

## **IDENTIFYING PHYSICAL AND CHEMICAL PHENOMENA WITH GRAVIMETRIC WATER SORPTION ANALYSIS**

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### **Abstract**

The technique of gravimetric water sorption was used to identify samples which appear to interact with water as a chemical reagent. These were distinguished from those which take up moisture purely physically. In the latter case water acts as a probe which aids the characterization of the sample surfaces and their hydration states. After identifying the features in the sorption behavior which allow this distinction to be made, we drew the following conclusions:

1. Few if any of the samples investigated interact chemically with water.
2. The demonstration of chemical interaction of a sample with water and other vapors by sorption studies alone is not always straightforward.
3. Chemical interaction of water with samples appears to be relatively rare. The major problems associated with high humidity in the production, storage and handling of samples therefore seem to be due to physical rather than chemical degradation.

**Keywords:** chemical adsorption, isotherm, physical adsorption, water sorption analysis

### **Introduction**

Water sorption analysis has been used for many years to investigate physical as well as chemical phenomena of solid and liquid samples. Water is thereby used as a physical probe, as a chemical reagent, as a solvent or as catalyst. This is possible because of the unusual combination of properties of water. The sorption of water vapor onto the surfaces of solid samples is therefore an important process.

### **Experimental**

The CISorp Automatic Water Sorption Analyser [1] was used to study a variety of solid samples. The equipment works gravimetrically, i.e. by continuous weighing of the samples while the relative humidity is maintained or changed automatically. The equipment has two balances which are exposed to the same conditions. This facilitates comparative

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studies. In an experimental sequence the humidity can be set to change in an infinite number of steps between 0 and 100% and the experimental temperature to values between 5 and 65°C. This allows the determination of water sorption profiles as a function of time (kinetic studies), of the relative humidity (isotherms), and of temperature (temperature tests) [2].

## Theory

A number of processes need to be considered in the interaction of vapors with solid or liquid samples.

1. In the first instance, vapor molecules interact with the surfaces of solid or liquid samples purely physically through weak forces such as van der Waals or hydrogen bonding. The process is comparable with the condensation of vapors observed in everyday life. It occurs to a greater or lesser extent in all systems and is usually reversible.

2. In some cases vapors and samples react with each other chemically. In these instances, chemical bonds are broken and/or formed. The energy changes involved are therefore at least one order of magnitude greater than those involved in physical adsorption.

3. In the special case of water, this is also important as a hydrating agent. This means that many ionic compounds such as salts have different hydration states, i.e. different numbers of water molecules associated with them, depending on the availability of the vapor. The interactions are physical but strong, i.e. electrostatic.

4. Adsorbed vapors such as water may act as solvents. In this capacity, they can be chemical reagents such as water in hydrolysis. They may also be catalysts and have a plasticizing effect by facilitating rearrangements such as crystal (trans-)formations.

These changes may be physical or chemical, depending on the types of bonds which are affected.

### *Summary characteristics of physical adsorption*

The phenomenon of physical adsorption can be summarized by the following characteristics:

- The forces between the solid (adsorbent) surfaces and the vapor molecules (adsorbate) are weak, i.e. van der Waals, hydrogen bonds etc., with maximum energy changes in the region of 40 kJ mol<sup>-1</sup>.
- Bond lengths are those of physical interactions, i.e. longer than chemical bonds.
- The process is always exothermic and therefore enhanced at lower temperatures.
- The process usually releases free energy despite a decrease in the entropy.
- There is no energy barrier, but rates may be limited through diffusion effects.
- The process is usually reversible by raising the temperature and/or lowering the vapor pressure, although hysteresis (a discrepancy between the ad- and desorption branches) may arise.

- Several vapor layers can form on the surfaces. The process can therefore be compared with the condensation of the vapor and provide valuable information about the sample surfaces.

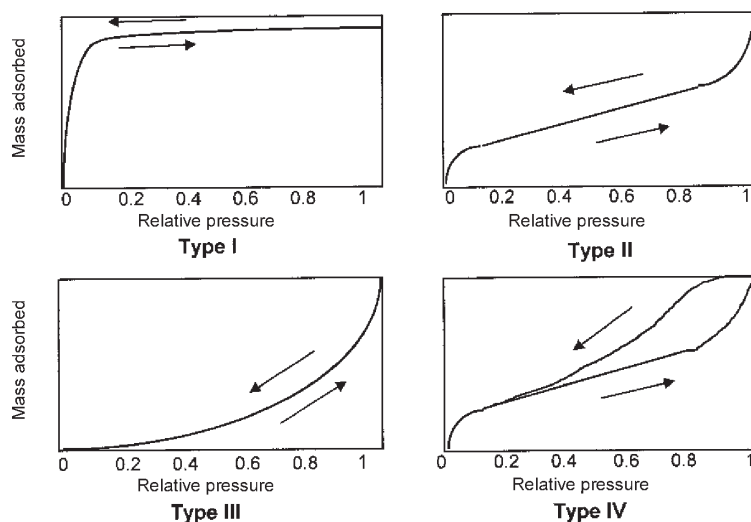
#### *Summary characteristics of chemical adsorption*

The phenomenon of chemical adsorption can be summarized by the following characteristics:

- The forces are those involved in chemical reactions and are therefore much greater than those in physical adsorption. Bond lengths are much shorter.
- Chemical adsorption is always preceded by physical adsorption.
- The process may be exo- or endothermic. Usually there is a decrease in the entropy.
- Rates may be limited by energy barriers, as well as by diffusion effects.
- The process is usually irreversible, depending on the equilibrium position.
- Chemical interactions can occur only in a single surface layer. However, physical vapor sorption can take place on the new product(s).

#### *Case 1: reversible water sorption*

As mentioned earlier, reversible adsorption is indicative of relatively weak, physical processes which can be used for the characterization of sample surfaces. As long ago as 1940, Brunauer, Deming, Deming and Teller classified reversible physical adsorption isotherms according to their shapes (Fig. 1) [3]. This classification is still widely used today.



**Fig. 1** Some types of isotherms in the BDDT classification

## Type II/IV isotherms

Figure 2 shows a typical Type IV water sorption isotherm. Its interpretation is that the surfaces of this sample are more polar than water molecules and therefore show increased water uptake at low relative humidities (0 to 10%). Once a single (mono-)layer of water has formed, additional adsorption increasingly resembles the condensation of water. At high humidities, i.e. above 70%, adsorption is enhanced due to the presence of tiny surface pores (mesopores, pore diameters 2 to 50 nm [4]). These attract water molecules on more than one side, i.e. by 'capillary condensation' [5]. This leads to hysteresis in this humidity region caused by the reluctant release of the adsorbed water. (The hysteresis at lower humidities is an experimental effect caused by inadequate equilibration of the sample [2].)

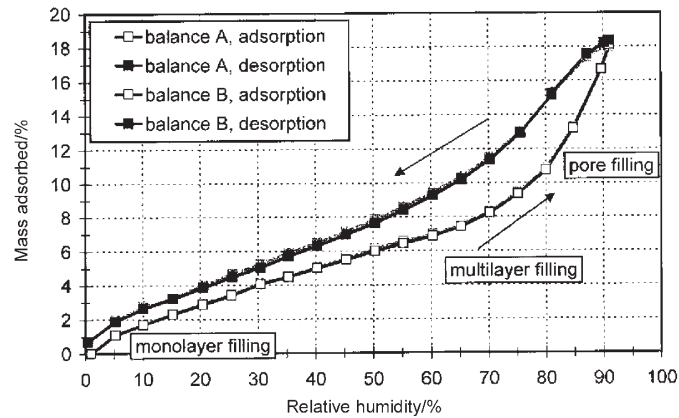


Fig. 2 Type IV water sorption isotherms of powdered sample

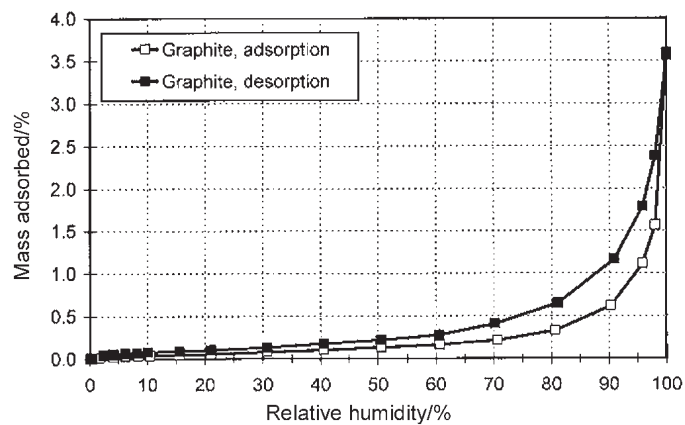


Fig. 3 Type III water sorption isotherms of graphite powder

This type of isotherm can be used for the determination of a host of physical quantities about the sample such as the 'water surface', i.e. the area with a high affinity for water and the volume and size distribution of pores accessible to water. If very accurate data at low RH are recorded or isotherms are measured at different temperatures, the enthalpy and entropy changes due to water sorption can also be determined [2, 5].

#### Type III/V isotherms

Graphite (Fig. 3) gives a Type III isotherm. The reduced water sorption onto the dry surfaces confirms the non-polar nature and thereby low affinity of the sample for water. The lack of hysteresis indicates that the sample is largely non-porous. The same type of qualitative but less quantitative information about the sample surfaces can therefore be gained from this type of isotherm.

#### Type I isotherms

A Type I isotherm like that of zeolite NaY (Fig. 4) is typical of microporous samples (pore diameters less than 2 nm [4]). Such small pores can accommodate only a few water layers which are all strongly bound. Once the pores are filled the effective surface area and thereby the amount of water sorption is greatly reduced. The point of inflection in this type of isotherm therefore corresponds to micropore filling and can be used to determine the micropore volume. This type of isotherm is typical of many heterogeneous catalysts such as zeolites.

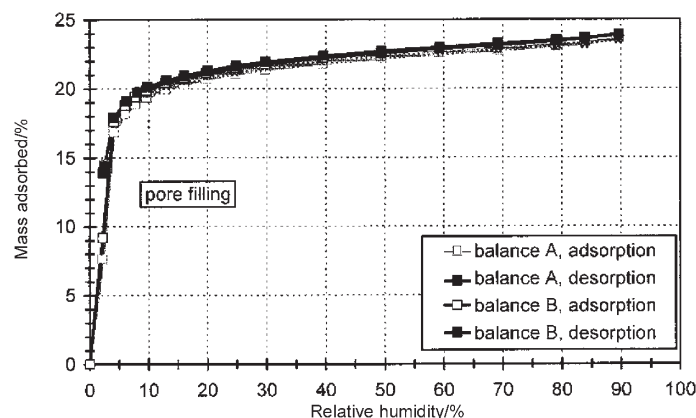


Fig. 4 Type I water sorption isotherms of zeolite NaY

#### Case 2: irreversible water sorption

There are many situations where water is taken up irreversibly by samples. However, this does by no means imply that the interaction is chemical.

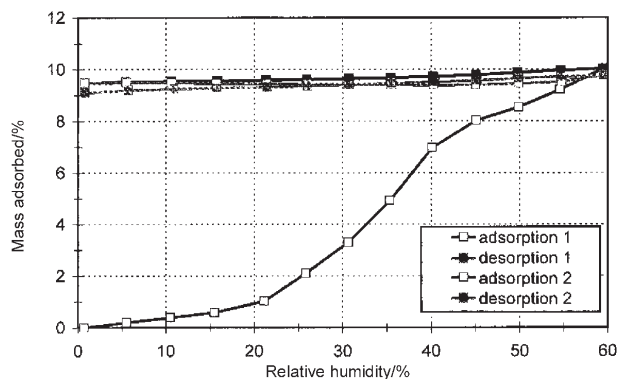


Fig. 5 Irreversible water sorption isotherms of a freeze-dried powder

#### Specially prepared samples

Freezing, milling and other methods of drying remove moisture from samples with great efficiency. Exposing such samples even to relatively moderate RH rehydrates them irreversibly (Fig. 5). The water removed and re-adsorbed by such methods is usually physically bound although it may be held quite strongly.

#### Changes in hydration states

Hysteresis, i.e. a discrepancy between the ad- and desorption branches, often has origins other than sample porosity. A common cause is the changes in the hydration states of salts such as in copper sulphate (Fig. 6). This salt changes from the mono- to the trihydrate near 25% RH and to the pentahydrate near 42% relative humidity. The changes are reversed only once the humidity is reduced to the lower limit for that hydration state. Since these changes do not involve chemical bonds, they should be considered as physical.

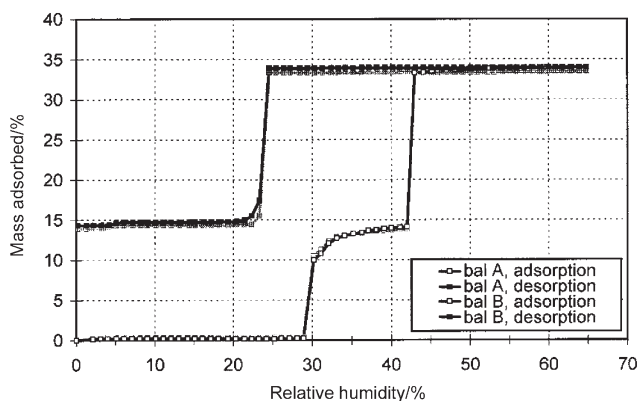


Fig. 6 Water sorption isotherms of copper sulphate

### Crystal (trans)formations

Many compounds such as sugars, salts and quartz are crystalline in form. Depending on their chemistry they may be atomic, molecular or ionic. Of the above, atomic crystals such as quartz, are rarely affected by water. Many molecular crystals such as sugars, by contrast, readily dissolve and recrystallize when the humidity is changed. Although the process is reversible, dissolution and crystallization follow different paths in terms of the rate and humidity levels (Fig. 7). In a similar way, crystalline compounds such as sucrose which have been made amorphous, readily crystallize in the presence of moderate amounts of water vapor with an accompanying expulsion of some water (Fig. 8). These processes are purely physical since they affect only the physical bonds between molecules and not the chemical bonds within them. The bonds in ionic crystals such as those of salts are strong and chemical. However, in polar solvents such as water they are easily broken. In a similar way to molecular crys-

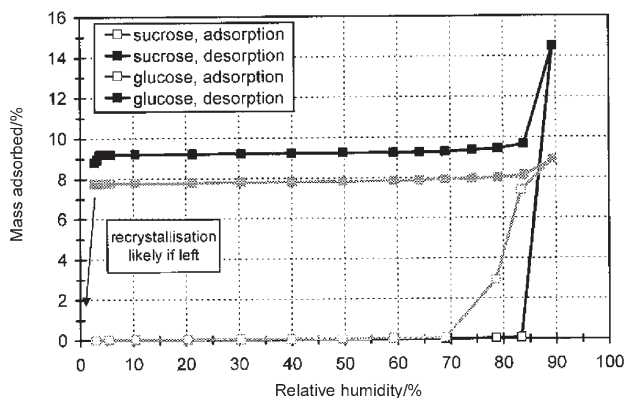


Fig. 7 Water sorption isotherms of sugars

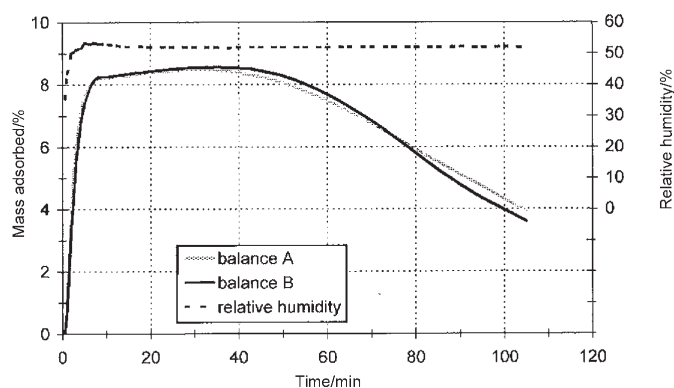


Fig. 8 Water sorption kinetics of amorphous sucrose

tals, this process is reversible along different paths (Fig. 6). Ionic dissolution can be considered as a chemical reaction since the crystals dissolve into their constituent ions. Chemical bonds are therefore broken and reformed. The process can be used for the formation of new (ionic) compounds if several dissolved materials are present. In this situation the solvent acts as a catalyst, reducing the energy required to break chemical bonds without itself being consumed or changed.

### Case 3: complex compounds

In reality it is not usually so easy to identify the physical or chemical processes which underlie the vapor sorption profiles of samples. Many real samples such as processed foods or pharmaceutical compounds have several constituents which undergo different processes and may interact with each other.

According to Ahlneck and Zografis [6], even low levels of adsorbed water can have a plasticizing effect on crystals, allowing the molecules or ions within the struc-

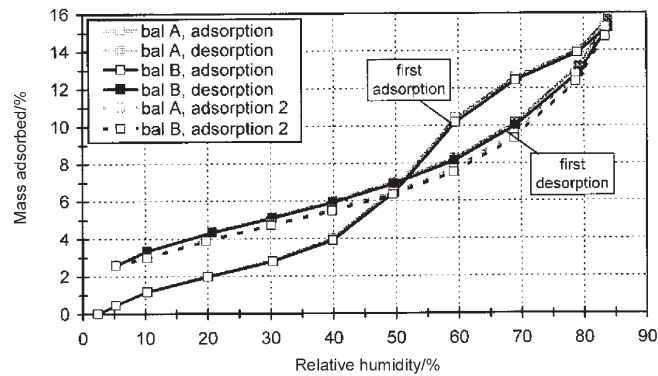


Fig. 9 Water sorption isotherms of milk powder

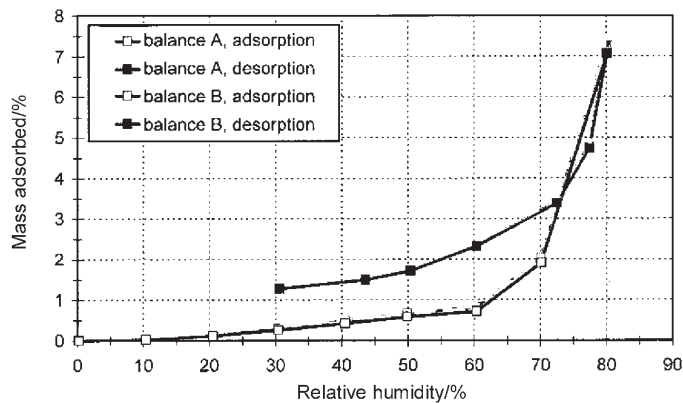


Fig. 10 Water sorption isotherms of chocolate flakes



ture to become mobilized and rearrange themselves. This is important when considering the effects of humidity on mixed compounds such as milk powder [7]. Here the water released during crystallization may cause local increases in the humidity which may affect nearby molecules (Fig. 9). Whether such effects are physical or chemical depends on the nature of the components of the substance. Similarly, the sugar contained in processed foods such as in chocolate has a different physical structure from that of pure sugar. When such samples are exposed to critical levels of humidity for a sufficiently long time, the sugar is able to recrystallize. Such samples therefore show irreversible water sorption profiles (Fig. 10).

## Conclusions

The above examples show that water as an adsorbate can interact with solid and liquid samples in a multitude of ways. Some interactions are easily identifiable as weak and physical without permanent effects on the samples. Others are also physical but their effects are less easily reversed. In a third case, the sample may interact with the adsorbate as a solvent, as a catalyst, or even as a chemical reagent.

Without a good prior knowledge of the sample, it is not always possible to understand the interactions between the adsorbent and adsorbate from the sorption profile. However, for many practical applications such as the determination of suitable storage conditions, an empirical understanding of these interactions is often all that is required.

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