

PART 1

## Water and Other Food Constituents

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Water is the most abundant constituent of the majority of foods. It therefore plays a crucial role in the physicochemical characteristics and properties of the plant and animal foods we eat. These characteristics can be desired due to their contribution to food quality (the texture of fruit, vegetables and meat, which depends, among other things, on cell turgidity as well as on specific and complex interactions between water and other constituents). However, they can also contribute to food spoilage through biochemical and microbiological processes. As a result, several food preservation methods are based, at least partially, on lowering the water activity ( $a_w$ ) or the water availability.

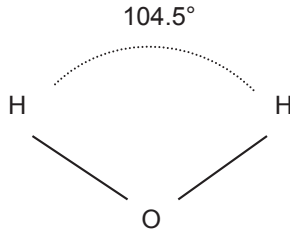
## 1.1. Structure and state of water

The water molecule, composed of two hydrogen atoms and one oxygen atom ( $H_2O$ ), can exist, like many substances, in three different states: solid, liquid or gas.

In the liquid and vapor state, the water molecule is a polar monomer (see Figure 1.1).

In the solid state (i.e. ice), water molecules are linked by hydrogen bonds and form a crystalline polymer in which each monomer molecule is connected to four other molecules by hydrogen bonds. The distance between two oxygen atoms is 0.276 nm. At temperatures below  $-173^\circ C$ , all hydrogen

atoms are involved in hydrogen bonds, whereas at 0°C only around 50% are involved, and at 100°C only a small percentage are involved.



**Figure 1.1.** *Water molecule*

Certain water properties can be attributed to these intermolecular bonds, in particular the boiling point, melting point, latent heat of fusion, latent heat of vaporization, specific heat, surface tension and the dielectric constant. However, water in a liquid state behaves like a monomer in terms of viscosity and the diffusion coefficient (Tables 1.1 and 1.2).

Properties	Unit	Value
Molar mass	$\text{g mol}^{-1}$	18.01528
Melting point (at 101,325 Pa)	°C	0.00
Boiling point (at 101,325 Pa)	°C	100.00
Maximum density	$\text{kg m}^{-3}$	999.95
Temperature of maximum density	°C	4.00
Triple-point temperature	°C	0.01
Triple-point density (liquid)	$\text{kg m}^{-3}$	999.78
Triple-point density (gas)	$10^{-3} \text{ kg m}^{-3}$	4.88
Latent heat of sublimation at the triple point	$10^3 \text{ J kg}^{-1}$	2800
Critical temperature	°C	373.99
Critical pressure	MPa	22.064
Critical density	$\text{kg m}^{-3}$	322
Specific volume at the critical point	$10^{-3} \text{ m}^3 \text{ kg}^{-1}$	3.11
Latent heat of freezing at 0°C	$10^3 \text{ J kg}^{-1}$	335

**Table 1.1** *Properties of water*

Different theoretical models have been proposed to explain the liquid and solid state behavior of water. Monomers as well as higher-energy molecules exist in a static equilibrium: each molecule is involved in one to four hydrogen bonds; the latter can form short-lived labile clusters.

Properties	Units	Frozen water		Liquid water						Water vapor	
Temperature	(°C)	-20	0	0	20	40	60	80	100	100	200
Density	kg m <sup>-3</sup>	919.3	916.8	999.8	998.2	992.2	983.2	971.8	958.4	0.589	0.452
Viscosity	10 <sup>-6</sup> Pa s	-	-	1,793	1,002	653	466	354	281	12.5	16.4
Surface tension	10 <sup>-3</sup> N m <sup>-1</sup>	-	-	75.64	72.75	69.60	66.24	62.67	58.91	-	-
Vapor pressure	(Pa)	103.4	611.3	611.3	2,338.8	7,381.4	19,932	47,373	101,325	-	-
Specific heat C <sub>p</sub>	J.kg <sup>-1</sup> k <sup>-1</sup>	1,954	2,101	4,217	4,182	4,178	4,184	4,196	4,216	2,041	1,960
Energy of vaporization	10 <sup>3</sup> J kg <sup>-1</sup>	-	-	2,494	2,448	2,402	2,357	2,309	2,258	-	-
Thermal conductivity	W m <sup>-1</sup> °K <sup>-1</sup>	2.43	2.22	0.561	0.598	0.630	0.654	0.670	0.679	0.0248	0.0391
Diffusivity in the air	10 <sup>-6</sup> m <sup>2</sup> s <sup>-1</sup>	-	-	21.8	24.6	27.5	30.5	33.7	-	-	-
Thermal diffusivity at 10 <sup>5</sup> Pa	10 <sup>-6</sup> m <sup>2</sup> s <sup>-1</sup>	-	-	0.135	0.143	0.151	0.161	0.164	0.170	19.6	32.6

**Table 1.2.** *Properties of water*

The structure of water is largely influenced by its organic and inorganic environment:

- electrolytes such as Na<sup>+</sup>, K<sup>+</sup> and Cl<sup>-</sup> are highly hydrated in solution, and lower the number of hydrogen bonds between water molecules, whereas hydrocarbon chains and non-polar groups of protein side-chains tend to increase it;

– substances in solution (carbohydrates and amino acids), which can themselves form hydrogen bonds, can modify the bonds between water molecules depending on their geometric compatibility with the existing network, e.g. urea has a strong effect whereas ammonia has none;

– substances with several different functional groups (e.g. amino acids, proteins, fatty acids and carbohydrates) affect the structure of water.

The effect of the environment is very pronounced in highly concentrated solutions and weakly hydrated systems. Water can form crystalline hydrates (clathrates) above 0°C with some gases (e.g. freon and propane). The formation of these hydrates can be used in the concentration or demineralization of aqueous solutions. Table 1.3 shows the different binding energies of water.

Type of bond	Binding energy (kJ mol <sup>-1</sup> )
Covalent bond	460
Hydrogen bond (liquid water)	< 20
Hydrogen bond (frozen water)	23
Hydration of polar group (monolayer)	4–6
Hydration of polar group (multilayer)	1–3
Van der Waals bond	0.5
Water retained by capillary forces	0.3

**Table 1.3.** *Binding energy of water [FAI 03]*

Water also affects properties such as the structure, diffusion and reactivity of substances in solution. For example, the role of water in the structure and functional properties of macromolecular compounds such as proteins is known [LEM 02]. The main functions of water in food are shown in Table 1.4.

Role of water	Example
Solvent	Molecule dissolution
Reaction medium	Enzymatic reactions
Mobility of reagents	Maillard reactions
Reagent	Lipid hydrolysis
Anti-oxidant	Hydrogen bond with peroxides blocking the oxidation of lipids, for low $a_w$
Pro-oxidant	<ul style="list-style-type: none"> <li>– Swelling of proteins and accessibility of oxidizable sites</li> <li>– Sources of free radicals in irradiated foods</li> </ul>
Structural role	<ul style="list-style-type: none"> <li>– Formation of hydrogen bonds between texturing molecules</li> <li>– Acts on lipid/protein bonds in bakery products</li> <li>– Acts on the conformation and interactions between gelling agents and proteins</li> </ul>

**Table 1.4.** *Functions of water in food [DUC 76, FAI 03]*

## 1.2. Properties of water

Among the physical and physicochemical properties of water, some greatly influence phase transitions as well as mass and heat transfers. Examples include specific heat, latent heat of fusion, latent heat of vaporization, thermal conductivity and viscosity. They determine the design and control of heat treatment (sterilization, cooking, etc.), concentration, drying or freezing processes. Others relate to the solvent properties of water: dielectric constant, surface tension or dipole moment. Water is, in fact, the dilution medium for many chemical species that can diffuse and react with each other. In addition to this, water can diffuse and participate in various reactions, such as hydrolysis. The introduction of different chemical species in solution or colloidal suspension in water also creates the so-called colligative properties, which depend on the number of molecules present. This is the case, for example, with lowering the freezing point and surface tension, increasing the boiling point and viscosity, and establishing osmotic pressure gradients through semi-permeable membranes.

The fact that the water present in food is more or less in interaction with the other constituents gives rise to concepts of “free water” and “bound water”. Various observations show that the so-called bound water can itself be bound to varying degrees and the state of water is just as important for the stability of a foodstuff as the total water content. This concept of “bound water” is also underpinned by the knowledge of the dipolar nature of water and its possible interactions with different chemical groups of other constituents.

In order to determine to what extent the concept of “bound water” is a physical reality, two categories of properties can be used to characterize this potential binding state: molecular mobility and thermodynamic properties. Of these, water activity ( $a_w$ ) has attracted the most attention in food science and technology. The ability of water to freeze has also long been considered an indication of the binding state of water. These concepts are now combined with dynamic data (glass transition –  $T_g$ ) to establish the state diagram [SIM 02]. These three concepts ( $a_w$ ,  $T_g$  and the phase diagram) are explained hereafter.

### **1.2.1. Water activity ( $a_w$ )**

#### **1.2.1.1. Definition**

The  $a_w$  of a food product is characterized by the ratio of the partial vapor pressure in a food product ( $P_p$ ) and the saturated vapor pressure ( $P_w$ ) at the same temperature  $\theta$ :

$$a_w = \frac{P_p}{P_w} \quad [1.1]$$

The  $a_w$  is, therefore, a non-dimensional ratio and is thus a relative measure compared to a standard (pure water). Consequently, the  $a_w$  of pure water is equal to 1, with every other product having an  $a_w$  value below 1. The decrease in water activity can be explained by the fact that the solubilized chemical components partially mobilize the water and, therefore, decrease its capacity to vaporize; they also alter the chemical reactivity of water, which is exactly proportional to  $a_w$ .



The  $a_w$  of a food product should not be confused with its relative humidity ( $H_R$ ). The  $H_R$  is the ratio of the partial vapor pressure in air ( $P_a$ ) and the saturated vapor pressure ( $P_{sv}$ ) at the same temperature  $\theta$ :

$$H_R = \frac{P_a}{P_{sv}} \times 100 \quad [1.2]$$

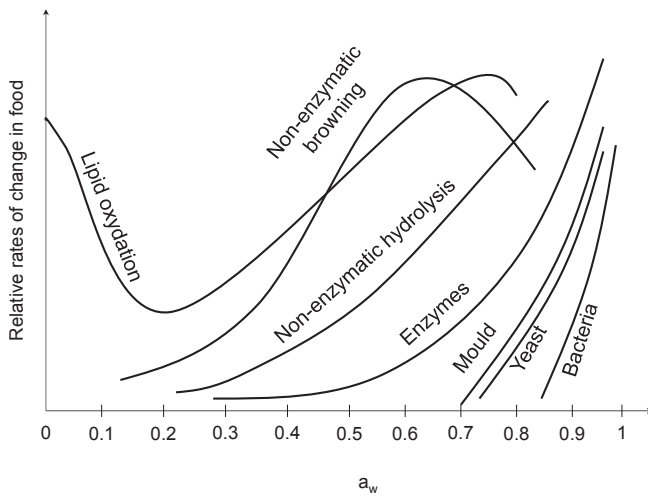
At equilibrium,  $P_p = P_a$  and  $P_w = P_{sv}$  for a given food product and at a given temperature  $\theta$ . The  $a_w$  or the  $H_R$  at equilibrium ( $H_{RE}$ ) of a food product is the  $H_R$  of an atmosphere in equilibrium with the product. In other words, the  $a_w$  of a solution or a food is equal to the relative partial pressure of water vapor of the solution or food in a confined atmosphere at equilibrium. Therefore,  $H_R$  at equilibrium and  $a_w$  are proportional physical quantities linked by the following equation:

$$H_{RE} = a_w \times 100 \quad [1.3]$$

Some authors believe that such a thermodynamic equilibrium is never reached in the case of food. The  $a_w$  values obtained from measurements on food should therefore not be considered as absolute.

The  $a_w$  of a food product accounts for the availability of water as a solvent or a reagent. As a result,  $a_w$  is crucial in estimating the stability of food during processing and storage. The relative rates of change in food as a function of  $a_w$  are clearly illustrated in Figure 1.2. For low  $a_w$  values ( $< 0.1$ ), the risk of lipid oxidation is very high. This negative correlation with  $a_w$  in this range can be explained by the fact that a monolayer of water molecules around the lipid fraction constitutes a resistance to oxygen transfer and, thus, a protective shell against lipid oxidation. For  $a_w$  values between 0.3 and 0.8, the reaction rates linked to non-enzymatic browning (maximum of 0.6–0.7  $a_w$ ), non-enzymatic hydrolysis and enzymatic activity gradually increase with  $a_w$ . There is very little microorganism growth when  $a_w$  is less than 0.6. Efstathiou *et al.* [EFS 02] estimated an optimum stability range for  $a_w$  values of between 0.2 and 0.3.

During freezing, the  $a_w$  of ice is calculated by using the vapor pressure value of subcooled water at the corresponding temperature as a reference [BLO 02]. It is equal to 1 at 0°C and decreases with temperature (see Table 1.5).



**Figure 1.2.** Relative rate of change in food as a function of  $a_w$

Temperature (°C)	Vapor pressure of pure liquid water (Pa)	Vapor pressure of ice (Pa)	$a_w = \frac{P_{\text{ice}}}{P_{\text{liquid water}}}$
0	610.48	610.48	1.000
-5	421.70	401.70	0.953
-10	286.51	259.98	0.907
-15	191.45	165.45	0.864
-20	125.72	103.46	0.823
-25	80.93	63.46	0.784
-30	51.06	38.13	0.747
-40	18.93	12.93	0.683
-50	6.40	4.00	0.625

**Table 1.5.** Vapor pressure of water and ice measured at different temperatures

As it can be assumed that the cryo-concentrated phase and the ice phase are in equilibrium,  $a_w$  is the same in both phases: it depends, therefore, on the temperature of the frozen product regardless of its nature. The  $a_w$  value is

not a very significant criterion for stabilization (even at temperatures below 0°C). If a product preserves better at a lower storage temperature, and therefore has a weak  $a_w$ , the shelf-life variability of various frozen products clearly shows that this parameter cannot be considered as the sole index of stability. Chemical stability is related more to the mobility of solutes and the diffusion of oxygen than the availability of water. Another interesting aspect about the  $a_w$  of a product is its link with the initial freezing temperature. At this temperature, there is an equilibrium between the  $a_w$  and the temperature of ice. This parameter should be considered in the development of complex products that combine a frozen phase with another low-humidity and, therefore, ice-free phase, such as ice cream in a wafer; the difference in their  $a_w$  is the cause of water migration, which is inevitable without a barrier between the two phases.

#### 1.2.1.2. Method

The methods for determining the  $a_w$  of food products involve placing the product in equilibrium with the atmosphere of a microchamber and then measuring the manometric or hygrometric characteristics of the air in equilibrium with the product [LAB 68, LAB 76, GAL 81].

$a_w$	Ideal molality	NaCl	CaCl <sub>2</sub>	Sucrose	Glycerol
0.995	0.280	0.150	0.101	0.272	0.277
0.990	0.566	0.300	0.215	0.534	0.554
0.980	1.13	0.607	0.418	1.03	1.11
0.960	2.31	1.20	0.87	1.92	2.21
0.940	3.54	1.77	1.08	2.72	3.32
0.920	4.83	2.31	1.34	3.48	4.44
0.900	6.17	2.83	1.58	4.11	5.57
0.850	9.80	4.03	2.12	5.98	8.47
0.800	13.90	5.15	2.58		11.50
0.750	18.90		3.00		14.80
0.700	23.8		3.40		18.3
0.650	30.0		3.80		22.0

**Table 1.6.** Molality (number of moles of solute per kg of solvent) of various solutes and corresponding  $a_w$  values at 25°C

	10°C	20°C	25°C	30°C	40°C	50°C	60°C	70°C	80°C
LiBr	0.07	0.07	0.06	0.06	0.06	0.05	0.05	0.05	0.05
NaOH		0.07	0.07	0.07	0.07	0.06	0.05		
KOH	0.12	0.09	0.08	0.07	0.06	0.06	0.05	0.05	
LiCl	0.13	0.11	0.11	0.11	0.11	0.10	0.10	0.10	0.10
LiI	0.21	0.19	0.18	0.17	0.15	0.12			
CH <sub>3</sub> COOK	0.23	0.23	0.22	0.22					
CaCl <sub>2</sub>		0.33	0.30	0.22	0.19	0.17			
MgCl <sub>2</sub>	0.34	0.33	0.33	0.32	0.32	0.31	0.29	0.28	0.26
NaI	0.42	0.39	0.38	0.36	0.33	0.29	0.26	0.24	0.23
K <sub>2</sub> CO <sub>3</sub>	0.43	0.43	0.43	0.43		0.41	0.39	0.37	0.35
Mg(NO <sub>3</sub> ) <sub>2</sub>	0.57	0.54	0.53	0.51	0.48	0.45			
SrCl <sub>2</sub>		0.73	0.71	0.69		0.57	0.52	0.46	0.41
NaNO <sub>3</sub>	0.78	0.75	0.74	0.73	0.71	0.69	0.67	0.65	0.63
NaCl	0.76	0.75	0.75	0.75	0.75	0.75	0.74	0.74	0.74
KCl	0.87	0.85	0.84	0.84	0.82	0.81	0.79	0.78	0.77
BaCl <sub>2</sub>	0.92	0.91	0.90	0.90	0.89	0.88	0.87	0.86	0.85
K <sub>2</sub> SO <sub>4</sub>	0.98	0.98	0.97	0.97	0.96	0.96	0.96	0.96	0.96
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	0.98	0.98	0.98	0.98					

**Table 1.7.** Saturated salt solutions used to determine sorption curves

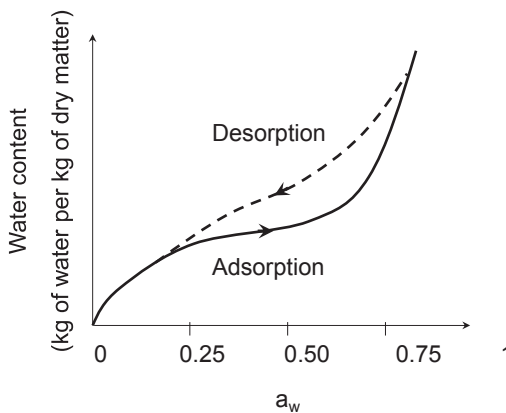
According to Dumoulin *et al.* [DUM 04], there are several methods for determining water activity, such as directly measuring the vapor pressure of water using a manometer or measuring the dew-point temperature or relative humidity of the air in equilibrium with the product using polyamide fiber or electrical hygrometers, for example.

Table 1.6 shows the ideal molality (number of moles of solute per kg of solvent) corresponding to  $a_w$  with experimental values for solutions of sodium chloride, calcium chloride, sucrose and glycerol. In reality, most solutes reduce  $a_w$  by more than would be expected theoretically. There are different reasons for this behavior: strong associations between water and solute molecules, almost complete dissociation of electrolytes and forces acting on the water structure.

Table 1.7 shows the  $a_w$  values of saturated salt solutions as a function of temperature:  $a_w$  is equal to 1 and 0 for pure water and saturated  $P_2O_5$ , respectively. The  $a_w$  values generally have an accuracy of  $\pm 0.02$  [BIM 02].

### 1.2.1.3. Sorption isotherm

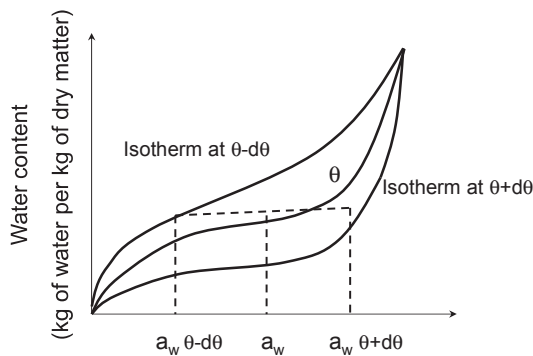
In addition to measuring  $a_w$ , it is also possible to establish a relationship between  $a_w$  and the water content of a product (kg of water per kg of dry matter) at a given temperature  $\theta$ . This relationship is represented by a sorption isotherm (adsorption or desorption) in the shape of a sigmoidal curve (Figure 1.3). Sorption isotherms reflect the adsorption capacity of water as well as the water retention capacity of the product. This information is very important for the food technology sector.



**Figure 1.3.** Water adsorption and desorption isotherm

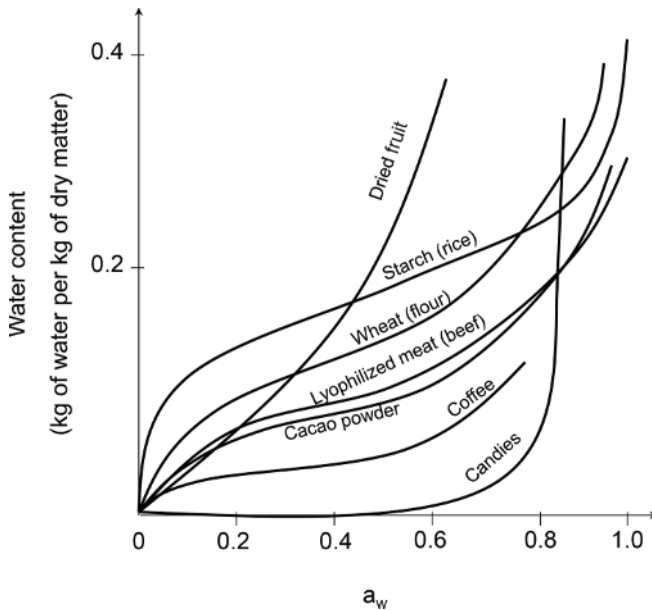
Measuring these curves generally involves placing a product sample in an atmosphere of known  $H_R$  (Table 1.7) until equilibrium has been reached and then measuring the water content of the sample by weight. Depending on whether a high or low moisture product is used, a desorption or an adsorption isotherm is obtained, respectively. These are not superimposable. The gap between the two curves is referred to as hysteresis: for a product with the same water content, equilibrium is obtained during desorption, at each point, at a lower  $a_w$  value than during adsorption. Hysteresis occurs mainly in the intermediate regions of the isotherms where water is only “weakly bound”. It is linked to water condensation in the pores of the product. It also corresponds to the relationship, defined by the Kelvin equation, between the partial vapor pressure and the contact angle (which depends on the surface tension) or the pore diameter. The liquid–solid contact angle is greater when a liquid wets a dry surface (adsorption) than when it evaporates from a wet surface (desorption). The supersaturation phenomenon of sugars in solution may also partly explain the hysteresis observed in fruit and vegetables. Water activity drops rapidly during dehydration because sugars do not crystallize but form a supersaturated solution. In contrast, sugars only dissolve above a certain water content during rewetting.

Sorption isotherms vary with temperature (Figure 1.4). In theory,  $a_w$  does not depend on the temperature but solely on the composition of the solution. In reality, for most products and at a constant water content,  $a_w$  increases with temperature, but with a reverse reaction for products high in fat or soluble sugars [BIM 02].



**Figure 1.4.** Influence of temperature on the water adsorption isotherm

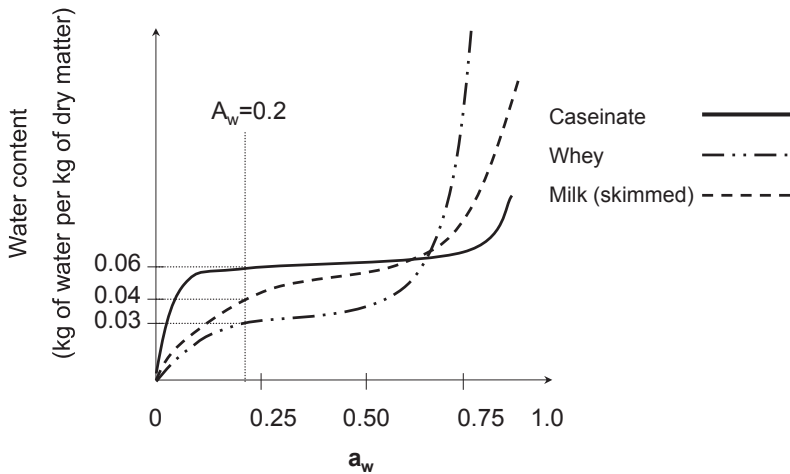
Sorption isotherms also vary from one food to another (Figure 1.5). They are the result of the behavior of various chemical constituents of food with water. Proteins and starches retain more water in the lower region of the isotherms than fats and crystalline substances (e.g. sugar). Dried fruit high in sugar is particularly hygroscopic, but only above a certain  $H_R$ .



**Figure 1.5.** Water adsorption isotherm of various foods

The physical states (i.e. amorphous, intermediate or crystalline) of the matrix influence water retention. This physical state largely depends on the type of technological process, and the manner in which these operations are carried out can cause variations in the isotherms of dried products. Particle size also influences water retention.

Using the theoretical sorption isotherms given in Figure 1.6, it is possible to determine the ideal water content for the optimum preservation of a given powder. For an  $a_w$  of 0.2, the water content would be 4% for milk powder (maximum regulatory requirement), between 2 and 3% for whey powders and 6% for caseinate powders (maximum regulatory requirement).



**Figure 1.6.** *Theoretical water adsorption isotherm for milk powders*

Sigmoidal sorption curves can be divided into three sections:

- The first section ( $a_w$  from 0 to 0.2) corresponds to the sorption of a monolayer of water molecules with strong hydrogen bonds (between 4 and 60 KJ mol<sup>-1</sup>). These water molecules are bound to the polar groups of certain compounds, mainly NH<sub>3</sub><sup>+</sup> and COO<sup>-</sup> groups of proteins and OH groups of starches; this section also includes water of crystallization of salts and sugars (e.g. lactose). These water molecules are, therefore, very strongly bound, which means they are quite difficult to remove by dehydration and cannot undergo freezing.

- The second section ( $a_w$  from 0.2 to 0.6), the linear portion of the curve, corresponds to the additional water layers or multilayers with weaker hydrogen bonds (between 1 and 3 KJ mol<sup>-1</sup>), representing more mobile water molecules with increasing  $a_w$ .

- The third section ( $a_w$  above 0.6) represents the condensed water in the pores of the food (energy 0.3 KJ mol<sup>-1</sup>): this water allows the dissolution of soluble elements and can serve as a support to biological agents such as enzymes and microorganisms (Figure 1.2). This section is almost asymptotic and therefore very difficult to model.

However, some researchers believe that beyond the second section of the isotherm and despite an  $a_w$  as low as 0.2 to 0.3, water molecules have the



same properties apart from a few exceptions (ability to evaporate in particular). There would, therefore, be no fundamental difference between weakly bound water and unbound water (free water), where the property of water is very close to that of pure water, and its availability, as a solvent or reagent, would increase continuously with  $a_w$ . It is likely that weakly bound water and free water are able to rapidly interchange.

Many attempts have been made to establish mathematical models of sorption isotherms based on theoretical considerations and experimental observations. Despite this, and given the complexity of the phenomena, none of these models offers the ideal solution that covers the entire sorption field.

The most commonly used model is the Brunauer–Emmett–Teller model (BET; [BRU 38]) with two parameters, which is of particular significance in the study of curves corresponding to an  $a_w$  below 0.5. It is based on the following equation:

$$\frac{a_w}{M(1-a_w)} = \frac{1}{M_1C} + \frac{a_w(C-1)}{M_1C} \quad [1.4]$$

where  $M$  and  $M_1$  are the values for the water content of the product and the monolayer, respectively (g per 100 g of dry matter), and  $C$  is the BET constant defined by:

$$C = e^{\left[ \frac{H_m - H_n}{RT} \right]} \quad [1.5]$$

where  $H_m$  is the heat of sorption of the monolayer ( $\text{J mol}^{-1}$ ),  $H_n$  is the heat of adsorption of the second and higher layers ( $\text{J mol}^{-1}$ ),  $R$  is the ideal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the absolute temperature (K).

Using equation [1.4],  $M_1$  and  $C$  can be calculated, with  $M$  and  $a_w$  determined experimentally. Plotting  $\frac{a_w}{M(1-a_w)}$  (y-axis) as a function of  $a_w$  (x-axis) results in a straight line (Figure 1.7), giving values for the intersection and slope of  $\frac{1}{M_1C}$  and  $\frac{C-1}{M_1C}$ , respectively. The advantage of this model is that it is possible to calculate  $M_1$  and  $(H_m - H_n)$ .

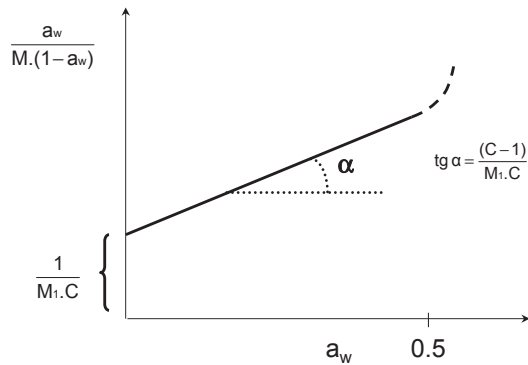


Figure 1.7. Representation of the Brunauer–Emmett–Teller equation

Another commonly used model is the Guggenheim–Anderson–de Boer model (GAB; [VAN 81]) with three parameters. It is often considered an extension of the BET model and can represent sorption curves up to an  $a_w$  of 0.85:

$$M = \frac{M_1 C K a_w}{[1 - (K a_w)][1 - (K a_w) + (C K a_w)]} \quad [1.6]$$

where  $M$  and  $M_1$  are the water content values of the product and the monolayer, respectively (g per 100 g of dry matter), and  $C$  and  $K$  are the temperature-dependent parameters such as:

$$\begin{cases} C = C_0 e^{\frac{\Delta H_c}{RT}} \\ K = K_0 e^{\frac{\Delta H_k}{RT}} \end{cases} \quad [1.7]$$

where  $C_0$  and  $K_0$  are constant, and  $\Delta H_c$  and  $\Delta H_k$  are defined by:

$$\begin{cases} \Delta H_c = H_m - H_n \\ \Delta H_k = L - H_n \end{cases} \quad [1.8]$$

where  $H_m$  and  $H_n$  are, respectively, the heat of sorption values of the monolayer and multilayer of water ( $\text{J mol}^{-1}$ ), and  $L$  is the heat of condensation of pure water ( $\text{J mol}^{-1}$ ).

More recently, Pisecki [PIS 97] proposed an empirical model to directly estimate the  $a_w$  values of skimmed milk powder:

$$a_w = e^{\left[ -\frac{b}{M^a} \right]} \quad [1.9]$$

where  $M$  is the water content of the product (g per 100 g of dry matter) and  $a$  and  $b$  are two adjusted coefficients ( $a = 2.0544$  and  $b = 54.387$  for desorption, and  $a = 1.7764$  and  $b = 24.8439$  for adsorption). This type of model, even though not explicative, still manages to closely match adsorption and desorption isotherms.

## 1.2.2. Glass transition

### 1.2.2.1. Principle

Glass transition has long been recognized for its technological importance for mineral and organic substances as well as food products. The concept, originally developed and used by physical chemists in the field of polymer science, characterizes the mobility of water in amorphous products (i.e. non-crystallized). A distinction can be made between:

- products in a glassy state, that are relatively hard, and present weak water mobility;
- products in a flaccid state (rubbery and sticky), having a higher water mobility and that are, therefore, less stable in terms of storage.

The gradual shift from one state to another is called “glass transition”: it occurs when there is a variation in temperature or water content. According to Genin and René [GEN 95], cooling a pure liquid can, in most cases, result in the formation of a crystalline solid. In theory, this change of state happens for a given product at a fixed temperature, known as the crystallization temperature ( $T_c$ ). However, no change of state is observed during cooling even when the  $T_c$  has been exceeded. There are two possible outcomes if the temperature is lowered further:

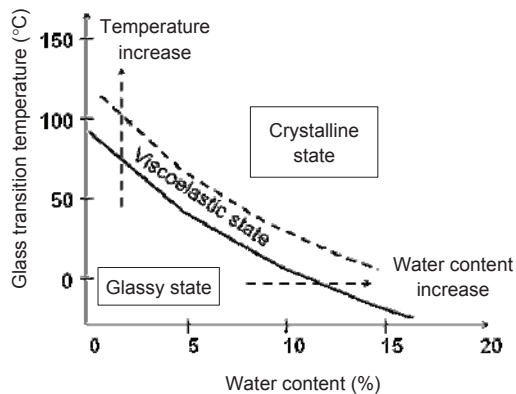
- crystallization occurs, but at a temperature below  $T_c$ ;
- the liquid state remains until solid-like behavior occurs (no change of state in a thermodynamic sense) at a given temperature known as the “glass transition temperature ( $T_g$ )”.

This frozen liquid is called a glass or an amorphous solid. In terms of energy, it is a metastable state; a small amount of energy can switch it to a more stable state, which can be a liquid or a crystalline state.

The glass state can be achieved in two ways:

- when cooling is fast enough to avoid the appearance of ice crystals;
- when the dynamic viscosity affects the rate of crystal growth by lowering the diffusivity (dynamic viscosity and diffusivity vary inversely).

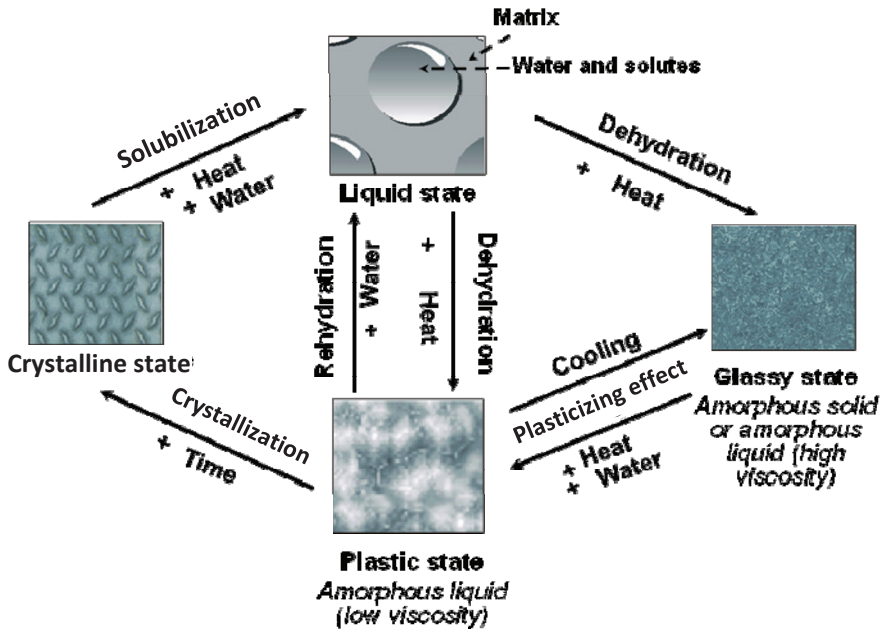
In the amorphous solid state, the molecules are not ordered and the system is said to be in a glassy state: the material has a high internal viscosity. During reheating above  $T_g$ , the system passes from a glassy state to a viscoelastic state where molecular mobility is higher [BHA 96]. This change can also be obtained at a constant temperature by increasing the water content: this is referred to as the plasticizing effect. Generally, the higher the water content is, the lower the  $T_g$ . This influence of the water content on  $T_g$  was observed for many products: amorphous lactose, skimmed milk powder, etc. [JOU 94a, LEM 90]. Water availability in a food matrix therefore depends on many different factors: water content, solute composition, hygroscopicity, viscosity and  $T_g$  (Figure 1.8).



**Figure 1.8.** Representation of the glass transition temperature as a function of water content [ROO 97, ROO 02]

Thus, a change in temperature and water content around the  $T_g$  value will significantly alter the mechanical properties of the material [JOU 94b,

ROO 97]. Even though glass transition has been used to predict the stability of frozen or dried products, the complexity and variety of products make the interpretation difficult. Sugars, proteins and fat are affected by glass transition [ROO 91a, ROO 91b]. Figure 1.9 summarizes the relation between amorphous and crystalline structures.



**Figure 1.9.** Representation of the relation between amorphous and crystalline structures [ROO 97, ROO 02]

The nature and range of molecular movements as well as the kinetics of the changes depend on the product temperature ( $T$ ) in relation to  $T_g$  ( $T - T_g$ ). For temperatures below  $T_g$ , only local, non-cooperative movements of small amplitude are possible (rotation movements and bond vibrations). Conversely, cooperative molecular movements of a higher amplitude occur at temperatures above  $T_g$ . Molecular mobility is enhanced in this case (translational movements), thus encouraging several reactions [LEM 01].

Table 1.8 gives some  $T_g$  values for dried ingredients. These values vary significantly from one ingredient to another (lactose/casein) and within the

same constituent category (lactose/galactose). For example, monosaccharides generally have a lower  $T_g$  than disaccharides.

Ingredients	$T_g$ (°C)
Glucose	+36
Galactose	+30
Fructose	+10
Sorbitol	-2
Lactulose	-2
Maltose	+43
Sucrose	+67
Lactose	+97
Skim milk	+92
Whole milk	+92
Hydrolyzed milk	+49
Casein	+144
Sodium caseinate	+130
Maltodextrin DE 6	+168
Maltodextrin DE 33	+130
Maltodextrin DE 47	+103

**Table 1.8.** Glass transition temperature ( $T_g$ ) of various dried food ingredients

Table 1.9 gives some examples of foods where sugars can affect the glassy state by causing visible modifications of food systems.

Food	Glassy state created by:	Types of sugars	Problems and solutions
Ice cream	Freezing	Sucrose–lactose	Grains (formation of lactose crystals, promoted by storage between $-17$ and $-23^{\circ}\text{C}$ ). Avoid an excessive level of lactose in the formulae (lactose/water below 10% (w/w)).
Skim milk powder	Dehydration	Lactose (representing 50% of dry matter)	Sticking resulting in aggregates. Should be stored in waterproof packaging below the $T_g$ in order to maintain stability. Possibility of instantizing.
Sweets	Concentration by boiling–cooling	Sucrose–glucose–invert sugar	Sedimentation – formation of grains (crystals) – sticky surface. Avoid a high hygroscopic sugar content and storing at overly high temperatures and/or relative humidity levels.
Lyophilisate	Dehydration	Different types	Partial liquefaction. Caking may occur during freeze-drying and slow it down. This also makes rehydration more difficult. Avoid overly high temperatures and relative humidity levels.

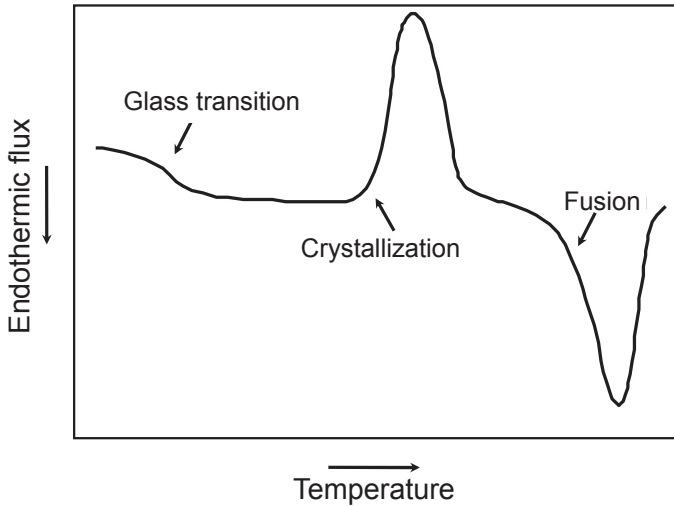
**Table 1.9.** *Sugars in the glassy state in foods: instability and approaches to overcome this*

### 1.2.2.2. Measurement and calculation

$T_g$  can be measured in various ways; for example, in rheological measurements,  $T_g$  is defined as the temperature at which viscosity decreases. However, these measurements are often difficult in the agri-food sector because the glass phase is generally involved in a solid phase, rendering obsolete the notion of viscosity. Another method is to measure the dielectric

constant of the medium, which changes significantly during glass transition. In practice,  $T_g$  is measured by following the change in the specific heat flux as a function of temperature, generally by differential scanning calorimetry (Figure 1.10). Using this analysis, three successive thermal events can be identified during the heating of a pure substance in the amorphous state [SEN 95]:

- at  $T_g$ , a change in specific heat (endothermic), denoted by  $\Delta C_p$ ;
- at the crystallization temperature, an exothermic phase transition;
- at the melting temperature, an endothermic phase transition.



**Figure 1.10.** Change in specific heat flux as a function of temperature by differential scanning calorimetry. Transition of a sugar from the glassy state to the crystalline state

It is also possible to estimate a  $T_g$  value by using equations that link the glass transition temperature of a mixture to its composition and to the glass transition temperatures of its pure constituents. The Gordon and Taylor equation is as follows:

$$T_g = \frac{\sum_i W_i \cdot T_{gi}}{\sum_i W_i} \quad [1.10]$$



where  $W_i$  is the mass fraction of constituent  $i$  in solution (%) and  $T_{gi}$  is the glass transition temperature of the pure compound  $i$  ( $^{\circ}\text{C}$ ). In general, this equation slightly overestimates the  $T_g$ .

A more accurate  $T_g$  can be obtained using the Couchman–Karasz equation, modified and extended to ternary solutions of proteins, carbohydrates and water:

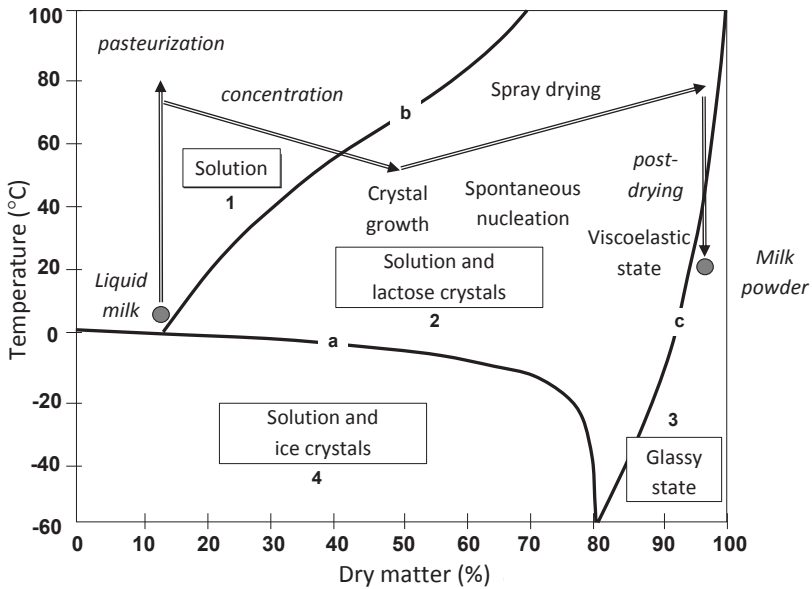
$$T_g = \frac{\sum_i W_i \Delta C_{pi} \cdot T_{gi}}{\sum_i W_i \Delta C_{pi}} \quad [1.11]$$

where  $T_{gi}$  is the glass transition temperature ( $^{\circ}\text{C}$ ) of constituent  $i$  at zero  $a_w$ ,  $\Delta C_{pi}$  is the change in specific heat of constituent  $i$  at  $T_{gi}$  ( $\text{J kg}^{-1}\text{C}^{-1}$ ) and  $W_i$  is its mass fraction (%). The  $T_{gi}$  values, referred to as “dry  $T_g$ ”, are obtained by extrapolating the  $T_g$  and  $\Delta C_p$  values measured at different  $a_w$  levels. In this model, water is one of the constituents measured, with  $T_g$  and  $\Delta C_p$  values equal to  $-139^{\circ}\text{C}$  and  $1.94 \text{ kJ kg}^{-1}\text{C}^{-1}$ , respectively. The reliability of the calculation of the overall  $T_g$  directly depends on the consideration of all the product constituents (water, proteins, amino acids, carbohydrates, minerals, etc.), subject to the availability of their thermodynamic characteristics,  $T_{gi}$  and  $\Delta C_{pi}$ . This is a limiting factor in using equation [1.11].

### 1.2.3. Phase diagram

The phase diagram is a widely used tool in the agri-food sector. It is possible, for example, in the production of whole milk powder to relate temperature ( $\theta$ ) and dry matter concentration in the phase transitions for water and lactose, as shown in Figure 1.11:

- the freezing curve (a) starting from  $0^{\circ}\text{C}$  for water and gradually falling to around  $-6^{\circ}\text{C}$  at around 50% dry matter, then extrapolated to 80% dry matter;
- the lactose solubility curve (b), adapted to whole milk;
- the glass transition curve (c) for lactose in milk according to Roos [ROO 97], using the Gordon and Taylor equation.



**Figure 1.11.** Phase diagram of whole milk [VUA 02]

The three curves define the main phase changes of lactose and water in four different areas:

- lactose solution;
- lactose solution with lactose crystals;
- solid amorphous lactose;
- lactose solution with ice crystals.

If we take into account the kinetic dimension of mutarotation and lactose crystallization, this dynamic phase diagram is particularly useful for describing the different processing stages (e.g. pasteurization, concentration, homogenization, spray drying, fluidized bed drying and cooling; Figure 1.11).