# Heat-of-Sorption

## – White Paper 25-01

## 1. Introduction

Temperature plays an important role in water vapor sorption as the interaction between a material and moisture changes with temperature. Several factors contribute to this correlation which are explained below:

In general, moisture sorption decreases at higher temperatures. Such behavior is observed in materials where the adsorption process is associated with an exothermic reaction, meaning heat is released.
As the surrounding temperature rises, the system attempts to adjust by adsorbing less moisture to maintain equilibrium. The physical phenomenon is described by the principle of "Le Chatelier". [1,2]

Furthermore, an increase in temperature leads to an increase in thermal motion, resulting in higher kinetic energy for water vapor molecules. This leads to increased molecular mobility and wider intermolecular distances. Consequently, the probability of molecules binding to the material via attractive forces, such as van der Waals or hydrogen bonds, decreases. Additionally, at elevated temperatures, these bonds become more susceptible to rupture, causing water molecules to revert to their gaseous state. [3-6]

In terms of water vapor sorption, an increase in temperature makes the desorption of bound water molecules more likely. An increase in temperature generally results in a decrease in the amount of bound water, assuming constant $a_w$ values. [3,4,7]

Due to the factors mentioned above, moisture sorption isotherms recorded at different temperatures are typically shifted downward as the temperature rises. This is illustrated schematically in Fig. 1. Therefore, at a constant $a_w$ value, the moisture content of the sample increases as the temperature decreases. Conversely, at a constant moisture content, the water activity of the sample increases with temperature.

## 2. Heat-of-Sorption

The term "Heat-of-Sorption" refers to the heat either released during adsorption or the energy required for the desorption of water vapor molecules. The stronger the interaction and binding force between water vapor molecules and a material's surface, the more energy is released or required for desorption.

Factors influencing the Heat-of-Sorption, i.e., the binding strength between adsorbed water vapor molecules and the surface, include:

1. the characteristics of the materials: e.g. the chemical composition associated with the presence of hydrophilic groups, the porosity and specific surface or whether the material is in a crystalline or amorphous state.
2. the moisture content: For dry materials, water vapor molecules bind directly to the surface of the material through interaction with the active groups present. The binding strength in this monolayer state is very strong, resulting in a large Heat-of-Sorption. With higher moisture load, a multimolecular sorption layer is formed and the attractive forces, the binding strength as well as the released heat during sorption are reduced. [8,9]
3. Temperature: An increase in temperature is associated with an increase in the kinetic energy of the vapor molecules. This leads to a reduction in the probability of adsorption, consequently decreasing the total mass of the bound water vapor molecules [9]. Thus, an increase in temperature typically corresponds to a decrease in binding strength, resulting in lower heat release.

From a practical standpoint, understanding the interaction with water vapor, as well as controlling the moisture content and $a_w$ -value, is crucial for ensuring shelf life, sensory properties, and safety.

In this context, it is important to consider temperature changes during processing and storage. Furthermore, the correlation between moisture content and Heat-of-Sorption is particularly relevant to the design and energy efficiency of industrial drying processes since removing water from materials, especially in a low-moisture state, requires a high energy input.

As explained above, the Heat-of-Sorption is a useful measure of the interaction between a material and water vapor and can also serve as an indicator of the processes involved in sorption or desorption processes.

## 3. Theory and Calculation

DVS measurements provide a convenient and reliable method for determining the Heat-of-Sorption. The method involves measuring the equilibrium moisture content at defined relative humidities using at least two different temperatures [7].

A well-established approach to calculating the Heat-of-Sorption from sorption data is the Clausius-Clapeyron-Equation (Eq. 1). In general, the equation provides a relationship between the vapor pressure of a substance dependent on the temperature. To calculate the sorption heat, the approach describes the dependency between temperature and the sorption isotherm. For this approach to be valid, the following assumptions must be met: (1) the Heat-of-Sorption must be independent of temperature, and (2) the moisture content must remain constant. [4].

$$\left(\frac{d \ln P}{dT}\right)_x = \frac{\Delta H_{sorp}}{R \cdot T^2} \qquad \text{Eq. 1}$$

After integration, the equation becomes:

$$ln\, p = -\frac{\Delta H_{sorp}}{R} \cdot \frac{1}{T} + C \qquad \text{Eq. 2}$$

$p$: Equilibrium vapor pressure at temperature T
$T$: Absolute temperature in Kelvin
$\Delta H_{sorp}$: Isosteric Sorption enthalpie [J/mol]
$R$: Ideal gas constant (8.314 J/mol·K)
$C$: Integration constant (dependent on moisture load

To calculate the Heat-of-Sorption from experimental DVS data, the temperature-dependent $a_w$ values at the same moisture load must first be determined from the sorption curves as exemplary shown in Fig. 1.

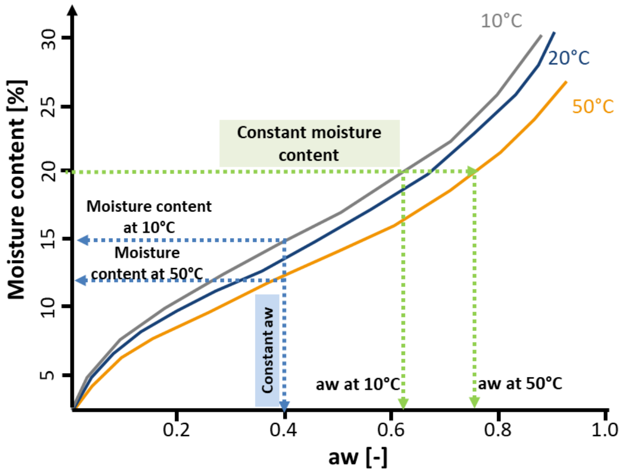

Fig. 1: Relationship between moisture content and water activity as a function of temperature. Exemplary calculation of the Heat-of-Sorption from DVS data

After plotting ln($a_w$) against 1/T, the slope m is obtained by a linear regression. This slope corresponds to:

$$m = \left(\frac{\ln(aw)}{1/T}\right) = -R \cdot \Delta H_{sorp} \qquad \text{Eq. 3}$$

afterwards $\Delta H_{sorp}$ can be calculated by Eq. 4:

$$\Delta H_{sorp} = -m * R\ [\mathrm{kJ/mol}] \qquad \text{Eq. 4}$$

## 4. Experiments & Results

The influence of temperature on moisture adsorption was investigated using dynamic vapor sorption analysis. The proUmid SPS devices can cover a temperature range from 5 °C to 60 °C, making them ideally suited for investigating the temperature-dependent sorption behavior.

The experiment involves a simple preparation procedure: First, the device is set to the desired temperature. Then, the samples are placed into the previously tared sample dishes and weighed. Here, the multisample option allows up to 23 samples to be measured simultaneously. Finally, the measurement is started, and the set moisture/temperature profile runs fully automatically.

The sorption behavior was measured at various temperatures, and the relative humidity (RH) profile was adjusted from 0 to 90 % RH for both sorption and desorption.

The Heat-of-Sorption was investigated for different samples ranging from food powders to building materials. The obtained data were evaluated as explained in Chapter 3.

Fig. 2 shows the sorption isotherms of cement powder from 0 to 90 % RH at 20 and 25 °C. The sorption data were fitted using the GAB model. The fitting parameters obtained are summarized in Table 1.

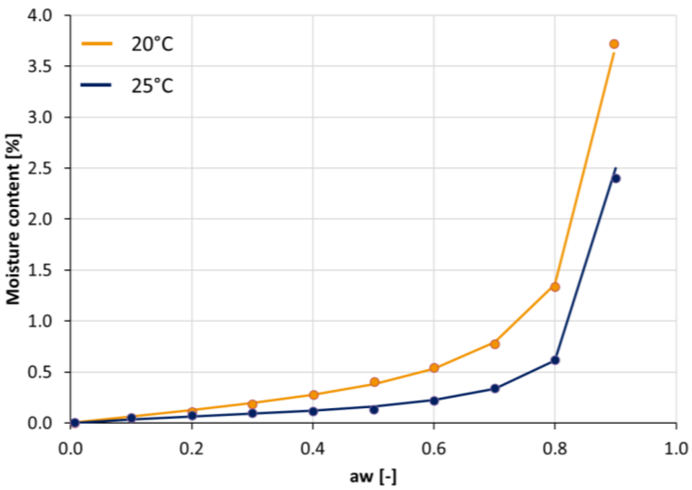

Fig. 2: Sorption isotherms of cement powder at 20 °C and 25 °C in the RH range from 0-90 %. Dots represent the experimental data; the lines represent the curve fitting by the GAB model.

Table 1: GAB parameter: Sorption of cement powder

| GAB parameter | 20 °C | 25 °C |
|---|---|---|
| m0 | 0.243 | 0.091 |
| C | 2.732 | 4.485 |
| k | 1.042 | 1.071 |
| $R^2$ | 1.000 | 1.000 |

As expected from theory, the 25 °C curve lies below the 20 °C curve throughout the complete sorption range.

From these data, the Heat-of-Sorption was calculated using Clausius Clapeyron's equation. Fig. 3 shows their dependence on moisture content, with values ranging from 110 kJ/mol to 5 kJ/mol.

In accordance with literature, this indicates that the binding strength, and consequently the heat release, decreases with increasing moisture loading. [1,10]

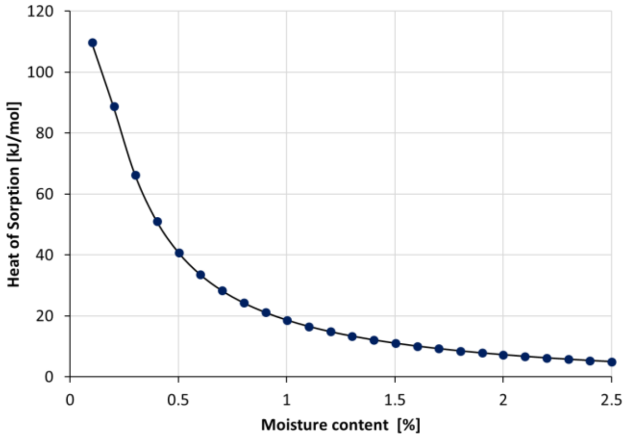

Fig. 3: Heat-of-Sorption dependent on the moisture content of cement powder.

Fig. 4 shows the moisture sorption behavior of potato starch at relative humidities between 0 and 90 % and temperatures within the range of 25 to 60°C. As in previous results, the amount of moisture adsorbed decreases with higher temperature.

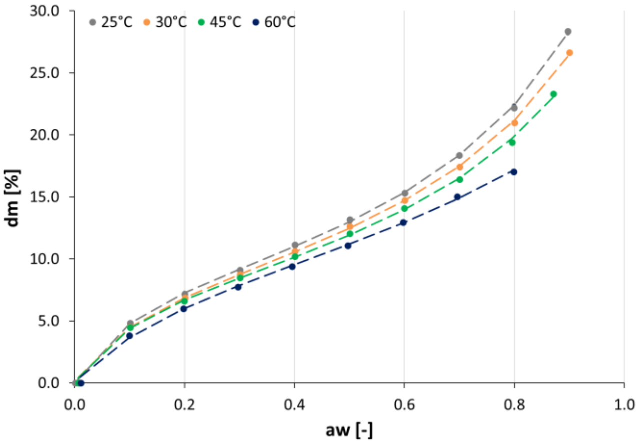

Fig. 4: Sorption isotherm of potato starch at 25 °C, 30 °C, 45 °C and 60 °C.

The sorption curves were fitted using the GAB equation to describe the relationship between relative humidity and moisture content of the material. The fitting parameters are summarized in Table 2.

Table 2: GAB parameter: Sorption of potato starch powder

| GAB parameter | 25 °C | 30 °C | 45 °C | 60 °C |
|---|---|---|---|---|
| m0 | 9.163 | 9.06 | 8.69 | 10.07 |
| C | 9.537 | 9.017 | 10.27 | 10.699 |
| k | 0.559 | 0.539 | 0.548 | 0.377 |
| R2 | 1.000 | 0.999 | 0.999 | 0.999 |

As shown in Table 2, the monomolecular moisture content (m0) decreases from 25 °C to 45 °C because less moisture is bound to the material. A higher value was determined at 60 °C, which could be explained by temperature-related changes in the material that affect the starch powder's moisture adsorption capacity.

The GAB fit was used to calculate the Heat-of-Sorption dependent on moisture. Results are shown in Fig. 5.

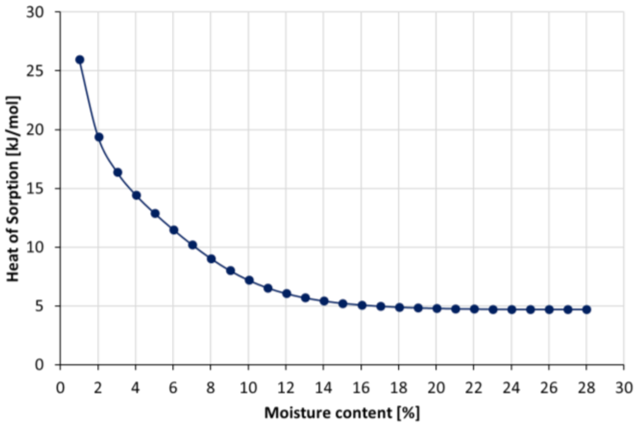

Fig. 5: Heat-of-Sorption dependent on moisture content for potato starch

Compared to cement powder, the Heat-of-Sorption is lower for potato starch at low moisture contents. This can be explained by differences in the sorption mechanism. Since moist cement pastes were used in the experiment, hydration processes occurred, involving chemical reactions between active cement groups and water [11]. This chemisorption releases more energy. In contrast, starch polymers mainly bind water by physisorption, resulting in lower binding strengths [12].

As a further example, Fig. 6 shows the Heat-of-Sorption compared to the Heat-of-Desorption of gluten, a protein component of various cereals.

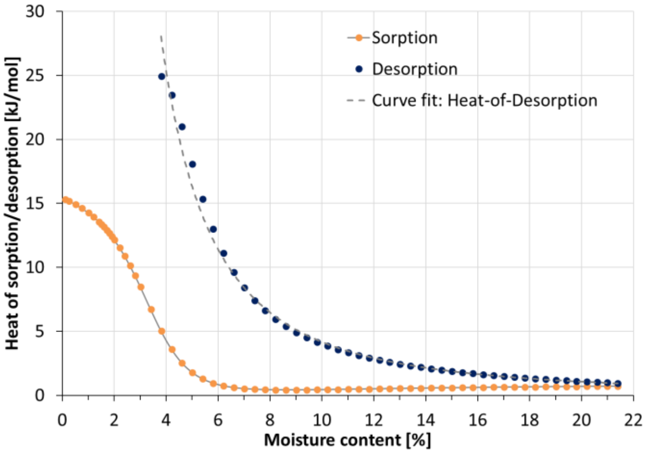

Fig. 6: Heat-of-Sorption and Heat-of-Desorption of gluten

The Heat-of-Desorption is an important parameter for estimating the energy requirements of the drying process. For these types of applications, the desorption isotherm should be used in the calculation. Fig. 6 shows that the energy required for sorption and desorption differs. This difference can be explained by the unique properties of gluten, which is known for its water-binding and water-retaining capacity. This quality is crucial for the baking properties of flour.

This strong water binding requires more energy to remove moisture, resulting in a higher Heat-of-Desorption than the exothermic release of energy during sorption.

## Calculation of the energy required for drying

Since the Heat-of-Desorption depends on the moisture content of the material, this relationship must first be determined. For example, as shown in Fig. 6, a power-law fit (Eq. 5) was used to mathematically describe the desorption isotherm of gluten.

$$\Delta H_{Desorp}(x) = 356.94 \cdot x^{-1.937} \qquad \text{Eq. 5}$$

x: Water content; $\Delta \mathrm{H}_{\mathrm{Desorp}}$: Sorption enthalpy [kJ/mol]

Assuming a drying process of 1 kg gluten from 21 % to 4 % product moisture, the required energy can be calculated as shown below.

### Given parameters:

| | |
|---|---|
| Product moisture at start (kg/kg): | 0.21 |
| Target moisture (kg/kg): | 0.04 |
| Mol mass water (g/mol): | 18.015 |
| Evaporation enthalpy (kJ/mol): | 40.7 |

### Calculation of the sorption energy:

$$\mathrm{Q_{Desorp}} = \frac{1}{18{,}015} \cdot \int_{0.04}^{0.21} 356.94 \cdot \mathrm{x}^{-1.937}\,\mathrm{dx}$$

$$\int x^{-1.937} dx = \frac{\mathrm{x}^{(-1.937+1)}}{-0.937} = \frac{\mathrm{x}^{(-0.937)}}{-0.937}$$

$$\mathrm{Q_{Desorp}} = \frac{356.94}{18{,}015 \cdot (-0.937)} \cdot \left(\mathrm{x}^{(-0.937)}\Big|_{0.04}^{0.21}\right) \mathrm{Q_{Desorp}}$$

$$= \frac{356.94}{-16.878} \cdot (4.69 - 21.32)$$

$$= -21.14 \cdot (-16.63)$$

$$= \mathbf{351.7\ kJ}$$

### Calculation of the evaporation energy:

Moisture to remove:

$$\mathrm{m_{H_2O,\,remove}} = 0.21 - 0.04 = 170\ \mathrm{g}$$

$$\mathrm{n} = \frac{170}{18.015} = 9.44\ {}^{\mathrm{g}}/_{\mathrm{mol}}$$

$$\mathrm{Q_{evap.}} = 9.44 \cdot 40.7 = \mathbf{384.5\ kJ}$$

### Total energy requirement:

$$Q_{total} = Q_{Desorp.} + Q_{evap.} = 351.7 + 384.5 = \boldsymbol{736\ kJ}$$

## 5. Conclusions

The adsorption of water vapor is a complex process that depends on various factors. These factors include the powder's physical properties, such as particle size, pore size, and pore size distribution, as well as its surface properties, such as the presence of functional groups with water-binding affinity. Temperature is another important factor. As explained above and demonstrated by the results, higher temperatures generally lead to a lower $a_w$ value and lower moisture adsorption by the powder. [13,14]

However, exceptions may occur if the powder experiences temperature-related structural changes or if its soluble components liquefy. This phenomenon is particularly evident in materials that contain sugar or salt. [13,14]

Due to this correlation, investigating the temperature-dependent sorption behavior of materials is useful for their detailed characterization. Additionally, determining the sorption behavior at different temperatures allows for the identification of energetic processes.

In industrial drying processes, for instance, this parameter allows for the calculation of necessary energy consumption and the optimization of the drying process in terms of energy and product quality.

Another important aspect in this context is the storage stability of products, as an increase in temperature due to exothermic adsorption processes negatively affects the product quality.

Within the scope of this study, a method for determining the Heat-of-Sorption using dynamic water vapor sorption was demonstrated for various materials. Additionally, the energy requirement for a drying process was calculated as an example.

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