Water is the main ingredient in many foods. It has a significant effect on a food's microbial, chemical, and structural stability. To achieve consistent, reliable quality in every batch and product, food manufacturers need a scientifically accurate way of measuring water relationships. In many cases, water activity is the best measurement to use.

Fundamentals of Water Activity

This paper discusses the scientific origins and attributes of water activity, reviews the regulations which specify water activity as a measurement, and details some of the most common applications using water activity. ▶

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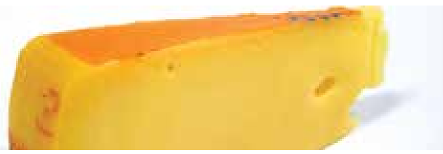
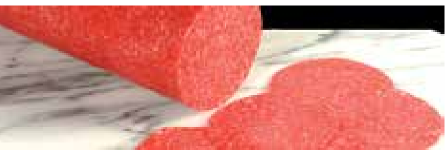
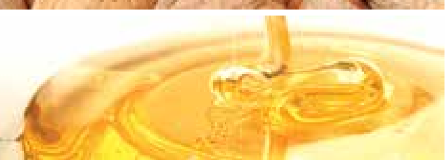
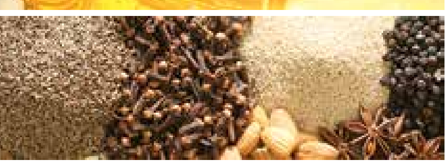
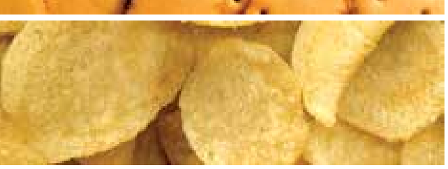
Water Activity and Growth of Microorganisms in Food*

	Range of a_w	Microorganisms Generally Inhibited by Lowest a_w in This Range	Foods Generally within This Range
	1.00–0.95	Pseudomonas, Escherichia, Proteus, Shigella, Klebsiella, Bacillus, Clostridium perfringens, some yeasts	Highly perishable (fresh) foods and canned fruits, vegetables, meat, fish, milk, and beverages
	0.95–0.91	Salmonella, Vibrio parahaemolyticus, C. botulinum, Serratia, Lactobacillus, Pediococcus, some molds, yeasts (Rhodotorula, Pichia)	Some cheeses (Cheddar, Swiss, Muenster, Provolone), cured meat (ham), bread, tortillas
	0.91–0.87	Many yeasts (Candida, Torulopsis, Hansenula), Micrococcus	Fermented sausage (salami), sponge cakes, dry cheeses, margarine
	0.87–0.80	Most molds (mycotoxigenic penicillia), Staphyloccocus aureus, most Saccharomyces (bailii) spp., Debaryomyces	Most fruit juice concentrates, sweetened condensed milk, syrups, jams, jellies, soft pet food
	0.80–0.75	Most halophilic bacteria, mycotoxigenic aspergilli	Marmalade, marzipan, glacé fruits, beef jerky
	0.75–0.65	Xerophilic molds (Aspergillus chevalieri, A. candidus, Wallemia sebi), Saccharomyces bisporus	Molasses, raw cane sugar, some dried fruits, nuts, snack bars, snack cakes
	0.65–0.60	Osmophilic yeasts (Saccharomyces rouxii), few molds (Aspergillus echinulatus, Monascus bisporus)	Dried fruits containing 15-20% moisture; some toffees and caramels; honey, candies
	0.60–0.50	No microbial proliferation	Dry pasta, spices, rice, confections, wheat
	0.50–0.40	No microbial proliferation	Whole egg powder, chewing gum, flour, dry beans
	0.40–0.30	No microbial proliferation	Cookies, crackers, bread crusts, breakfast cereals, dry pet food, peanut butter
	0.30–0.20	No microbial proliferation	Whole milk powder, dried vegetables, freeze dried corn

* Adapted from L.R. Beuchat, Cereal Foods World, 26:345 (1981).

Water Activity: Measuring Energy

In 1953, William James Scott showed that microbial growth in food is governed not by water content, as most people thought, but by water activity. Four years later, he established the concept of a minimum water activity for microbial growth. Water activity is now routinely used by food manufacturers to determine whether or not a product is susceptible to microbial proliferation.

Scott's work is relevant to every product from fresh tree nuts and wheat berries to processed cheese and pharmaceuticals. The microbial growth limits he and his colleagues established apply to dried meats, cheesecake, powdered drink mix, and dog food, but also to non-food products like tree bark, hand lotion, and insulation.

Why Water Activity Predicts Microbial Growth

Like all organisms, microorganisms rely on water for growth. They take up water by moving it across the cell membrane. This water movement mechanism depends on a water activity gradient—on water moving from a high water activity environment outside the cell to a lower water activity environment within the cell.

When water activity outside the cell becomes low enough, it causes osmotic stress: the cell cannot take up water and becomes dormant. The microorganisms are not eliminated, they just become unable to grow enough to cause infection. Different organisms cope with osmotic stress in different ways. That's why there are different growth limits for each organism. Some types of molds and yeasts have adapted to withstand very low water activity levels.

Controlling Water Activity

If you measure the water activity of any material, you will know which bacteria, molds, or fungi can grow on and in it. By reducing water activity, you can rule out the growth of certain classes of microbes. At low water activities you can preclude the growth of anything at all.

Water activity is not a kill step. It's a control step, and an integral part of many HACCP plans.

The chart on page 2 shows the water activity limits for many common microorganisms. These well-established microbial growth limits have been incorporated into FDA and other regulations (see pages 4 and 12).

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Table A. Interaction of pH and a_w for control of spores in food heat-treated to destroy vegetative cells and subsequently packaged.

a_w Values	pH Values		
	4.6 or less	> 4.6 - 5.6	> 5.6
0.92 or less	Non-PHF*/Non-TCS**	Non-PHF/Non-TCS	Non-PHF/Non-TCS
> 0.92 - 0.95	Non-PHF/Non-TCS	Non-PHF/Non-TCS	PA***
> 0.95	Non-PHF/Non-TCS	PA	PA

* PHF: Potentially Hazardous Food
** TCS: Time/Temperature Control for Food Safety
*** PA: Product Assessment Required

Table B. Interaction of pH and a_w for control of vegetative cells and spores in food not heat-treated or heat-treated but not packaged.

a_w Values	pH Values			
	> 4.2	> 4.2 - 4.6	> 4.6 - 5.0	> 5.0
> 0.88	Non-PHF*/Non-TCS**	Non-PHF/Non-TCS	Non-PHF/Non-TCS	Non-PHF/Non-TCS
> 0.88 - 0.90	Non-PHF/Non-TCS	Non-PHF/Non-TCS	Non-PHF/Non-TCS	PA***
> 0.90 - 0.92	Non-PHF/Non-TCS	Non-PHF/Non-TCS	PA	PA
> 0.92	Non-PHF/Non-TCS	PA	PA	PA

* PHF: Potentially Hazardous Food
** TCS: Time/Temperature Control for Food Safety
*** PA: Product Assessment Required

2009 Food Code Definition of Potentially Hazardous Foods

Water activity is the only moisture related measurement that is an accepted HACCP critical control point. It is particularly important in intermediate, shelf-stable food products. In combination with pH, water activity determines which of these intermediate-moisture foods are considered potentially hazardous by the FDA.

Let's use a thought experiment to better understand water activity. Take a glass of water, and a dry sponge. Dip the corner of the sponge into the glass of water. The water will, of course, move from the glass into the sponge.

What is the difference between the water in the glass and the water in the sponge? The answer is that the water in the glass is free, while that in the sponge is, to some extent, bound. It has a lower energy state than the water in the glass. We know that, because to retrieve the water from the sponge we need to do work on it (squeeze the sponge).

That reduction in the water's energy reduces its vapor pressure, increases its boiling point, and reduces its freezing point. In other words, the water in the sponge is different from the water in the glass in measurable ways.

Let's consider the reduction in vapor pressure. We can calculate the change in energy that accompanies a change in pressure using the first law of thermodynamics. If we let the symbol U represent the energy in a system, and calculate the change in U that occurs when we change the volume, at constant pressure (we assume no heat is added or removed) we can write

$$dU = -pdV$$

dU represents a small change in energy, and dV represents a small change in volume. The relationship between pressure and volume, called the ideal gas law, is

$$pV = nRT$$

where n is the number of moles of gas, R is a constant, known as the gas constant (8.31 J/mol K) and T is the temperature of the gas in kelvins. We can differentiate the ideal gas law to get dV:

$$dV = -nRT\frac{dp}{p^2}$$

Combining this with the first law we get

$$dU = nRT\frac{dp}{p}$$

Now, the energy required to go from the vapor pressure of the pure water in the glass, which we call the saturation vapor pressure or p_0, to the vapor pressure of the water in the sponge is

$$U = nRT\int_{p_0}^{p}\frac{dp}{p} = nRT\ ln\left(\frac{p}{p_0}\right)$$

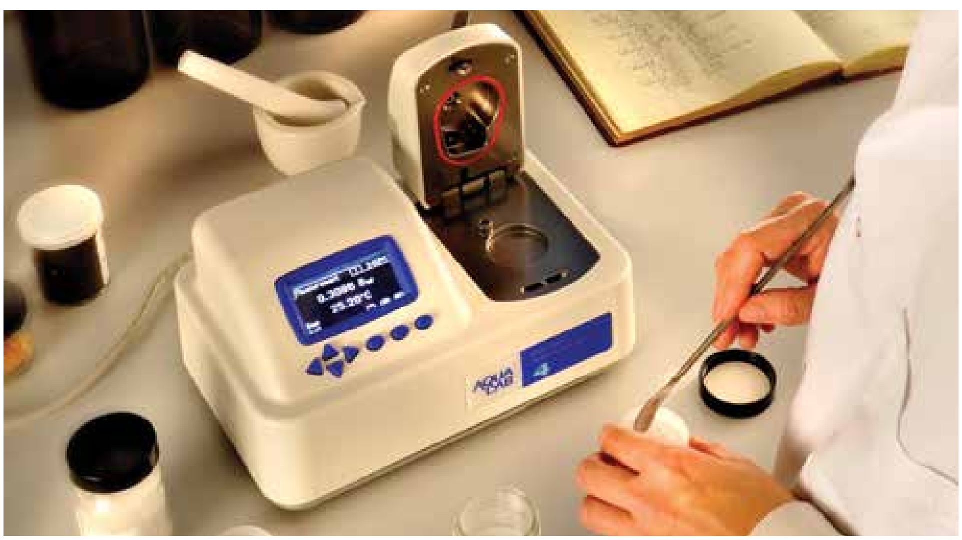
The ratio p/p_o is called the water activity, a_w, when we are talking about the water in the sponge, or water in foods or other solids or liquids. We call it the relative humidity when we apply it to water in the air, and sometimes multiply it by 100 to express it as a percent. The ratio U/n is the energy per mole of water and is called the water potential, with the symbol Ψ. Water potential has units of Joules/mole. With this substitution we finally arrive at the equation relating the energy of the water in the sponge and its water activity

$$\Psi = RT\ ln\ a_w$$

The equation tells us that we can express the energy state of the water in a product either as a water potential or as a water activity. Some fields of science use water potential and others use water activity (some also use freezing point depression or osmolality, but these are all equivalent concepts). There are advantages and disadvantages to each, but the important thing to understand is that both are measures of the energy state of the water and have a strong theoretical basis. We focus on water activity here because that is the measure most widely used in food science and engineering.

What determines water activity?

Now consider what factors influence water activity. We can lower the water energy by adsorbing the water in the sponge. Water adsorbed onto any surface lowers its energy state. The water is bound by hydrogen bonds, capillary forces and van der Waals - London forces, so it has less energy than free water. We call these effects matrix effects. The water energy can be decreased in another way as well. We can dilute the water with solutes. Since work is required to restore the water to its pure, free state, this also reduces the water activity and water potential. We call these effects osmotic effects. We sum the reduction in energy from matric and osmotic effects to get the total change in energy.



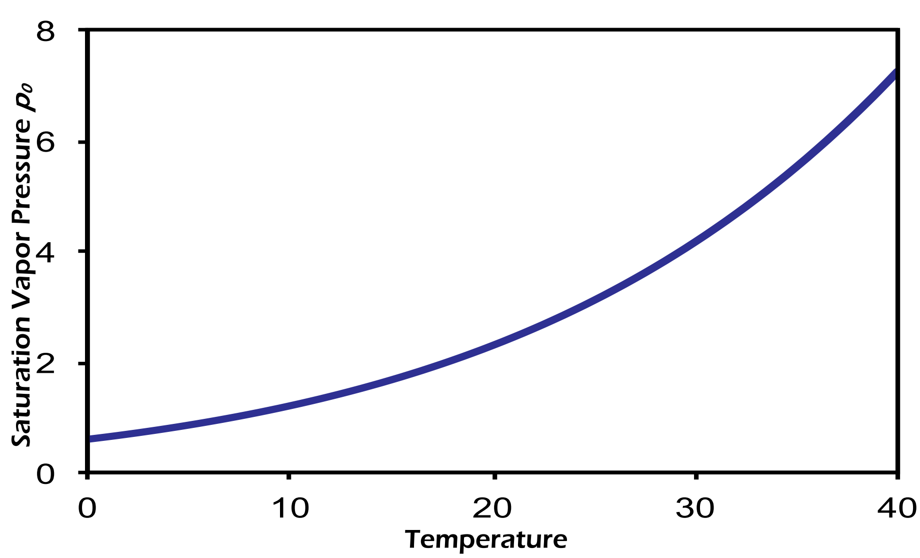
AquaLab determines water activity by measuring the temperature of the sample and the dew point of the air in a sealed head space.

How do we measure water activity? The equation we just derived also provides a convenient way of measuring water potential or water activity. If we enclose a sample in a sealed container the relative humidity of the head space will equilibrate with the water activity of the sample. At equilibrium the two will be equal, and we can measure the relative humidity of the head space to know the water activity of the sample.

Early water activity meters used this method. Primitive hygrometers used changes in length of hair or swelling and shrinking of specially prepared membranes to measure humidity. These devices were sealed into chambers with food samples to determine humidity, and thus water activity. More recently electric hygrometers, measuring either electrical capacitance or electrical resistance are sealed into the head space of the sample to measure humidity.

The best method, though, is suggested by the ratio p/p_0. The saturation vapor pressure p_0 depends only on the temperature of the sample, as shown in the accompanying graph. If we know the sample temperature we know p_0. The vapor pressure of the water in the sample can be measured by measuring the vapor pressure of water in the sealed head space of the sample.

The most accurate way of measuring that vapor pressure, and one that goes back to first principles, is to measure the dew point of the air. AquaLab dew point instruments measure the vapor pressure using the dew point temperature, thus giving a direct and fundamental measurement of water activity. If you want water potential, it is easy to convert between the two measurements.

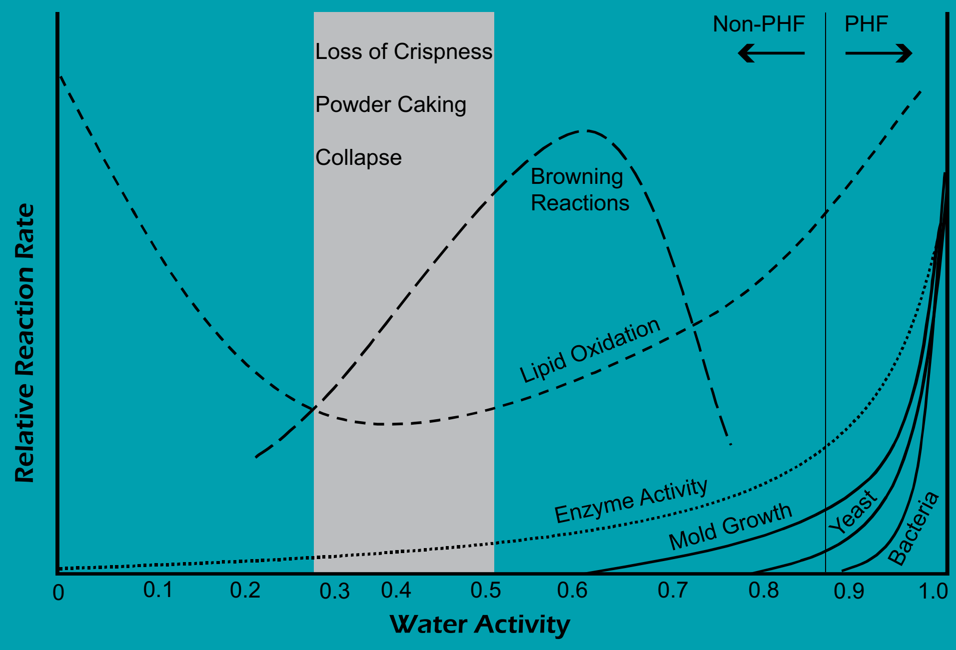


Saturation Vapor Pressure p_0 is temperature dependent.

Chemical Stability

Chemical reactions can affect the taste, appearance, and nutritional value of food products. They can also reduce the effectiveness of active ingredients in pharmaceuticals.

Water can affect these chemical reactions in several ways. It can be a reactant, it can act as a solvent, and it can affect the rate of diffusion-limited reactions by changing the molecular mobility of the reactants. Chemical reactions can be complex and the mechanisms are not always completely understood. However, a food's chemical stability often correlates better with water activity than with moisture content. In many cases you can use established mathematical models to maximize shelf life, establish packaging standards, and set release specifications. The models predict the rate of degradative reactions that occur in a specific food or pharmaceutical at a specific water activity. These calculations can help establish water activity values that will maximize shelf life, determine packaging needs, and set release specifications that minimize degradative effects.



This figure shows how physical, chemical, and microbial stability relate to water activity.

Physical Stability

Water plays a critical role in the stability of foods near glass transition. In these foods, changes in water can affect both structure and texture. The result of structural degradation can be seen in phenomena like crystallization, caking, deliquescence, and collapse. Textural degradation results in effects such as loss of crispness, hardening, and stickiness.

It is difficult to separate the effects of water content, water activity, and temperature on the physical stability of foods. Physical stability is best understood through a moisture sorption isotherm—a graph of the relationship between moisture content and water activity at constant temperature. Each product has a different isotherm. The isotherm can be used in various models to find the critical water activity associated with glass transition.

Moisture Movement Between Components

Multi-component products such as creme-filled cakes, iced cookies, or nut-filled bars present special challenges. Water will move between the components until their water activities are equal. Sometimes this can cause structural changes, chemical reactions, or microbial susceptibility. Water activity is the only measurement that can predict how moisture will move. An ingredient mixing model can establish the water activity at which all the components will be in equilibrium and set targets for each ingredient.

Target Water Activity

Especially for intermediate-moisture foods, setting a target water activity is a critical step in formulating for safety and quality. The specification can be set to avoid microbial proliferation, chemical reactions, physical and structural degradation, and moisture migration. Once it has been set, other models can help determine shelf life based on storage conditions and packaging.

How To Use Water Activity Data

PREDICT AND MAXIMIZE SHELF LIFE, MAKE PACKAGING DECISIONS, AND AVOID DEGRADATIVE REACTIONS.

STABILITY	REACTIONS ending shelf life	INPUTS modeling data	OUTPUTS model prediction
Microbial	Pathogenic Bacteria Yeasts Mold	Microbial counts under different environmental conditions including water activity.	Days until growth or growth rate.
Chemical	Vitamin Degradation Loss of Active Ingredient Maillard Browning Reaction Lipid Oxidation Enzyme Stability	Concentration data of measurable attribute related to the reaction taken at different temperatures and water activities. Minimum acceptable level for reactant or product.	Shelf life in days. Most stable a_w for product.
Physical	Moisture Migration in Multi-component Products (Raisin bran, cream-filled cakes)	Isotherm data for each ingredient. Wet mass of each ingredient.	Best equilibrium condition for product components Final moisture content for each ingredient.
	Caking/Clumping/ Crystallization	Isotherm data	Critical a_w limit for glass transition
	Deliquescence	Isotherm data	Critical a_w limit for deliquescence.

Shelf Life

Determining Shelf Life

Shelf life testing requires knowing what event ends shelf life for a particular product and finding a way to quantify and track that event. For example, reactions can be tracked by quantifying changes in the concentration of one of the reactants or one of the products of the reaction.

Scientific models can then predict the shelf life of a product at a specific water activity and temperature. They can also predict the water activity of a product based on ingredients, determine how much humectant should be added to achieve a specific water activity, and calculate packaging requirements. The chart on page 10 shows some of the predictive modeling possible with water activity measurements and details the data needed for each model.

Conclusion

Water activity is a thermodynamic measure of the energy of water in a product. It is directly related to the microbial susceptibility of food products. It is also well-correlated with degradative chemical and physical reactions that end shelf life in foods. It can be used to predict and maximize shelf life, to make packaging decisions, to avoid glass transition, and in many other facets of formulation. Because it is measured on a scale with a known standard, it is particularly well-suited to being a safety and quality specification. It is cited in several FDA regulations and guidelines, and is the only measurement that can be used as a HACCP critical control point. ◀

Vapor sorption analysis is the best way of understanding physical stability.

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Fundamentals of Water Activity

Government Compliance Regulations for Microbiological Control

FOOD STANDARDS

2009 Food Code definition of Potentially Hazardous Foods

21CFR 110
Current food manufacturing practice in manufacturing, packing, or holding human food

21CFR 113
Thermally processed low-acid foods packaged in hermetically sealed containers

21CFR 114
Acidified foods

HACCP
Critical control point

ANSI/NSF Standard 75
Shelf-Stable Baked Goods

PHARMACEUTICAL STANDARDS

21CFR 211.113
Control of microbiological contamination

USP <1112>
Microbiological attributes of non-sterile pharmaceutical products

ICH Guidelines

COSMETICS STANDARDS

ISO 29621
Guidelines for the risk assessment and identification of microbiologically low-risk products

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