

## Introduction to water activity theory

### What is water activity?

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:  $\mu$  ( $\text{J mol}^{-1}$ ) 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  $T$  ( $^{\circ}\text{K}$ );  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ );  $f$  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 ( $f \sim p$ ) so;

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

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 ( $\text{H}_3\text{O}^+$  or  $\text{OH}^-$ ), 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 for determining microbial water relations and therefore their growth rates.

### ***Why is water activity important?***

Water activity ( $a_w$ ) is one of the most critical factors in determining quality and safety of the goods you consume every day. Water activity affects the shelf life, safety, texture, flavor, and smell of foods. It is also important to the stability of pharmaceuticals and cosmetics. While temperature, pH and several other factors can influence if and how fast organisms will grow in a product, water activity may be the most important factor in controlling spoilage. Most bacteria, for example, do not grow at water activities below 0.91, and most molds cease to grow at water activities below 0.80. By measuring water activity, it is possible to predict which microorganisms will and will not be potential sources of spoilage. Water activity--not water content--determines the lower limit of available water for microbial growth. In addition to influencing microbial spoilage, water activity can play a significant role in determining the activity of enzymes and vitamins in foods and can have a major impact their color, taste, and aroma. It can also significantly impact the potency and consistency of pharmaceuticals.

### ***Free water versus bound water.***

Water activity describes the continuum of energy states of the water in a system. The water in a sample appears to be "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. These terms are easier to conceptualize, although they fail to adequately define all aspects of the concept of water activity. Water activity instruments measure the amount of free (sometimes referred to as unbound or active) water present in the sample. A portion of the total water content present in a product is strongly bound to specific sites on the chemicals that comprise the product. These sites may include the hydroxyl groups of polysaccharides, the carbonyl and amino groups of proteins, and other polar sites. Water is held by hydrogen bonds, ion-dipole bonds, and other strong chemical bonds. Some water is bound less tightly, but is still not available (as a solvent for water-soluble food components). Many preservation processes attempt to eliminate spoilage by lowering the availability of water to microorganisms. Reducing the amount of free--or unbound--water also minimizes other undesirable chemical changes that occur during storage. The processes used to reduce the amount of free water in consumer products include techniques like concentration, dehydration and freeze drying. Freezing is another common approach to controlling spoilage. Water in frozen foods is in the form of ice crystals and therefore unavailable to microorganisms for reactions with food components. Because water is present in varying degrees of free and bound states, analytical methods that attempt to measure total moisture in a sample don't always agree. Therefore, water activity tells the real story.

### ***Controlling non-enzymatic reactions.***

Foods containing proteins and carbohydrates, for example, are prone to non-enzymatic browning reactions, called Maillard reactions. The likelihood of Maillard reactions browning a product increases as the water activity increases, reaching a maximum at water activities in the range of 0.6 to 0.7. In some cases, though, further increases in water activity will hinder Maillard reactions. So, for some samples, measuring and controlling water activity is a good way to control Maillard browning problems.

### ***Slowing down enzymatic reactions.***

Enzyme and protein stability is influenced significantly by water activity due to their relatively fragile nature. Most enzymes and proteins must maintain conformation to remain active. Maintaining critical water activity levels to prevent or entice conformational changes is important to food quality. Most enzymatic reactions are slowed down at water activities below 0.8. But some of these reactions occur even at very low water activity values. This type of spoilage can result in formation of highly objectionable flavors and odors. Of course, for products that are thermally treated during processing, enzymatic spoilage is usually not a primary concern.

### **Measuring water activity**

There is no device that can be put into a product to directly measure the water activity. However, the water activity of a product can be determined from the relative humidity of the air surrounding the sample when the air and the sample are at equilibrium. Therefore, the sample must be in an enclosed space where this equilibrium can take place. Once this occurs, the water activity of the sample and the relative humidity of the air are equal. The measurement taken at equilibrium is called an equilibrium relative humidity, or "ERH".

### ***Choosing a measurement tool***

Two different types of water activity instruments are commercially available. One uses chilled-mirror dewpoint technology while the other measures relative humidity with sensors that change electrical resistance or capacitance. Each has advantages and disadvantages. The methods vary in accuracy, repeatability, speed of measurement, stability in calibration, linearity, and convenience of use.

Which sensor works best for measuring the water activity of products? The major advantages of the chilled-mirror dew point method are accuracy, speed, ease of use and precision. The range of Decagon's AquaLab, for example, is from 0.030 to 1.000 $a_w$ , with a resolution of  $\pm 0.001a_w$  and accuracy of  $\pm 0.003a_w$ . Measurement time is typically less than five minutes. Capacitance sensors have the advantage of being inexpensive, but are not typically as accurate or as fast as the chilled-mirror dewpoint method. Capacitive instruments measure over the entire water activity range—0 to 1.00  $a_w$ , with a resolution of  $\pm 0.005a_w$  and accuracy of  $\pm 0.015a_w$ . Some commercial instruments can measure in five minutes while other electronic capacitive sensors usually require 30 to 90 minutes to reach equilibrium relative humidity conditions.

### ***Chilled-mirror theory***

In chilled mirror dewpoint instruments, a sample is equilibrated within the headspace of a sealed chamber containing a mirror, an optical sensor, an internal fan, and an infrared temperature sensor. At equilibrium, the relative humidity of the air in the chamber is the same as the water activity of the sample. A thermoelectric (Peltier) cooler precisely controls the mirror temperature. An optical reflectance sensor detects the exact point at which condensation first appears. A beam of infrared light is directed onto the mirror and reflected back to a photodetector, which detects the change in reflectance when condensation occurs on the mirror. A thermocouple attached to the mirror accurately measures the dew-point temperature. The internal fan is for air circulation, which reduces vapor equilibrium time and controls the boundary layer conductance of the mirror surface. Additionally, a thermopile sensor (infrared thermometer) measures the sample surface temperature. Both the dew point and sample temperatures are then used to determine the water activity. During a water activity measurement, the instrument repeatedly determines the dew-point temperature until vapor equilibrium is reached. Since the measurement is based on temperature determination, calibration is not necessary, but measuring a standard salt solution checks proper functioning of the instrument. If there is a problem, the mirror is easily accessible and can be cleaned in a few minutes.

### ***Capacitive sensor theory***

Some  $a_w$  instruments use capacitance sensors to measure water activity. Such instruments use a sensor made from a hygroscopic polymer and associated circuitry that gives a signal relative to the ERH. The sensor measures the ERH of the air immediately around it. This ERH is equal to sample water activity only as long as the temperatures of the sample and the sensor are the same. Since these instruments relate an electrical signal to relative humidity, the sensor must be calibrated with known salt standards. In addition, the ERH is equal to the sample water activity only as long as the sample and sensor temperatures are the same. Some capacitive sensors need between 30 and 90 minutes to come to temperature and vapor equilibrium. Accurate measurements with this type of system require good temperature control.

### ***Evaluating Instrumentation***

When evaluating water activity measurements, precision and accuracy are, of course, important considerations. But equally important to consider is how susceptible the sensor is to contamination and how frequently calibration is required. Also, when comparing water activity instruments, be sure to evaluate precision and accuracy over the entire range of water activities most commonly found in your specific products.

### ***Water activity--accepted and approved***

For many products, water activity is an important property. It predicts stability with respect to physical properties, rates of deteriorative reactions, and microbial growth. The growing recognition of measuring water activity in foods is illustrated by the U.S. Food and Drug Administration's incorporation of the water activity principle in the definition of non-potentially hazardous foods (Potentially Hazardous Foods means food with a finished equilibrium pH greater than 4.6 and a water activity greater than 0.85). They use this and other criteria to determine whether a scheduled process must be filed for the thermal destruction of *Clostridium botulinum* (Botulism). In the past, measuring water activity of foodstuffs was a frustrating experience. New instrument technologies have vastly improved speed, accuracy and reliability of measurements.

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