Water Activity in Muscle and Related Tissues

Owen Fennema*, Leader
John Carpenter, Recorder

Water activity is a better indication than water content of microbial growth and stability of sensory attributes of meat and meat products. Thus it is important to understand what water activity is, how it relates to various other terms of importance, and how it influences the growth of microorganisms and the stability of various attributes of food.

It is evident from Fig. 1 that water activity, a_w, is the partial pressure of water above the sample divided by the vapor pressure of water at the same temperature. It is also necessary that equilibrium conditions prevail and this is difficult to achieve when dealing with large (more than about 25 g) samples. It is also evident that a_w is numerically equal to the equilibrium relative humidity (ERH) divided by 100. Furthermore, a_w is equal to the mole fraction of water, N, in the sample. This point is of significance since it allows one to calculate a_w from freezing point data (freezing point depression is mathematically related to the moles of water in the sample.)

It should be noted that water activity as defined in Fig. 1 is an approximation. Water activity is accurately defined in terms of fugacities, but the error involved in using partial pressures and vapor pressures is not significant in practical situations that apply to foods.

Figure 1.

Water Activity, a_w

$$a_w = \frac{P}{Po} = \frac{ERH}{100} = N = \frac{n_1}{n_1 + m}$$

where

P is the partial pressure of water above the sample.

Po is the vapor pressure of pure water at the same temperature.

ERH is the equilibrium relative humidity of the atmosphere expressed as a percent.

N is the mole fraction of water with n_1 and n_2 representing moles of solvent and solute respectively.

*O.R. Fennema, University of Wisconsin, Madison, WI 53706

J.A. Carpenter, University of Georgia, Athens, GA 30602

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Knowing what water activity is, it is now appropriate to deal with why one should be interested in this term. As briefly alluded to at the outset, water activity is a better indicator than water content of: microbial growth, stability of nutrients, stability of color, stability of flavor and textural properties. In addition, a_w is useful for predicting the water content of a food which will provide optimum storage stability.

Water activity is not, however, a perfect indicator of microbial growth and food stability. This is true since other factors, such as oxygen concentration, water mobility, pH and the types of solutes present, also influence microbial growth and food stability. In spite of these shortcomings, water activity is still a useful indicator under most circumstances of the properties mentioned.

Several methods exist for increasing water activity: 1) methods based on freezing point depression; 2) methods based on direct measurement of relative humidity or the sample atmosphere once a small sample has come to equilibrium in a small, closed container, and 3) methods based on placing the sample in a small closed container, the internal atmosphere of which is maintained at a constant relative humidity by means of a solution saturated with a suitable solute, allowing the sample to come to equilibrium with the atmosphere, then determining the moisture content of the sample. Method 1 is most applicable to liquid samples. Many commercial instruments are available which function in accord with Method 2. Method 3 is slow, but can be done inexpensively in any laboratory. Achieving equilibrium conditions (and, therefore, accuracy) can be troublesome with Methods 2 and 3, unless the sample is very small (a few grams with a large surface area).

It is appropriate at this point to list the water activities of various meats and meat products (Table 1). The fact that fresh meat has an average a_w of 0.99 means that the most easily removable or least bound water molecules behave essentially like pure water ($a_w = 1.0$). It follows that water from fresh meat will be easily removable during drying (at least during the early stage) and that the water in fresh meat will be readily available to support the growth of microorganisms and to participate in chemical reactions. As indicated in Table 1, meat products generally exhibit water activities somewhat lower than that of fresh meat, and these products are, therefore, correspondingly more stable.

One of the most useful ways to utilize water activity data is to use it to plot a moisture-sorption isotherm (plot of water content versus water activity at a constant temperature). An example for meat is shown in Fig. 2. The desorption isotherm is prepared by incremental drying, and the adsorption iso-

Table 1. Water Activity of Meats and Meat Products

Product	A_w Minimum	Maximum	Average
Fresh meat	0.98	0.99	0.99
Bologna type sausage	0.93	0.98	0.97
Liver sausage	0.95	0.97	0.96
Blood sausage	0.93	0.97	0.96
Fermented sausage	0.72	0.95	0.91
Raw ham	0.88	0.96	0.92
Dried beef	0.86	0.94	0.90

Leistner and Rödel, 1975

Figure 2

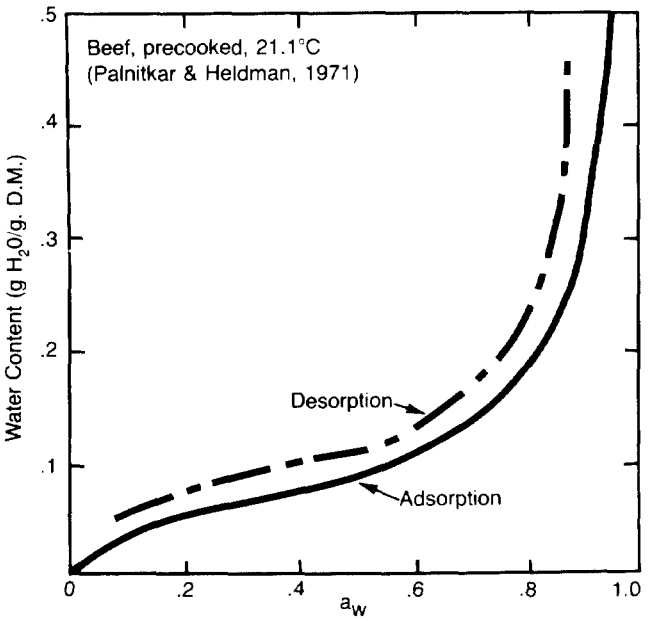

Figure 2. Relationship between water content and water activity in meat.

therm, which is displaced from the desorption isotherm, is prepared by incremental moistening of a previously dried sample. The fact that the two isotherms are not superimposable is an indication that some of the changes during drying irreversibly alter the water-solute relationships in the sample. The shape of the isotherms is qualitatively typical of most foods.

A more generalized isotherm is shown in Fig. 3, which has been divided into three zones that are separated by indistinct boundaries. These zone boundaries are purposely indistinct because there is, in fact, no abrupt change at the boundaries and because the locations change somewhat, depending on the type of food and on whether an adsorption or desorption mean was used. Let us consider these zones by starting with a dry product to which water is gradually added. Water in Zone I is the most strongly adsorbed and the most immobile. This water associates with the most polar, most accessible sites by means of strong water-ion or water-dipole bands. Water in Zone I has no solvent capacity, no plasticizing ability, is unfreezable down to a temperature of −40° C and exhibits

Figure 3.

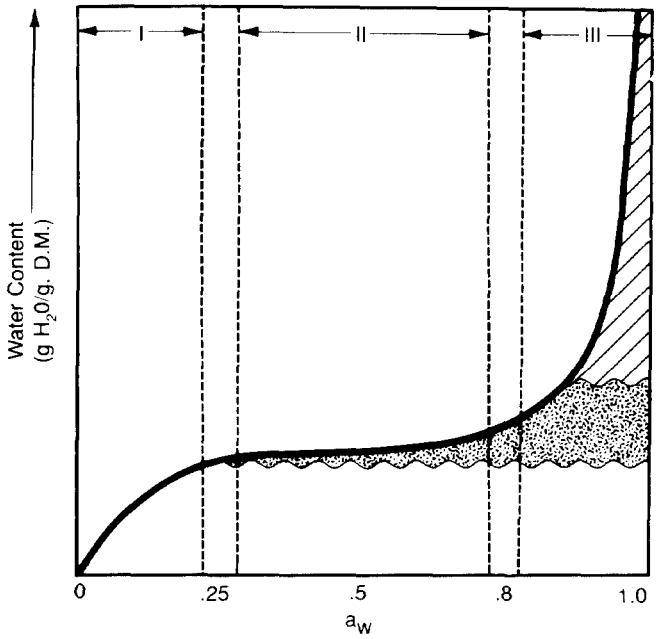

Figure 3. Relationship between water content and water activity – three zones of activity.

an enthalpy of vaporization greater than that of pure water.

The boundary between Zones I and II represents the monolayer moisture value. At this water activity, water is present in sufficient amount to cover, in a monolayer, all of the accessible polar sites on the dry food matrix. This water activity and the associated water content usually provides optimum stability for the food, i.e., either greater or smaller water activities will result in more rapid chemical degradation.

If additional water is added to the sample, it occupies Zone II. Water in Zone II occupies the remaining accessible first-layer sites and also forms multilayers. Water-solute or water-water hydrogen binding are the primary means of intermolecular association. Zone II water exhibits a slightly elevated enthalpy of varporization compared to pure water, is largely unfreezable down to −40° C and is present in sufficient quantity to lend some plasticity to the product, to cause some swelling, to initiate reactant mobility and solution processes and to increase reaction rates. By way of perspective, in a high-moisture food, the water occupying Zones I and II typically represents less than 5% of the total water.

If water continues to be added, eventually the boundary of Zones II and III will be reached and further added water will become Zone III water. This water is the least strongly bound and most mobile of the three kinds of water in Fig. 3. It is freezable, easily removable, available as a solvent and readily supports chemical reactions and growth of microorganisms. This water is sometimes referred to as bulk-phase water. It has properties like water in a dilute salt solution. In cells or gels, this water may be physically entrapped so its flow is impeded. In a high-moisture sample, Zone III water will constitute about 95% of the total water.

The various shadings used in Fig. 3 are intended to convey the notion that Zone I water remains essentially intact as Zone II water is added, and both Zones I and II water remain essentially intact as Zone III water is added. However,

the three zones are in a state of dynamic equilibrium so that water molecules can move between zones with the various movements balancing out so the quantity of water in each zone remains constant.

One should also be aware that water activity values and moisture sorption isotherms are affected by temperature (Fig. 4). A one-degree change in temperature (C°) will cause the a_w value to change about 0.01. Thus, a large change in temperature can alter a_w significantly, and this in turn will alter food stability. This can occur without a change in moisture content (any horizontal line drawn through Fig. 4).

Figure 4

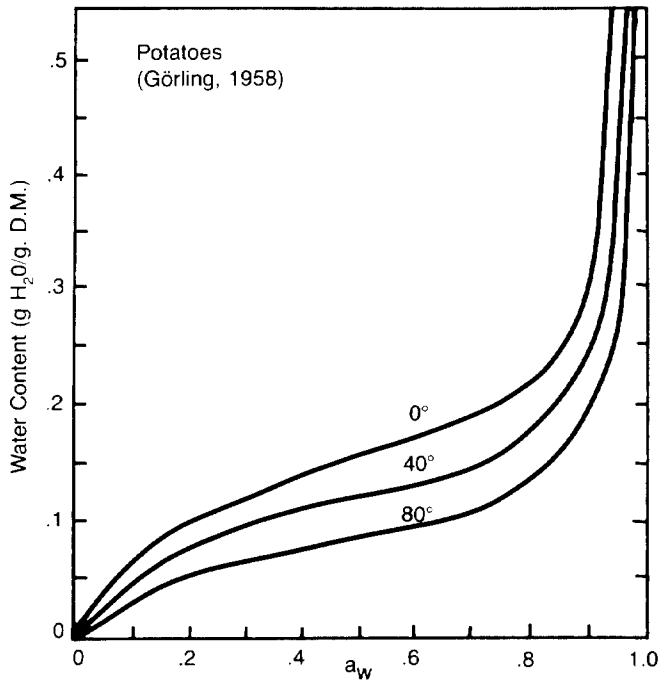

Figure 4. Effect of temperature on water activity in foods.

With this background, it is now appropriate to look at a series of graphs in which curves for the rates of various reactions are superimposed on an idealized moisture sorption isotherm (dashed curve). In each graph, the abscissa is common to all curves, the right ordinate relates to the isotherm and the left ordinate relates to the curves for reaction rates. Fig. 5A deals with enzymatic hydrolysis and it is apparent that these types of reactions are effectively stopped by lowering the water activity to or below the monolayer value. Raising the water activity above the monolayer value results in a rather rapid increase in rates of enzymatic hydrolysis, and this relates to the properties of Zone II water, as discussed earlier. Degradation of chlorophyll and Vitamin B_1, also follow a similar pattern (Fig. 5B). The tendency of the vitamin B_1 curve to turn downward above an a_w of about 0.6 is believed to occur because water is now present in sufficient quantity to solute and mobilize constituents and additional water simply dilutes the reactants. This behavior is quite common, but usually occurs at somewhat higher a_w values, as in Fig. 5C.

Data in Fig 5C relates to the loss of lysine as a result of carbonyl-amine reactions (nonenzymatic browning). Again,

Figure 5A

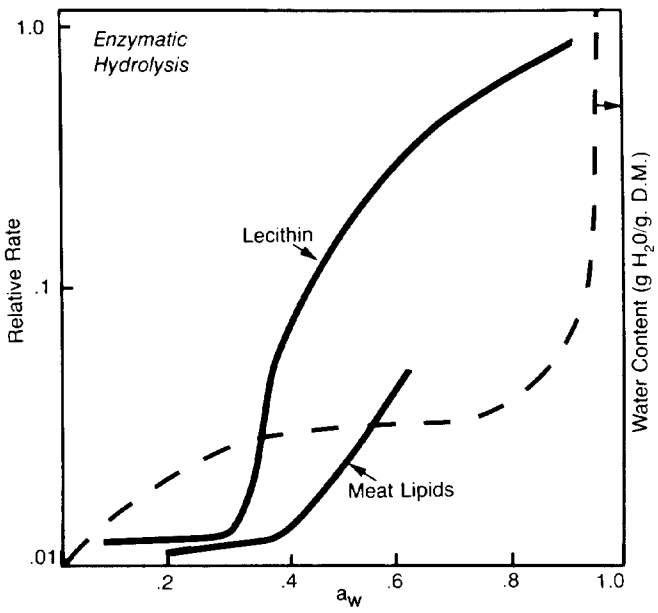

Figure 5A. Effect of water activity on enzymatic hydrolysis.

Figure 5B

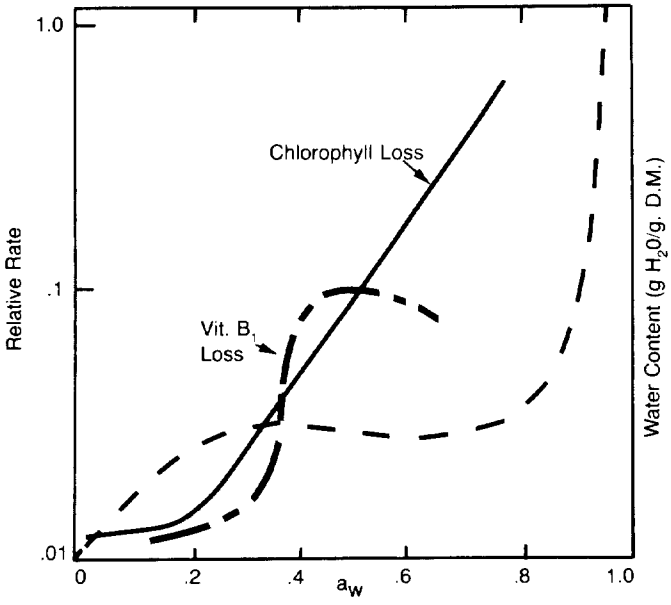

Figure 5B. Effect of water activity on losses of Chlorophyll and Vitamin B_1.

the rate is minimal at or below the monolayer value and rises abruptly as Zone II water becomes abundant.

Oxidative reactions as a function of a_w behave quite differently, as shown in Fig. 5D.

Above the monolayer value, the behavior corresponds approximately to that observed in Fig. 5A-C, but below the monolayer value a marked difference is apparent. The upper curve for oxidation of lipids in potato chips is the relevant one since data below a_w 0.3 were not collected for Vitamin C. The pattern observed for oxidation of potato lipids is common, indicating that rates of oxidation increase as the a_w is

Figure 5C

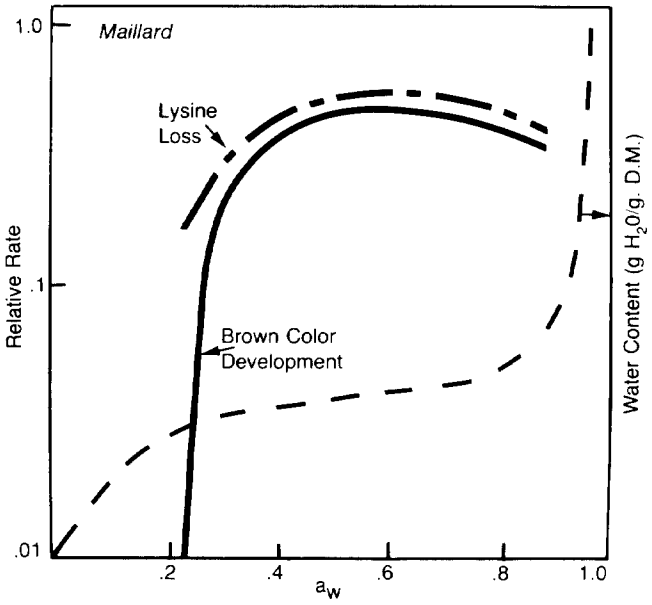

Figure 5C. Effect of water activity on lysine loss and the development of brown color.

Figure 5D

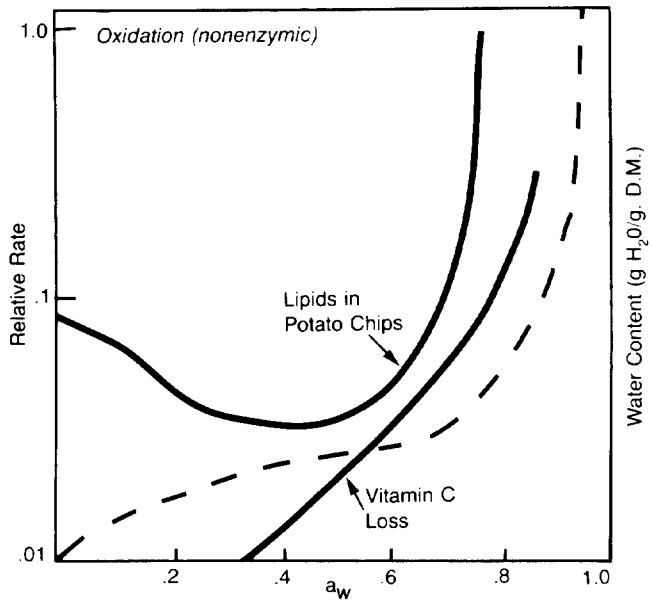

Figure 5D. Effect of water activity on oxidation reactions.

lowered below the monolayer value. The reasons for this behavior are not conclusively known, although several theories have been advanced.

Because of lipid oxidation, it is possible to over dry foods (i.e., decrease their stability by an excessively low a_w). Thus, selection of the monolayer a_w as an approximation of optimum stability is a compromise selected to cause all kinds of chemical reactions to proceed slowly.

Consideration of all graphs in Fig. 5 reveals that many reactions exhibit maximum rates near a_w 0.8. This, unfortunately, is in the a_w range of intermediate moisture foods.

Figure 6

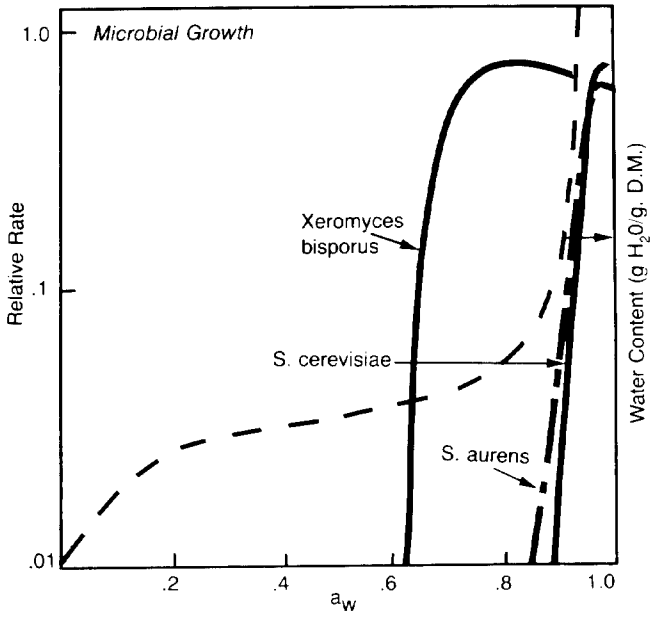

Figure 6. Effect of water activity on microbial growth.

Figure 7

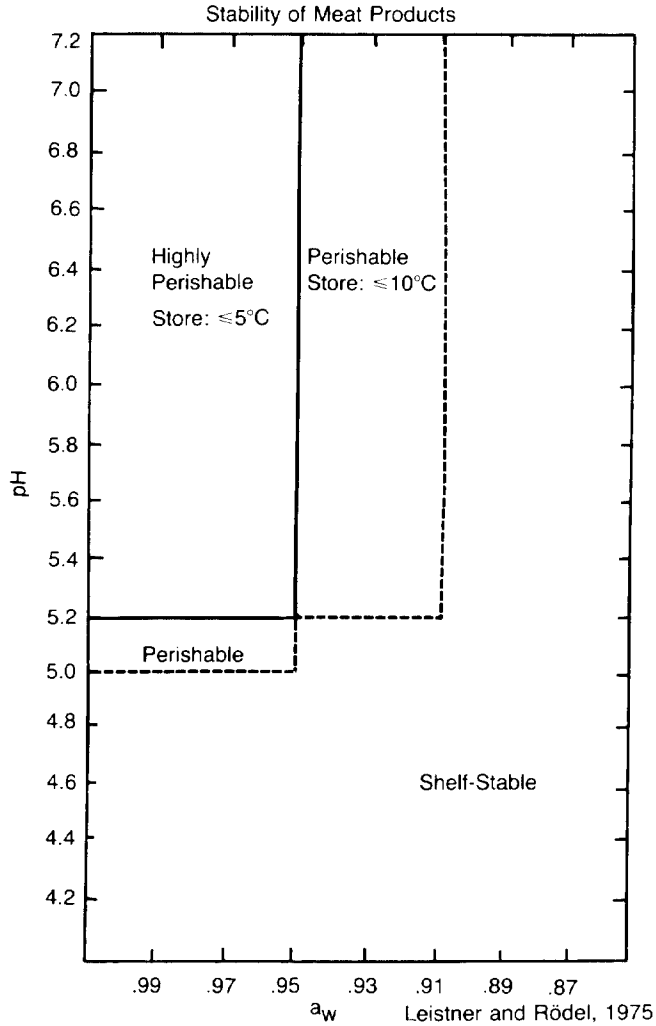

Figure 7. Effect of water activity and pH on the stability of meat products.

The situation with respect to growth of microorganisms is shown in Fig. 6. Below about 0.65 a_w, microbial growth is not a problem. Above this a_w some molds and yeast will begin to grow and at somewhat higher water activities, bacteria will grow. Growth of most microorganisms requires the presence of Zone III water, i.e., the a_w must be above about 0.8-0.85.

The last figure, and the one that has the greatest relevance to most meat and meat products, is Fig. 7. This figure represents the work of Leistner and Rödel at Karlsruhe, Germany. In this figure, the stability of meat and meat products is defined in terms of a_w *and* pH. As mentioned earlier, a_w alone is not always an accurate predictor of food stability, and in the case of meat, the combination of a_w and pH is much superior. Knowing the pH and a_w of a meat product, one can with ease determine from Fig. 7 the storage conditions that are most suitable. It is apparent that at any a_w above 0.91, reducing the pH to a value below 5.0-5.2 greatly enhances the stability of meat.

EDITOR'S NOTE: Due to the inability to transcribe satisfactorily the discussions which followed this presentation, the manuscript above was rewritten by the author to include answers to most of the questions posed in the discussion periods.

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