

BASIC CONCEPTS

Colligative Properties

Colligative properties, by definition, are properties which depend on number but not nature of particles in a system (Adamson, 1973). The term "colligative" originates from the Latin "colligatus" or collected together. A general system exhibiting colligative properties is a solution in equilibrium with the solute or solvent. For ideal solutions, colligative properties are independent of the chemical nature of the solute. Vapor pressure lowering, freezing point depression, boiling point elevation and osmotic pressure are commonly observed colligative properties (Andrews, 1976). Before discussing each property, especially vapor pressure lowering in more details, a brief review of the thermodynamic basis is presented.

Chemical Potential and Activity Coefficient: For a closed system, the Gibb's free energy is defined by,

$$G = H - TS = E + PV - TS \quad (1)$$

where H is the enthalpy, S the entropy, E the internal energy, T the absolute temperature, P the pressure and V the volume. In differential form,

$$dG = dH - Tds - SdT = VdP - SdT \quad (2)$$

For a multicomponent system in which chemical species may be gained or lost, G is a function of T, P and n. which denotes the number of moles of the ith species. The differential change for G becomes

$$dG = VdP - SdT + \sum_i \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j} dn_i \quad (3)$$

The partial molal Gibbs' free energy (G), or chemical potential (μ_i) of the ith species is defined as

$$\mu_i = \bar{G}_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j} \quad (4)$$

In other words, chemical potential is the change in free energy of the system corresponding to an infinitesimal change in number of moles of a constituent i when temperature, pressure and mole quantities of other constituents are held constant. Chemical potential indicates the escaping tendency of the constituent. For two systems with different chemical potentials, there is a driving force for mass transfer from the system with a higher μ_i to a system with a lower μ_i . At equilibrium, μ_i is equal for all systems and states.

The partial derivative of μ_i with respect to P can be written as

$$\left(\frac{\partial \mu_i}{\partial P} \right)_T = \frac{\partial}{\partial P} \left(\frac{\partial G}{\partial n_i} \right)_{T,P} = \frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial P} \right)_T = \left(\frac{\partial V}{\partial n_i} \right)_{T,P} = \bar{V}_i \quad (5)$$

Where \bar{V}_i is the partial molal volume. For ideal gas,

$$\left(\frac{\partial \mu_i}{\partial P} \right)_T = \bar{V}_i = \frac{RT}{P_i} \text{ or } d\mu_i = RT d(\ln P_i) \quad (6)$$

Thus

$$\mu_i = \mu_i^0 + RT \ln P_i \quad (7)$$

where μ_i^0 is the chemical potential of the gas in its standard state ($P = 1 \text{ atm}$).

In the case of a real gas, the pressure term (P) in Eq. (6) is replaced by fugacity (f) which takes into account of any nonideality of the vapor. Fugacity is a measure of the escaping tendency of a component. This concept is applicable to any mixture of solid, liquid or gas. For a pure real gas, fugacity can be computed by (Kirkwood and Oppenheim, 1961)

$$f = P^2 / P_0 \quad (8)$$

where P is the pressure of the real gas, and P_0 is the pressure of the ideal gas at the same temperature.

For real gases, Eq. (6) can be rewritten as

$$d\mu_i = RT d(\ln f_i) \quad (9)$$

Integration of Eq. (9) yields

$$\mu_i - \mu_i^0 = RT \ln (f_i/f_i^0) \quad (10)$$

where μ_i and f_i are the chemical potential and fugacity, respectively, of component i at the standard state. Usually the standard state of fugacity is taken as 1 atm. By defining activity of component i (a_i) as

$$a_i = f_i/f_i^0 \quad (11)$$

Eq. (10) becomes

$$\mu_i - \mu_i^0 = RT \ln a_i \quad (12)$$

It should be noted that f_i approaches P_i as pressure approaches zero. This is because real (nonideal) gases approach ideal behavior at low pressure (Acree, 1984).

For real gases at very low pressure or ideal gases, activity can be expressed as

$$a_i = P_i/P_i^0 \quad (13)$$

When a solution and its vapor phase are in equilibrium, the chemical potential of a component is the same in two phases. Thus,

$$\mu_i(l) = \mu_i(g) \quad (14)$$

where $\mu_i(l)$ and $\mu_i(g)$ are the chemical potentials of the i component in liquid and gas phases, respectively. If the vapor behaves as an ideal gas,

$$\mu_i(l) = \mu_i(g) = \mu_i^0 + RT \ln P_i \quad (15)$$

According to Raoult's law for ideal solutions,

$$P_i = X_i P_i^0 \quad \text{or} \quad X_i = P_i/P_i^0 \quad (16)$$

where X_i is the mole fraction of component i . Substituting Raoult's law into Eq. (15),

$$\mu_i(g) = \mu_i^0 + RT \ln P_i^0 + RT \ln X_i \quad (17)$$

$$\mu_i(l) = \mu_i^0 + RT \ln P_i^0 + RT \ln X_i$$

$$\mu_i(l) = \mu_i^* + RT \ln X_i \quad (18)$$

where $\mu_i^* = \mu_i^0 + RT \ln P_i^0$ is a constant at a given temperature and pressure.

For nonideal and nonelectrolyte solutions, the chemical potential of component i is

$$\mu_i = \mu_i^0 + RT \ln a_i \quad (12)$$

The nonideality of the solution is corrected for by introducing activity coefficient (γ) which is defined as

$$a_i = \gamma_i X_i \quad (19)$$

Now Eq. (12) becomes

$$\mu_i = \mu_i^0 + RT \ln \gamma_i X_i \quad (20)$$

The activity coefficient of component i is a function of temperature, pressure and concentration. The activity coefficient of the solvent in a solution approaches unity (ideal solution) as its mole fraction approaches unity. For a more thorough discussion of this subject, the readers are referred to Acree's (1984) book on thermodynamic properties of nonelectrolyte solutions.

Water Activity: The concept of water activity (a) becomes obvious when the i th constituent is replaced by water in Eq. (11), (19) and (20). Thus,

$$a_w = f_w / f_w^0 \quad (21)$$

$$a_w = \gamma_w X_w \quad (22)$$

$$\mu_w = \mu_w^0 + RT \ln \gamma_w X_w \quad (23)$$

Assuming that the vapor pressure correction factor for the solution and water to be the same, the ratio f_w / f_w^0 may be replaced by P / P_0 (Robinson and Stokes, 1965). Water activity as defined by food scientists

$$a_w = P_w / P_w^0 \quad (24)$$

where P_w is vapor pressure of water in equilibrium with food, and P_w^0 is vapor pressure of pure water at the same temperature. Equilibrium relative humidity (ERH) is related to water activity by:

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

At subfreezing temperature, water activity is defined somewhat differently (Fennema, 1981):

$$a_w = P_w / P_{sw}^0 \quad (25)$$

where P_w is the vapor pressure of water generated by the frozen sample and P_{sw}^0 is the vapor pressure of pure supercooled water at the same temperature. From a thermodynamic standpoint, supercooled water is the preferred reference state (Franks, 1982). If vapor pressure of ice were to be used as P_0 , all samples containing ice would have a a_w of unity. In the presence of an ice phase, a_w becomes independent of chemical composition and depends solely on temperature (Fennema, 1981).

The movement of water molecules between a food material and its environment is illustrated in Figure 1. In this particular case, the water activity of the food is higher than that of the environment. The dynamic exchange of water molecules between the food and its surrounding will result in a net decrease in water from the food until the chemical potential or water activity of the two becomes the same. When the dynamic equilibrium condition is reached, the number of water molecules moving in and out of the food material should be equal. Water activity can be directly measured by determining the partial vapor pressure of water in equilibrium with the food material.

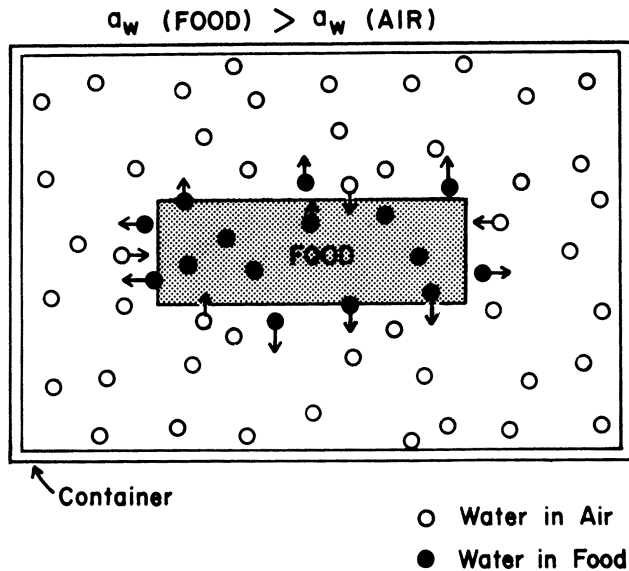


Fig. 1 A Schematic Diagram Illustrating The Movement of Water Molecules Between the Food Material and Its Surrounding.

Although the concept of water activity originates from thermodynamics, real food systems do not always fulfill the requirement of true equilibrium state. For example, many multicomponent food systems consist of two or more phases (e.g., solid, liquid, aqueous, oil) which may not be in thermodynamic equilibrium with each other (Van den Berg and Bruin, 1981). Therefore, a_w may not be a valid thermodynamic parameter for most food systems. Franks (1982) pointed out the presence of hysteresis loop in water sorption isotherms of foods as an indication of irreversible, non-equilibrium conditions, and cast doubt on the meaning of water activity. While water activity has been an extremely useful concept in food, caution should be taken in interpreting its theoretical basis.

Freezing Point Depression: The freezing point depression of a solution caused by addition of solutes can be derived from the equilibrium condition $\mu_j(s) = \mu_j(l)$ and Eq. (20). For small freezing point depressions, heat of fusion may be considered independent of temperature. By assuming the solution to be ideal, the following equation can be obtained:

$$-\ln X_1 = \frac{\Delta H_f (T_0 - T)}{RTT_0} \cong \frac{\Delta H_f \Delta T_f}{RT_0^2} \quad (27)$$

where X_1 is the mole fraction of the solvent, T the freezing point of solution, T_0 the freezing point of solvent, ΔT_f the freezing point of depression, ΔH_f the heat of fusion, and R the gas constant.

For dilute solutions,

$$-\ln X_1 = -\ln(1 - X_2) = X_2 + 1/2 X_2^2 + 1/3 X_2^3 + \dots \quad (28)$$

where X_2 is the mole fraction of the solute. Assuming the second and higher terms to be negligible, Eq. (27) becomes

$$\Delta T_f = \frac{RT_0^2}{\Delta H_f} X_2 = \frac{RT_0^2 M m}{1000 \Delta H_f} = K_f m \quad (29)$$

where M is the molecular weight of the solvent, m the molality of the solute and K_f the freezing point depression constant. The value of K_f for water is 1.86 (Adams, 1973).

Freezing point depression can be related to water activity (a_w) by the following equation (Robinson and Stokes, 1965):

$$-\ln a_w = \frac{\Delta H_f}{RT_f^2} \Delta T_f + \frac{J}{2R} \frac{\Delta T_f}{T_f^2} \quad (30)$$

where J is the difference in molal heat capacities between liquid water and ice. By expanding the term $\Delta T_f / T_f^2$, Eq. (29) can be approximated to

$$-\log a_w = 0.004207 \Delta T_f + 2.1 \times 10^{-6} \Delta T_f^2 \quad (31)$$

For example, a freezing point depression of 10°C corresponds to a a_w of 0.903. Water activity values calculated from freezing point depression agree well with the measured a_w data reported in the literature for sucrose, glycerol, sodium chloride and other solutions (Fontana and Chirife, 1981a).

Boiling Point Elevation: Boiling point elevation of a solution caused by addition of a nonvolatile solute can be derived from the equilibrium condition $j_i(g) = j_i(l)$ and Eq. (12) (Adams, 1973). By assuming the solution to be ideal and making approximations similar to those for freezing point depression, the boiling point elevation can be determined by

$$\Delta T_b = \frac{RT_b^2 M}{1000 \Delta H_v} m = K_b m \quad (32)$$

where T_b is the original boiling point, M the molecular weight of the solvent, ΔH_v the heat of vaporization, m the molality of the solute, and K_b the boiling point elevation constant. The value of K_b for water is 0.51. Boiling point elevation can be related to water activity by the following equation:

$$-\log a_w = 0.01526 \Delta T_b - 4.862 \times 10^{-5} \Delta T_b^2 \quad (33)$$

Since the molal elevation of the boiling point for water is about one-quarter the molal depression of the freezing point, boiling point must be measured with nearly four times the accuracy of freezing points to obtain similar accuracy for a_w (Robinson and Stokes, 1965).

Osmotic Pressure: When a solution and pure solvent are separated by a semi-permeable membrane, which is permeable to the solvent (A) but not the solute (B), the solvent will move toward the solution side. The mechanical pressure required to prevent any net flow of solvent is known as the osmotic pressure π . At equilibrium, the chemical potential of the solvent (μ_A) is equal on both sides of the membrane. Due to the presence of the solute, μ_A in the solution is lowered by

$$\Delta \mu = RT \ln \left(\frac{P_A}{P_A^0} \right) = RT \ln a_A \quad (34)$$

the decrease in μ_A in the solution is counteracted exactly by the increase in μ_A due to the imposed osmotic pressure. Therefore,

$$\Delta\mu = -RT \ln a_A \int_0^{\Pi} \frac{1}{V_A} dP \quad (35)$$

where V_A is the molar volume of the solvent. Assume that V_A is independent of pressure,

$$-RT \ln a_A = \Pi \bar{V}_A \quad (36)$$

For an ideal solution,

$$\Pi \bar{V}_A = -RT \ln X_A = -RT \ln(1 - X_B) \quad (37)$$

where X_A and X_B are the mole fractions of the solvent and the solute, respectively. If the solution is dilute, X_B is very small compared to X_A . Using the approximation

$$-\ln(1 - X_B) \cong X_B \cong n_B/n_A \quad (38)$$

Eq. (37) can be written as

$$\Pi = n_B RT/V_A = C_B RT \quad (39)$$

where n is the number of moles, C_B is the molar concentration of the solute and $V_A = n V_A$. Eq. (39) is known as the Van Hoff's Law of osmotic pressure. A comparison of the observed and calculated osmotic pressure of sucrose solutions is shown in Table 1.

For nonideal solutions, the term osmotic coefficient (ϕ) is defined as,

$$\phi = \frac{-m_A \ln a_A}{v m_B} \quad (40)$$

where v is the number of moles of ions formed from one mole of electrolyte, and m_A and m_B are the molal concentrations of solvent and solute, respectively. Osmotic coefficient of a solution can be calculated if the water activity is known, or vice versa. Combining Eq. (36) and Eq. (40),

$$\Pi = \frac{RT \phi v m_B}{m_A V_A} \quad (41)$$

Osmotic coefficients of sucrose solutions at 25°C are given in Table 2. Note that $\phi \rightarrow 1$ as $m \rightarrow 0$. Osmotic coefficients of electrolytes have been compiled by Robinson and Stokes (1965).

Table 1. The Osmotic Pressure of Sucrose Solutions at 20°C.

Sucrose Concentration (mol/L)	Observed Osmotic Pressure (KPa)	Calculated Osmotic Pressure (KPa)	
		Eq. (37)	Eq. (39)
0.098	262	247	239
0.192	513	553	469
0.282	771	792	689
0.370	1030	1035	901
0.453	1290	1278	1100
0.533	1560	1820	1300
0.610	1840	1763	1490
0.685	2120	2003	1670
0.757	2400	2244	1840
0.825	2700	2480	2000

Source: Moore (1962).

Table 2. Osmotic Coefficients, Water Activities and Activity Coefficients of Sucrose Solutions at 25°C.

Molality (Moles Sucrose/ kg Water)	Osmotic Coefficient	Water Activity	Mole Fraction of Water	Activity Coefficient of Water
0.1	1.008	0.9982	0.9982	1.0000
0.5	1.041	0.9907	0.9964	0.9943
1.0	1.088	0.9806	0.9823	0.9983
1.4	1.129	0.9719	0.9754	0.9964
2.0	1.189	0.9581	0.9652	0.9926
2.5	1.240	0.9457	0.9569	0.9883
3.0	1.288	0.9328	0.9488	0.9831
3.5	1.334	0.9193	0.9407	0.9773
4.0	1.375	0.9057	0.9328	0.9709
4.5	1.414	0.8917	0.9251	0.9639
5.0	1.450	0.8776	0.9144	0.9566
5.5	1.482	0.8634	0.9099	0.9489
6.0	1.511	0.8493	0.9025	0.9410

Source: Adapted from Robinson and Stokes (1965).

WATER SORPTION PROPERTIES

Bound Water

It is generally recognized that water in food can be categorized as "bound" and "free" (Kuprianoff, 1958). Many physical properties of water change substantially when it is associated closely with a host substance such as solutes or macromolecules. The term bound water is ill-defined and its exact meaning varies depending on the physical properties studied and the techniques used (Karel, 1975; Fennema, 1976; Labuza, 1977; Leung, 1981; Labuza, 1985). The unusual properties of bound water include unfreezability, unavailability as solvent, lower vapor pressure, higher heat of adsorption, reduced nuclear magnetic relaxation times, and different infrared and dielectric absorption as compared to free or bulk water (Cooke and Kuntz, 1974). Bound water contents determined using different criteria may vary considerably for the same food material.

The term bound water covers a wide spectrum of degree of binding. It may be used to denote tightly bound water such as the monolayer moisture to very loosely bound water such as water held in a macromolecular gel network. The most widely used criterion of bound water is its unfreezability at low temperatures (e.g. -50°C). Interestingly, unfreezable water of food systems correspond to equilibrium moisture contents at water activity of 0.8 - 0.9 based on differential thermal analysis (Duckworth, 1972) and nuclear magnetic resonance measurement (Leung and Steinberg, 1979). Therefore, unfreezable water is not strongly bound to food materials and is available for chemical reactions and microbial growth.

The water sorption isotherm is a convenient way of studying water binding. It is usually divided into three ranges: very tightly bound water corresponding to an a_w of 0.2 - 0.3 and less, moderately bound water (a_w 0.3 - 0.7), and loosely bound water corresponding to an a_w of 0.7 - 0.8 and higher (Van den Berg and Bruin, 1981).

Water Potential

While water activity is popular among food scientists and microbiologists, a similar concept, "water potential", has been used widely by soil and plant scientists (Papendick and Campbell, 1980). By definition, water potential Ψ is the difference between the chemical potential of the water in a system and that of pure water (μ_w^0) at the same temperature, divided by the partial molal volume of water V_w (1.8×10^{-6} m³/mol at 4°C) (Slatyer, 1967). Recall that,

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \bar{V} \quad (6)$$

It follows that,

$$\mu_w - \mu_w^0 = V_w (P - P^0) \quad (42)$$

or

$$\Psi_w = P - P^0 = (\mu_w - \mu_w^0) / V_w \quad (43)$$

In principle, $P - P^0$ can be considered to be the suction required on pure

water to reduce its activity to that of the soil (or food) at the same temperature. Water potential is related to water activity (a_w) by [see Eq. (12)]

$$\Psi_w = \frac{RT}{V_w} \ln a_w \quad (44)$$

Water activities corresponding to some water potential values at 20°C are given in Table 3.

Table 3. Relationship Between Water Potential and Water Activity at 20°C.

Water Potential (Pa)	Water Activity
-10^3	1.0000
-10^4	0.9999
-10^5	0.9993
-10^6	0.9926
-10^7	0.9286
-2×10^7	0.8624
-5×10^7	0.6906

Insight into water relations of foods may be gained by examining the factors contributing to water potential in soil and plant systems. The major components of water potential are: (1) the osmotic potential due to solutes, (2) the matric potential due to adsorption and capillary effects of the solid phase, and (3) the pressure potential resulting from external gas or hydraulic pressure applied to water such as turgor of plant cells. In food systems, osmotic potential is contributed by solutes such as salt and sugar, matric potential by macromolecules and porous surface, and pressure potential by turgor of plant cells as in fruits and vegetables. The concept of water potential was applied by Labuza and Lewicki (1978) to study water binding of food gels.

Factors Affecting Water Activity

Activity of water in food systems may be reduced by dissolved solutes, formation of hydrogen bonds at hydrophilic sites, capillary forces, and other long range forces in a solution, suspension or gel. The nature of the last type of attractive force is unclear. Ling (1972) suggested that water in macromolecular systems exists in polarized multi-layers.

Surface interaction between water and food components plays an important role in lowering water activity at low moisture content. The water molecules are bound to various chemical groups of the food molecules by hydrogen bonds, hydrophobic bonds, ionic bonds and other forces. As a result, the vapor pressure of water is lowered considerably. At low moisture content such as the monolayer value, the activity of the water is reduced by so much that it is not available for microbial growth and most chemical reactions.

In the capillary condensation theory, the bulk of the adsorbed water is considered to fill up the pores or capillaries of a material. The vapor pressure of water inside a capillary is lower than that of regular water. Water activity can be related to the pore size of the capillaries by the Kelvin's Equation (Labuza, 1975),

$$a_w = \exp - \frac{2\gamma \bar{V} \cos \theta}{r RT} \quad (45)$$

where

- y = surface tension
- V = molar volume of liquid
- θ = contact angle
- r = capillary radius
- R = gas constant
- T = absolute temperature

This theory has been used to relate porosity and water potential of soil (Papendick and Campbell, 1980). For food materials, most pores are in the 10 - 300 μ m range (Labuza, 1984). Assuming complete wetting ($\cos \theta = 1$) and pure water ($\gamma = 0.723$ N/m) in the pores, the range as calculated from the Kelvin's Equation is 0.989 - 0.9999. Van den Bweg and Bruin (1981) believed capillary condensation does not play any significant role in foods at a w higher than 0.95.

Binding of water to specific polar sites of proteins by hydrogen bond has been studied extensively. Bull and Breese (1968) concluded that about six water molecules are associated with each polar side chain when proteins are exposed to a w of 0.92. This type of interaction should play an important role in lowering water activity in food.

One of the most well known factor of water activity in food is the depression of a by dissolved solute. For ideal solution, the effect can be predicted using the Raoult's law,

$$a_w = X_w \quad (46)$$

for nonideal solution,

$$a_w = \gamma_w X_w \quad (47)$$

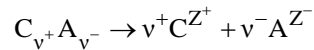
where γ is the activity coefficient of water which corrects for deviation from ideality. Table 2 lists the activity coefficients of water in sucrose solutions of different concentrations at 25°C. Note that sucrose solution approaches ideality ($\gamma = 1.0$) at dilute concentration (e.g., 0.1 m). In the case of the salt, the total number of positive and negative ions are considered in water activity depression. For instance 1 mole of sodium chloride is counted as two moles of kinetic units (Na and Cl). The solubility limits and minimum activities of several solutions at 25°C (room temperature) are presented in Table 4.

Table 4. Solubility limits and minimum water activities of some solutions at 25°C.

Solute	Solubility limit (% w/w)	Water Activity
Sucrose	67	0.86
Glucose	47	0.915
Invert sugar	63	0.82
Sucrose (37.6%) + Invert sugar (62.4%)	75	0.71
Sodium chloride	27	0.74

Source: Karel (1973)

Electrolytes behave very differently from nonelectrolyte solutions such as sugar solutions. Due to interaction of charged particles and formation of ion clouds around each ion, electrolytes deviate from ideal solutions even at very low concentrations. Separate ions follow Raoult's law up to about 0.4 m (Van den Berg and Bruin, 1981) corresponding to an a_w of 0.993. Consider an ion that dissociates as



where C is the cation and A is the anion, v^+ and v^- are the respective numbers of positive and negative ions and Z^+ and Z^- are the respective charge numbers. The mean activity coefficient of a dilute electrolyte solution can be calculated according to the Debye-Huckel limiting law (Moore, 1962).

$$\log \gamma_{\pm} = -A |Z^+ Z^-| I^{1/2} \quad (48)$$

where

- γ_{\pm} = mean activity coefficient
- A = constant
- I = ionic strength
- m_i molality of ion i

The Debye-Huckel limiting law is exact only at ionic strength of less than 0.01. At higher concentrations, the thermodynamics becomes more complicated. Based on the derivation of Bromley (1973) for electrolytes of high concentrations, Van den Berg and Bruin (1981) constructed a series of graphs relating water activity to ionic strength. A simple empirical method for predicting activity coefficients of strong electrolyte has been presented by Meissner (1980).

SORPTION ISOTHERMS

Hysteresis

Water sorption isotherms are plots of equilibrium moisture contents of a material as a function of water activity at constant temperature. The adsorption isotherm refers to adsorption of moisture by a dry material exposed to higher water activity. The desorption isotherm refers to desorption of moisture from a wet material exposed to lower water activity. For many food materials, adsorption and desorption isotherms do not follow the same path (Kapsalis, 1981). The hysteresis effect of freeze dried rice at 4.4% (Wolf et al., 1973) is illustrated in Figure 2. The desorption isotherm always lies above the adsorption isotherm, forming a hysteresis loop. Therefore, more water is retained in the desorption cycle as compared to adsorption.

The extent and type of hysteresis vary widely among different dehydrated foods (Wolf et al., 1972). In air dried apple, hysteresis occurs mainly in the monolayer region. In freeze-dried pork, a moderate hysteresis begins at an a_w of 0.85 and extends to zero water activity. In rice, a large hysteresis occurs from a a_w of 0.9 to zero (Figure 2). Increasing temperature decreases the hysteresis loop.

In the case of a food product subjected to changing moisture, the question arises as to which isotherm (adsorption or desorption) should be used. Labuza (1984) suggested the use of "working isotherm" based on the actual drying and humidification cycle the food undergoes. In other words, the adsorption isotherm should be followed if the food is wetted, and the desorption isotherm used if the food is dried. Sometimes the working isotherm may include a crossover between the adsorption and desorption branches.

While different theories have been suggested for sorption hysteresis (Rao, 1941; Everett, 1967), the general consensus is that the desorption isotherm represents a metastable state. Thus the sorption process is irreversible and fails to meet the requirement of equilibrium condition in thermodynamics. Based on this argument, Franks (1982) questioned the validity of the concept of water activity in foods. It should be pointed out that water activity and sorption isotherm have been extremely useful in food even though reversible thermodynamics do not always apply to complex food systems.

Effect of Temperature

Increasing temperature results in a downward shift of the sorption isotherm. This effect is illustrated in Figure 3 for sliced potatoes at 10, 25 and 40% (Mazza, 1980). Knowing the water sorption at different temperatures, the isosteric heat of adsorption can be calculated from the Clausius-Clapeyron Equation as follows:

$$\frac{d \ln P}{d(1/T)} = -\frac{\Delta H}{R} \quad (49)$$

$$\Delta H = \frac{RT_1 T_2}{T_2 - T_1} \ln \frac{P_1}{P_2} \quad (50)$$

$$\Delta H = \Delta H_v + Q_s \quad (51)$$

where ΔH is the differential heat of adsorption, ΔH_v the heat of evaporation of water, Q_s the excess heat of interaction, P_1 and P_2 , the partial vapor pressures of water at temperatures T_1 and T_2 respectively. The Gibb's free energy of adsorption is:

$$\Delta G = RT \ln (P/P') \quad (52)$$

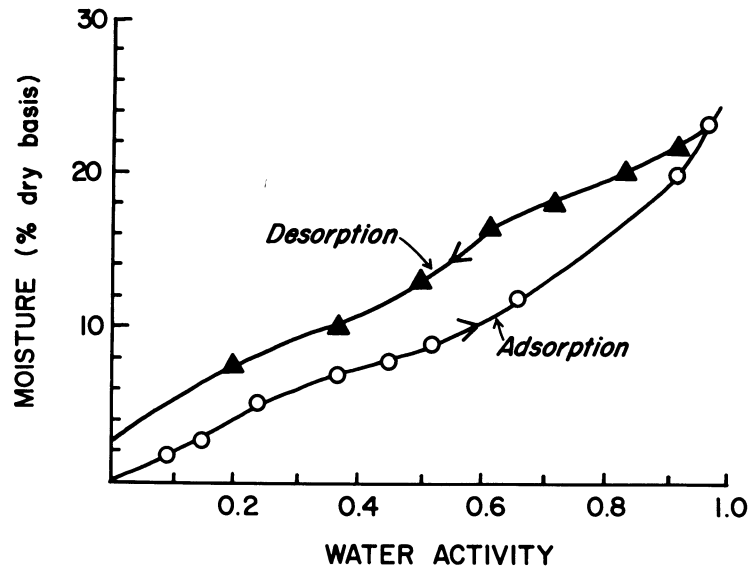


Fig. 2 Water vapor sorption hysteresis of freeze-dried rice at 4.4°C (Wolf et al., 1972).

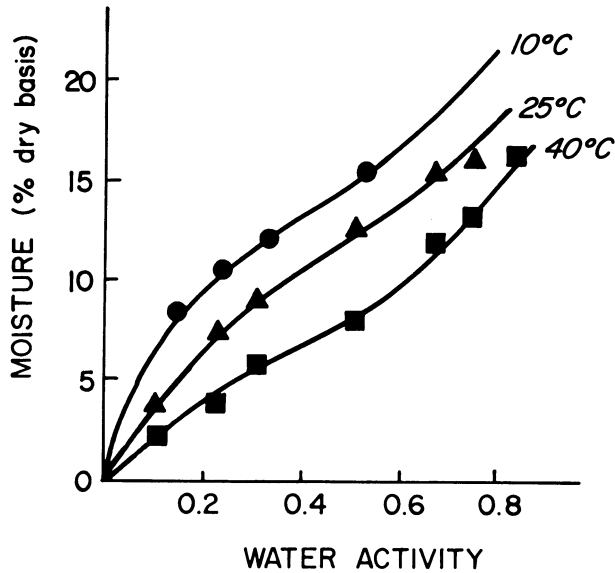


Fig. 3 Effect of temperature on desorption isotherms of sliced potatoes (Mazza, 1980).

where P' is the atmospheric pressure, and P is the vapor pressure of water in equilibrium with the hydrated material. The entropy of adsorption is then:

$$\Delta S = (\Delta H - \Delta G)/T \quad (53)$$

For condensation of water vapor to liquid water at 25°C, $\Delta G = -8.62$ KJ/mol, $\Delta H = -43.96$ KJ/mol, $\Delta S = -118.9$ KJ/mol.

Figure 4 shows the variation of differential ΔH , ΔG and ΔS with moisture content for adsorption of water vapor on amylo maize (high amylose corn starch) at 25°C (Morsi et al., 1967). The moisture level at which maximum ΔH and ΔS occur coincides with the BET monolayer value (Brunauer et al., 1938), which represents the amount of water covering the primary polar sites by one layer. Similar phenomena were also observed by other workers (Duckworth, 1972; Leung and Steinberg, 1979). The observation was rationalized by Bettelheim et al. (1970) who stated that when the most accessible sites are saturated, water vapor will be sorbed on primary sites in the least accessible region with the highest polymer segment density. Thus, one expects a maximum heat of sorption just before the completion of a monolayer. The same authors also compared the isosteric (differential) heats of sorption calculated from isotherms and calorimetric heats of sorption determined experimentally. Although maxima in both functions occur at monolayer coverage, the calorimetric and isosteric heats for three biopolymers are different. They attributed the discrepancies to irreversibility of the sorption process, swelling and changes in crystallinity of the polymers.

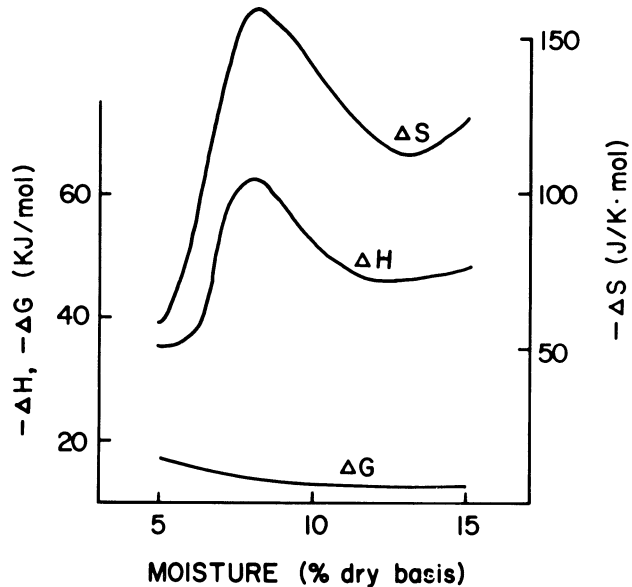


Fig. 4 Variation of differential ΔH , ΔS and ΔG with water vapor adsorption on amylo maize as a function of moisture content (Morsi et al., 1960).

BET Equation

The BET isotherm (Brunauer et al., 1938) is probably the most popular isotherm in characterizing water sorption in foods. The equation gives an estimate of the monolayer value of water adsorbed on a material. This monolayer value has been shown to correspond to the moisture content at which many food systems have the maximum stability in regards to chemical reactions (Salwin, 1959; Labuza, 1971). The multimolecular adsorption model was derived on the basis that the rate of condensation on top on the first layer is equal to the rate of evaporation from the second layer. It was assumed that the binding energy of all of the water molecules on the first layer is the same, and that the binding energy of the other layers are the same as those of pure liquid water (heat of liquefaction). Brunauer et al. (1938) also assumed a uniform surface and no lateral interaction between adsorbed molecules. Although some of the assumptions are known to be incorrect (Brunauer et al., 1969), the BET model provides a useful tool in analyzing isotherms in foods. The BET can be written as:

$$\frac{a}{(1-a)m} = \frac{1}{m_0 C} + \frac{(C-1)}{m_0 C} a \quad (54)$$

where a is water activity, m is moisture content, m_0 the monolayer moisture value and C a constant. A plot of $a/(1-a)m$ versus a yields a straight line with an intercept (I) of $1/m_0 C$ and a slope (S) of $(C-1)/m_0 C$. The monolayer value can be calculated as $m = 1/(I+S)$. However, Eq. (54) deviates from linearity when a is greater than 0.3 - 0.5, above which the theory no longer holds. As mentioned before, the monolayer values have been shown to coincide with the moisture contents at which maxima of isothermic heat of adsorption occurs (Figure 4).

A survey of van der Waals adsorption of gases by Brunauer et al. (1940) yielded five different types of isotherms (Figure 5). Eq. (54) represents a Type II isotherm when $C \gg 1$ or $E_1 > E_L$, and a Type III isotherm when $E_1 < E_L$ where E_1 is the binding energy of the first layer and E_L is the binding energy between water molecules. Type II, or the S-shaped isotherm is the most common in food.

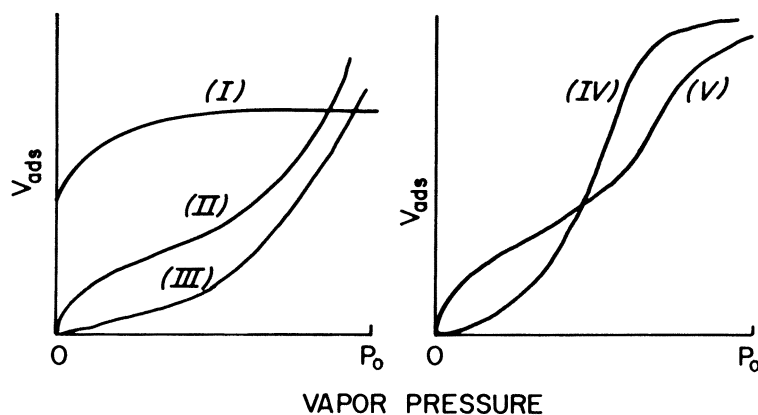


Fig. 5 The five typical shapes of isotherms for physical adsorption (Brunauer et al., 1940).

Isotherm Equations

More than 200 isotherm equations have been proposed for biological materials (Van den Berg and Bruin, 1981). Some of the equations are derived based on sorption models such as the BET Equation. Some of them, however, are simply empirical equations with two or three fitting parameters. In fact, some of the seemingly different isotherm equations turn out to have the same form after rearrangement (Boquet et al., 1980). The empirical equations are useful in predicting water sorption properties of foods, although they provide little insight into the interaction of water and food components. Due to the large number of isotherm equations reported in the literature, only a few selected ones are covered in this review. The readers are referred to Van den Berg and Bruin (1981) and Chirife and Iglesias (1978) for a more complete listing of the equations.

In the following equations, a denotes water activity, m moisture content on dry basis, m_0 the monolayer value, and T absolute temperature.

1. The Harkins-Jura Equation (1944)

This equation is based on the two dimensional gas theory and applies up to a of about 0.4 - 0.5.

$$\ln a = B - A/m^2 \quad (55)$$

where A and B are constants.

2. The Bradley Equation (1936)

The Bradley Equation was derived on the basis of polarization theory. The induced dipoles in the first layer of adsorbed molecules induce dipoles in the next layer and so on until several layers are built up.

m

$$-\ln a = K_2 K_1^m \quad (56)$$

where K_1 and K_2 are constants.

3. The Henderson Equation (1952)

$$\ln(1 - a) = -K T m^n \quad (57)$$

where K and n are constants. The Henderson Equation is one of the commonly used empirical equations for fitting water sorption isotherms of foods. The original equation can be simplified by eliminating the temperature term

$$\ln(1 - a) = -K' m^n \quad (58)$$

where K' and n are constants.

4. The Smith Equation (1947)

The Smith Equation has been shown to be useful in describing water sorption isotherms of various biopolymers and food products at a_w of 0.3 - 0.5 and higher.

$$m = A - B \ln(1 - a) \quad (59)$$

where A and B are constants.

5. The Oswin Equation (1946)

The Oswin Equation is a mathematical series expansion for S-shaped curves.

$$m = A [a / (1 - a)]^n \quad (60)$$

where A and n are constants.

6. The Chen Equation (1971)

The Chen Equation was derived based on diffusion and drying theory.

$$a = \exp [K + A \exp(Bm)] \quad (61)$$

where K, A and B are constants.

7. The Halsey Equation (1948)

The Halsey Equation was developed based on condensation of multilayers assuming that the potential energy of a molecule is proportional to the inverse rth power of its distance from the surface.

$$a = \exp(-A / RT \theta^r) \quad (62)$$

where A, and r are constants, R is gas constant and θ is m/m_0 . This equation was simplified to

$$a = \exp(-A' / \theta^r) \quad (63)$$

by Iglesias and Chirife (1976), who found that it provides a good fit for 220 isotherms from 69 different food materials.

8. The Kuhn Equation (Kuhn, 1964) - rearranged

$$m = A / \ln a + B \quad (64)$$

where A and B are constants.

The Kuhn Equation was derived based on multilayer film adsorption and capillary condensation. It was found to give a good fit for water sorption in potato chips (Quast and Karel, 1972).

9. The Iglesias and Chirife Equation (Iglesias and Chirife, 1978).

$$\ln[m + (m^2 + m_{0.5})^{1/2}] = A a + B \quad (65)$$

where A and B are constants, and $m_{0.5}$ is the equilibrium moisture content at $a = 0.5$.

This empirical equation is applicable to most fruits and high-sugar foods.

10. The Guggenheim-Anderson-DeBoer (GAB) Equation (Guggenheim 1966)

The GAB Equation is a significant improvement over the BET model (Van den Berg and Bruin, 1981; Bizot, 1983). It is a multilayer model that takes into account of the different properties of sorbate (e.g. water) in the multilayer region. Different values of heat of sorption are used for the monolayer, the multilayers and the pure gas molecules (heat of condensation). It is considered to be the best equation for fitting water-sorption isotherm of many food materials (Bizot, 1983; Van den Berg, 1985). The equation can be written as:

$$\frac{m}{m_0} = \frac{CKa}{(1 - Ka)(1 - Ka + CKa)} \quad (66)$$

where

C = the Guggenheim constant
C = C' exp [(AH1-AH1)/RT]
K = K' exp [(AH1-AH2)/RT]
ARL = heat of condensation of water
AH 1 = heat of sorption of the monolayer
AH 2 = heat of sorption of the multilayers
R = gas constant.
C', K' = constants.

It is interesting to note that Eq. (66) is identical to the modified BET Equation (Brunauer et al., 1969). However, the derivation and the model are different. The modified BET Equation employs a parameter K as a measure of the attractive force of the adsorbent. The monolayer value of the GAB model is generally higher than that of the BET model. For potato starch, the GAB monolayer value is closer than the BET value to what is expected theoretically (Van den Berg, 1985).

Water sorption isotherm equations are useful in shelf life prediction of food products. For example, deterioration of some food materials packaged in flexible film is directly related to moisture gain or loss during storage, which is governed by the moisture permeability of the film and the hygroscopic properties of the food. A simple linear isotherm equation has been shown to be adequate in predicting shelf life of snack foods undergoing moderate change in moisture (Labuza, 1982). For more complex food systems, computer solutions using non-linear isotherm equations would be necessary.