

# Thermodynamic Analysis of Solubility Data: Phase Diagrams of Systems Salt Hydrate + Water

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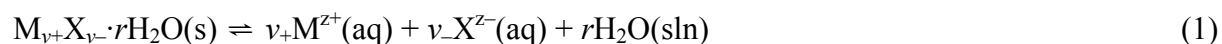
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Solubility equilibria between solid salts, salt hydrates and water play an important role in different branches of applied chemistry such as, for example, hydrometallurgy, geochemistry and oceanography. The continuous interest in this field is reflected by volumes 85, 87 and 89 of the IUPAC-NIST Solubility Data Series (SDS) [1].

Temperature – composition phase diagrams are widely used for a concise description of solubility equilibria according to complete dissociation into the ionic constituents and water as indicated by eq. (1).



A rapid and reliable way to obtain the necessary fitting equations for the dependence on temperature and composition of solid salt and salt hydrate solubilities in aqueous solutions has been comprehensively described in [2], concisely summarized in [3] and is further developed in this work.

The solubility product of reaction (1) is (writing w for H<sub>2</sub>O):

$$-\Delta_{sln}G^\circ(T)/RT = \ln K_s = \ln(a_M^{v+} a_X^{v-} a_w^r) \quad (2)$$

As composition variables for the ionic system it turned out advantageous to use  $x_+$ ,  $x_-$ , the ionic (species) mole fractions,  $x_w$ , the mole fraction of water and  $x$ , the mole fraction of the anhydrous salt  $M_{v+}X_{v-}$ , where  $v = v_+ + v_-$ . The right-hand side of eq. (3) depends on  $\tau = T / T_{fus}$  only, where  $T_{fus}$  is the melting temperature of  $M_{v+}X_{v-} \cdot rH_2O(s)$ .

$$Y[x(T)] = \ln \left\{ \frac{x^v (1-x)^r (v+r)^{v+r}}{r^r [1+(v-1)x]^{v+r}} \right\} = - \int_{T_{fus}}^T \frac{\Delta_{sln}H^\circ}{R} d\left(\frac{1}{T}\right) - \ln \left[ \left( \frac{f}{f^*} \right) \left( \frac{f_w}{f_w^*} \right) \right] \quad (3)$$

Usually three or four term Clarke-Glew type of equations suffice to represent  $Y = Y(\tau)$ . Once optimal values for the Clarke-Glew parameters have been obtained by nonlinear regression analysis the  $x$  and  $T$  part of eq. (3) can be solved simultaneously to result in  $T = f(x)$ . These calculations, which are the basis for construction of  $x$ ,  $T$  phase diagrams, have been performed using the mathematic software package Maple [4].

The ratio of the slopes to liquidus curves intersecting at isobaric invariants, e.g. eutectic or peritectic points, has been estimated by adapting Pelton's [5] thermodynamic arguments to electrolyte systems. By this method the consistency of phase diagrams can be checked and the interpretation of experimental data will be improved.

The recently compiled and evaluated data of the systems  $LiNO_3 + H_2O$ ,  $Ni(ClO_3)_2 + H_2O$  and  $LaBr_3 + H_2O$  provide examples to apply the refined procedure for calculation and optimization of phase diagrams from solubility data. The phase diagram of the system  $LiNO_3 + H_2O$ , see Fig. 1, was the first for which the slopes to the liquidus curves at the eutectic points were calculated using thermodynamically predicted slope ratios.

## References

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