Calorimetric Determination of Thermodynamics and Kinetics of Water Vapor Sorption

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Depending on the partial pressure of the water vapor, the sorption of water vapor on solid phases can lead to the formation of hydrates or saturated solutions. The increasing degree of hydration causes changes in physical chemical properties. Adsorption and hydration behavior in relation to relative humidity are therefore decisive criteria for the quality assurance of pharmaceuticals, fertilizers and similar products. Their behavior toward water vapor is normally determined hygrostatically or isopiestically. These methods require chemical equilibrium to be established and are therefore very time-consuming.

The water vapor sorption on solid phases can be rapidly determined using DSC with regard to the beginning of a reaction with water vapor and to hydrate formation under equilibrium partial pressure while increasing water vapor pressure. Furthermore the kinetics of sorption reactions by means of the calorimetric determination of the sorption rate as a function of the water vapor pressure can be characterized. This is done by exposing the sample under isothermal conditions to a gas flow saturated with water vapor whose partial vapor pressure increases linearly during the experiment. The measured heat flow q is proportional to the sorption rate of the sample substance.

$$q = \Delta H (dn/dt)_{\rm T} \tag{1}$$

$$(dn/dt)_{\rm T} = k A (p_{\rm H2O} - p^{\rm c}_{\rm H2O})$$
 (2)

$$(dq/dp_{H2O})_{\rm T} = k \ A \ \Delta H \tag{3}$$

From the plot of q against p_{H2O} , the increase representative for the different curve sections (k, A, Δ H) can be determined. This characterizes the individual reactions with regard to adsorption, hydration and formation of saturated solutions. The investigation of the temperature dependence of k provides information on kinetics in accordance with the Arrhenius equation.

The results of the investigations on the hydration of inorganic salts, the characterization of drugs and the stability of fertilizers will be discussed.^{1,2}

Literature:

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