

## Water Activity Definition

Water activity is derived from fundamental principles of thermodynamics and physical chemistry. As a thermodynamic principle there are requirements in defining water activity that must be met. These requirements are; pure water ( $a_w = 1.0$ ) is the standard state, the system is in equilibrium, and the temperature is defined. In the equilibrium state:

$$\mu = \mu_o + RT \ln (f/f_o)$$

where:  $\mu$  (J mol<sup>-1</sup>) is the chemical potential of the system i.e. thermodynamic activity or energy per mole of substance;  $\mu_o$  is the chemical potential of the pure material at the temperature T (°K); R is the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>); f is the fugacity or the escaping tendency of a substance; and  $f_o$  is escaping tendency of pure material (van den Berg and Bruin, 1981). The activity of a species is defined as  $a = f/f_o$ . When dealing with water, a subscript is designated for the substance,

$$a_w = f/f_o$$

$a_w$  is activity of water, or the escaping tendency of water in system divided by the escaping tendency of pure water with no radius of curvature. For practical purposes, under most conditions in which foods are found, the fugacity is closely approximated by the vapor pressure ( $f \approx p$ ) so;

$$a_w = f/f_o \cong p/p_o$$

Equilibrium is obtained in a system when  $\mu$  is the same everywhere in the system. Equilibrium between the liquid and the vapor phases implies that  $\mu$  is the same in both phases. It is this fact that allows the measurement of the vapor phase to determine the water activity of the sample.

Water activity is defined as the ratio of the vapor pressure of water in a material (p) to the vapor pressure of pure water ( $p_o$ ) at the same

temperature. Relative humidity of air is defined as the ratio of the vapor pressure of air to its saturation vapor pressure. When vapor and temperature equilibrium are obtained, the water activity of the sample is equal to the relative humidity of air surrounding the sample in a sealed measurement chamber. Multiplication of water activity by 100 gives the equilibrium relative humidity (ERH) in percent.

$$a_w = p/p_o = \text{ERH} (\%) / 100$$

Water activity is a measure of the energy status of the water in a system. There are several factors that control water activity in a system. Colligative effects of dissolved species (e.g. salt or sugar) interact with water through dipole-dipole, ionic, and hydrogen bonds. Capillary effect where the vapor pressure of water above a curved liquid meniscus is less than that of pure water because of changes in the hydrogen bonding between water molecules. Surface interactions in which water interacts directly with chemical groups on undissolved ingredients (e.g. starches and proteins) through dipole-dipole forces, ionic bonds (H<sub>3</sub>O<sup>+</sup> or OH<sup>-</sup>), van der Waals forces (hydrophobic bonds), and hydrogen bonds. It is a combination of these three factors in a food product that reduces the energy of the water and thus reduces the relative humidity as compared to pure water. These factors can be grouped under two broad categories osmotic and matric effects.

Due to varying degrees of osmotic and matric interactions, water activity describes the continuum of energy states of the water in a system. The water appears “bound” by forces to varying degrees. This is a continuum of energy states rather than a static “boundness”. Water activity is sometimes defined as “free”, “bound”, or “available water” in a system. Although these terms are easier to conceptualize, they fail to adequately define all aspects of the concept of

water activity.

Water activity is temperature dependent. Temperature changes water activity due to changes in water binding, dissociation of water, solubility of solutes in water, or the state of the matrix. Although solubility of solutes can be a controlling factor, control is usually from the state of the matrix. Since the state of the matrix (glassy vs. rubbery state) is dependent on temperature, one should not be surprised that temperature affects the water activity of the food. The effect of temperature on the water activity of a food is product specific. Some products increase water activity with increasing temperature, others decrease  $a_w$  with increasing temperature, while most high moisture foods have negligible change

with temperature. One can therefore not predict even the direction of the change of water activity with temperature, since it depends on how temperature affects the factors that control water activity in the food.

As a potential energy measurement it is a driving force for water movement from regions of high water activity to regions of low water activity. Examples of this dynamic property of water activity are; moisture migration in multidomain foods (e.g. cracker-cheese sandwich), the movement of water from soil to the leaves of plants, and cell turgor pressure. Since microbial cells are high concentrations of solute surrounded by semi-permeable membranes, the osmotic effect on the free energy of the water is important