Water Activity Fundamentals

<u>What is water activity?</u>

We could 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. Now answer the question: 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:

$$dV = -nRT\, dp/p^2$$

Combining this and the first law we get

$$dU = nRT\, dp/p$$

Now, the energy required to go from the vapor pressure of the pure water in the glass, which we call the saturation vapor pressure, and give the symbol p_o, to the vapor pressure of the water in the sponge is

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

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. It 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

$$\psi = RT \ln a_w$$

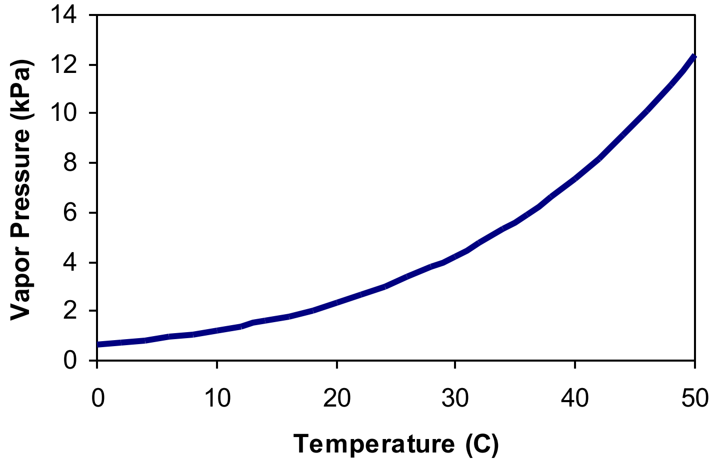
The equation tells us that we can express the energy state of the water in a product either as a water potential or as a water activity. Some fields of science use water potential and others use water activity (some also use freezing point depression or osmolality, but these are also equivalent concepts). 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 Walls -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.

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 headspace of the sample to measure humidity. The best method, though, is suggested by the ratio p/p_o. The saturation vapor pressure p_o depends only on the temperature of the sample, as shown in the accompanying graph. If we know the sample temperature we know p_o. 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 measuring the dew point of the air. AquaLab dew point instruments measure those two variables, so give a direct and fundamental measurement of water activity. If you want water potential, it is easy to convert between the two measurements.


Vapor Pressure (kPa)
14
12
10
8
6
4
2
0
0
10
20
30
40
50
Temperature (C)

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