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CRYSTALLIZATION AND HYDRATION PRESSURE OR FORMATION PRESSURE OF SOLID PHASES

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The pressure produced by a crystal growing in a solution can be described by an equation of the following form:

$$P = P_s - P_s^o = \frac{R \cdot T}{V_m} \cdot \ln A \qquad (1)$$

where P is the crystallization pressure, R the gas constant, T the absolute temperature and V_m the molar volume of the solid phase. It is possible to consider the change of the interface energy in the above formula (1).

The term A can be defined in different manners:

1) Correns (2) used a supersaturation ratio c/c_s, where c ist the actual concentration of the growing phase in the solution and c_s is the solubility in the state of equilibrium. This equation was widely used, especially in the investigation of the decay of natural stones (3,4,5). In the derivation of the equation the concentrations are assumed to be proportional to the osmotic pressures. This is only an approximation, because the osmotic pressure is proportional to $\varphi \cdot c$. φ is the osmotic coefficient, which is a function of the chemical composition of the solution. The discrepancies between measured and calculated values of the crystallization pressure reported by Correns may be explained by this.

2) Dron and Brivot (6) investigated the crystallization pressure of ettringite. They defined A as a solubility product ratio s_A/s_B, where s_B is the solubility product of the solid reaction product and s_A is the solubility product of the solid reactants, given by the reaction equation (in the original paper of Dron and Brivot a somewhat different form of equation 1 was used).

3) Xie and Beaudoin (7,8) also investigated the crystallization pressure of ettringite. A discussion of their paper was given by Dron (9). They defined A as a solubility product ratio K_{sp}/K_{sp}^o, where K_{sp} is the solubility product of the solid phase if the whole system is in equilibrium at the pressure P_s. K_{sp}^o is the solubility product of the solid phase at the pressure P_s^o of the solution, normally 1 bar. They presented a complete and detailed derivation of their equation from thermodynamic theory.

The way of derivation of equation 1 given by Dron and Brivot and Xie and Beaudoin is different, but they received equivalent expressions. For the practical calculation of crystallization pressures K_{sp} is the actual existing ion product of the reaction product (e.g. ettringite) in the solution. It is possible to define this actual ion product both as the solubility product of the reactants and as the solubility product of the solid phase if the whole system would be in equilibrium at the pressure P_s.

The purpose of this letter is to point to the following items:

1) The above formula is not restricted to crystallization processes. This was already suggested in (9), but it seems not to be a common knowledge. The equation describes a state of thermodynamic equilibrium between solid phases and the surrounding solution. The solid phases can be crystalline or amorphous. It may be better to speak of a formation pressure of a solid phase than to use the limited term crystallization pressure.

2) Activities must be used instead of concentrations to calculate the ion products resp. the solubility products. The calculation of activity coefficients of dissolved species from the measured concentrations is possible by the use of the Pitzer-theory (10,11,12).

3) The Ca^{2+} - $CaOH^{+}$ equilibrium must be considered in the case of the alkaline concrete pore solution (13,14).

4) The pressure produced by a hydration process can be described by the analogous equation (4,15):

$$P = \frac{n \cdot R \cdot T}{V_h - V_o} \cdot \ln \frac{P_w}{P'_w} \qquad (2)$$

where n is the number of moles of water consumed during the reaction (related to 1 mol solid), V_h and V_o are the molar volumes of the hydrated and the original substance, and P_w and P'_w are the vapor pressures of water and the hydrated substance at the given temperature. This equation is also an approximation. Fugacities must be considered instead of the vapor pressures for an exact calculation. This equation is also not restricted to crystalline phases.

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