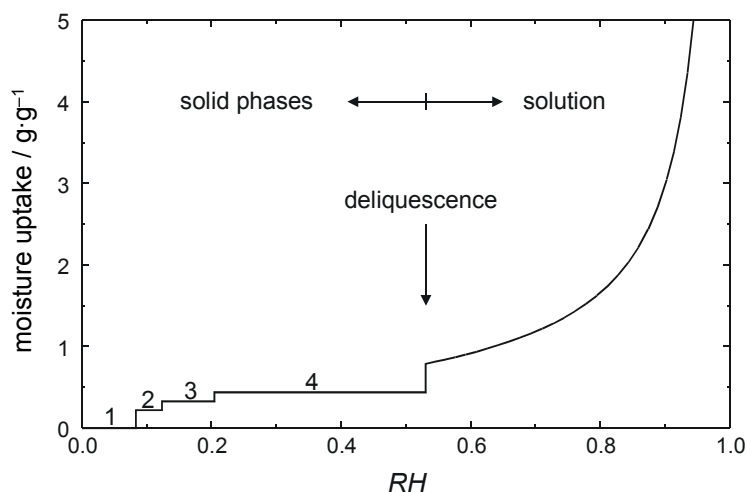


Figure 3: Moisture uptake (g water / g salt) of calcium nitrate at 20 °C; solid phases are: (1) Ca(NO₃)₂, (2) Ca(NO₃)₂ · 2H₂O, (3) Ca(NO₃)₂ · 3H₂O, (4) Ca(NO₃)₂ · 4H₂O.

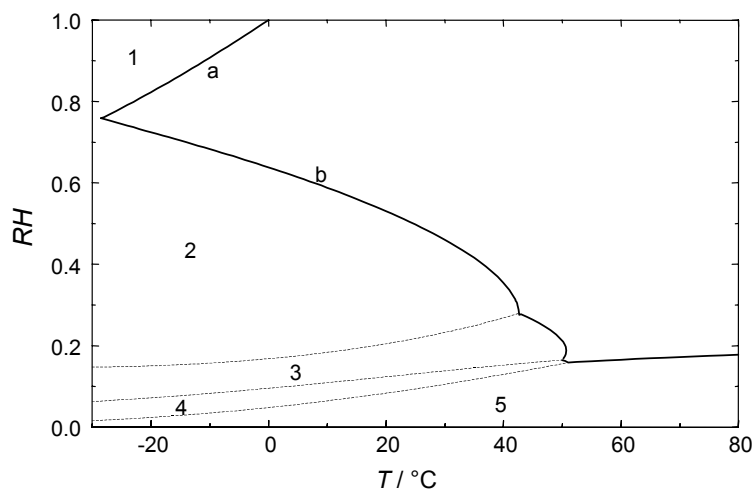


Figure 4: Humidity–temperature diagram of the system Ca(NO₃)₂–H₂O; solid and dashed lines represent solid–solution and hydration–dehydration equilibria, respectively; solid phases are: (1) ice, (2) Ca(NO₃)₂ · 4H₂O, (3) Ca(NO₃)₂ · 3H₂O, (4) Ca(NO₃)₂ · 2H₂O, (5) Ca(NO₃)₂.

If a solute is dissolved in the liquid phase, then μ_l is decreased ($a_w < 1$, cf. Fig. 2). 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 μ_l due to both, the drop in temperature and the addition of solute. An expression can be derived [3,4] relating the depression of the freezing point to the water activity, a_w , which was used to calculate curve a in Fig. 4.

According to eq. (1) the freezing point of a salt solution is directly related to the relative humidity. This is illustrated in Fig. 5 depicting freezing points and saturation humidities of various salts [5]. The stability field of ice in the humidity–temperature diagram is shown as the hatched area. Solid lines are the deliquescence humidities of several salts. For example, at 45 °C and a relative humidity of 75 % (point A in Fig. 5), K_2SO_4 , KNO_3 , $MgSO_4 \cdot 7H_2O$, and KCl remain in crystalline form as their deliquescence humidities are above 75 %. The remaining salts shown in Fig. 5, i.e. $NaNO_3$, $Ca(NO_3)_2$, and $CaCl_2$ are deliquescent at 75 % and 45 °C, hence, they exist as solutions. Upon cooling at constant RH under equilibrium conditions, $NaNO_3$ and $Ca(NO_3)_2 \cdot 4H_2O$ crystallize out at 21 °C and –26.5 °C, respectively. In contrast, in the case of the $CaCl_2$ solution at 75 % RH , ice is the first solid to be precipitated (at –28.5 °C). Further decreasing the temperature causes continuous deposition of ice. Only at about –50 °C antarcticite ($CaCl_2 \cdot 6H_2O$) crystallizes out and a solution is not stable any more at lower temperatures.

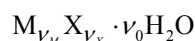
The deliquescence or saturation humidities are closely related to the solubilities of the salts. As the water activity continuously decreases with increasing concentration (molality) of a solution (cf. Fig. 2), it is not surprising that the most soluble salts show the lowest deliquescence humidities. For example, calcium sulfate, e.g. in the form of anhydrite ($CaSO_4$) or gypsum ($CaSO_4 \cdot 2H_2O$), is only slightly soluble and the water activities of saturated calcium sulfate solutions are not substantially lower than that of pure water ($a_w > 0.999$). In contrast, calcium chloride solutions are very soluble and their saturation humidities are quite low. Deliquescence humidities of most salts decrease with increasing temperature (see Fig. 5). This is the result of a solubility increase with temperature which is typical for hydrated salts and the anhydrous nitrates of sodium and potassium.

As the dissolution/crystallization equilibrium is of fundamental importance with respect to the salt damage mechanism, both solubility equilibria in aqueous electrolyte solutions and vapour-liquid equilibria at saturation have to be considered. As an example, the temperature dependence of the solubilities of the various hydrated forms of calcium nitrate are depicted in Fig. 6. Note that the corresponding water activities of these saturated solutions are shown in Fig. 4. From the type of phase diagrams discussed so far, the properties of a single salt present in a porous material can be easily predicted. Crystallization damage may be avoided by maintaining the relative humidity of the air at a value other than the deliquescence or saturation humidity. If the RH is kept below the saturation humidity a salt remains in solid form, at humidities above the saturation value the salt remains in solution all time. Similar arguments apply for hydration.

3 Modeling of Phase Equilibria of Salt Mixtures

Contamination with a single salt is very uncommon. The salt accumulations usually found in porous materials are comprised of many different ions. Typically, the chlorides, nitrates and sulfates of sodium, potassium, magnesium and calcium have to be considered. Unfortunately, the situation becomes a lot more complicated for mixtures compared to pure salts as the concept of the saturation humidities of the individual salts does no longer apply to mixtures [6, 7]. Salt efflorescences on walls containing complex salt mixtures have been observed at considerably lower relative humidities than would have been expected from the saturation humidities of the pure salts [1]. In order to predict the properties of salts in mixtures it is impractical to conduct the necessary measurements for a huge number of mixture compositions. In order that phase equilibria can be predicted, a model approach appears to be more appropriate [6–8].

The theoretical treatment of solubility equilibria is well known. Given a salt of general composition



consisting of ν_M positive ions, M , of charge z_M , ν_X negative ions, X , of charge z_X , and ν_0 molecules of water the equilibrium constant of the dissolution reaction

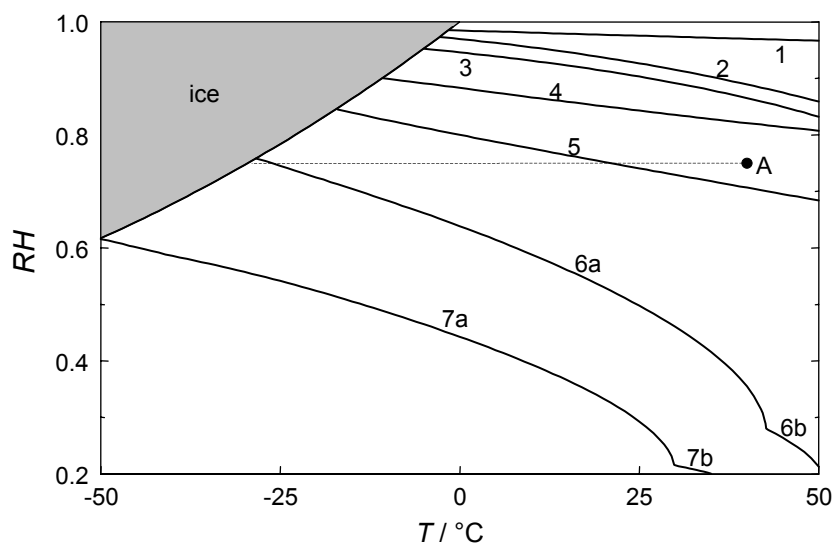


Figure 5: Freezing point depression and saturation humidities of several salts: (1) K_2SO_4 , (2) KNO_3 , (3) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, (4) KCl , (5) NaNO_3 , (6a) $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, (6b) $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, (7a) $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, (7b) $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, redrawn from reference [5].

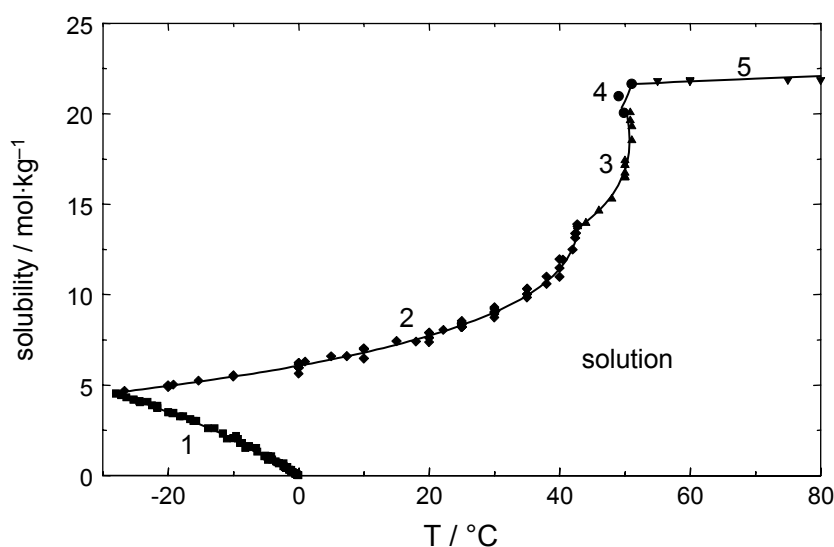
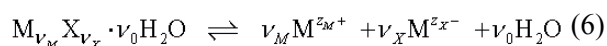


Figure 6: Solubilities and freezing points in the system $\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O}$; symbols represent experimental solubilities and freezing points from the literature; solid phases are: (1) ice, (2) $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, (3) $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, (4) $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, (5) $\text{Ca}(\text{NO}_3)_2$.



is given by

$$\ln K_{MX} = v_M \ln m_M + v_M \ln \gamma_M + v_X \ln m_X + v_X \ln \gamma_X + v_0 \ln a_w \quad (7)$$

where γ_M and γ_X represent the ion activity coefficients.

From eq. (7) it is apparent that calculations of solubility equilibria in mixed salt systems require (a) values of the equilibrium constants, K_{MX} , in the

temperature range of interest, and (b) activity coefficients of the aqueous species as a function of solution composition and temperature. There has been considerable progress in the thermodynamic treatment of concentrated electrolyte solutions during the last decades. In particular the ion interaction approach of Pitzer [9] proved very helpful in modeling various thermodynamic properties. Details of the model are not discussed here but may be found in reference [9]. Briefly, the Pitzer ion interaction approach is a set of equations to calculate thermodynamic properties of aqueous electro-

lyte solutions. The model was introduced more than 25 years ago [10] and, since then, found wide acceptance and was applied in a number of research areas [11,12]. The Pitzer model is a semi-empirical model, i.e. the form of the ion interaction equations arises from theoretical considerations while there remain empirical parameters which have to be determined from experimental data. Values of these parameters are obtained by fitting thermodynamic data of binary and common ion ternary systems. These thermodynamic data are preferably taken from the published literature.

Data used for the parameterization include water activities, activity coefficients, enthalpies (heat of solution, heat of dilution) and heat capacities. Such data are used to determine the binary ion interaction parameters as functions of temperature. For the parameterization of ternary interaction parameters the same type of thermodynamic data in common ion ternary systems, i.e. mixtures containing three different ions, may be used. For most practical applications, however, solubility data are most appropriate for the determination of ternary parameters. Once the binary and ternary interaction parameters and their temperature dependence have been parameterized, the model can be used to predict the thermodynamic properties of complex mixtures.

To perform solubility calculations in mixed systems, values of the equilibrium constants in the temperature range of interest are required. These can be either taken from thermodynamic databases if available, or, may be parameterized from solubility data in the respective binary systems. For example, the equilibrium constants for $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}(\text{NO}_3)_2$ may be determined from literature solubilities as shown in Fig. 6 by using eq. (7) and the experimental molalities together with calculated activity coefficients and water activities from the Pitzer model. In a similar way the equilibrium constants for double salts may be obtained from solubility data in the respective ternary system, e.g., the equilibrium constant for the double salt darapskite ($\text{NaNO}_3 \cdot \text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$) is determined together with the ternary interaction parameters from solubility data in the mixed system $\text{NaNO}_3\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$.

If all interaction parameters and equilibrium constants are known, the model can be used to calculate solubilities in mixed salt systems. The calculation of phase equilibria in multicomponent systems requires numerical techniques which have been reviewed by Van Zeggeren and Storey [13]. Two

main techniques may be distinguished: (1) optimization techniques minimizing the Gibbs free energy function and (2) the numerical solution of a set of simultaneous non-linear equations. Both approaches may be used for the calculation of phase equilibria of salt mixtures in porous materials. Calculations presented in the present paper were made using a method of the second type to calculate the equilibrium concentrations of saturated salt solutions. The method involves the simultaneous solution of a set of mass action and mass balance equations. The mass action expressions are the solubility constants of the dissolution reactions (eq. 7).

The mass balance equations include the total charge balance

$$\sum_M z_M m_X = \sum_X z_X m_X \quad (8)$$

where the sums are over all cations, M, and anions, X, respectively. The set of eqs. (7) and (8) can be simultaneously solved for the unknown molalities by Newton-Raphson iteration [13] yielding initial values, $m_i^{(0)}$, for the equilibrium molalities of all ions in the solution. At this point of the calculation the Pitzer equations are used to correct for the non-ideality. The Newton-Raphson iteration is repeated using the activities, $a_i^{(0)} = \gamma_i^{(0)} m_i^{(0)}$, and the water activity, $a_w^{(0)}$, as starting values, yielding new molalities $m_i^{(1)}$ which are used to calculate $\gamma_i^{(1)}$ and $a_w^{(1)}$. This procedure is repeated until satisfactory convergence in all γ_i and m_i is obtained.

It has been shown [6–8] that the Pitzer ion interaction model together with an appropriate numerical technique for the calculation of phase equilibria can be used to analyze the behaviour of salt mixtures in porous building materials. The model can be used to predict crystallization sequences, including hydration–dehydration equilibria, as a result of changes in temperature or relative humidity. Examples of such calculations are depicted in Figs. 7 and 8 and were subject to a detailed discussion in previous papers [7,8,14,15]. Briefly, the crystallization properties of salt mixtures are strongly dependant on the mixture composition. For example, consider the solutions of compositions A and C in the ternary system $\text{NaCl}\text{--NaNO}_3\text{--H}_2\text{O}$ depicted in Fig. 7. If the relative humidity decreases, water will evaporate and the solutions will become more concentrated (lines AB and CD). At points B and D the solutions are saturated with respect to NaNO_3 (point B) and NaCl (point D), respectively. Any further evaporation of water will lead to supersaturation and crystallization of one salt. Upon further

evaporation, this salt continues to crystallize and the solution composition moves along the lines CE or DE, respectively. Finally, reaching point E any further decrease of RH will lead to complete drying.

In effect, the crystallization of one salt from a mixed solution does not occur at a specific value but rather across a range of relative humidities [6–8]. This is illustrated in Fig. 7 for the mixtures A and C of NaCl and NaNO₃ discussed before. The

deliquescence humidities of the pure salts at 19 °C are nearly identical ($a_w = 0.75$). In the presence of the second salt the saturation humidities are decreased. For the solutions of composition B and D the values of a_w are 0.72 and 0.71, respectively. The saturation humidity at the drying point which is always the endpoint of the crystallization path is $a_w = 0.675$, a value considerably lower than the deliquescence humidities of the pure salts.

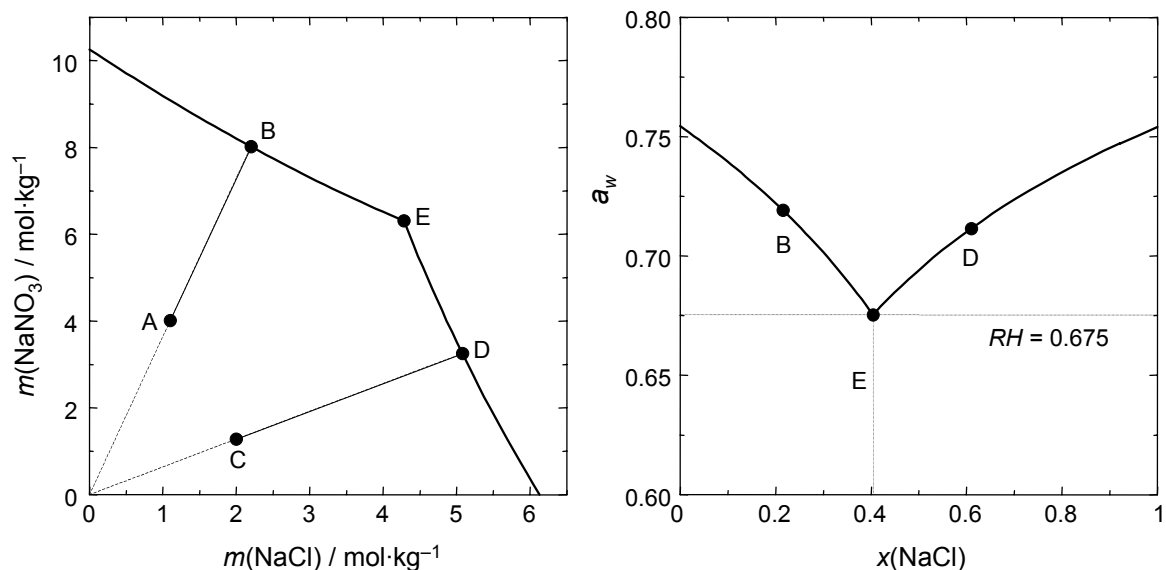


Figure 7: Solubilities (left) and saturation humidities, a_w , vs. mole fraction of NaCl, $x(\text{NaCl})$, (right) in the system NaNO₃–NaCl–H₂O at 19 °C.

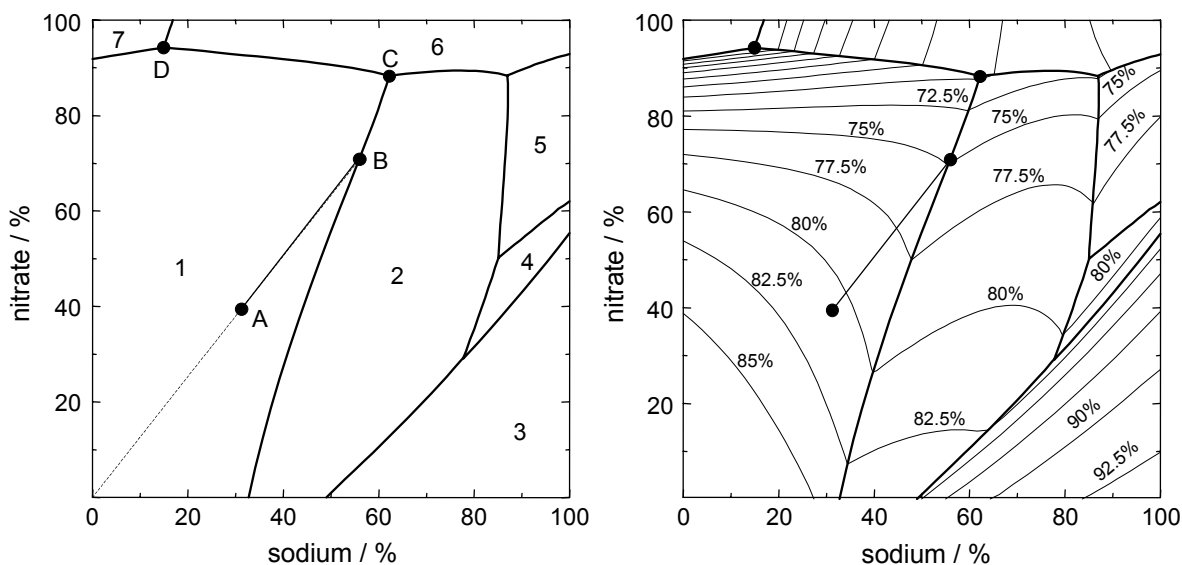


Figure 8: Solubilities (left) and saturation humidities (right) in the system Na⁺–Mg²⁺–NO₃[–]–SO₄^{2–}–H₂O at 25 °C; solid phases are: (1) MgSO₄ · 7H₂O, (2) Na₂SO₄ · MgSO₄ · 4H₂O, (3) Na₂SO₄ · 10H₂O, (4) Na₂SO₄, (5) NaNO₃ · Na₂SO₄ · H₂O, (6) NaNO₃, (7) Mg(NO₃)₂ · 6H₂O, redrawn from reference [15]

In a similar way more complex mixtures can be treated using the model approach. Fig. 8 provides an example of the solubility equilibria in a salt system containing four different ions (a quaternary system). All possible solution compositions in the system $\text{Na}^+ - \text{Mg}^{2+} - \text{NO}_3^- - \text{SO}_4^{2-} - \text{H}_2\text{O}$ can be expressed as the percentage contribution of each cation to the total amount of positive charges and the contribution of each anion to the total amount of negative charges (Jaenecke projection). The lines in the interior of the square are the saturation curves for solutions coexisting with two solid phases. They define the crystallization fields of the stable solids at 25 °C, i.e. NaNO_3 (nitratine), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (nitromagnesite), $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (mirabilite), Na_2SO_4 (thenardite), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (epsomite) and the double salts $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ (astrakanite) and $\text{NaNO}_3 \cdot \text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (darapskite).

For any composition of a solution the crystallization pathway can be readily predicted from the phase diagram of Fig. 8. For example, epsomite would crystallize out first from a solution of composition A. Due to the crystallization of epsomite the solution becomes depleted in magnesium and sulfate. Hence, the solution composition moves along line AB, being also saturated with respect to astrakanite at point B. Further removal of water then causes the simultaneous crystallization of epsomite and astrakanite until at point C the solution is also saturated with respect to nitratine. The solution is now saturated with respect to three solids. However, point C is not the crystallization end-point for a solution of initial composition A, but C is rather a transformation point. Assuming full equilibrium between the solution and the solids already precipitated, further removal of water would lead to the dissolution of astrakanite and the precipitation of nitratine instead. Then, the solution composition moves along the line CD. Point D is the drying point of the solution of initial composition A. It is important to note, however, that completely different crystallization pathways result for other solution compositions. Several examples are discussed in detail in references [7] and [14].

The equilibrium model can be also used to calculate the saturation humidity of a solution of any composition. Saturation humidities are depicted as lines of equal saturation humidity in Fig. 8. It is obvious that the addition of other ions causes a considerable decrease in the saturation humidities of the different solids. Such diagrams can be used to obtain critical ranges of relative humidity within which fluctua-

tions cause crystallization or other phase changes. For instance, it can be seen from Fig. 8 that in a solution of composition A epsomite starts to crystallize at about 81% RH, which has to be compared to the saturation humidity of 90.3 % of a pure MgSO_4 solution at the same temperature. Upon further decreasing the relative humidity, the solution becomes also saturated with astrakanite at 75 % RH. However, at about 70 % RH the double salt re-dissolves and nitratine precipitates instead. Finally, the crystallization end-point is reached at a relative humidity of 50 % RH.

Salt mixtures typically found in historic buildings are even more complex [1]. Salt systems containing the ions sodium, potassium, calcium, chloride and nitrate are often found in the ground moisture zone of old buildings. The complete solubility diagram of that system cannot be shown in a simple two-dimensional diagram. However, it is possible to display several useful projections in simplified diagrams. As an example, Fig. 9 depicts the solubility diagram of the quinary $\text{Na}^+ - \text{K}^+ - \text{Ca}^{2+} - \text{Cl}^- - \text{NO}_3^- - \text{H}_2\text{O}$ system at 25 °C showing all solution compositions that are saturated with respect to halite (NaCl). For the sake of simplicity straight lines were used to connect the isothermal invariant points which are the intersections of these lines, i.e. the compositions of solutions that are saturated with respect to halite and three additional salt minerals. Such diagrams are extremely useful to derive the crystallization pathways of complex mixtures. For example, it can be seen from Fig. 9 that halite, sylvite (KCl) and nitratine (NaNO_3) cannot coexist in stable equilibrium.

The saturation humidities of some invariant points are also shown in Fig. 9. It is obvious that with increasing complexity of the salt composition the effect of the decrease in the saturation humidities becomes more pronounced. In particular, with increasing amounts of calcium the mixtures become more and more hygroscopic. Then, even sodium and potassium salts can remain dissolved at very low humidities. All calcium containing solids except the double salt $\text{KNO}_3 \cdot \text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ would only precipitate at extremely low humidities (<20 % RH) and will, therefore, not occur in crystalline form as efflorescences under typical ambient conditions. The double salt $\text{KNO}_3 \cdot \text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ has not yet been found in porous building materials. Also in laboratory experiments it was observed that this salt has the tendency to form highly supersaturated solutions of extremely high viscosity. Similar effects are

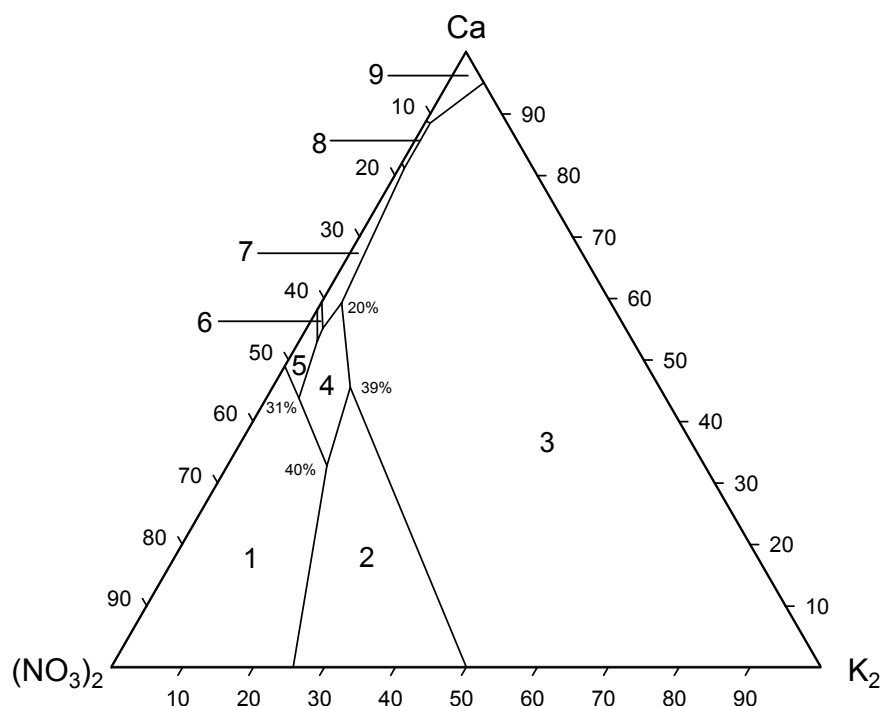


Figure 9: Solubilities in the $\text{Na}^+ - \text{K}^+ - \text{Ca}^{2+} - \text{Cl}^- - \text{NO}_3^- - \text{H}_2\text{O}$ system at 25 °C, all solutions are also saturated with halite; solid phases are: (1) NaNO_3 , (2) KNO_3 , (3) KCl , (4) $\text{KNO}_3 \cdot \text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, (5) $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, (6) $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, (7) $\text{CaCl}_2 \cdot \text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, (8) $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, (9) $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.

known from other solids containing calcium nitrate [16, 17]. Hence, the occurrence of efflorescences containing calcium nitrate or calcium chloride is very unlikely.

4 Application of Thermodynamic Models

There are various useful applications of thermodynamic models in conservation. First of all, equilibrium calculations can be used to interpret the results of salt measurements in building materials. An analysis of the crystallization pathways is very helpful to understand the behaviour of a particular salt mixture and to assess the effects of the ambient environment on the dynamics of salt damage due to repeated phase transitions. In such a study the model predictions can be validated by comparison with phenomenological observations of salt behaviour, e.g. seasonal changes in the efflorescences occurring on wall surfaces [18].

The modeling approach is particularly useful as a predictive tool. In instances where other measures to prevent salt damage, e.g. desalination, are not applicable, preventive conservation might be the only option to prevent or mitigate salt damage. After appropriate measurements of the salt contam-

ination of an object have been carried out, careful application of a thermodynamic model will allow to predict the conditions, i.e. temperature and relative humidity, that would minimize the frequency of occurrence of undesired phase changes inducing crystal growth in porous materials.

Sometimes model simulations can be extremely helpful in order to predict the effects of changes in room climate due to an envisaged change in the usage of an object. Very often salt damage is dramatically accelerated or even initiated by the installation of a heating system in rooms that have not been used in the past and have therefore never been heated. This author has successfully used computer simulations for several objects in order to demonstrate the deleterious effects that would result from the installation of a heating system in a previously unheated room with salt contaminated walls. In such instances thermodynamic modeling is preferable to any experimental approach.

Currently, a computer program, ECOS (Environmental Control of Salts) exists [19] facilitating the use of thermodynamic modeling to conservators and conservation scientists. ECOS involves the mole fraction based thermodynamic model of Pitzer [9] instead of the molality based model used

for the calculations in the present work. Recent research demonstrated both the abilities of the practical application of the ECOS program [20] and potential problems encountered with its use [21].

Other applications of thermodynamic modeling include the evaluation of experimental conditions used in salt damage simulation studies. A thorough review of such laboratory simulation studies is now available [22]. The interpretation of the results from such studies suffers from the fact that the experimental conditions are often not comparable or even not appropriate for the particular purpose of the study. A careful analysis of the phase equilibria of single salts or salt mixtures will allow to optimize the experimental conditions in future studies. For that purpose a chemical equilibrium model should be very helpful.

The use of equilibrium models is always based on the assumption that salt systems are in equilibrium with the environment at all times. Hence, the major limitations of such models arise from non-equilibrium conditions [19]. Kinetic effects are of particular importance. The tendency of some salts to form supersaturated solutions as described before, may lead to metastable crystallization pathways resulting in mineral assemblies that are in disagreement with model predictions. However, this is not a general restriction, as an equilibrium model can be also used to calculate metastable phase equilibria. Hence, the model can be used to simulate possible deviations from the equilibrium situation and alternative crystallization pathways including metastable equilibria.

More severe is the fact that pore solutions are subject to transport in porous materials, whilst solid deposits are not. In other words, the assumption that the solution phase is in equilibrium with the salts already deposited at all times is violated. In principle, this can be handled by assuming that a solid phase once deposited is completely removed from the system, i.e. prohibiting reactions causing the dissolution of one solid and the crystallization of another one as discussed for the crystallization sequence in the $\text{Na}^+ - \text{Mg}^{2+} - \text{NO}_3^- - \text{SO}_4^{2-} - \text{H}_2\text{O}$ system (cf. point C in Fig. 8). In reality the situation will strongly depend on the transport properties of the porous material, its moisture content and the dissolution and crystallization kinetics of the various salts. This problem can be only addressed by a combined thermodynamic and kinetic approach, i.e. a model of the coupled heat, moisture and salt transport in porous materials. Such research is in

progress [23]. The thermodynamic model is coupled to an existing model of moisture transport in porous materials. The chemical model, however, is only used to calculate if the system is in an equilibrium state. Any deviation from equilibrium results in processes such as crystallization, dissolution, evaporation or condensation, which are treated by a separate kinetic model.

5 Conclusions

In conclusion, thermodynamic modeling provides a powerful tool in improving our understanding of salt behaviour and salt damage in porous materials. Existing models are very useful to calculate phase equilibria, but need to be refined and extended in order to be of general use to conservators and conservation scientists. There are limitations of equilibrium models which cannot be applied to non-equilibrium conditions. Extended models including transport processes and kinetics might be helpful in improving our understanding of the combined effects of transport and phase transformations, these being the most important factors determining the distribution and behaviour of salts in porous materials.

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