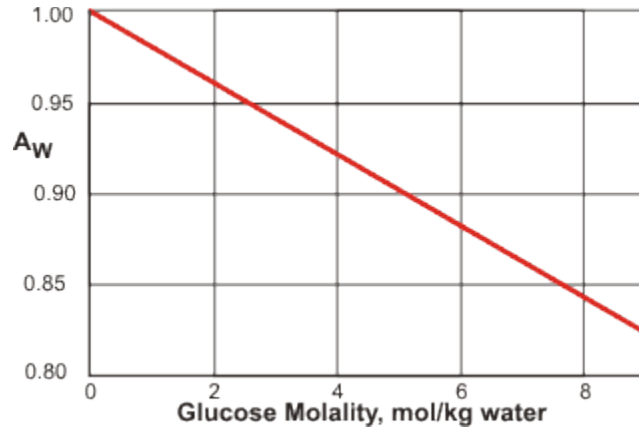
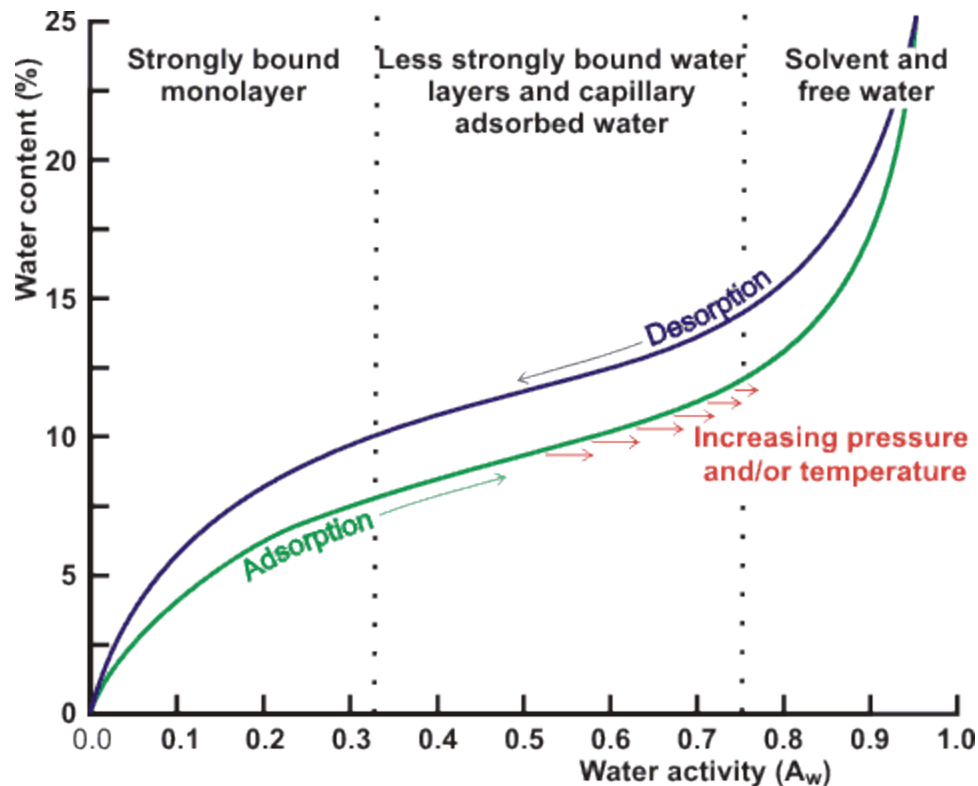


Water Activity



The term 'water activity' (a_w) describes the (equilibrium)ⁱ amount of water available for hydration of materials. When water interacts with solutes and surfaces, it is unavailable for other hydration interactions. A water activity value of unity indicates pure water whereas zero indicates the total absence of 'free' water molecules; addition of solutes always lowering the water activity. Water activity has been reviewed in aqueous [788] and biological systems [1813] and has particular relevance in food chemistry and preservation. Water activity is the effective mole fraction of water, defined as $a_w = \lambda_w x_w = p/p_0^a$ where λ_w is the activity coefficient of water, x_w is the mole fraction^g of water in the aqueous fraction, p is the partial pressure of water above the material and p_0 is the partial pressure of pure water at the same temperature (that is, the water activity is equal to the equilibrium relative humidity (ERH), expressed as a fraction). It may be experimentally determined from the dew-point temperature of the atmosphere in equilibrium with the material [473, 788]; for example, by use of a chilled mirror (in a hygrometer) to show the temperature when the air becomes saturated in equilibrium with water.^{f, h} A high a_w (that is, > 0.8) indicates a 'moist' or 'wet' system and a low a_w (that is, < 0.7) generally indicates a 'dry' system. Water activity reflects a combination of water-solute and water-surface interactions plus capillary forces. The nature of a hydrocolloid or protein polymer network can thus affect the water activity, crosslinking reducing the activity [759]. Note that the water activity of any aqueous solution in equilibrium with ice (a_w^i) is equal to the water vapor pressure over ice to the water pressure over pure liquid water and does not depend on the solute's nature or concentration [457]. Solutions with the same ice melting point therefore have the same water activity.



Shown right is an indicative water activity isotherm displaying the hysteresis often encountered depending on whether the water is being added to the dry material or removed (drying) from the wet material. This hysteresis is due to non-reversible structural changes and non-equilibrium effects. There are many empirical equations (and tables) that attempt to describe this behavior but, although indicative, none predict with sufficient accuracy and the water activity isotherm should be experimentally determined for each material. In the food industry, such empirical equations combine contributions from the ingredients to give an estimate of a_w which is then used to estimate the mold-free shelf life (MFSL; $\text{Log}_{10}(\text{MFSL, days}) = 7.91 - (8.1 \times a_w)$, 21 °C, [443]).

The water activity (a_w) usually increases with temperature and pressure increases.^g For small temperature increases ($T_1 \rightarrow T_2$) at low a_w , an often-applicable relationship

is:
$$\ln\left(\frac{a_w^{T_2}}{a_w^{T_1}}\right) = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$
 where ΔH is an enthalpy change (for example, absorption or mixing), R is the [gas constant](#) and T is in Kelvin. A similar equation is derived on the [colligative properties](#) page. Such changes in water activity may cause water migration between food components. Increasing the temperature reduces the mold-free shelf life.

The multi-ingredient nature of food and its processing (for example, cooking) commonly result in a range of water activities being present. Foods containing macroscopic or microstructural aqueous pools of differing water activity will be prone to time and temperature dependent water migration from areas with high a_w to those with low a_w ; a useful property used in the salting of fish and cheese but in other cases may have disastrous organoleptic consequences. Such changes in water activity may cause water migration between food components. As the humidity of the air is typically

50-80% ($a_w = 0.5-0.8$), foods with lower a_w will tend to gain water whilst those with higher a_w tend to lose water.

Control of water activity (rather than water content) is very important in the food industry as low water activity prevents microbial growth (increasing shelf life), causes large changes in textural characteristics such as crispness and crunchiness (for example, the sound produced by 'crunching' breakfast cereal disappearing above about $a_w = 0.65$) and changes the rate of chemical reactions (increasing hydrophobe lipophilic reactions but reducing hydrophile aqueous-diffusion-limited reactions). The balance between these factors is such that there is an optimum water activity for dehydrated foods, which is usually equated with a monolayer coverage of water and an a_w of about 0.2 - 0.3 [1127]. Highly perishable foodstuffs have $a_w > 0.95$ (equivalent to about 43 % w/w sucrose), Growth of most bacteria is inhibited below about $a_w = 0.91$ (equivalent to about 57 % w/w sucrose); similarly most yeasts cease growing below $a_w = 0.87$ (equivalent to about 65 % w/w sucrose) and most molds cease growing below $a_w > 0.80$ (equivalent to about 73 % w/w sucrose). The absolute limit of microbial growth is about $a_w = 0.6$.^b As the solute concentration required to produce $a_w < 0.96$ is high (typically $> 1\text{molal}$), the solutes (and surface interactions at low water content) will control the structuring of the water within the range where a_w knowledge is usefully applied. Changes in the natural clustering of water due to low concentrations of solutes will only occur at $a_w > 0.98$. Although low density water (ES) will possess less a_w than collapsed water clustering (CS) and the consequences are very important in biological systems, such changes in the absolute value of a_w are small.

Indicative values of water activities			
Substance	λ_w	x_w	a_w
Seawater	1.0	0.98	0.98
Saturated LiCl	0.19	0.57	0.11
Saturated MgCl ₂	0.83	0.40	0.33
Saturated SrCl ₂	1.03 ^c	0.69	0.71
Saturated BaCl ₂	1.18 ^c	0.76	0.90
Bread	-	35 ^d	0.96
Cheese	-	37 ^d	0.97
Dried fruit (for example, sultanas)	-	18 ^d	0.76
Raw meat	-	60 ^d	0.98
Dry pasta	-	12 ^d	0.50
Cooked pasta	-	72 ^d	0.97
Preserves (for example, jam)	-	28 ^d	0.88

The safe storage of food is also controlled by the pH at lower water activities; thus for example at a water activity of 0.92, only pH's above pH 4.2 present potential microbiological hazards in non-heat-treated food [1127].

Footnotes

^a Water activity is defined as equal to the ratio of the fugacity (the real gas equivalent of an ideal gas's partial pressure) of the water to its fugacity under reference conditions, but it approximates well to the more easily determined ratio of partial pressures under normal working conditions. The activity coefficient (λ_w) has dependence on the partial molar volume and hydrogen bond strength (which includes dependence on the temperature and dielectric constant) of the water and only in dilute solutions (that is, $a_w > 0.95$) can it be approximated by unity. The water activity (a_w) is related to the [chemical potential](#) (μ_w ; at equilibrium, μ_w of liquid water and its vapor phase are identical) by $\mu_w = \mu_w^\circ + RT \ln(a_w)$ where μ_w° is the standard chemical potential of water. Prediction equations for the water activity of multicomponent systems have been developed [\[552\]](#), based on

$$VdP - SdT - \sum_{i=1}^N n_i d\mu_i = 0$$

the Gibbs-Duhem equation, which at constant temperature and

$$\sum_{i=1}^N n_i d\mu_i = 0 \quad \text{and therefore} \quad \sum_{i=1}^N n_i d(\ln a_i) = 0$$

pressure simplifies to, where the terms n_i are the relative proportions of components n of chemical potential μ and activity a . The resultant equations, although starting on this firm theoretical base, require empirical simplifications due to the problems involving the interactions between the components and the paucity in our knowledge of the molecular interactions of the components with water. Water activity prediction may also be achieved by combining the effects of the chemical groups (rather than molecules) present, where suitable parameters are available [\[557\]](#). In conclusion, prediction of the water activity of mixed components presents difficulty and, except in cases of simple interpolation, is best determined experimentally.

^b Note that the required a_w necessary to prevent growth will depend somewhat on the solutes present; for example, glycerol lowers a_w efficiently but still may allow microbial growth.

^c An activity coefficient (λ) less than unity for ions may be due to non-ideal behavior caused removal of water by binding to the ions (see [colligative properties page](#)). An activity coefficient (λ) greater than unity for ions may be due to non-ideal behavior caused by the volume taken up by large ions (and other solutes, for example, sucrose) at high concentrations [\[442\]](#). An activity coefficient (λ_w) greater than unity for water may be simply seen as due to the removal of some of the ions as separate solutes by the formation of ion-pairs (see for example, [\[997\]](#)).

^d % w/w.

^e In some materials (for example, salts and some sugars) water activity may reduce with temperature increase. At high pressures, water behaves similar to solutions with increasing salt content in that the water activity apparently reduces with increased pressure [\[457\]](#).

^f There is a number of methods for measuring water content [\[470\]](#) including the poorly understood Karl Fischer titration [\[471\]](#).

^g The [mole fraction](#) of water equals the number of moles of water divided by the total number of moles of all materials, including water, in the same volume.

^h The activity coefficients for solutes may be determined in several ways, including [boiling point elevation](#), [freezing point depression](#), [equilibrium vapor pressure](#), equilibrium relative humidity (RH, $a_w \sim \text{RH}/100$), [osmotic pressure](#) ($a_w = \exp(-\Pi V_m/RT)$), heat of dilution and excess heat capacity [\[929\]](#) and the Raman absorption at 180 cm^{-1} [\[1963\]](#). Due to deviations from the theoretical relationships applied, different methods may give different results, particularly at high solute concentrations.

ⁱ The activity coefficient is an equilibrium property. Note that most food (and other biological) materials during preparation and/or processing will not be at equilibrium and so their properties may diverge from those expected from their activity coefficients. Although varying with water content, water activity is a distinct property. Activity values are empirical values determined by experiment.

Source: <http://www1.lsbu.ac.uk/water/activity.html>