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Water Activity and Food Preservation

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20.1 Basics of Water Activity

Water is an important constituent of all foods. Why water activity and not water content? In the middle of the nineteenth century, scientists began to discover the existence of a relation between water in a food and its relative tendency to spoil. They also began to realize that the *active water* could be much more important to the stability of food than the total amount of water present. Scott [130,131] clearly identified that water activity of a medium correlated well with the deterioration of food stability due to the growth of microorganism. Thus, it was possible to develop generalized rules or limits for the stability of foods by using water activity. This was the main reason why food scientists started to emphasize water activity rather than water content. Since then, the scientific community has explored the great significance of water activity in determining the physical characteristics, processes, shelf life, and sensory properties of foods. The water activity of fresh foods, as shown by Chirife and Fontan [34], is 0.970–0.996. Other applications of water activity are: (i) process design and control, (ii) ingredient selection, and (iii) packaging selection. Water activity data are important to food processing, such as osmotic dehydration and air drying. In drying operations, desorption isotherms at the process temperature are needed for design and control purposes. The endpoint of drying or osmotic dehydration process can be determined from the equilibrium moisture content. In the drying process, the foods equilibrate with air equilibrium relative humidity; in osmotic or salting process, foods equilibrate with the osmotic solution water activity. Hence, water activity plays an important role in designing, operation, and control of drying processes and reverse osmosis. Water activity's depressing power of solutes needs to be considered when selecting ingredients or additives for food product formulation. When food materials are packed in a semipermeable membrane, the food will (a) collect moisture if its water activity is lower than the external relative humidity of the air or (b) lose moisture if its water activity is higher than the relative humidity. The sorption isotherm is necessary to predict the moisture transfer rate through the packaging film and edible food coating, so that shelf life can be predicted. The mathematical equations used to determine the isotherms for moisture transfer through packaging material are available in the literature [44,114].

20.1.1 Basic Terminologies

A number of basic terminologies related to water activity have been developed over the last 5 decades. It is important to understand these terminologies for proper utilization of water activity concept in food preservation and processing.

20.1.1.1 Water Activity

Water activity, a thermodynamic property, is defined as the ratio of vapor pressure of water in a system and the vapor pressure of pure water at the same temperature, or the equilibrium relative humidity of the air surrounding the system at the same temperature. A number of methods have been reported in literature to measure or estimate the water activity of foods. Water activity measurement methods include the following: (i) equilibrium sorption rate method (isopiestic method), (ii) vapor pressure measurement method, and (iii) hygrometric instrument method. In addition, water activity can be predicted from other thermodynamic properties such as freezing point. The accuracy of most methods lies in the range of 0.01–0.02 water activity units [118]. Details of the various measurement techniques are described by Labuza et al. [80], Rizvi [118], Rahman [109], Rahman and Sablani [112], Rahman et al. [113], Fontana [53], and Sablani et al. [124]. Water activity can be lowered or controlled by several methods such as separating out of water and adding solutes. Processes that can be used to remove water are drying, concentration, and dewatering by centrifuge. Other unit operations such as baking, extrusion, and frying also reduced the water activity to some extent. Solutes can be added to foods to reduce water activity as well as improve the

TABLE 20.1

Some Criteria for Humectants to be Used in Foods

Safe
Approved by regulatory agencies
Effective at reasonable concentrations
Compatible with the nature of the food
Flavorless at concentrations of use
Colorless and imparts no color changes in the food

functional and sensory properties of foods, for example, adding salt to meat and fish, and adding sugars to fruits. When only solutes are used to reduce water activity, then the specific antimicrobial effects and the cost of solutes or humectants should be considered for food product formulation. The factors affecting the selection of humectants are summarized in Table 20.1.

20.1.1.2 Sorption Isotherm

The moisture sorption isotherm is the dependence of moisture content on the water activity of one of the samples at a specified temperature. It is usually presented in a graphical form or as an equation. Brunauer et al. [19] classified adsorption isotherms of materials into five general types (Figure 20.1). If water-soluble crystalline components are present in foods, e.g., sugars or salt, the isotherm appears as concave shape type III. Most other foods result sigmoid isotherm type II. The inflection point of the isotherm indicates the change of water-binding capacity or of the relative amounts of free and bound water. Type I is indicative of a nonswelling porous solid, such as silicate anticaking agents. For practical purposes, the isotherm is presented in an empirical or theoretical model equation. However, none of the isotherm models in the literature is valid over the entire water activity scale of 0–1. The Guggenheim-Anderson-de Boer (GAB) model is one of the most widely accepted models for foods over a wide range of water activities from 0.10 to 0.9. The details of the isotherm models with their parameters are compiled by Rizvi [118], Okos et al. [106], Lomauro et al. [91,92], and Rahman [109].

20.1.1.3 Hysteresis

The difference in the equilibrium moisture content between the adsorption and desorption curves is called hysteresis and is shown in Figure 20.2. In region II of this figure, the water is held less tightly and is usually present in small capillaries, whereas in region III, the water is held loosely in large capillaries or is free [53]. Hysteresis in sorption has important theoretical and practical implications in foods. The theoretical implications are evidence of irreversible of the sorption process and the validity of the equilibrium thermodynamic process. The practical implications deal with the effects of hysteresis on chemical and microbiological deterioration and its importance on low- and intermediate-moisture foods [70]. Strasser [140] and Wolf et al. [154] maintained that changes in hysteresis could be used as an index of quality deterioration, since hysteresis loops of foods change with storage time, but this is a poor method of evaluation. Rahman and Al-Belushi [111] presented more reviews on the sorption hysteresis in foods.

20.1.1.3.1 Factors Affecting Hysteresis

The desorption hysteresis loop usually ends at the monolayer, but in some cases it extends down to an activity of zero [77]. In foods, a variety of hysteresis loop shapes can be observed depending on the type of food and the temperature [152]. The principal factors affecting hysteresis are composition of the product, isotherm temperature, storage time before isotherm measurement, pretreatments, drying temperature, and the number of successive adsorption and desorption cycles.

20.1.1.3.1.1 Types of Foods Affecting Hysteresis Variations in hysteresis can be grouped into three types of foods [70]: (i) Hysteresis in high-sugar foods—in high-sugar or high-pectin foods such as air-dried apple, hysteresis occurs mainly in the monomolecular layer of water region, below the first inflection point of isotherm region I in Figure 20.2 [106]. Although the total hysteresis is large, there is no hysteresis above 0.65. (ii) Hysteresis in high-protein foods—in pork, a moderate hysteresis begins at about

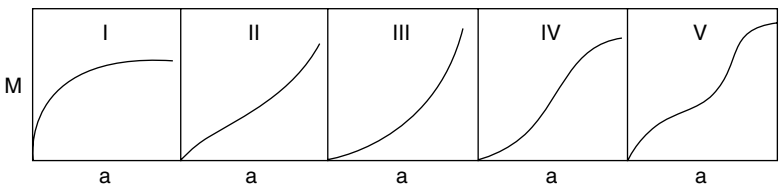

FIGURE 20.1 The five types of van der Waals adsorption isotherms proposed by Brunauer et al. [19].

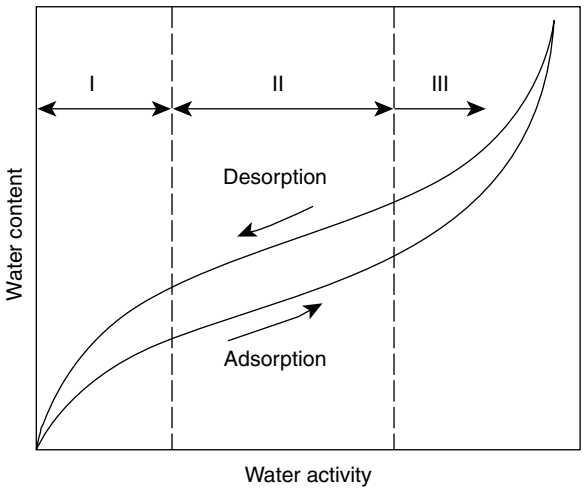

FIGURE 20.2 Sorption isotherm for typical food product showing hysteresis.

0.85 (i.e., in the capillary condensation region) [69]. (iii) Hysteresis in high-starch foods—in starchy foods a large hysteresis loop occurs, with a maximum water activity of about 0.70, which is within the capillary condensation region [106].

20.1.1.3.1.2 Temperature Effects on Hysteresis Total hysteresis decreases as sorption temperature increases [152]. Desorption isotherms usually give a higher water content than adsorption isotherm. Chinachoti and Steinberg [28] found hysteresis in sugar containing starch up to 0.60 and Bolin [13] in resin (with very high sugar content) up to 0.30. Tsami et al. [145] observed significant hysteresis below 0.5 or 0.6 and at temperatures above 30°C in case of fruits (raisin, currant, fig, prune, and apricot) and mentioned that absence of hysteresis at higher temperatures was due to the dissolution of sugars at high temperatures. The water activity below which a significant hysteresis effect was manifested was inversely proportional to the sugar content of the fruits [145]. In high-sugar or high-pectin foods such as air-dried apple, hysteresis occurs mainly in the monomolecular layer of water region [106]. Although the total hysteresis is large, there is no hysteresis above 0.65. In case of pork, a moderate hysteresis begins at about 0.85 (i.e., in the capillary condensation region) [69]. In starchy foods, a large hysteresis loop occurs with a maximum water activity of about 0.70, which is within the capillary condensation region [106], whereas in case of kudzu starch hysteresis continues up to 0.90 [12]. Increasing the temperature decreases the total hysteresis [154]. Iglesis and Chirife [64] estimated and compared the isosteric heats of water adsorption and desorption for a number of foods and reported that the effect of temperature on the magnitude of hysteresis varied. There was no direct relationship between the observed differences in adsorption and desorption heats and the distribution of hysteresis along the isotherm. For some foods (thyme, winter savoy, sweet marjoram, cooked trout, raw and cooked chicken, and tapioca), increasing temperature decreased or eliminated hysteresis, while for others the total hysteresis remained constant (ginger and nutmeg) or even increased (anise, cinnamon, chamomile, and coriander) [70].

20.1.1.3.1.3 Effects of Physicochemical Nature The type of changes encountered upon adsorption and desorption depends on: (i) initial state of the sorbent (amorphous versus crystalline), (ii) transitions taking place during adsorption, (iii) final water activity adsorption point, and (iv) sorption rate. If the saturation point has been reached and the material has gone into sorption, rapid desorption may preserve the amorphous state due to supersaturation [70]. Some water remained after desorption at dry conditions even after prolonged storage due to hydrogen-bonded trapped water in the amorphous sugar microregions as well as water of crystallinity [42,154].

20.1.1.3.1.4 Effects of the Sorption Cycle on Hysteresis In some cases hysteresis seems to be reproducible a second time [5,140], and for some cases the second sorption–desorption cycle resulted in the elimination of hysteresis [4]. Elimination of hysteresis upon the second or subsequent cycles may take place for a variety of reasons, including change in crystalline structure when a new crystalline form persists in subsequent cycles [6], swelling and increased elasticity of capillary walls resulting in a loss of power of trapping water [115,116], denaturation [39], surface-active agents [122], and even mechanical treatment, which may affect the capillary structure [70].

20.1.1.3.2 Theories of Sorption Hysteresis

Several theories have been formulated to explain the phenomenon of hysteresis but at present no theory has given a complete insight into the several mechanisms responsible [145], and no quantitative prediction of hysteresis is available in literature. The theories proposed in the literature on the causes of hysteresis are discussed in the following sections.

20.1.1.3.2.1 Capillary Condensation This can mainly explain hysteresis in nonswelling porous solids. Capillary condensation can be explained using the Kelvin equation. Owing to the presence of impurities, such as dissolved gas, the contact angle of the receding film upon desorption is smaller than that of the advancing film upon adsorption. Therefore, capillary condensation along the adsorption branch of the moisture sorption isotherm is at a higher relative vapor pressure [69].

20.1.1.3.2.2 Ink Bottle Theory Rao [117] assumed capillaries to be composed of narrow necks with a large pore, somewhat like an ink bottle. On adsorption, the capillary does not completely fill until the water activity corresponding to the large radius of the pore is reached. During desorption, the smaller radius of the pore neck controls the emptying of the capillary, so that activity is lowered considerably [77]. This theory was confirmed by Labuza and Rutman [83] for a cellulose model system. Cohan [41] elaborated upon the open-pore theory by extending the bottleneck theory, including considerations of multilayer adsorption. This was based on the difference as affected by the shape of the meniscus.

20.1.1.3.2.3 Mechanisms of Physicochemical Changes The physicochemical changes in food components also cause hysteresis, such as deformability and elastic stresses of the sorbent, a deformation of the polypeptide chains within the protein molecule [70], and the energy surplus of unfolding (swollen) protein phase transition [23]. Kapsalis [70] discussed that adsorption from the dry state by biopolymers is due to: (i) side chain amino groups, (ii) end carboxylic and other groups, (iii) peptide bonds, and (iv) secondary structures. In general, below 0.5 water activity the main sites of sorption are the polar side chain groups. The contribution of the polypeptide chain becomes progressively more important at higher activities, for example, at 0.80 activity the peptide bonds account for almost half the adsorbed water in wool keratin. Deamination of methylation of side chain groups in wool and benzoylation in casein did not show any appreciable changes of hysteresis [100]. This suggested that it was the main chains of the biopolymers that were primarily responsible [70]. Sheehof et al. [133] supported the polar group interpretation of hysteresis, where binding mainly involves the free basic groups of the protein. Kapsalis [70] showed a correlation between the maximum amount of hysteresis with the sum of arginine, histidine, lysine, and cystine groupings. Besides the free basic groups of the protein molecule, sulfur linkages are also of prime importance in hysteresis [137]. In contrast to this work, hysteresis in casein was observed to be independent of the content of free amino groups [100]. Thus, a twofold nature of hysteresis was proposed: constant hysteresis, independent of the relative humidity desorption point; and hysteresis proportional to the amount adsorbed above the upper adsorption break of the isotherm [70]. In a swelling polymer, hysteresis depends on the mechanical constants contributed by the elastic properties and cannot be interpreted by capillary condensation [7]. Van Olphen [148] described retardation of adsorption due to the development of elastic stress in crystallites during the initial peripheral penetration of water between the unit layers. The shift toward higher relative vapor pressure during adsorption is caused by the activation energy required to open the unit layer stacks. The glass–rubber transition during adsorption and desorption may also cause hysteresis due to the nonequilibrium state of phase transition.

20.1.1.3.2.4 Structural Collapse With sorption, the capillary pores of the adsorbent become elastic and swell. Upon desorption, the removal of water causes shrinkage, and a general collapse of the capillary porous structure occurs. Alteration of structure causes elimination of hysteresis due to the absence of capillary condensation [70]. The collapse of capillaries during desorption also affects sorption hysteresis.

20.1.1.4 Water Activity Shift in Isotherm

The isotherm shift due to temperature can usually be estimated by the well-known Clausius–Clapeyron equation [50,81]:

$$\ln\frac{(a_w)_2}{(a_w)_1} = \frac{q+\lambda_w}{R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right] \tag{20.1}$$

The slope of a plot of ln a_w versus $1/T$ should give the value of $(q + \lambda_w)/R$, where q is the excess heat of sorption (kJ/kg) and λ_w the latent heat of vaporization for water (kJ/kg). Typical water activity shift due to temperature at constant moisture content is shown in Figure 20.3. The water activity shift caused by temperature is mainly due to the change in water binding, dissociation of water, physical state of water, or increase in the solubility of solute in water. It is widely accepted that an increase in temperature results in decreased equilibrium moisture content (Figure 20.3a). Tsami et al. [145] found similar results for the dried fruits up to a water activity of about 0.55–0.70. In that region, the curves for several temperatures intersect. At water activity values higher than 0.7, there was an inversion in the effect of temperature (i.e., equilibrium moisture content increased with temperature) due to an increase in solubility of sugars in water. The intersection (or inversion) point depends on the composition of the food and the solubility of sugars [152]. For sultana raisin and currant, the inversion point was about 0.55, likewise, 0.65 for fig, 0.70 for prune, 0.75 for apricot (possessing the lowest sugar content of fruit) [145], 0.55 for quince jam (ferbar brand), and 0.65 for quince jam (tapada nova) [123]. A similar intersection was also found by Saravacos et al. [128] for sultana raisin and by Weisser et al. [151] for sugar alcohol. Apple (low sugar fruit) does not show intersection [121]. For products with protein or starch content, there is also no intersection point with the increase of temperature [4].

20.1.1.5 Water Activity Break

In a pure component isotherm, the change of solute from the amorphous state to a crystal affects the isotherm. A break is observed in the isotherm, as shown in Figure 20.4. In some foods, one part of the solute (salts and sugar) is bound to a polymer (protein and starch) and the other part is crystalline or amorphous. Bound and free forms of solutes are in equilibrium, which is strongly dependent on the actual water activity. If change in water activity takes place slowly, this equilibrium may be maintained, whereas during rapid changes nonequilibrium conditions are likely to be attained. Bound, crystalline, and amorphous solutes produce characteristic changes (i.e., break and shift) in the water sorption isotherm [57]. A typical curve showing break is shown in Figure 20.4b, where a break is also observed due to transformation of

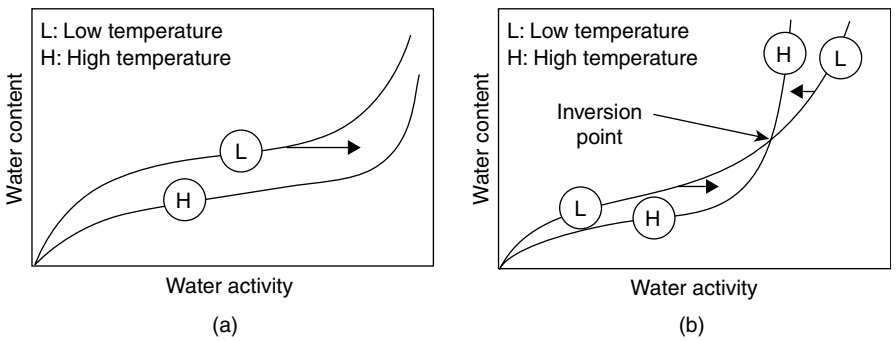

FIGURE 20.3 Water activity shift of food due to temperature. (a) Shift without intersection. (b) Shift showing the point of intersection or inversion point.

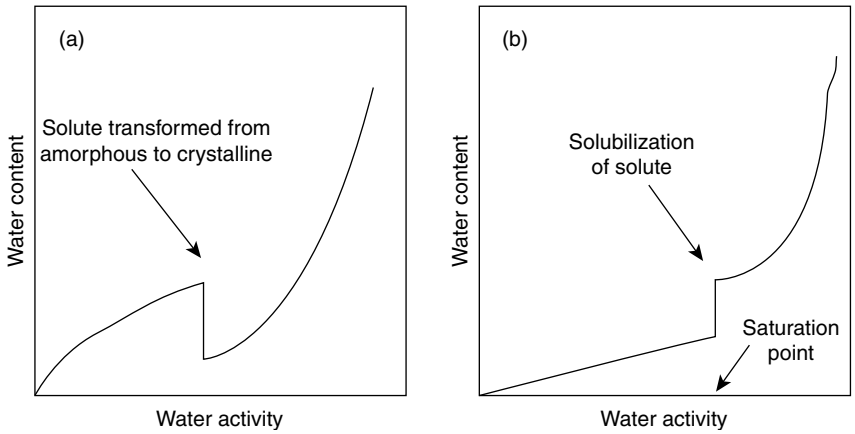

FIGURE 20.4 Water activity shift of food due to physicochemical parameters. (a) Shift with solute transformation from amorphous to crystalline. (b) Shift with solubilization of solute.

the solute from an amorphous to a crystalline state. This break was observed for sodium chloride–starch mixture [27]; sucrose–starch mixtures [26]; and sucrose, albumin, and gluten mixtures [29].

20.1.1.6 Concept of Local Isotherm

Rockland [119] proposed the concept of local isotherm to characterize the physical state or special type of water binding in foods [65]. The local isotherm can be identified by graphical analysis of experimental sorption data according to Henderson's equation. The three localized isotherms may be distinguished by plotting experimental sorption data as $\ln[-\ln(1-a)]$ versus $\ln M_w$. Three straight lines rather than a single straight line are observed, each being identified as a local isotherm. The three regions are identified as three types of water. Iglesias and Chirife [64] analyzed 235 isotherms based on this concept and concluded that although in a broad sense the local isotherms proposed by Rockland [119] may be related to the different modes of water binding, they cannot be used to give a precise and unequivocal definition of the physical state of water in foods. Moreover, the original Henderson equation should give only one curve during complete water activity range. In reality more linear segments in the curve present a poor fit.

20.1.1.7 Thermodynamic Properties Prediction

Thermodynamic properties such as the freezing point, boiling point, and heat sorption can also be predicted from water activity. For example, the freezing point (Equation 20.2) and boiling point (Equation 20.3) can be estimated as follows [51]:

$$\ln a_w = 9.6934 \times 10^{-3}\delta + 4.761 \times 10^{-6}\delta^2 \tag{20.2}$$

$$\ln a_w = 1.1195 \times 10^{-4}\delta^2 - 3.5127 \times 10^{-2}\delta \tag{20.3}$$

where δ is the freezing point depression or boiling point depression. The above equation could be very useful when measurement of freezing point is very fast and easy.

20.1.1.8 Porous Structure Investigation

Water sorption can be influenced by the surface area and porosity of the food material. The characteristics of a material (e.g., porous or nonporous) can be determined from sorption isotherms. It has been proposed in the literature that water activity could be used to calculate the food surface area as well as the pore size. However, Nagai and Yano [103] found the surface area and pore size calculated from the water sorption to be misleading. They suggested that water adsorption not only occurred on the surface, but also mainly on the water-binding sites inside the structure that does not increase with an increase in surface area.

20.1.2 Factors Affecting Water Activity

20.1.2.1 Food Components

Protein and starch adsorb much more water at low water activities than do fatty materials or crystalline substances like sugar. Pretreatment, such as heating, has little effect on proteins. On the other hand, such pretreatment increases the amount of water-impenetrable crystalline starch at the expense of amorphous starch. The smaller active site for adsorption means that less water can be adsorbed [77]. Sugars and salts present a difficult problem because the change from an amorphous to a crystalline state occurs fairly rapidly at normal temperature [94]. This change releases water, which may be picked up by other materials if the sugar is present in a mixture such as dried milk. The material would then become sticky and lumpy, making it undesirable. Salwin [127] observed that the equilibrium condition obtained is not an equal moisture content in all components in multicomponent mixture, but an equal activity.

20.1.2.2 Physicochemical State of Food Components

Many food components may be present in several states: crystalline solids, amorphous solids either rubbery or glassy , aqueous solution, or bound to other components. Sorption in such systems is complex. Crystalline sugars adsorb very little water, but amorphous sugars adsorb substantially more water at the same conditions. The adsorption of water results in breaking of some hydrogen bond and an increase in mobility of sugar molecules, resulting eventually in the sugars transforming to the crystalline state. In this process the sugar loses water [71]. However, the sugar–polymer interaction and physical state play an important role in separating out water from the system. Gelatinization followed by freeze drying results in only minor differences in water-binding behavior of water activity up to 0.94; above 0.95 the gelatinized samples adsorb considerably more water [147]. Saltmarch and Labuza [126] studied the effects of water activity and temperature on the transition of lactose from the amorphous to the crystalline state. Results from scanning electron microscopy indicated that lactose crystallized at 0.40, 0.33, and 0.33 water activity after 1 week at 25°C, 35°C, and 45°C, respectively. Water activity also influences protein conformation. The annealing effect of water, time, and temperature can alter the structural and functional properties of cereal starch (Figures 20.5 and 20.6). When crystalline starch is transformed to amorphous form, polar sites develop in the starch molecule, which could form hydrogen bonds with water molecules [102].

20.1.2.3 Porous Structure of Foods

Structure or pore size and distribution of material may also affect the sharply increasing region at higher water activity.

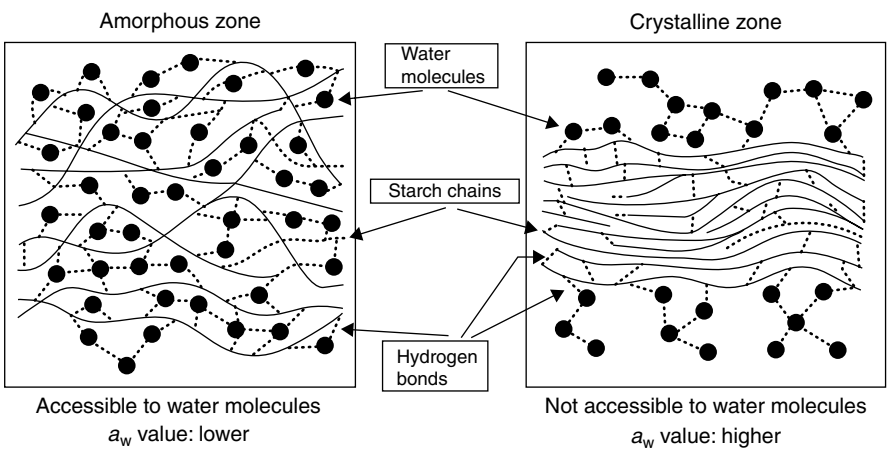

FIGURE 20.5 Schematic model of starch structure during amorphous and crystalline states. (From Munzing, K. 1991. *Thermochim. Acta* 193: 441–448.)

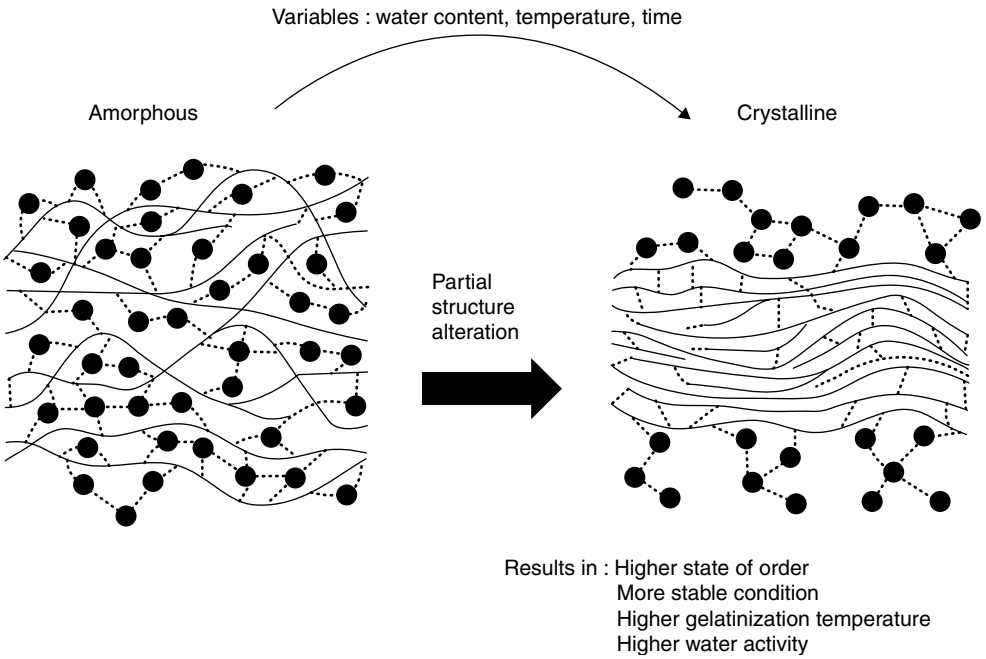

FIGURE 20.6 Annealing effects of starch induced by water, temperature, and time. (From Munzing, K. 1991. *Thermochim. Acta* 193: 441–448.)

20.1.2.4 Temperature

20.1.2.4.1 Above Freezing

The isotherm shift due to temperature can be estimated by Clausius–Clapeyron equation as discussed earlier.

20.1.2.4.2 Below Freezing

Information in the literature on water activity of the frozen state below freezing is limited [70]. The vapor pressures of animal tissues over the temperature span of −26°C to −1°C ranged from 13% to 20% lower than those of pure ice at the same temperature [46,63]. Other researchers demonstrated that the vapor pressures of frozen biological materials were equal to the vapor pressure of ice at the same temperatures [47,49,93,139]. Water activity values at subfreezing temperatures can be calculated (rather than measured) as [70]

$$a_w = \frac{\text{Vapor pressure of solid water (ice)}}{\text{Vapor pressure of liquid supercooled water (not ice)}} \tag{20.4}$$

The equation indicates that water activity does not depend on the composition, but only on the temperature. In a two-phase system (ice and solution) at equilibrium, the vapor pressure of solid water as ice crystals and the interstitial concentrated solution are identical; thus, water activity depends only on the temperature, and not on the nature and initial concentration of solutes, present in the third or fourth phase (i.e., irrespective of the kind of food). This creates a basis to estimate the water activity of foods below freezing using Equation 20.4. Thus, Fennema [49] concluded that changes in properties could occur below freezing without any change in water activity. These include changes in diffusion properties, addition of additives or preservatives, and disruption of cellular systems. The water activity data of ice from 0°C to −50°C are correlated with an exponential function as

$$a_w = 8.727\left[\exp\left(-\frac{595.1}{T}\right)\right] \tag{20.5}$$

where T is in K. The maximum error in prediction is 0.012 unit water activity and the average is 0.0066, respectively. The data of Fennema [49] were used to develop the above correlation.

20.1.2.5 Pressure

The effect of pressure on the sorption isotherm is relatively small and negligible at reasonable pressure levels [106]. At constant moisture content, the variation of water activity with pressure can be derived thermodynamically as [106]

$$\ln\frac{a_2}{a_1} = \frac{\lambda_w}{\rho_w RT}(P_2 - P_1)$$

where a_1 and a_2 are the water activity at P_1 and P_2, R is the gas constant (82.05×10^{-3} m^3 atm/kg mole K or 8.314×10^3 m^3 Pa/kg mole K), T the temperature (K), and P_1 and P_2 are total pressure (atm or Pa).

20.1.2.6 Surface Tension

The effect of capillary action on water activity can be estimated from the Kelvin equation as

$$a_w = \exp\left(-\frac{\Delta P\, V_m}{RT}\right)$$

For spherical interface

$$\Delta P = \gamma_s\left[\frac{1}{r_1} + \frac{1}{r_2}\right]\cos\theta$$

where ΔP is the pointing pressure (Pa), V_m the liquid molar volume (18 m^3/kg mole), R the gas constant (8.314 Nm/kgmolK), T the temperature (K), γ_s the surface tension (N/m), cos θ the contact angle, and r the radius of curvature (m). If the droplet is spherical, then $r_1 = r_2$ and the above equation can be written as

$$a_w = \exp\left[-\frac{2\gamma\cos\theta\, V_m}{rRT}\right]$$

If surface tension is reduced by a factor of 0.5, the ratio of the water activities at the two conditions can be calculated using the above equation. The ratio is 0.995 at 20°C, thus the effect of surface tension cannot be measured. Chen and Karmas [25] reported that in case of intermediate food solutions, water activity increased very little as the surface tension decreased. They suggested that ingredients that result in reduction of surface tension should be avoided to attain low water activity. In contrast to Chen and Karmas [25], Alzamora et al. [1] found that surface tension did not appear to have any significant effect on water activity, at least within the range of apparatus error from 0.004 to 0.005 water activity unit.

20.2 Water Activity in Food Preservation

20.2.1 Monolayer Concept

The monolayer value can be determined from Brunaur-Emmett-Teller (BET) isotherm and is widely used to determine the stability of foods. The BET equation can be derived from kinetic, statistical mechanics, or thermodynamic considerations. The equation can be written as

$$\frac{a_w}{M_w(1-a_w)} = \left(\frac{C-1}{M_m}\right)a_w + \frac{1}{M_m C}$$

where a_w is the water activity, M_m the BET monolayer, and C the temperature dependence for sorption excess enthalpy. The value of C indicates how strongly water is bound to the polar sites of the solid matrix and can be related with temperature as

$$C = \alpha\left[\exp\left(-\frac{Q_s}{RT}\right)\right]$$

where Q_s is the excess heat of sorption (kJ/kg) and α the preexponent factor. The monolayer can be estimated from the slope of the linear line of the plot $a_w/M_w(1-a_w)$ versus a_w. The BET equation is valid only within 0.05–0.50 water activity. Thus, values within that range should be used to estimate the

monolayer value. The monolayer value is generally around a water activity of 0.2–0.4 [78]. In addition, the BET monolayer calculation is an effective method for estimating the amount of bound water to specific polar sites in dehydrated food systems [98]. The BET monolayer values usually vary from 0.01 to 0.14 (dry basis) in case of foods and food components. Macromolecules such as starch, protein, and agar usually have higher BET monolayer whereas high fat content foods such as avocado, peanuts, and whole milk showed lower monolayer. Iglesias and Chirife [64] found that monolayer values decreased significantly with increasing temperature after studying 100 foods and food components. This may be due to the thermodynamics where higher temperatures increase the escaping tendencies of gas molecules. In recent years, the most widely accepted and represented model for sorption isotherms for foods has been the GAB. This is mainly due to its accuracy and its validity over a wide range of water activities from 0.1 to 0.9. The GAB isotherm was developed by Gugenheim, Anderson, and De Boer and can be written as

$$M_w = \frac{M_{gm} C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)}$$

where C and K are the model parameters and are related to the temperature. The GAB isotherm equation is an extension of the two-constant BET model and takes into account the modified properties of the sorbate in the multilayer region and bulk liquid properties through the introduction of a third constant K. The GAB model parameters and monolayer values have been compiled by Rahman [109] for a number of food products. It is important to point that BET monolayer has more physical meaning and acceptability to be used for food stability compared to the GAB monolayer, although GAB provides better mathematical prediction of isotherm over the wide range of water activities. Recently, the advantages were discussed by Rahman and Al-Belushi [111].

20.2.2 Food Stability Diagram

The moisture sorption isotherm is an extremely valuable tool for food scientists because of its usefulness in predicting food stability. Most foods have a critical moisture content below which the rate of quality loss is negligible. Quality is understood to include growth and toxin production by microorganisms as well as chemical deterioration and decrease of sensory intensity, such as crispness, hardness, caking, texture, color, flavor or aroma [78]. A global food stability map is presented in Figure 20.7 [84,120]. As discussed by Labuza [78], the rate of quality loss begins to increase above water activity 0.2–0.3 for most chemical reactions (Figure 20.7). At this water activity, the amount of water adsorbed on surfaces and in capillaries is enough to affect the overall dielectric properties such that the water can now behave as a solvent. Thus, chemical species can dissolve, become mobile, and are reactive. The higher the water activity, the faster the reaction rate because of the greater solubility and increased mobility of the reactants. However, at some higher water activity no further species dissolve, and therefore an increase in water activity decreases the concentration of the reacting species. Since the rate of a reaction is proportional to concentration on a molecular basis, the rate should reach a maximum and then fall as in Figure 20.7. Between this maximum and the monolayer, a semilog plot of rate versus water activity generally results in a straight line. For most dry foods, an increase of 0.1 water activity unit in this region decreases shelf life two to three times [78].

20.2.3 Microbial Activity

20.2.3.1 Minimum Water Activity Limit

The minimum water activity is the limit below which a microorganism or group of microorganisms can no longer reproduce. Hypothetical curves showing effects of water activity are presented in Figure 20.8. The initial portion of this growth curve is composed of a lag phase during which the physiological machinery is created for later growth. The lag period is increased with an increase in solute content or a decrease in water activity. The growth or logarithmic phase is also affected by water activity as shown in Figure 20.8 [143]. Secondary metabolites are produced by some microorganisms that are highly toxic and carcinogenic to humans. The factors that affect spore formation can influence the formation of these metabolites. Beuchat [9] summarized the effects of water activity on spore formation and germination as well as toxin production by microorganisms commonly associated with foods and food spoilage. Minimal water activity values for

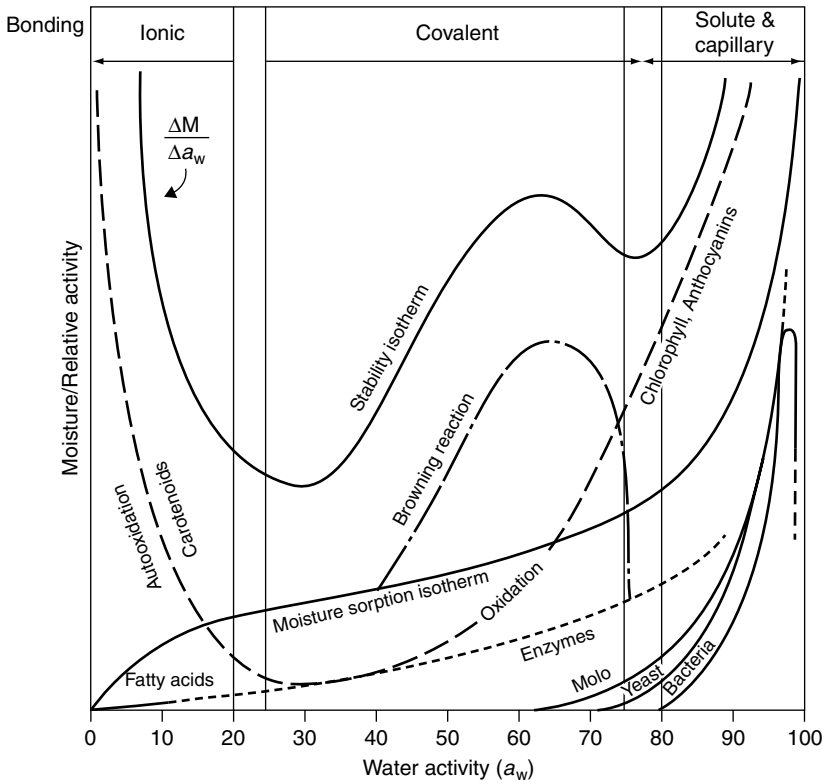

FIGURE 20.7 Food stability as a function of water activity. (From Rockland, L. B. and Beuchat, L. R. 1987. In: *Introduction, Water Activity: Theory and Applications to Food*. Rockland, L. B. and Beuchat, L. R. eds. Marcel Dekker, New York. p. v.)

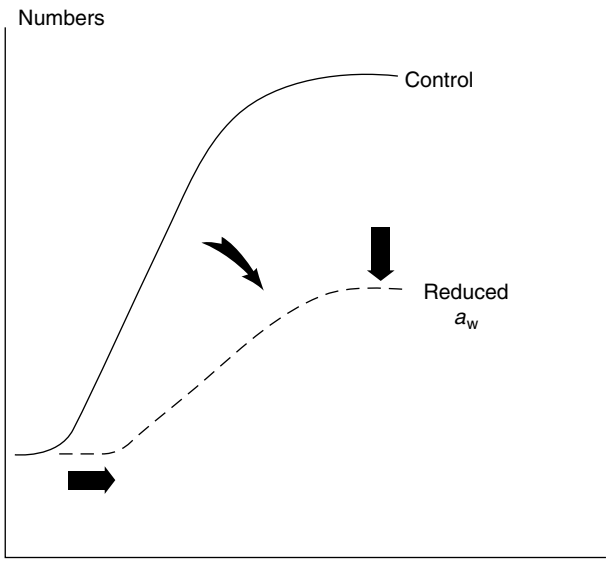

FIGURE 20.8 Hypothetical curves showing effects of water activity reduction on bacterial growth. (From Troller, J. A. 1987. In: *Water Activity: Theory and Applications to Food*. Rockland, L. B. and Beuchat, L. R. eds. Marcel Dekker, New York. pp. 101–117.)

growth and toxin production by microorganisms of public health significance are listed in Tables 20.2 through 20.7. The concern of food safety increases with increasing water activity. The water activity values of some foods cause their susceptibility to spoilage microorganisms as shown in Table 20.7 [8]. There is a critical water activity below which no microorganisms can grow. For most foods, this is in the 0.6–0.7 water activity range. Pathogenic bacteria cannot grow below a water activity of 0.85–0.86, whereas yeast and molds are more tolerant to a reduced water activity of 0.80, but usually no growth occurs below a water activity of about 0.62 [32]. The critical limits of water activity may also be shifted to higher or lower levels by other factors, such as pH, salt, antimicrobial agents, heat treatment, and temperature of storage. Leistner and Rodel [88] found the rate of microbial death during frozen storage to be reduced by a decrease in temperature without fluctuation. Thus, they suggested that the microbiological quality of frozen foods could be improved by initial storage of foods at −10°C (a_w = 0.90) to reduce the number of undesirable organisms followed by freezing at very low temperature (i.e., −30°C) [89]. In case of selected penicillia, spores produced on media at 0.99 water activity appeared more heat resistant compared to those produced at 0.88 water activity [11]. All treated spores were more sensitive to benzoate and sorbate but more resistant to cycloheximide. McClure [97] provided a review on the effect of water activity on the growth of microorganisms.

20.2.3.2 Mode of Action

For many years, scientists believed these mechanisms relied mainly on the influx and outflow of small, charged inorganic particles, primarily the ions of sodium, potassium, hydrogen, and chloride. Cell physiologists are coming to appreciate that changes in a cell's volume compromise more than just the shape or even the integrity of a cell. Any imbalance in the number of dissolved particles between a cell's interior and exterior can cause water either to rush in and burst the cell's membrane, or to seep out, causing the cell

TABLE 20.2

Minimal a_w for Growth and Toxin Production by Bacteria of Public Health Concern

	Minimal Water Activity for		
Bacteria	**Growth**	**Toxin Production**	**Toxin**
Bacillus cereus	0.93–0.95	–	–
Clostridium botulinum	0.93–0.95	0.94–0.95	Type A
	0.93–0.94	0.94	Type B
	0.95–0.97	0.97	Type E
Clostridium perfringens	0.93–0.95	–	–
Salmonella spp.	0.92–0.95	–	–
Staphylococcus aureus	0.86–0.87	0.87–0.90	Enterotoxin A
	0.86–0.87	0.97	Enterotoxin B
Vibrio parahaemolyticus	0.94	–	

Source: Beuchat, L. R. 1981. *Cereal Foods World* 26: 345–349.

TABLE 20.3

Minimal a_w for Growth of Foodborne Pathogens in Laboratory Media at Optimum pH and Temperature

Pathogen	**Minimal a_w**	**Pathogen**	**Minimal a_w**
Campylobacter jejuni	0.990	*Salmonella* spp.	0.940
Aeromonas hydrophilia	0.970	*Escherichia coli*	0.935
Clostridium botulinum E	0.965	*Vibrio parahaemolyticus*	0.936
Clostridium botulinum G	0.965	*Bacillus cereus*	0.930
Shigella spp.	0.960	*Listeria monocytogenes*	0.920
Yersinia enterocolitica	0.960	*Staphylococcus aureus* (anaerobic)	0.910
Clostridium perfringens	0.945	*Staphylococcus aureus* (aerobic)	0.860
Clostridium botulinum A and B	0.940		

Source: Chirife, J. 1993. *Food Control* 4: 210.

TABLE 20.4

Sodium Chloride versus Glycerol in Minimum Water Activity Supporting Growth of Pathogenic Bacteria

	a_w Adjusted with	
Bacteria	**Sodium Chloride**	**Glycerol**
Clostridium botulinum E	0.966	0.943
Clostridium botulinum G	0.966	–
Escherichia coli	0.945	0.940
Clostridium perfringens	0.945	0.930
Salmonella spp.	0.941	–
Clostridium botulinum A and B	0.940	0.930
Vibrio parahaemolyticus	0.932	0.911
Bacillus cereus	0.930	0.920
Listeria monocytogenes	0.920	0.900
Staphylococcus aureus	0.860	0.890

Source: Chirife, J. and Buera, M. D. P. 1996. *Crit. Rev. Food Sci. Nutri*. 36(5): 465–513.

TABLE 20.5

Minimal Water Activity for Growth of Pathogenic Bacteria[a]

Bacteria	**NaCl**	**KCl**	**Sucrose**	**Glucose**
Listeria monocytogenes	0.920	–	0.920	–
Vibrio parahaemolyticus	0.935	0.936	0.940	–
Clostridium botulinum G	0.965	–	0.965	–
Clostridium botulinum E	0.972	0.972	0.972	0.975
Clostridium perfringens	0.945	–	–	0.946
Staphylococcus aureus	0.864	0.864	0.867	–

[a]In laboratory media, water activity adjusted with salts (NaCl and KCl) or sugars (sucrose and glucose).
Source: Chirife, J. 1994. *J. Food Eng*. 22: 409–419.

TABLE 20.6

Minimal a_w for Growth of and Toxin Production by Molds of Public Health Concern

	Minimal Water Activity for		
Mold	**Growth**	**Toxin Production**	**Toxin**
Alternaria alternate	–	<0.90	Altenuene, alternariol, alternariol monomethyl ether
Aspergillus flavus	0.78–0.80	0.83–0.87	Aflatoxin
Aspergillus parasiticus	0.82	0.87	Flatoxin
Aspergillus orchraceus	0.77–0.83	0.83–0.87	Ochratoxin
Byssochlamys nivea	0.84	–	–
Penicillium cyclopium	0.81–0.85	0.87–0.90	Ochratoxin
Penicillium viridicatu	0.83	0.83–0.86	Ochratoxin
Penicillium ochraceus	0.76–0.81	0.80–0.88	Penicillic acid
Penicillium cyclopium	0.82–0.87	0.97	Penicillic acid
Penicillium martensii	0.79–0.83	0.99	Penicillic acid
Penicillium islandicum	0.83	–	–
Penicillium urticae	0.81–0.85	0.85–0.95	Patulin
Penicillium expansum	0.83–0.85	0.99	Patulin
Stachybotrys atra	0.94	0.94	Stachybotrym
Trichothecium roseum	0.90	–	Trichothecine

Source: Beuchat, L. R. 1981. *Cereal Foods World* 26: 345–349.

TABLE 20.7

Water Activity of Some Foods and Susceptibility to Spoilage by Microorganisms

Range of a_w	Microorganisms Generally Inhibited by the Lowest a_w in This Range	Examples of Foods Generally within This Range of a_w
1.00–0.95	*Pseudomonas, Escherichia, Proteus, Shigella, Klebsiella, Bacillus*, *Clostridium perfringens*, some yeasts	Highly perishable foods (fresh and canned fruit, vegetables, meet fish) and milk; cooked sausages and breads
0.95–0.91	*Salmonella*, *Vibrio parahaemolyticus, C. botulinum, Serratia*, *Lactobacillus, Pediococcus*, some molds, *Rhodotorula, Pichia*	Some cheeses (Cheddar, Swiss, Muenster, provolone), cured meat, some fruit juice concentrates
0.91–0.87	Many yeasts (*Candida*, *Torulopis, Hansenula*), *Micrococcus*	Fermented sausage (salami), sponge cakes, dry cheeses, margarine
0.87–0.80	Most molds (mycotoxigenic penicillia), *Staphylococcus aureus*, most *Saccharomyces* (billii) ssp., *Debaryomyces*	Most fruit juice concentrates, sweetened condensed milk, chocolate syrup, maple and fruit syrup, rice, pulses, fruit cakes, country-style ham, fondants, high sugar cake
0.80–0.75	Most halophilic bacteria, mycotoxigenic aspergilli	Jam, marmalade, marzipan, glace fruit, some marshmallows
0.75–0.65	Xerophilic molds (*Aspergillus chevalieri*, *A. candidus,Wallemia sebi*), *Saccharomyces bisporus*	Rolled oats, grained nougats, fudge, marshmallows, jelly, molasses, raw can sugar, some dried fruits, nuts
0.65–0.60	Osmophilic yeasts (*Saccharomyces rouxii*), a few molds (*Aspergillus echinulatus*, *Monascus bisporus*)	Dried fruits, some toffees and caramels, honey
0.50	No microbial proliferation	Noodles, spaghetti, dried spices
0.40		Whole egg powder
0.30		Cookies, crackers, bread crusts
0.20		Whole milk powder, dried vegetables, corn flask, dehydrated soup, some cookies, crackers

Source: Beuchat, L. R. 1981. *Cereal Foods World* 26: 345–349.

to shrink. In case of hypertonic solution, the cells shrink whereas in case of hypotonic solution, cells expands [85]. A decrease in water activity in the environment increases the osmotic stress of microbial cells because the cells always try to maintain a slightly lower internal osmolality (i.e., water activity). This causes an influx of water into the cell to maintain surface integrity. It is the disruption of this process by solutes that leads to cell damage and death. In addition to osmotic stress, solutes may have other effects on microorganisms, including enzyme inhibition, cytoplasmic coagulation, and damage to the cell wall. Brown [18] showed that high levels of salt with antibiotics like penicillium and cycloserine caused prokaryotic cell walls to become fragile while strong-walled eukaryotes survived. In the above case, the controlling mode of action was damage to the cell wall. Water activity can explain only the osmotic stress. Genetic control is closely tied to the amino acid pool, especially betaine and praline, and the potassium level in the cell.

20.2.3.3 Adaptation

A variety of mechanisms may help avoid water loss or gain from microorganisms [58]. Such mechanisms are reviewed by Troller [143].

20.2.3.3.1 Sensing and Translation

While potassium may or may not be the trigger that initiates the process of osmoregulation, its transport into the cell is the primary modulatory event [61]. Helmer et al. [62], in a series of experiments, demonstrated that at least two and probably four K^+ transport systems exist in *Escherichia coli*. The first system is accomplished, in part, by a series of three high-affinity genes. The first three genes of the inner membrane proteins of various molecular weights act as gatekeepers. The fourth gene alters its conformation in a manner that permits and intensifies transcription to maintain cytoplasmic K^+ content [47]. The second system is constitutive and requires ATP and a proton motive force to supply energy for net K^+ uptake. Helmer et al. [62] identified a proton motive force as supplying the primary energy to drive this reaction, whereas ATP supplies the energy to turn off K^+ transport. Another system, the K^+ export model, has only been postulated and is of some interest because of the potential existence of export-blocking proteins that might be synthesized by the cell in response to osmotic challenge. In this case, K^+ would not be pumped out of the cell but would be retained to trigger a metabolic response or to provide primary iso-osmotic conditions across the membrane [143].

20.2.3.3.2 Accommodation

Christian [37] and Christian and Waltho [38] observed first that growth of *Salmonella oranienburg* at low water activity was stimulated by the addition of the amino acid proline. They observed a reversal of plasmolysis when exogenous proline was supplied to the bacteria growing at low water activity. Although uptake from the media may be one method of accumulating proline in response to water stress, most organisms appear to be able to synthesize proline. In fact, synthesis probably is the most common mechanism for accumulating proline in osmotically inhibited bacteria [144]. This is called compatible solute. A number of osmoregulatory solutes protect proteins against denaturation by heat [58]. Measures [99] and Gould and Measures [60] showed that K^+ was required to maintain electrical neutrality or to balance the charges within cells exposed to environments with low water activity in which various amino acids, such as α-ketoglutarate and glutamic acid, accumulate intracellularly. The principal reaction involves conversion of α-ketoglutarate to glutamic acid by glutamate dehydrogenase, an enzyme activated by K^+. Glutamic acid reduces the intracellular water activity to reverse plasmolysis by reducing relative amounts of K^+ and glutamate dehydrogenase. This leaves the cell at a balanced, osmotic null point by virtue of the increased glutamic acid pool. For some bacteria the process stops at this point, but for other organisms glutamic acid is converted to γ-aminobutyric acid or proline, neither of which is highly charged. Accumulation of high concentrations of glutamic acid would require concomitant acquisition of K^+ to keep the system at neutrality. This excessive amount of K^+ could be detrimental to the organism and at the very least, costly in terms of energy expenditure. Both γ-aminobutyric acid and proline are remarkably efficient at reducing intracellular water activity without interfering in the cell's metabolism and for this reason have been termed compatible solutes [17]. Compatible protoplasmic solutes in bacteria include glycylbetaine, proline, glutamic acid, γ-aminobutyric acid, and glycerol. Polyols of various types are compatible protoplasmic solutes in many fungi (Table 20.8). Exactly how these solutes avoid interference is not fully understood [143]. Gould [58] suggested that specific binding between solutes and intracellular enzymes is not the mechanism. Jones and Pollard [66] suggested that as these solutes may be excluded from the hydration sphere of proteins, the term benign solutes might more accurately describe the nonparticipatory nature of these materials.

20.2.3.3.3 Genetic Adaptation

The genetic components controlling osmoregulation in microorganisms are being investigated. *Escherichia coli* appears to have evolved a particularly advanced scheme for protection against osmotic stress through a proline-overproduced mutation, which confers osmotolerance. *Klebsiella pneumoniae* experiences an increase in intracellular-free proline when it is exposed to high levels of sodium chloride. Thus an enhanced level of osmoresistance in the organism results in its ability to fix nitrogen while under osmotic stress Troller [143].

20.2.3.3.4 Changing Cell Metabolism

An important role of the membrane may be to exclude Na^+, which if permitted to enter the cell can quickly inactivate a number of vital enzymatic systems. Na^+ alters the types and amount of phospholipids within the membrane [143]. How a bacterial spore maintains such low cytoplasmic water content or water activity even when suspended in pure water is not yet understood [58].

TABLE 20.8

Compatible Protoplasmic Solutes in Fungi

Solute	Genus	Solute	Genus
Mannitol	*Geotrichum*	D-Galactosyl-(1,1)-glycerol	*Ochromonas*
	Platymonas	Glycerol	*Chlamydomonas*
	Aspergillus		*Aspergillus*
	Dendryphiella		*Dunaliella*
	Penicillium		*Saccharomyces*
Cyclohexanetetrol	*Monochrysis*		*Debaromyces*
Arabitol	*Dendryphiella*	Erythritol	*Aspergillus*
	Saccharomyces		*Penicillium*
Sorbitol	*Stichococcus*		

Source: Brown, A. D. and Simpson, J. R. 1972. *J. Gen. Microbiol*. 2: 589.

20.2.4 Fat Oxidation

Figure 20.7 shows a quality loss by oxidation below monolayer value. If a food is susceptible to oxidation of unsaturated fats, e.g., cereal grains, the rate increases as water activity decreases below the monolayer. Oxidation and rancidity are aggravated by drying of foods to very low moisture levels [127]. An oxygen attack is also responsible for pigment instability, loss of vitamins, and sometimes initiates nonenzymatic browning reactions [138]. The attachment of an oxygen molecule to a binding site of a protein would produce an incongruity in the aqueous covering sheath, which could distribute the hydration structure of neighboring sites [75]. Competition with oxygen is not the sole basis for explaining the protective effects of water. The bond energy of the adsorbed water would inhibit interactions between polar groups on adjacent carbohydrate or protein molecules and thereby preserve rehydration ability, reconstitution ability, and texture of foods [127]. Moreover, with respect to fat oxidation, the catalytic effect of metallic compounds is reduced when they form coordination spheres with polar groups [146]. Water is important in lipid oxidation because it acts as a solvent, mobilizes reactants, and interacts chemically or by hydrogen bonding with other species. The basic protective function that water exhibits when the moisture content increases the absolute dry state can be accounted for by two factors: (i) water interacts with metal catalysts, making them less effective through changes in their coordination sphere, and (ii) water hydrogen bonds with hydroperoxides, tying them up so that they are no longer available for decomposition through initiation reactions. When moisture content is higher than the value at the monolayer, the solvent and mobilization properties of water become more important and the catalysts present are more easily mobilized and possible swelling of solid matrix exposes new catalytic sites, making oxidation rates even higher [77,82]. Thus, foods having unsaturated fat should be kept at the critical water activity to maximize shelf life. The water activity at BET monolayer can be defined as *critical water activity*. Autoxidation of lipids occurs rapidly at low water activity levels, decreasing until a water activity range of 0.3–0.5 is reached [142]. At low water content especially in porous substrates in the complete absence of water, peroxidation of unsaturated lipids proceeds very rapidly. The addition of small quantities of water tends to produce a protective effect if the substrate is still free of oxidation products and reactive intermediates. However, reactions of oxidation products with proteins follow a more complex pattern [71]. In a model system consisting of methyl linoleate and lysozyme, the free radicals and other reactive species formed by the linoleate react with the protein, resulting in increased fluorescence, decreased enzyme activity, and decreased protein solubility. Water activity has an inhibitory effect on the initial oxidation of the lipid, but the secondary reactions of the lipid degradation products with the protein are accelerated by increasing water activity [68]. Schaich [129] showed that the free radical formed in proteins reacted with peroxide lipids and found that the amount and type of free radicals formed in the proteins were strongly affected by water activity. It appears that water facilitates recombination of free radicals and as a consequence the steady-state concentration of radicals, whereas various radical-initiated processes such as protein cross-linking increase at high water content. In case of freeze-dried model systems, certain amino acids, including histidine, β-amino-butyric acid, lysine, and cysteine, showed substantial antioxidant activity [72].

20.2.5 Nonenzymatic Activity

Browning reactions in foods affect nutritional value as well as color and texture [79]. The induction period, defined as the time to visually detectable browning, is inversely proportional to water activity [76,150]. Browning reactions are influenced by the types of reactant sugars and amines, pH, temperature, water activity, and the types of solutes or humectants used to adjust the water activity [142].

20.2.5.1 Types of Browning

There are three major pathways by which nonenzymatic browning can occur: high-temperature caramelization, ascorbic acid oxidation, and the Maillard reaction [79]. The browning reaction of sugars heated above their melting point in the absence of proteins or amino acids is called caramelization. This can be either beneficial or detrimental to the quality of a food product and can be prevented by avoiding high-temperature processing and low storage temperatures. It is enhanced in alkaline or acid conditions and is used to make commercial caramel colorings and flavors. Ascorbic acid (vitamin C) oxidation, a second type of browning reaction, is catalyzed by low pH and elevated temperatures. The decomposition products resulting from the oxidation of ascorbic acid cause a brown discoloration as well as decreased nutritional value. The Maillard reaction is a result of reducing compounds, primarily sugars, reacting with proteins or free amine groups. This changes both the chemical and the physiological properties of the protein. In general, the accumulation of brown pigments is the most obvious indication that Maillard browning has occurred in a food containing both carbohydrate and protein. It is used as an indicator of excessive thermal processing in the milk industry [79]. In the early stages of the Maillard reaction, the carbonyl group of the reducing sugar reacts with the free amino group of the amino acid to form a Schiff base and then the *N*-substituted glycosylamine as well as a molecule of water. Glycosylamines are converted to 1-amino-1-deoxy-2-ketose by Amadori rearrangement (cyclization and isomerization) [90]. The Maillard reactions forming Amadori compounds do not cause browning but do reduce the nutritive value [96]. The advanced Maillard reaction has five pathways. The first pathways start from the 1,2-enol or 2,3-enol forms of the Amadori product, yielding various flavor compounds. The third pathway is Strecker degradation, which involves oxidative degradation of amino acids by the dicarbonyls produced in the first two pathways. The fourth pathway involves transamination of the Schiff base. The fifth pathway starts with a second substitution of the amino-deoxyketose. The final step of the advanced Maillard reaction is the formation of many heterocyclic compounds, such as pyrazines and pyroles [90]. Brown melanoidin pigments are produced in the final stage of the Maillard reaction. The pigments are formed by polymerization of the reactive compounds produced during the advanced Maillard reaction, such as unsaturated carbonyl compounds and furfural. The polymers have a molecular weight greater than 1000 and are relatively inert [96]. These pathways depend upon environmental conditions such as temperature and pH.

20.2.5.2 Factors Affecting Browning

The browning reaction rate increases sharply from water activity at BET to a maximum, and then decreases (Figure 20.7). Water can retard the rate of the initial glycosylamine reaction of which it is a product. This results in product inhibition by some of the intermediate reactions. A second factor is the dilution of reactive components with increasing water content. The mobility of the reactive species increases due to a decrease in viscosity with increasing water activity. However, the first two factors eventually overcompensate for the decreased viscosity at higher water activity, and thus the overall rate of browning decreases [79]. Wolf et al. [153] demonstrated that losses of free lysine and methionine were highly dependent on water activity, protein, and sugar. Thermal degradation of both amino acids followed first-order kinetics, and rates decreased at 65°C and 115°C with increasing water activity. A more rapid decrease of lysine, tryptophan, and threonine at higher water activity is observed in model systems when heated to 95°C [87]. The retention of tryptophan was greater than lysine at water activity 0.75, but lysine retention was greater than that of tryptophan at water activity 0.22. At higher water activity, the Maillard reaction predominates and a rapid loss of lysine occurs. At lower water activity, browning proceeds at a slower rate and reactions involving the indole ring of tryptophan become significant [90]. Glucose utilization in a model system consisting of glucose, monosodium glutamate, corn starch, and lipids during nonenzymatic browning was investigated by Kamman and Labuza [67]. The rates of glucose utilization at water activity 0.81 were higher than at 0.41.

Lipid accelerated the reaction rates at 0.41 but had virtually no effect at 0.81 water activity. Liquid oil is more effective than shortening in increasing the degradation rate of glucose. These can be explained by the mobility of solutes in both water and oil [90]. Cerrutti et al. [24] studied browning in a model system consisting of lysine, glucose, sodium chloride, and phosphate buffer. They showed that water had little or no effect on the rate of glucose loss at water activity 0.90–0.95, but the rate was highly dependent on temperature and pH. Similar behavior was observed on accumulation of 5-hydroxymethylfurfural, fluorescent compounds, and brown pigments. Seow and Cheah [132] found that nonenzymatic browning decreased with an increase in water activity and temperature in a water-glycerol-sorbate-glycine model system at pH 4. In case of dehydrated orange juice (a_w = 0.44) stored at 30°C and 50°C, the total amino acids lost due to nonenzymatic browning were 30% and 65% of initial concentration [21].

20.2.5.3 Maximum Browning Region

The region where the maximum browning occurs is usually near 0.65–0.80 water activity. In model freeze-dried foods, the maximum browning rate is in the range of 0.40–0.67 [39], in whey powders at 0.44 [79], and in dehydrated foods in the range of 0.65–0.75 [149]. Petriella et al. [107] found that water had relatively less effect on the browning rates at water activity of 0.90–0.95. At this range, pH and temperature were the determining factors. At very high water content, i.e., water activity greater than 0.95, moisture strongly inhibits the browning rate by diluting the reactive species [142]. Warmbier et al. [149] studied the influence of solutes on the maximal range of browning. For example, if glycerol is employed to reduce water activity, the range of maximal browning shifts from 0.65–0.75 to 0.40–0.50. They concluded that glycerol can influence the rate of browning at lower water activity values by acting as an aqueous solvent and thereby allowing reactant mobility at much lower moisture values than would be expected for water alone. The overall effect of glycerol or other liquid humectants on the maximum for nonenzymatic browning is to shift it to a lower water activity [79]. Obanu et al. [105], on the other hand, observing browning in glycerol–amino acid mixtures stored at 65°C, concluded that glycerol itself might participate in the browning reaction. Moreover, Troller [142] pointed that product quality relative to browning could be improved by reducing the water activity and, more importantly, the temperature during the final stage of drying. It is somewhat paradoxical that at water activity levels that minimize browning, autoxidation of lipids is maximized.

20.2.6 Enzymatic Activity

Enzyme-catalyzed reactions can proceed in foods with relatively low water contents. Karel [71] summarized two features of the results mentioned in the literature as follows: (i) The rate of hydrolysis increases with increasing water activity, with the reaction being extremely slow at very low activities. (ii) At each water activity, there appears to be a maximum extent of hydrolysis, which also increases with water content. The apparent cessation of the reaction at low moisture cannot be because of irreversible inactivation of the enzyme, but because upon humidification to a higher water activity, hydrolysis is resumed at a rate characteristic of the newly obtained water activity [71]. Silver [134] investigated a model system consisting of avicel, sucrose, and invertase and found that the reaction velocity increased with water activity. Complete conversion of the substrate was observed for water activities greater than or equal to 0.75. Below water activities of 0.75, the reaction continued to 100% hydrolysis. In solid media, water activity can affect reactions in two ways: lack of reactant mobility and alteration of active conformation of substrate and enzymatic protein [141]. Effects of varying the enzyme-to-substrate ratios on reaction velocity and the effect of water activity on the activation energy for the reaction could not be explained by a simple diffusion model, but required more complex postulates [71]: (i) The diffusion resistance is localized in a shell adjacent to the enzymes. (ii) At low water activities, the reduced hydration produces conformational changes in the enzyme affecting its catalytic activity. Tome et al. [141] tested the simple diffusion-related hypothesis on the basis of experiments in liquid systems in which water activity was reduced by the addition of glycerol, ethylene glycol, propylene glycol, diethylene glycol, sorbitol, methanol, or ethanol. In these solutions, the effects of polyphenoloxidase on tyrosine were very similar to those obtained in solid systems. The optimum pH of activity is shifted slightly toward alkaline values. Three characteristic curves were observed: (i) for low water activity, there was almost a total inhibition, (ii) in the intermediate range, reaction rate was very dependent on water activity, and (iii) for high water activity zones, activity was weakly affected by organic

TABLE 20.9

Minimum Water Activity Values for Enzymatic Reactions in Selected Food Systems

Product/Substrate	Enzyme	*T* (°C)	Water Activity Threshold
Grains	Phytases	23	0.90
Wheat germ	Glycoside hydrolases	20	0.20
Rye flour	Amylases	30	0.75
	Proteases	–	–
Macaroni	Phospholipases	25–30	0.45
Wheat flour dough	Proteases	35	0.96
Bread	Amylases	30	0.36
	Proteases	–	–
Casein	Trypsin	30	0.50
Starch	Amylases	37	0.40/0.75
Galactose	Galactosidase	30	0.40–0.60
Olive oil	Lipase	5–40	0.25
Triolein, triaurin	Phospholipases	30	0.45
Glucose	Glucose oxidase	30	0.40
Lenoleic acid	Lipoxygenase	25	0.50/0.70

Source: Drapron, R. 1985. In: *Properties of Water in Foods.* (Simato, D. and Multon, J. L., eds.) Martinus Nijhoff Publishers, Dordrecht.

additives. In general, the rate increased rapidly with increasing water activity, and the reaction stopped at a certain level before all reactants were consumed; the higher the water content, the higher the plateau. The authors were unable to find a correlation of enzyme activity with viscosity, solubility of oxygen and tyrosine, or dielectric constant. It also appeared that the more the mixture deviated from ideality, the more the enzymatic activity was inhibited, regardless of whether the deviation was positive or negative. Thus, solvent–water interaction is the main parameter in polyphenoloxidase inhibition. The minimum water activities for enzymatic reactions in selected food systems are given in Table 20.9.

20.2.7 Vitamin Loss

The nutrition loss of dehydrated foods depends on the storage temperature, light, oxygen, and water activity. The loss of thiamine due to heating is affected by (i) the state of thiamin molecule (incorporated into the enzyme or protein bound), (ii) pH (the rate of destruction increases especially in the alkaline region), (iii) metals (free metals act as catalysts to increase the rate of thiamine destruction), and (iv) oxygen (oxygen can accelerate thiamine destruction especially in solutions above 70°C) [48]. The thiamine destruction during heat treatment strongly depended on pH and insignificant influence of water activity within 0.9–1.0 values [54]. Products with a pH value of 3 show excellent thiamine retention, while those with a pH value approaching 7 showed a strong instability during the thermal process. The destruction of thiamine in the model system was less than 5% at storage temperatures ≤ 37°C and was independent of water activity at $a_w \leq 0.65$. A significant increase in the thiamine loss occurred in the model system stored at 45°C when the water activity was at or above 0.24. Riboflavin is considered more heat stable than thiamine but highly sensitive to degradation by light. The stability of riboflavin in dry products is considered to be excellent in the absence of light [74]. With only one expectation, the reaction rates of vitamins A, B1, B2, and C increased with increasing water activity 0.24–0.65 [90]. The B vitamins are more stable than vitamins A and C at various water activity values [90].

20.2.8 Texture

Rockland [119] defined food texture as a function of localized moisture sorption isotherms as follows: (i) region I (low water activity)—dry, hard, crisp, and shrunken, (ii) region II (intermediate water activity)—dry, firm, and flexible, (iii) region III (high water activity)—moist, juicy, soft, flaccid, swollen,

TABLE 20.10

Critical Values for Ingredients in Model Food Products

Moistness	Crispness	Chewiness	Toughness
Cereal		<0.40	>0.50
Fruit	>0.30	<0.50	<0.30
Nuts		<0.65	

Source: Bourne, M. C. 1987. In: *Water Activity: Theory and Applications to Food*. Rockland, L. B. and Beuchat, L. R. eds. Marcel Dekker, New York. pp. 75–99.

stickiness. Table 20.10 shows textural characteristics of model food products as water activity. The effect of water activity on textural measurements for different types of foods is reviewed by Bourne [14]. Presently, there are insufficient data to predict what the textural properties of a given type of food will be at a given water activity, and no sound theories exist to predict in advance the textural properties of a food at a given water activity. Cenkowski et al. [22] studied the mechanical behavior of canola kernels by bringing them to equilibrium, adsorption or desorption, at the same final moisture. The ratio of elasticity was 18%–38% higher for kernels brought to equilibrium through adsorption than those through desorption for a moisture range of 9.5%–7.5% (dry basis). At higher moisture contents, the differences in modules of elasticity were not significant. In case of dry snacks, the loss of crispness occurred close to BET monolayer [77]. In case of potato chips [108] and corn chips [15], the *critical water activity* when the product was unacceptable was found to be 0.40 water activity. The change in sensory crispness of potato chips, popcorn, puffed corn curls, and saltines generally fell in the 0.35–0.50 water activity range [73]. Instron analysis showed that the force–deformation curve changed distinctly near critical a_w for saltines and puffed corn curls, while the curve changed more gradually with increasing a_w for popcorn.

20.3 Water Activity Concepts and Other Alternatives

20.3.1 Limitations Identified

Two major drawbacks of the water activity concepts are identified in the literature. These are: validity of equilibrium conditions, discontinuity or break in the isotherm, and effects of different solutes.

20.3.1.1 Validity of Equilibrium Conditions

Water activity is defined at equilibrium, whereas foods with low and intermediate water content may not be in a state of equilibrium. Instead they may be in an amorphous multistate, which is very sensitive to changes in moisture content and time. In low- and intermediate-moisture foods, the concept of water activity may be meaningless because the measured vapor pressure of water is no longer the equilibrium vapor pressure as defined in the literature. A stationary state may be reached under a given set of environmental conditions and mistaken for equilibrium. In moisture-sorption studies, the situation is further complicated if the amorphous material undergoes a glass–rubber transition during the course of the measurement. Chirife and Buera [33] believe that an analysis of various literature data may throw some light on these aspects. An important comprehensive collaborative study within the framework of European Corporation in the Field of Scientific and Technical Research (COST) was conducted to determine the precision of data (e.g., repeatability or reproducibility) in the determination of sorption isotherms. In the water activity range of interest to microbial growth (0.6–0.9), the average standard deviation of all data from 24 laboratories was ±2.6% for equilibrium moisture content of microcrystalline cellulose (MCC) and ±3.8% for potato starch, respectively. The repeatability was 2% for both MCC and potato starch. Chirife and Buera [33] also reported data on isotherms from different sources of the same material and found good reproducibility within a wide range of water activities. Lomauro et al. [92] concluded from a study of a large number of foods that a pseudoequilibrium was reached when the moisture content (dry basis) did not change by more than ±0.5% during three consecutive sample periods at an interval of no more than 7 days. This criterion for equilibrium moisture content was compared with the values obtained after 6 months of storage in closed

mason jars, which were considered to be very close to the equilibrium moisture content. Lomauro et al. [92] concluded that the foods tested reached (or were very close to) equilibrium within 1 month, based on the above criterion. Various authors reported their equilibrium times for isotherm determinations of different food systems using the gravimetric static method over saturated salt solutions, and their equilibrium times ranged mostly between 1 and 4 weeks, depending on the temperature and relative humidity. Bizot et al. [10] utilized a practical equilibrium time of about 7 days (±0.02% water per 24 h) for a 1 g sample, but they also stored their starch samples over saturated salt solutions for 2 years. They noted a slow drift in desorption pseudoequilibrium, but there was only a 1% difference in water content (dry basis) over this long time. Thus, water activities measured are likely to be close to equilibrium, and the differences should be within the uncertainties associated with the experimental determination of isotherm [33].

20.3.1.2 Break in the Isotherm

Chirife and Buera [33] reviewed sorption isotherms of fruits containing crystallizable sugars that constitute a nonequilibrium system. For example, in raisins the discontinuities in the isotherm are not noticed at water activity of 0.30–0.90, suggesting that sugars remained amorphous even at very large $T–T_g$. Sorption isotherm of other fruits reported in the literature does not show discontinuities [33,125]. Bolin [13] observed little effect on isotherm when raisins were sealed in glass jars held at 21°C or 32°C up to 12 months. This suggested that nonequilibrium effects are very slow, at least in their experiments. Chirife and Buera [33] also presented data on fruits, but they overlooked the crystallization of sugars in dairy products and formulated products having sugars or salts, as discussed in Chuy and Labuza [40] and Saltmarch and Labuza [126]. Recently developed dynamic sorption apparatus could measure the water activity within a couple of hours with a sample size in the range of μg. Although the break in isotherm poses a problem in the measurement, it provides a practical importance as far as detecting any change in structural components when stored on a specific water activity environment is concerned.

20.3.1.3 Effect of Solute Types

The microbial response may differ at a particular water activity when the latter is obtained with different solutes [32,33]. Thus, the proposed basis of water activity limit for growth may not be universal. Corry [43] reported that the survival of vegetative bacteria is influenced by nutrients in the food matrix. These influences show no consistent inhibitory pattern and are greatly affected by the matrix. Mugnier and Jung [101] studied the survival of bacteria and fungi in biopolymer gels with and without nutritive solutes. They observed that survival is increased at the point of mobilization of solute in the case of mannitol. While comparing a Gram-positive bacterium and a Gram-negative one, they concluded that low molecular weight compounds (C_3–C_5) had a deleterious effect on survival compared to higher molecular weight compounds (C_6–C_{12}), which had a protective effect. The glass–rubber state of solutes may also play an important role, since higher molecular weight solutes have higher glass transition temperatures than low molecular weight solutes. The degree of protective effect was in the order of mannitol > dextrin > ribose > glycerol. Above a certain amount of hydration (the mobilization point), there exists a second fraction of solute in the polymer system, which can serve as a true solvent for the microbial nutrient to maintain the organism's metabolic activity [89]. Brown [16] stated that freeze drying of microorganisms with a nonelectrolyte such as glycerol or sugar reduces mortality during dehydration, storage, and rehydration. This indicates that the nonelectrolyte functions directly as a solvent molecule for nutrients. Gould [58] acknowledged that in some instances solute effects might depend on the ability of the solute to permeate the cell membrane. Glycerol, for example, readily permeates the membrane of many bacteria and so does not initiate the same osmoregulatory response as nonpermeable solutes like sodium chloride and sucrose; therefore a different, usually lower, inhibitory water activity. Scott [131] noted that minimal water activity for the growth of microorganisms was independent of the solutes employed to adjust the water activity of a medium. It was observed later that some solutes were more inhibiting than others, thus water activity of a medium is not the only determining factor regulating microbial response. The nature of the solute used also plays an important role [36,59]. This is referred to as *specific solute effects* by Chirife [31]. Selected examples are discussed as follows. Figures 20.9 and 20.10 compare the minimal water activity supporting growth of various pathogenic bacteria when sodium chloride or glycerol is used to control the water activity. In all cases, glycerol is less

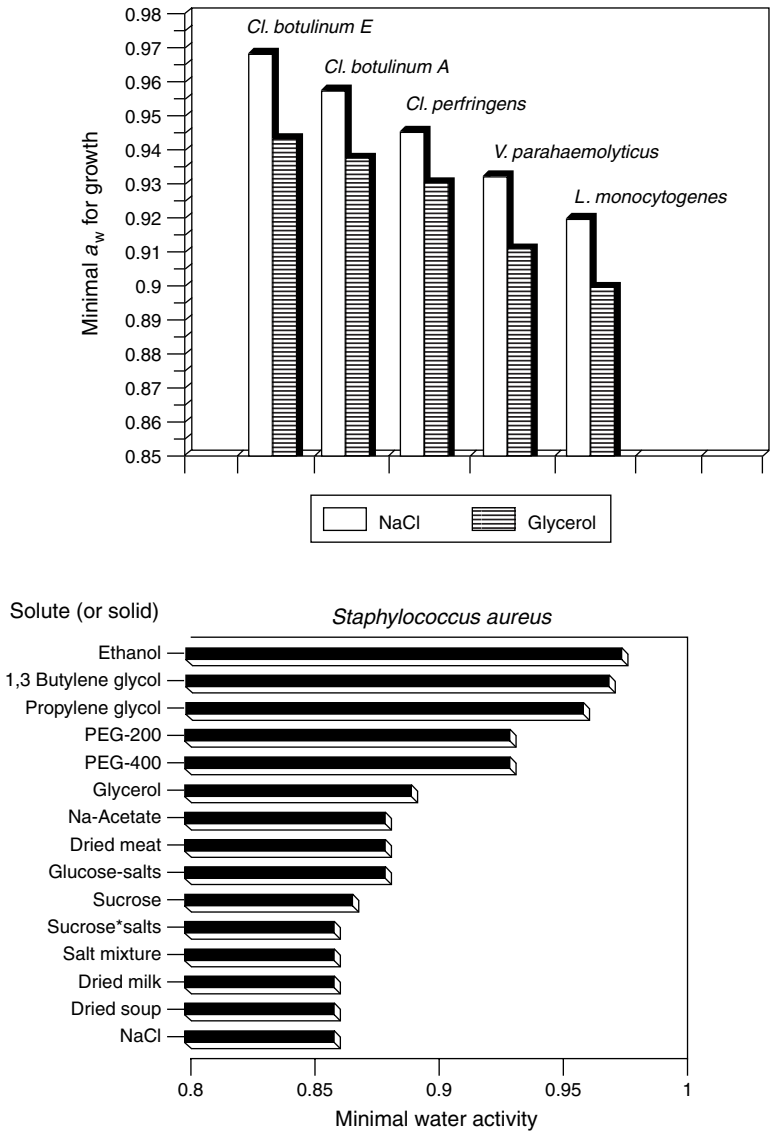

FIGURE 20.9 Effect of minimum water activity levels on growth of bacteria in different solutes. (From Chirife, J. and Buera, M. D. P. 1996. *Crit. Rev. Food Sci. Nutri*. 36(5): 465–513.)

inhibitory than sodium chloride. Glycerol readily permeates the membrane of bacteria and does not initiate the same osmoregulatory response as the nonpermeate solute sodium chloride [31]. It is conclusive that the water activity limit varies with the type of solute used and the microorganisms in the medium. Thus, it is important to identify the range of variations and the possible causes of variations. Table 20.5 shows the effects of solute types on *Staphylococcus aureus*. The range of water activities varies from 0.860 to 0.966. Propylene glycol is more effective in *S. aureus*, which is explained by Chirife [31]. The points in Figure 20.10 are distributed on both sides of the line, indicating a high correlation of water activity with growth and fluctuation due to other factors in the microorganisms. The effect of solute type on different microorganisms should be clearly identified to recognize generalized trends or at least the limitation of validity. Electron micrographs of *S. aureus* after growing in a medium containing different solutes were analyzed [31]. Microbial cells subjected to sodium chloride and sucrose ($a_w = 0.85$) did not show any important morphological changes in the cells; thus, the inhibitory effects of sucrose and sodium chloride against cells were

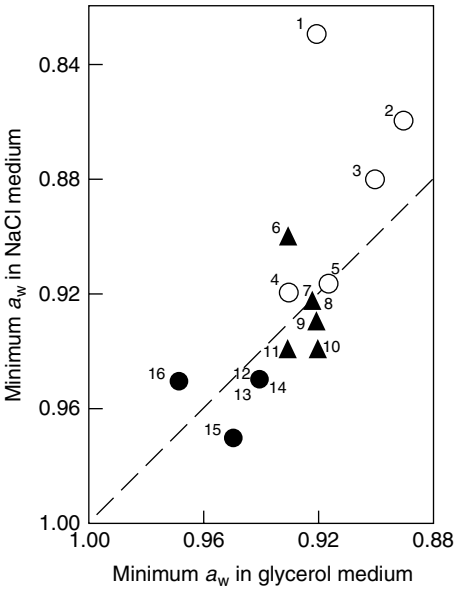

FIGURE 20.10 Relationship between the minimum water activity levels for growth of 16 species of bacteria in NaCl and in glycerol-adjusted medium. (From Christian, J. H. B. 1981. In: *Water Activity: Influences on Food Quality.* Rockland, L. B. and Stewart, G. F. eds. Academic Press, New York. pp. 825–854.)

primarily related to their ability to lower water activity, specific solute effects were not significant. Solutions of propylene glycol ($a_w = 0.92$), 1,4-butylene glycol ($a_w = 0.85$), and polyethylene glycol 400 and 1000 ($a_w = 0.85$) showed that these solutes caused dramatic morphological modifications in the cells. These antibacterial effects may be attributed mainly to the effects of these molecules on the membrane enzymes responsible for peptidoglycan synthesis. Anand and Brown [2] observed that polyethylene glycol was more inhibitory to yeast growth than were glucose and sucrose at a similar water activity. Marshall et al. [95] evaluated the inhibitory effects of sodium chloride and glycerol at the same water activity on 16 species of bacteria. They found that glycerol was more inhibitory than sodium chloride to relatively salt-tolerant bacteria and less inhibitory than sodium chloride to salt-sensitive species. Lenovich et al. [89] showed that the type of solute influences resistance to sorbate in *Saccharomyces rouxii*, thus indicating an interactive effect of solute type and preservative. Buchanan and Bagi [20] studied the effects of solutes (mannitol, sorbitol, and sucrose) in combination with four pH levels and three incubation temperatures on the growth of *Escherichia coli*. In addition to water activity, the growth kinetics was influenced by temperature and pH, and inhibition order followed as sorbitol > mannitol > sucrose. In addition at higher water activity levels, particularly when temperature and pH were nonlimiting, the differences between the humectants were minimal. However, as the environment was made more inhospitable, differences due to humectants were observed. Effects of solutes were insensitive to the *Lactobacillus casei* when sodium chloride or sorbitol was used to control the water activity [3]. The time of germination of spores appeared to vary depending on the water activity and solute type during spore production [11]. Resistance or susceptibility of microorganisms to antibiotics depends on the water activity and types of solutes. For example, resistance of *Streptococcus thermophilus* increased when water activity was lowered with glycerol, while susceptibility increased when water activity was adjusted with glucose and acid production was higher when sucrose was used. Susceptibility to gentamycin increased in both species (*Streptococcus thermophilus* and *Lactobacillus bulgaricus*) with reduced water activity [86]. Although there are differences in microbial stability when different solutes are used to achieve the same water activity, it does not mean that the concept of water activity is invalid [104]. It has been shown repeatedly in the literature that each microorganism has a critical water activity below which growth cannot occur. For example, pathogenic bacteria cannot grow below a water activity of 0.85–0.86; yeasts and molds are more tolerant of reduced water activity, but usually no growth exists below a water activity of about 0.6 (Table 20.7).

20.3.2 Glass Transition Concept

Recently, Rahman [110] reviewed the applications of glass transition concept in food product stability during storage. Slade and Levine [136] and Franks [55] proposed that water activity could serve as a useful, but not the sole indicator of microbial safety. Slade and Levine's [136] hypothesis stated that water dynamics or glass–rubber transition might be used instead of water activity to predict microbial stability. Slade and Levine [135] reported that for matched pairs of fructose and glucose at equal solute concentrations, fructose produced a much less stable system in which mold spores germinated much faster, i.e., the solute with lower ratio of melting temperature to glass transition temperature ($\alpha = T_m/T_g$) allowed faster germination. Thus, the following order of antimicrobial stabilization was predicted by Slade and Levine [136]: glycerol ($\alpha = 1.62$) > glucose ($\alpha = 1.42$) > mannose ($\alpha = 1.36$) > fructose ($\alpha = 1.06$) and sucrose ($\alpha = 1.43$) > maltose ($\alpha = 1.27$). The germination of *Aspergillus flavus*, *Aspergillus niger*, and *Eurotium herbariorum* did not follow the above sequence [35]. For example, germination times for all three molds in fructose or glucose were always greater than in glycerol. In all cases, germination time increased when the water activity decreased; the relative effect, however, depended both on the solute type and the mold. None of the molds studied germinated in solution of propylene glycol (at $a_w = 0.85$ or 0.90; $\alpha = 1.27$) after 70 days of incubation at 28°C [35]. This is simply because the behavior of propylene glycol cannot be explained on the basis of mobility or water activity effects alone, since this molecule possesses specific antimicrobial effects already recognized in the literature [35]. However, further studies from the microbiology groups could clarify the above-published results. Chirife and Buera [33] also showed evidence that above glass transition, microbial growth is inhibited in prunes and that below glass transition, microbial growth is possible in wheat flour. Overall both the water activity and glass transition concepts are not valid in all systems and conditions. Recent trends are to apply multiple concepts, such as water activity, glass transition, and pH, together to determine the chemical, physical, and microbial changes in foods. However, we are far from developing a more unified approach, including water activity, pH, glass transition, and preservatives. More discussions on glass transition concept and other factors are provided in the chapter on glass transition.

References

1. Alzamora, S. M., Chirife, J. and Fontan, C. F. 1981. Effect of surface active agents on water activity of IM food solutions. *J. Food Sci*. 46: 1974–1975.
2. Anand, J. C. and Brown, A. D. 1968. Growth rate patterns of the so-called osmophilic and nonosmophilic yeasts in solutions of polyethylene glycol. *J. Gen. Microbiol.* 52: 205.
3. Beker, M. E., Vigant, A. K., Marauska, M. K. and Klintsare, A. A. 1998. Osmotic sensitivity of the bacterium *Lactobacillus casei* var. *alactosus*. *Appl. Biochem. Microbiol*. 34(2): 146–148.
4. Benado, A. L. and Rizvi, S. S. H. 1985. Thermodynamics properties of water on rice as calculated from reversible and irreversible isotherms. *J. Food Sci*. 45: 1190.
5. Benson, S. W. and Richardson, R. L. 1955. A study of hysteresis in the sorption of polar gases by native and denatured proteins. *J. Am. Chem. Soc.* 77: 2585–2590.
6. Berlin, E., Anderson, B. A. and Pallansch, M. J. 1968. Water vapor sorption properties of various dried milks and whey. *J. Dairy Sci*. 51: 1339.
7. Bettelheim, F. A. and Ehrlich, S. H. 1963. Water vapor sorption of mucopolysaccharides. *J. Phys. Chem*. 67: 1948.
8. Beuchat, L. R. 1981. Microbial stability as affected by water activity. *Cereal Foods World* 26: 345–349.
9. Beuchat, L. R. 1987. In: *Water Activity: Theory and Applications to Food*. Rockland, L. B. and Beuchat, L. R. eds. Marcel Dekker, New York. p. 137–151.
10. Bizot, H., Buleon, A., Mouhous-Riou, N. and Multon, J. L. 1985. Some factors concerning water vapor sorption hysteresis in potato starch. In: *Properties of Water in Foods in Relation to Quality and Stability*. Simatos, D. and Multon, J. L. eds. Martinus Nijhoff, Dordrecht. p. 83.
11. Blaszyk, M., Blank, G., Holley, R. and Chong, J. 1998. Reduced water activity during sporogenesis in selected penicillia: impact on spore quality. *Food Res. Int*. 31(6–7): 503–509.
12. Boki, K. and Ohno, S. 1991. Moisture sorption hysteresis in kudzu starch and sweet potato starch. *J. Food Sci*. 56(1): 125–127.

13. Bolin, H. R. 1980. Relation of moisture to water activity in prunes and raisins. *J. Food Sci*. 45: 1190–1192.
14. Bourne, M. C. 1987. Effects of water activity on textural properties of food. In: *Water Activity: Theory and Applications to Food*. Rockland, L. B. and Beuchat, L. R. eds. Marcel Dekker, New York. pp. 75–99.
15. Brickman, C. L. 1957. Evaluating the packaging requirements of a product. *Package Eng*. 2(7): 19.
16. Brown, A. D. 1976. Microbial water stress. *Bacteriol. Rev*. 40(4): 803–846.
17. Brown, A. D. and Simpson, J. R. 1972. The water relations of sugar-tolerant yeasts: the role of intracellular polyols. *J. Gen. Microbiol*. 2: 589.
18. Brown, L. M. 1982. *Psychology* 21: 408.
19. Brunauer, S., Deming, L. S., Deming, W. E. and Teller, E. 1940. On a theory of the van der Waals adsorption of gases, *Am. Chem. Soc. J.* 62: 1723.
20. Buchanan, R. L. and Bagi, L. K. 1997. Effect of water activity and humectant identify on the growth kinetics of *Escherichia coli* O157:H7. *Food Microbiol*. 14: 413–423.
21. Castillo, M. D. D., Corzo, N., Polo, M. C., Pueyo, E. and Olano, A. 1998. Changes in the amino acid composition of dehydrated orange juice during accelerated non-enzymatic browning. *J. Agric. Food Chem*. 46: 277–280.
22. Cenkowski, S., Zhang, Q. and Crerar, W. J. 1995. Effect of sorption hysteresis on mechanical behavior of canola. *Trans. ASAE* 38(5): 1455–1460.
23. Cerofolini, G. F. and Cerorolini, M. 1980. Heterogeneity, allostericity, and hysteresis in adsorption of water by proteins. *J. Colloid Interface Sci*. 78: 65–73.
24. Cerrutti, P., Resnik, S. L., Seldes, A. and Ferro-Fontan, C. 1985. Kinetics of deteriorative reactions in model food systems of high water activity: glucose loss, 5-hydroxymethyl furfural accumulation and fluorescence development due to nonenzymatic browning. *J. Food Sci.* 50: 627.
25. Chen, C. C. and Karmas, E. 1979. Effect of surface active agents on water activity in intermediate moisture foods. *Food Sci. Technol*. 12: 68–71.
26. Chinachoti, P. and Steinberg, M. P. 1984. Interaction of sucrose with starch during dehydration as shown by water sorption. *J. Food Sci*. 49: 1604–1608.
27. Chinachoti, P. and Steinberg, M. P. 1985. Interaction of sodium chloride with raw starch in freeze-dried mixtures as shown by water sorption. *J. Food Sci*. 50: 825–839.
28. Chinachoti, P. and Steinberg, M. P. 1986. Moisture hysteresis due to amorphous sugar. *J. Food Sci*. 51: 153.
29. Chinachoti, P. and Steinberg, M. P. 1988. Interaction of sucrose with gelatin, egg albumin and gluten in freeze-dried mixtures as shown by water sorption. *J. Food Sci*. 53(3): 932–939.
30. Chirife, J. 1993. Physicochemical aspects of food preservation by combined factors. *Food Control* 4: 210.
31. Chirife, J. 1994. Specific solute effects with special reference to *Staphylococcus aureus*. *J. Food Eng*. 22: 409–419.
32. Chirife, J. and Buera, M. D. P. 1994. Water activity, glass transition and microbial stability in concentrated/semimoist food systems. *J. Food Sci*. 59(5): 921–927.
33. Chirife, J. and Buera, M. D. P. 1996. Water activity, water glass dynamics, and the control of microbiological growth in foods. *Crit. Rev. Food Sci. Nutri*. 36(5): 465–513.
34. Chirife, J. and Fontan, C. F. 1982. Water activity of fresh foods. *J. Food Sci*. 47: 661–663.
35. Chirife, J., Gonzalez, H. H. L. and Resnik, S. L. 1996. On water dynamics and germination time of mold spores in concentration sugar and polyol solutions. *Food Res. Int*. 28(6): 531–535.
36. Christian, J. H. B. 1981. Specific solute effects on microbial water relations. In: *Water Activity: Influences on Food Quality.* Rockland, L. B. and Stewart, G. F. eds. Academic Press, New York. pp. 825–854.
37. Christian, J. H. B. 1955. The water relations of growth and respiration of *Salmonella oranienburg* at 30°C. *Aust. J. Biol. Sci*. 8: 490.
38. Christian, J. H. B. and Waltho, J. A. 1964. The sodium and potassium content of nonhalophilic bacteria in relation to salt tolerance. *J. Gen. Microbiol*. 25: 97.
39. Chung, C. Y. and Toyomizu, M. 1976. Studies on the browning of dehydrated foods as a function of water activity. I. Effect of a_w on browning in amino acid-lipid systems. *Bull. Jap. Soc. Fisheries* 42: 697–702.
40. Chuy, L. and Labuza, T. P. 1994. Caking and stickiness of dairy based food powders related to glass transition. *J. Food Sci*. 59: 43.
41. Cohan, L. 1944. Hysteresis and the capillary theory of adsorption of vapors. *J. Am. Chem. Soc*. 66: 98.
42. Cohen, E. and Saguy, I. 1983. Effect of water activity and moisture content on the stability of beet powder pigments. *J. Food Sci*. 48: 703–707.
43. Corry, J. E. L. 1973. The water relations and heat resistance of microorganisms. *Prog. Ind. Microbiol*. 12: 73.

44. Desobry, S. and Hardy, J. 1993. Modelling of the total water desorption rate from packaging moist food. *Int. J. Food Sci. Technol*. 28: 347–359.
45. Drapron, R. 1985. Enzyme activity as a function of water activity. In: *Properties of Water in Foods*. Simato, D. and Multon, J. L. eds. Martinus Nijhoff Publishers, Dordrecht.
46. Dyer, D. F., Carpenter, D. K. and Sunderland, J. E. 1996. Equilibrium vapor pressure of frozen bovine muscle. *J. Food Sci*. 34: 196.
47. Epstein, W. and Lamins, L. 1980. Potassium transport in *Escherichia coli*: diverse systems with common control by osmotic forces. *Curr. Trends Biochem*. 5: 21.
48. Farrer, K. T. H. 1955. The thermal destruction of vitamin B1 in foods. *Ad. Food Res*. 6: 257–311.
49. Fennema, O. 1981. Water activity at subfreezing temperatures. In: *Water Activity: Influences on Food Quality*. Rockland, L. B. and Stewart, G. F. eds. Academic Press, Inc., New York. pp. 713–732.
50. Fennema, O. R. 1985. Water and ice. In: *Food Chemistry*, 2nd ed., Fennema, O. R. ed. Marcel Dekker, Inc., New York. pp. 23–67.
51. Fontan, C. F. and Chirife, J. 1981. The evaluation of water activity in aqueous solutions from freezing point depression. *J. Food Technol*. 16: 21–30.
52. Fontana, A. J. 2001. Dew-point method for the determination of water activity. In: *Current Protocols in Food Analytical Chemistry (CPFA)*. Wiley, New York. pp. A2.2.1–A.2.2.10.
53. Fortes, M. and Okos, M. R. 1980. Drying theories: their bases and limitation as applied to foods and grains. In: *Advances in Drying, Vol. 1,* Majumdar, A. S. ed. Hemisphere, Washington DC. pp. 119–154.
54. Fox, M., Loncin, M. and Weiss, M. 1982. Investigations into the influence of water activity, pH and heat treatment on the breakdown of thiamine in foods. *J. Food Qual.* 5: 161–182.
55. Franks, F. 1991. Water activity: a credible measure of food safety and quality. *Trends Food Sci. Technol*. 1: 68.
56. Gal, S. 1983. The need for and practical applications of sorption data. In: *Physical Properties of Foods*. Peleg, M. and Bagley E. B. eds. AVI Publishing Co., Westport, CT.
57. Gal, S. and Bankay, D. 1971. Hydration of sodium chloride bound by casein at medium water activities. *J. Food Sci*. 36: 800–803.
58. Gould, G. W. 1985. Osmoregulation: is the cell just a simple osmometer? The microbiological experience. In: *A Discussion Conference: Water Activity: A Credible Measure of Technological Performance and Physiological Viability?* Faraday Division, Royal Society of Chemistry, Girton College, Cambridge, UK. July 1–3.
59. Gould, G. W. 1988. Interference with homeostasis-food. In: *Homeostatic Mechanisms in Microorganisms*. Banks, J. G., Board, R. G., Gould, G. W. and Mittenbury, R. W. eds. Bath University Press, Bath, UK.
60. Gould, G. W. and Measures, J. C. 1977. Water relations in single cells. *Phil. Trans. R. Soc. Lond. B*. 278: 151.
61. Harold, F. M. 1982. Pumps and currents: a biological perspective. *Curr. Top. Membrane Transp*. 16: 485.
62. Helmer, G. L., Laimins, L. A. and Epstein, W. 1982. Mechanisms of potassium transport in bacteria. In: *Membranes and Transport*. Vol. 2. Martonosi, A. N. ed. Plenum Press, New York.
63. Hill, J. E. and Sunderland, J. E. 1967. Equilibrium vapor pressure and latent heat of sublimation for frozen meats. *Food Technol*. 21: 112–114.
64. Iglesias, H. A. and Chirife, J. 1976. On the local isotherm concept and modes of moisture binding in food products. *J. Agric. Food Chem*. 24(1): 77–79.
65. Isse, M. G., Schuchmann, H. and Schubert, H. 1993. Divided sorption isotherm concept: an alternative way to describe sorption isotherm data. *J. Food Eng*. 16: 147–157.
66. Jones, R. G. W. and Pollard, A. 1985. Towards a physical chemical characterization of compatible solutes. In: *Biophysics of Water.* Franks, F. and Mathias, S. F. eds. Wiley, Chichester.
67. Kamman, J. F. and Labuza, T. P. 1985. A comparison of the effect of oil versus plasticized vegetable shortening on rates of glucose utilization in nonenzymatic browning. *J. Food Proc. Pres*. 9: 217.
68. Kanner, J. and Karel, M. 1976. Changes in lysozyme due to reactions with peroxidizing methyl linoleate in a dehydrated model system. *J. Agric. Food Chem*. 24: 468.
69. Kapsalis, J. G. 1981. Moisture sorption hysteresis. In: *Water Activity: Influences on Food Quality*. Rockland, L. B. and Stewart, G. F. eds. Academic Press, New York. pp. 143–177.
70. Kapsalis, J. G. 1987. In: *Water Activity: Theory and Applications to Food*. Rockland, L. B. and Beuchat, L. R. eds. Marcel Dekker, New York. pp. 173–213.
71. Karel, M. 1979. The significance of moisture to food quality. In: *Developments in Food Science 2*. Chiba, H., Fujimaki, M., Iwai, K., Mitsuda, H. and Morita, Y. eds. Kodansha Ltd., Tokyo, pp. 378–383.

72. Karel, M., Tannenbaum, S. R., Wallace, D. H. and Maloney, H. 1966. Autoxidation of methyl linoleate in freeze-dried model systems. III. Effects of added amino acids. *J. Food Sci*. 31: 892–896.
73. Katz, E. E. and Labuza, T. P. 1981. Effect of water activity on the sensory crispness and mechanical deformation of snack food products. *J. Food Sci*. 46: 403–409.
74. Kirk, J. R. 1981. Influence of water activity on stability of vitamins in dehydrated foods. In: *Water Activity: Influences on Food Quality*. Rockland, L. B. and Stewart, G. F. eds. Academic Press, New York. pp. 531–566.
75. Klotz, I. M. and Heiney, R. E. 1957. Changes in protein topography upon oxygenation. *Proc. Natl. Acad. Sci. USA* 43: 717.
76. Kopelman, I. J., Meydau, S. and Weinberg, S. 1977. *J. Food Sci*. 42: 403.
77. Labuza, T. P. 1968. Sorption phenomena in foods. *Food Technol*. 22: 263–272.
78. Labuza, T. P. 1984. *Moisture Sorptions: Practical Aspects of Isotherm Measurement and Use*. Am Assoc. Cereal Chemists, St. Paul, MN.
79. Labuza, T. P. and Saltmarch, M. 1981. Kinetics of browning and protein quality loss in whey powders under steady state and nonsteady state storage conditions. *J. Food Sci*. 47: 92–96,113.
80. Labuza, T. P., Acott, K., Tatini, S. R., Lee, R. Y., Flink, J. and McCall, W. 1976. Water activity determination: a collaborative study of different methods. *J. Food Sci.* 41: 910–917.
81. Labuza, T. P., Kaanane, A. and Chen, J. Y. 1985. Effect of temperature on the moisture sorption isotherms and water activity shift of two dehydrated foods. *J. Food Sci*. 50: 385–391.
82. Labuza, T. P., Maloney, J. F. and Karel, M. 1966. Autoxidation of methyl linoleate in freeze-dried model systems. II. Effect of water on cobalt-catalyzed oxidation. *J. Food Sci*. 31: 885–891.
83. Labuza, T. P. and Rutman, M. 1967. The effect of surface active agents on sorption isotherms of model systems. Presented at *Ann. Can. Chem. Eng. Conference*, October. 18.
84. Labuza, T. P., Tannenbaum, S. R. and Karel, M. 1970. Water content and stability of low moisture and intermediate moisture foods. *Food Technol*. 24: 543.
85. Lang, F. and Waldegger, S. 1997. Regulating cell volume. *Am. Sci.* 85: 456–463.
86. Larsen, R. F. and Anon, M. C. 1989. Interaction of antibiotics and water activity on *Streptococcus thermophilus* and *Lactobacillus bulgaricus*. *J. Food Sci*. 54(4): 922–939.
87. Leahy, M. M. and Warthesen, J. J. 1983. The influence of a Millard browning and other factors on the stability of free tryptophane. *J. Food Proc. Pres.* 1: 25.
88. Leistner, L. and Rodel, W. 1979. Microbiology of intermediate moisture foods. In: *Proceedings of the International Meeting on Food Microbiology and Technology*. Jarvis, B., Christian, J. H. B. and Michener, H. D. eds. Medicina Viva Servizio Congress, Parma, Italy.
89. Lenovich, L. M. 1987. In: *Water Activity: Theory and Applications to Food*. Rockland, L. B. and Beuchat, L. R. eds. Marcel Dekker, New York. pp. 119–136.
90. Leung, H. K. 1987. Influence of water activity on chemical reactivity. In: *Water Activity: Theory and Applications to Food*. Rockland, L. B. and Beuchat, L. R. eds. Marcel Dekker, New York. pp. 27–54.
91. Lomauro, C. J., Bakshi, A. S. and Labuza, T. P. 1985. Evaluation of food moisture sorption isotherm equations. Part II: Milk, coffee, tea, nuts, oilseeds, spices and starchy foods. *Food Sci. Technol*. 18: 118–124.
92. Lomauro, C. J., Bakshi, A. S. and Labuza, T. P. 1985. Moisture transfer properties of dry and semimoist foods. *J. Food Sci*. 50: 397.
93. Mackenzie, A. P. 1995. The physico-chemical environment during freezing and thawing of biological materials. In: *Water Relations of Foods*. Duckworth, R. B. ed. Academic Press, New York.
94. Makower, B. and Dye, W. B. 1956. Equilibrium moisture content and crystallization of amorphous sucrose and glucose. *J. Agric. Food Chem*. 4(1): 72–77.
95. Marshall, B. J., Ohye, D. F. and Christian, J. H. B. 1971. Tolerance of bacteria to high concentrations of NaCl and glycerol in the growth medium. *Appl. Microbiol*. 21: 363.
96. Mauron, J. 1981. The Maillard reaction in food: a critical review from the nutritional standpoint. *Progr. Food Nutr. Sci.* 5: 5.
97. McClure, P. J. 1999. Predictive modeling of microbial growth: the microorganisms response to water activity. In: *Water Management in the Design and Distribution of Quality Foods*. Roos, Y. H., Leslie, R. B. and Lillford, P. J. eds. Technomic Publishing, Lancaster. pp. 375–393.
98. McLaren, A. D. and Rowen, J. W. 1952. Sorption of water vapor by proteins and polymers: a review. *J. Polym. Sci*. 7(2/3): 289–324.
99. Measures, J. C. 1975. Role of amino acids in osmoregulation of nonhalophilic bacteria. *Nature* 257: 398.
100. Mellon, E. F., Korn, A. H. and Hoover, S. R. 1948. Water adsorption of protein. II. Lack of dependence of hysteresis in casein on free amino groups. *J. Am. Chem. Soc*. 70: 1144.

101. Mugnier, J. and Jung, G. 1985. Survival of bacteria and fungi in relation to water activity and solvent properties of water in biopolymer gels. *Appl. Environ. Microbiol*. 50: 108.
102. Munzing, K. 1991. DSC studies of starch in cereal and cereal products. *Thermochim. Acta* 193: 441–448.
103. Nagai, T. and Yano, T. 1990. Fractal structure of deformed potato starch and its sorption characteristics. *J. Food Sci*. 55(5): 1334.
104. Nelson, K. 1993. Reactions kinetics of food stability: comparison of glass transition and classical models for temperature and moisture dependence. Ph. D. thesis. University of Minnesota.
105. Obanu, Z. A., Ledward, D. A. and Lawrir, R. A. 1977. Reactivity of glycerol in intermediate moisture meals. *Meat Sci.* 1: 177.
106. Okos, M. R., Narsimhan, G., Singh, R. K. and Weitnauer, A. C. 1992. Food dehydration. In: *Handbook of Food Engineering*. Heldman, D. R. and Lund, D. B. eds. Marcel Dekker, New York. pp. 437–562.
107. Petriella, C., Resnik, S. L., Lozano, R. D. and Chirife, J. 1985. Kinetics of deteriorative reactions in model food systems of high water activity: color changes due to nonenzymatic browning. *J. Food Sci*. 50: 1358–1359.
108. Quast, D. G. and Karel, M. 1972. Effects of environmental factors on the oxidation of potato chips. *J. Food Sci*. 37: 584.
109. Rahman, M. S. 1995. *Food Properties Handbook*. CRC Press, Inc. Boca Raton.
110. Rahman, M. S. 2006. State diagram of foods: its potential use in food processing and product stability. *Trends Food Sci. Technol*. 17: 129–141.
111. Rahman, M. S. and Al-Belushi, R. H. 2006. Dynamic isopiestic method (DIM): measuring moisture sorption isotherm of freeze-dried garlic powder and other potential uses of DIM. *Int. J. of Food Prop.* 9(3): 421–437.
112. Rahman, M. S. and Sablani, S. S. 2002. Measurement of water activity by electronic sensors. In: *Current Protocols in Food Analytical Chemistry (CPFA)*. Wiley, New York. pp. A2.5.1–A2.5.4.
113. Rahman, M. S., Sablani, S. S., Guizani, N., Labuza, T. P. and Lewicki, P. P. 2001. Direct manometric determination of vapor pressure. In: *Current Protocols in Food Analytical Chemistry (CPFA)*. Wiley, New York. pp. A2.4.1–A2.4.6.
114. Rangarao, G. C. P., Chetana, U. V. and Veerraju, P. 1995. Mathematical model for computer simulation of moisture transfer in multiple package systems. *Food Sci. Technol.* 28(1): 38–42.
115. Rao, K. S. 1939. Hysteresis in the sorption of water on rice. *Current Sci*. 8: 256.
116. Rao, K. S. 1939. Hysteresis loop in sorption. *Current Sci*. 8: 468.
117. Rao, K. S. 1941. Hysteresis in sorption-V. *J. Phys. Chem*. 45: 522.
118. Rizvi, S. S. H. 1995. Thermodynamic properties of foods in dehydration. In: *Engineering Properties of Foods*. 2nd ed., Rao, M. A. and Rizvi, S. S. H. eds. Marcel Dekker, New York.
119. Rockland, L. B. 1969. Water activity and storage stability. *Food Technol*. 23: 1241–1251.
120. Rockland, L. B. and Beuchat, L. R. 1987. In: *Introduction, Water Activity: Theory and Applications to Food*. Rockland, L. B. and Beuchat, L. R. eds. Marcel Dekker, New York. p. v.
121. Roman, G. N., Urbicain, M. J. and Rotstein, E. 1982. Moisture equilibrium in apples at several temperatures: experimental data and theoretical consideration. *J. Food Sci*. 47: 1484–1507.
122. Rutman, M. 1967. The effect of surface active agents on sorption isotherms of model systems. M.S. thesis, Massachusetts Institute of Technology, Cambridge, MA.
123. Sa, M. M. and Sereno, A. M. 1993. Effect of temperature on sorption isotherms and heats of sorption of quince jam. *Int. J. Food Sci. Technol*. 28: 241–248.
124. Sablani, S., Rahman, M. S. and Labuza, T. P. 2001. Measurement of water activity using isopiestic Methods. In: *Current Protocols in Food Analytical Chemistry (CPFA)*. Wiley, New York. pp. A2.3.1–A2.3.10.
125. Saltmarch, M. and Labuza, T. P. 1981. SEM investigation of the effect of lactose crystallization on the storage properties of spray dried whey. In: *Studies of Food Microstructure.* Holcomb, D. N. and Kalab, M. eds. Scanning Electron Microscopy Inc., IL. pp. 203–210.
126. Saltmarch, M. and Labuza, T. P. 1981. SEM investigation of the effect of lactose crystallization on the storage properties of spray dried whey. In: *Studies of Food Microstructure.* Holcomb, D. N. and Kalab, M. eds. Scanning Electron Microscopy Inc., IL. pp. 203–210.
127. Salwin, H. 1960. Defining minimum moisture contents for dehydrated foods. *Food Technol*. 13: 594–595.
128. Saravacos, G. D., Tsiourvas, D. A. and Tsami, E. 1986. Effect of temperature on the water adsorption isotherms of sultana raisins. *J. Food Sci*. 51: 381.
129. Schaich, K. M. 1974. Free radical formation in proteins exposed to peroxidizing lipids. D.Sc. thesis, Massachusetts Institute of Technology, Cambridge, MA.

130. Scott, W. J. 1957. Water relations of food spoilage microorganisms. *Adv. Food Res*. 7Z: 83–127.
131. Scott, W. J. 1953. Water relations of *Staphylococcus aureus* at 30°C. *Aust. J. Biol. Sci.* 6: 549.
132. Seow, C. C. and Cheah, P. B. 1985. Reactivity of sorbic acid and glycerol in nonenzymatic browning in liquid intermediate moisture model systems. *Food Chem.* 18: 71.
133. Sheehof, J. M., Keilin, B. and Benson, S. W. 1953. The surface areas of proteins, v. The mechanisms of water sorption. *J. Am. Chem. Soc*. 75: 2427.
134. Silver, M. E. 1976. The behavior of invertase in model systems at low moisture contents. Ph.D. thesis, Massachusetts Institute of Technology. Cambridge, MA.
135. Slade, L. and Levine, H. 1986. Non-equilibrium behavior of small carbohydrate-water systems. *Pure Appl. Chem*. 60: 1841.
136. Slade, L. and Levine, H. 1987. Structural stability of intermediate moisture foods—a new understanding, *Food Structure—Its Creation and Evaluation*. Mitchell, J. R. and Blanshad, J. M. V. eds. Butterworths, London. p. 115.
137. Speakman, J. B. and Stott, C. J. 1936. The influence of drying conditions on the affinity of wool for water. *J. Text. Inst*. 27: T186.
138. Stadtman, E. and Earl, R. 1948. Nonenzymatic browning in fruit products. *Adv. Food Res*. 1: 325.
139. Storey, R. M. and Stainsby, G. 1970. The equilibrium water vapour pressure of frozen cod. *J. Food Technol*. 5: 157–163.
140. Strasser, J. 1969. Detection of quality changes in freeze-dried beef by measurement of the sorption isobar hysteresis. *J. Food Sci*. 34: 18.
141. Tome, D., Nicolas, J. and Drapron, R. 1978. Influence of water activity on the reaction catalyzed by polyphenoloxidase from mushrooms in organic liquid media. *Food Sci. Technol*. 11: 38.
142. Troller, J. A. 1989. Water activity and food quality. In: *Water and Food Quality*. Hardman, T. M. ed. Elsevier Applied Science, London. pp. 1–32.
143. Troller, J. A. 1987. In: *Water Activity: Theory and Applications to Food*. Rockland, L. B. and Beuchat, L. R. eds. Marcel Dekker, New York. pp. 101–117.
144. Troller, J. A., and Christian, J. H. B. 1978. Microbial survival. In: *Water Activity and Food*. Academic Press, New York.
145. Tsami, E., Marinos-Kouris, D. and Maroulis, Z. B. 1990. Water sorption isotherms of raisins, currants, figs, prunes and apricots. *J. Food Sci*. 55(6): 1594–1625.
146. Uri, N. 1956. Metal ion catalysis and polarity of environment in the aerobic oxidation of unsaturated fatty acids. *Nature* 177: 1177.
147. Van Den Berg, C., Kaper, F. S., Weldring, J. A. G. and Wolters, I. 1975. Water binding by potato starch. *J. Food Sci*. 10: 589–602.
148. Van Olphen, H. 1965. Thermodynamics of interlayer adsorption of water in clay. I. Sodium vermiculite. *J. Colloid Sci*. 20: 822.
149. Warmbier, H. C., Schnickels, R. A. and Labuza, T. P. 1976. Nonenzymatic browning kinetics in an intermediate moisture model system: effect of glucose to lysine ratio. *J. Food Sci*. 41: 981–983.
150. Warren, R. and Labuza, T. P. 1977. Comparison of chemically measured availability by lysine with relative nutritive value measured by a tetrahymena bioassay during early stage of nonenzymic browning. *J. Food Sci*. 42: 429.
151. Weisser, H. 1985. Influence of temperature on sorption equilibria. In: *Properties of Water in Foods.* Simatos, D. and Multon, J. L. eds. Martinus Nijhoff Publishers, Dordrecht.
152. Weisser, H., Weber, J. and Loncin, M. 1982. Wasserdampf sorption isotherms von zuckerautauschstoffen im temperaturbereich von 25 bis 80°C. *Food Sci. Technol*. 33: 89.
153. Wolf, M., Thompson, D. R., Warthesen, J. J. and Reineccius, G. A. 1981. Relative importance of food composition in the free lysine and methionine loses during elevated temperature processing. *J. Food Sci*. 46: 1074.
154. Wolf, M., Walker, J. E. and Kapsalis, J. G. 1972. Water vapor sorption hysteresis in dehydrated foods. *J. Agric. Food Chem.* 20: 1073.