Boothroyd, R. G., *Flowing Gas-Solids Suspensions,* p. 24, Chapman and Hall, Ltd., London, England (1971).

Chowdry, A., and C. R. Westgate, "The Role of Bulk Traps in Metal-Insulator Contact Charging," *J. Phys. D.: Appl. Phys.*, 7, 713 (1974).

Krupp, H., "Particle Adhesion Theory and Experiment," *Advan. Collid Interface Sci.*, 1, 111 (1967).

Lifshitz, J. M., and H. Kolsky, "Some Experiments on Anelastic Rebound," *J. Mech. Phys. Solids.*, 12, 35 (1964).

Masuda, H., T. Komatsu, and K. Iinoya, "The Static Electrification of Particles in Gas-Solids Pipe Flow," *AIChE J.*, 22, 558 (1976).

Powell, F., and B. W. Quince, "The Kinetics of Impact in Drop-weight Experiments," *J. Phys. D.; Appl. Phys.*, 5, 1540 (1972).

Ramer, E. M., and H. R. Richards, "Correlation of the Electrical Resistivities of Fabrics With Their Ability to Develop and to Hold Electrostatic Charges," *Textile Research J.*, 38, 28 (1968).

Rose, G. S., and S. G. Ward, "Contact Electrification across Metal-Dielectric and Dielectric-Dielectric Interfaces," *Brit. J. Appl. Phys.*, 8, 121 (1957).

Sze, S. M., *Physics of Semiconductor Devices,* p. 90, Wiley, New York (1969).

Timoshenko, S. P., and J. N. Goodier, *Theory of Elasticity,* Chapt. 12, McGraw-Hill, New York (1951).

APPENDIX A: CONTACT AREA FOR $\phi \neq 0$

When the angle ϕ in Figure 1 is not zero, the equations in the text are replaced by following equations:

$$\dot{\rho_p} = \rho_p \beta^{-3} (\cos\phi)^2 \tag{A1}$$

$$S_e = 1.31\, \rho_p{}^{2/5} E^{-2/5} D_p{}^2 \beta^{4/5} v^{4/5} (\cos\phi)^{4/5} \tag{A2}$$

$$v_e = 1.29\, y^{5/2} \rho_p{}^{-1/2} \beta^{3/2} E^{-2} (\cos\phi)^{-1} \tag{A3}$$

$$S = 0.41\, \pi D_p{}^2 \sqrt{\frac{\rho_p \beta}{y}} \left\{ v - \left(\frac{1.29}{\cos\phi} - 1.25 \right) \sqrt{\frac{y^5 \beta^3}{E^4 \rho_p}} \right\} \tag{A4}$$

$$W_R = \frac{1}{2} m_p v^2 (1 - e^2)/p \tag{A5}$$

p in Equation (A5) is defined by (Powell and Quince, 1972) as

$$p = 1 + \frac{d^2}{k_o{}^2} \sin\phi (\sin\phi + \mu \cos\phi) \tag{A6}$$

where, d = distance between center of gravity and contact point, $m_p k_o{}^2$ = moment of inertia, μ = dynamic coefficient of friction.

$$e = \sqrt{1 - p\left(\frac{v - v_e}{v} \right)^2 - p\left(\frac{\alpha}{v} \right)^2} \tag{A7}$$

$$v^* = \left(\frac{1.29}{\cos\phi} - 1.25 \right) \sqrt{\frac{y^5 \beta^3}{E^4 \rho_p}} \tag{A8}$$

Manuscript received October 11, 1977; revision received May 2, and accepted June 8, 1978.

Prediction of the Sorptional Equilibrium Relationship for the Drying of Foodstuffs

ENRIQUE ROTSTEIN
and
ALAN R. H. CORNISH
Plapiqui (Uns-Conicet), Bahia Blanca, Argentina

After existing correlations were reviewed to predict the equilibrium of foodstuffs with moist air, it was found that they were not adequate. A new equilibrium expression is presented on the basis of equal chemical potentials in the external and internal phases. The resulting equation can be used over most of the range of moisture contents of sugar based foodstuffs including the high moisture region; it also provides simple analytical expressions for the partial derivatives of moisture content with respect to temperature and to water vapor activity.

SCOPE

Many practical design problems, such as dehydration, packaging, and storage, arise when a foodstuff is removed from an equilibrium situation and is required to attain a new one.

To model the kinetics of the rate processes involved, an equilibrium relationship is required in order to relate foodstuff moisture content to air-water vapor activity and temperature. In addition, partial derivatives of moisture content with respect to the two independent variables are required. Attempts to obtain mathematical descriptions of the equilibrium relationship have followed two main directions. In one of these, use has been made of theoretical expressions developed for the adsorption of gas molecules on nonvolatile solid surfaces, while in the other, empirical or semiempirical equations have been fitted to experimental data. The theoretical expressions for the adsorption of gas molecules on nonvolatile solid surfaces are applicable only at very low moisture contents, where the cells are no longer acting as water reservoirs. Most of the expressions that have been proposed were summarized by Labuza (1974). With a few exceptions (Henderson, 1952; Filonenko and Chuprin, 1967), the studies have been confined to a particular temperature and do not contain temperature explicitly as an independent variable. The behavior of the partial derivatives has not been studied, and, in fact, only a few of the existing expressions enable partial derivatives with respect to temperature to be readily obtained.

Enrique Rotstein is currently Visiting Professor at the Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota.

Alan R. H. Cornish is at the Imperial College of Science and Technology, London, England.

0001-1541-78-1682-0956-$01.35

In this paper, an equilibrium relationship is proposed which is based on a simplified description of vegetable tissues. As a test of its validity, the proposed relationship together with the existing expressions have been applied to specific foodstuffs.

CONCLUSIONS AND SIGNIFICANCE

It is shown that Equation (15) can be used over most of the range of moisture contents of sugar based foodstuffs including the high moisture region, a feature not provided by any of the known correlations, although high moisture content is the starting point for the study of the drying, packaging, and storage problems considered earlier. Equation (15) has been found to provide a simple analytical expression for $(\partial X/\partial T)_\phi$ and $(\partial X/\partial \phi)_T$ and to be well behaved at all moisture contents.

When the water content is close to the monolayer water content, the data are best represented by the BET equation. For some foodstuffs, the values thus predicted agree with those predicted by Equation (15), although there is no obvious thermodynamic justification for this.

The correlation is based on a simplified description of the composition of the food, so that it is sensitive to varietal or other composition differences. Its theoretical basis allows it to be used with a clear understanding of its possible limitations.

The correlation may be useful in two distinct situations. First, it provides a means of predicting the equilibrium behavior of sugar based foodstuffs when no data are available other than a knowledge of the average representative ratio of sugar to nonsugary dry matter together with the activity coefficient data reported below. Secondly, if experimental equilibrium data are available, they provide a simple model on which to base a correlation. In that case, α and A become the correlation parameters.

The drying of foodstuffs is a problem of coupled heat and mass transfer. Mathematical modeling results in a set of coupled partial differential equations. The coupling equation, Equation (1), is the equilibrium relationship which, at the prevailing temperature, relates the water content of the food to the moisture content of the surrounding air:

$$X = X(\phi, T) \tag{1}$$

In addition, the following derivatives of Equation (1) are required:

$$\left(\frac{\partial X}{\partial T}\right)_\phi = f_T(\phi, T) \tag{2}$$

$$\left(\frac{\partial X}{\partial \phi}\right)_T = f_\phi(\phi, T) \tag{3}$$

Applications of Equations (1) through (3) extend beyond air drying to packaging, conservation, cold storage, controlled atmosphere storage, as well as to alternative dehydration processes. The differences lie in the magnitudes of the variables (X, ϕ, T) as well as in the extent of changes in them.

REVIEW OF EXISTING EQUILIBRIUM RELATIONSHIPS

Equations of the form of (1), (2), and (3) have been obtained either by the use of theoretical expressions developed for the adsorption of gas molecules over nonvolatile solid surfaces or by means of empirical equations fitted to experimental data.

Equations that are applicable to foodstuffs are listed in Table 1. Their applicability has been tested against experimental data for the specific case of apples. Several authors have reported sorption equilibrium data for apples (Wolf, 1972; Taylor, 1961; Gane, 1950; Saravacos, 1967), but only Filonenko and Chuprin (1967) have reported data for desorption from fresh apples. Their data were used together with unpublished supplementary data obtained by one of the authors (Rotstein) using the chamber method (Labuza, 1974). When appropriate, a least-squares linear regression procedure was used to obtain the parameter values reported in Table 1.

It can be seen that Langmuir's equation and the BET equation provide an acceptable prediction for $\phi < 0.3$ (Figures 1 and 2). Outside of that range, the actual moisture content is significantly higher than predicted. For the same reason, the Rounsley equation cannot be used, and a comparison with cellulose equilibrium data (Rounsley, 1961) shows that only at low activities does the behavior approach that of conventional adsorption (Figure 3). A plot of the form proposed by Harkins and Jura (Figure 4) can be used only in a very restricted range of moisture content. As $\phi \rightarrow 1$, Equations (*a*) and (*i*) underpredict the full turgor moisture content, while the BET, Henderson, Kuhn, and Halsey expressions predict an infinite moisture content. Aside from this unrealistic behavior, Equations (*e*), (*f*), (*g*), and (*i*) provide an acceptable fit of the experimental data for $0.03 < X < 0.50$ kg/kg (Figures 5 and 6).

THE DERIVATIVES $(\partial X/\partial \phi)_T$ AND $(\partial X/\partial T)_\phi$

Expressions for the derivative $(\partial X/\partial \phi)_T$ are listed for each of the above equations in Table 2.

Analytical expressions for the derivative $(\partial X/\partial T)_\phi$ can only be obtained from Henderson's and Filonenko and Chuprin's expressions. The resulting equations are given in Table 3. To obtain the derivative $(\partial X/\partial T)_\phi$ for the other equations, it would be necessary to obtain correlations of the parameters as a function of temperature. At present, insufficient data are available for this purpose. Tables 4 and 5 give numerical values of the derivatives at different water vapor activities and are compared with experimental data. With the obvious exception of Langmuir's correlation, the predictions of the derivative with respect to ϕ for activities up to $\phi = 0.6$ are acceptable. As the activity increases, Equations (*m*), (*n*) and (*o*) increasingly overestimate the value of the derivative, while Equations (*k*) and (*l*) underestimate it. Moreover, for saturated air, a situation equivalent to fresh fruit at full turgor, all but Filonenko and Chuprin's correlation predict an infinite value for the derivative. Equation (*p*) yields acceptable predictions up to $\phi = 0.7$ for the derivation with respect to temperature. At higher activities, it

TABLE 1. EARLIER EQUILIBRIUM EXPRESSIONS

References	Equation	
Langmuir (1916, 1918)	$X = \frac{k_1 k_2 \phi}{1 + k_2 \phi}$	(a)
	$k_1 = 0.076$	
	$k_2 = 14.293$	
Brunauer et al. (1938)	$\frac{\phi}{X(1-\phi)} = \frac{1}{X_m c} + \frac{c-1}{X_m c}\phi$	(b)
	$X_m = 0.04094$ Kg/Kg	
	$c = 31.15873$	
Rounsley (1961)	$\frac{\phi(1-\phi^q)}{X(1-\phi)} = \frac{1}{B_1 C} + \frac{C-1}{B_1 C}\phi$	(c)
Harkins and Jura (1947)	$\ln \phi = D - \frac{C_1}{X^2}$	(d)
Henderson (1952)	$-\ln(1-\phi) = kT_R(100X)^n$	(e)
	$k = 1.3949 \times 10^{-4}$	
	$n = 0.86532$	
Kuhn (1964)	$X = \kappa \frac{1}{(-\ln\phi)^\xi} - B_2$	(f)
	$\xi = 0.9971$	
	$B_2 = 0.0003$	
	$\kappa = 0.0971$	
Halsey (1948)	$\ln \phi = -\frac{a_1}{RT}\left(\frac{X}{X_m}\right)^{-r_1}$	(g)
	$\frac{a_1}{RT} = 2.3858$	
	$r_1 = 0.9530$	
Filonenko and Chuprin (1967)	$X_I = \frac{a_2 + \phi}{k}$	(h)
	$X_{II} = \frac{B\Delta\phi}{b - \Delta\phi} + X_I$	(i)

Note: parameter values are for apples at 293°K.

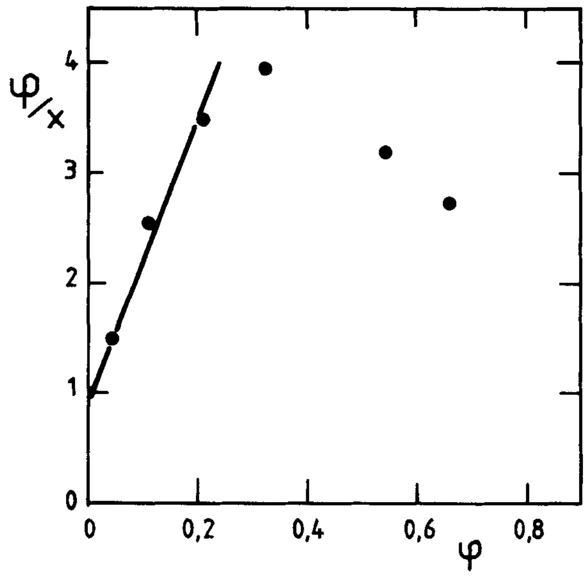

Fig. 1. Langmuir equation (apples, 293°K).

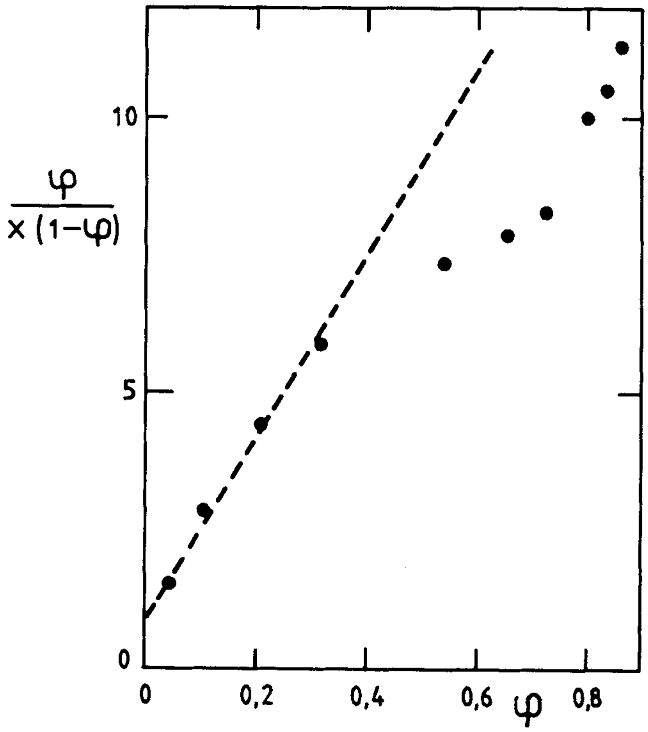

Fig. 2. BET equation (apples, 293°K).

overpredicts. Equation (q) is acceptable up to $\phi < 0.5$, but beyond that value it decreases rapidly and finally changes sign.

APPLICATION OF THE CHEMICAL POTENTIAL

To describe the equilibrium content of water in vegetable tissues, it is convenient to establish a model. In this case, the model is a simplified description of tissues and its components, the cells (Reeve, 1953; Slatyer, 1960; Nobel, 1974).

Tissues are regarded as assemblages of cells. Practically all cells have part of their surface abutting on intercellular air spaces. The generalized plant cell has an outside wall consisting of a mesh of cellulose microfibrils. Inside the outer wall there is cytoplasm, which consists mainly of proteins and water but which also contains lipids, salts, and other compounds. At the inner wall-cytoplasm interface, there is a membrane, plasmalemma, inside of which there is a large central aqueous phase which can occupy up to 90% of the volume of a mature cell, the vacuole. It is separated from the cytoplasm by a membrane known as the tonoplast.

Most of the water content of the cell resides in the vacuole and frequently reaches levels of about 98% of the vacuole volume (Slatyer, 1960; Stocking, 1956). The volumetric water content of the walls of turgid cells may be around 50% of the wall volume. The water is adsorbed on the solid surface and is retained in the interfibrillar spaces. The cytoplasm is even richer in water content. In the cytoplasm, water is bound to proteins and other hydrophilic colloids and also exists as free water. Most of the sugar in sugar based foodstuffs, to

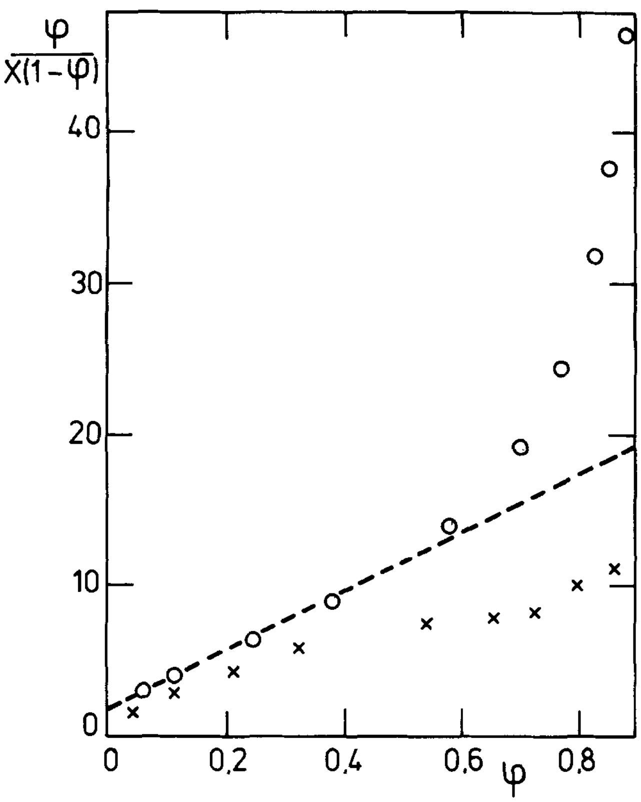

Fig. 3. Rounsley equation. ○ apples, × cellulose. ($T = 293$°K).

which the following analysis is confined, is contained within the vacuole. The vacuolar sap may be regarded as a solution (Slatyer, 1960).

WATER EQUILIBRIUM

When there is a change in water content, the solutes concentration as well as the sorptional force field resulting from the presence of the solid matrix and insoluble materials will be changed. The geometrical arrangement may also be altered.

This problem has some points of similarity with water-soil relationships. This was recognized by Slatyer (1960), who suggested that the thermodynamic approach used by Babcock (1963) would be applied to the above case.

If it is accepted that unique relationships can be established for the chemical potential of water as a function of volumetric water content, then a general expression for a differential change in chemical potential of water is as follows:

$$d\mu_w = -\bar{S}_w dT + \bar{V}_w dP + \left(\frac{\partial\mu_w}{\partial c_s}\right)_{T,P,nj,n_w} dc_s + \left(\frac{\partial\mu_w}{\partial\theta}\right)_{T,P,n_s} d\theta \qquad (4)$$

From a different standpoint, the number of moles of solute, of insoluble materials, and of water may be considered to be the relevant variables (Noy-Meir and Ginzburg, 1967):

$$d\mu_w = \bar{S}_w dT + \bar{V}_w dP + \left(\frac{\partial\mu_w}{\partial n_s}\right)_{nj,P,T} dn_s + \left(\frac{\partial\mu_w}{\partial n_m}\right)_{P,nj,T} dn_m + \left(\frac{\partial\mu_w}{\partial n_w}\right)_{P,nj,T} dn_w \qquad (5)$$

Equation (22) can be in integrated from the reference state of pure water at atmospheric pressure as expressed by the following set of initial conditions:

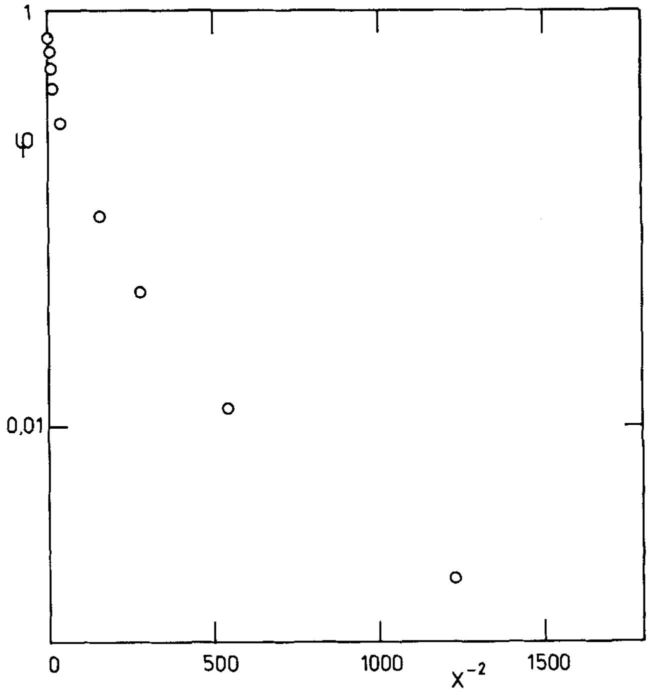

Fig. 4. Harkins and Jura equation (apples, 293°K).

$$P = P_o; \quad n_s = 0; \quad n_m = 0$$

where the water amount can be any nonnull quantity. If the temperature is taken to be constant, then in order to obtain an expression for the change in chemical potential, the term $(\partial\mu_w/\partial n_w)dn_m$ may be integrated at

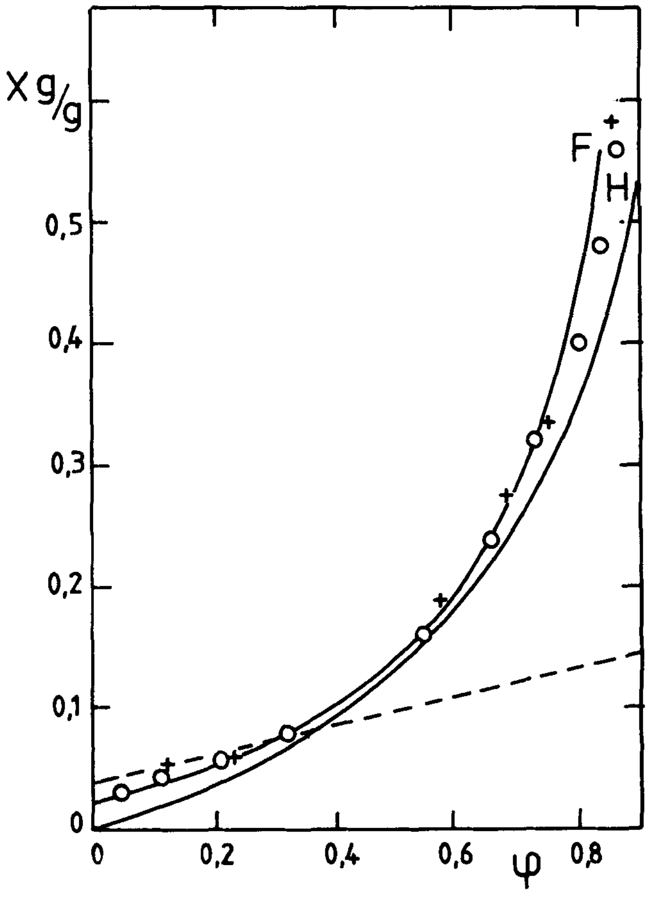

Fig. 5. Filonenko and Chuprin's (F) and Henderson's (H) equations (apples, 293°K).

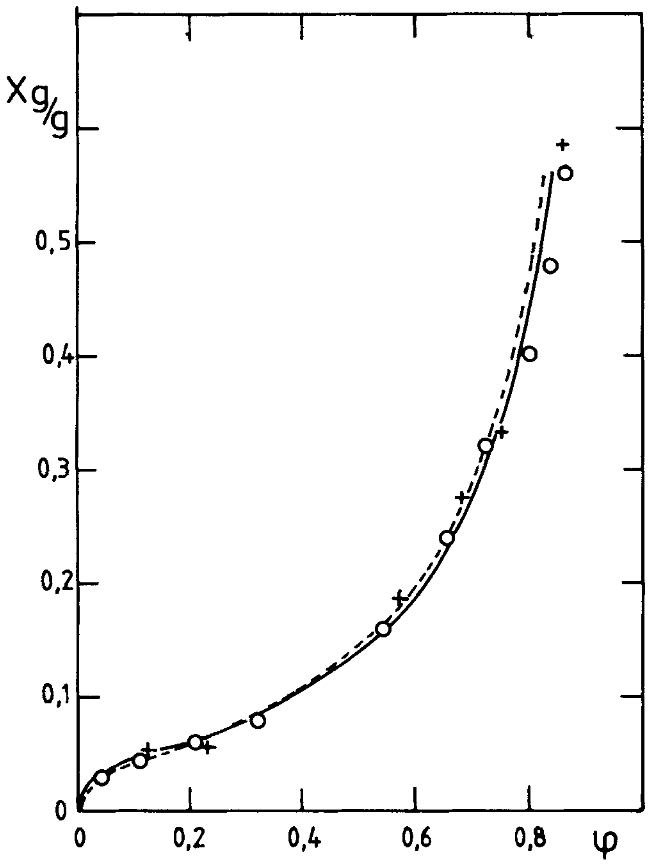

Fig. 6. Kuhn's (– – –) and Halsey's (——) isotherms (apples, 293°K). + Experimental data, ○ Filonenko and Chuprin (1967).

P_o, $n_s = 0$, n_w; the term $(\partial \mu_w / \partial n_s) dn_s$ at P_o, n_m, and n_w; and the $\overline{V}_w P$ term at n_s, n_m, n_w, between the reference state and the final state. Noy-Meir and Ginzburg (1967) discussed alternative partitions. While the pressure and solute terms of Equations (4) and (5) are readily integrable, the sorptional force field terms are not. For the purpose of the present discussion, the integrated effect of these terms will be lumped into a variable ψ_m (Slatyer, 1960; Nobel, 1974; Shepherd, 1975). Then, for constant $\overline{V}_w$

$$\mu_w - \mu_w{}^o = \overline{V}_w (P - P_o) + RT \ln a_w + \overline{V}_w \psi_m \qquad (6)$$

The problem under examination is that of equilibrium between tissue and humid air. Thus, the equilibrium isotherm is

$$RT \ln \phi = \overline{V}_w (P - P_o) + RT \ln \hat{a}_w + \overline{V}_w \psi_m \qquad (7)$$

where the gas phase is considered to be ideal, an acceptable assumption at atmospheric pressure. Equilibrium implies that the chemical potential has the same value in each of the phases in the cell as in the surroundings. The use of Equation (6) is not straightforward because of the complexity of the structure involved. The relative contributions of the terms to the value of the chemical potential value will be different for each of the phases; also, the values to be used will, of necessity, be spatial averages, since no techniques are available for the determination of cell properties on a microscale (Hellkvist et al., 1974).

TABLE 2. THE DERIVATIVE $\left(\dfrac{\partial X}{\partial \phi}\right)_T$

Original equation	$\left(\dfrac{\partial X}{\partial \phi}\right)_T$	
(a)	$k_1 k_2 / (1 + k_2 \phi)^2$	(j)
(b)	$\dfrac{X_m c \{1 + (c-1)\phi^2\}}{\{1 + (c-2)\phi - (c-1)\phi^2\}^2}$	(k)
(e)	$\dfrac{X}{n(1-\phi)\{-\ln(1-\phi)\}}$	(l)
(f)	$\dfrac{\kappa \xi}{\phi(-\ln \phi)^{1+\xi}}$	(m)
(g)	$\left(\dfrac{a_1}{RT}\right)^{1/r_1} \dfrac{X_m}{r_1} \dfrac{1}{\phi(-\ln\phi)^{1+1/r_1}}$	(n)
(i)	$\dfrac{bB}{(b - \Delta\phi)^2}$	(o)

TABLE 3. THE DERIVATIVE $\left(\dfrac{\partial X}{\partial T}\right)_\phi$

Original equation	$\left(\dfrac{\partial X}{\partial T}\right)_\phi$	
(e)	$-\dfrac{X}{nT}$	(p)
(i)	$\dfrac{(b - \Delta\phi)(BZ_1 + Z_2\Delta\phi) - BZ_1\Delta\phi}{(b - \Delta\phi)^2} - 0.0004$ $Z_1 = 10^{-4}(1.2T_c - 0.06T_c{}^2 - 4k)$ $Z_2 = -2.5 \times 10^{-6}\, T_c$	(q)

THE MATRIC POTENTIAL AND THE HYDROSTATIC PRESSURE TERMS

The matric potential term accounts for the capillarity, adsorption, and hydration forces. The water held by

TABLE 4. THE DERIVATIVE $(\partial X/\partial \phi)_T$

ϕ	Langmuir	BET	Experimental	Henderson	Kuhn	Filonenko	Halsey	$\phi = \gamma_w x_w$
0.01	0.832	0.9588		0.1163	0.4579	0.1264	0.4389	0.3084
0.10	0.184	0.1581	0.220	0.1845	0.1831	0.1517	0.1817	0.1889
0.20	0.073	0.1107	0.160	0.2332	0.1874	0.1889	0.1892	0.1852
0.30	0.039	1.1192	0.200	0.2867	0.2233	0.2445	0.2287	0.2102
0.40	0.024	0.1505	0.320	0.2988	0.2391	0.3266	0.3001	0.2595
0.50	0.016	0.2097	0.370	0.4452	0.4042	0.4583	0.4254	0.3468
0.60	0.012	0.3226	0.580	0.5812	0.6202	0.6891	0.6626	0.5107
0.70	0.009	0.5691	0.970	0.8085	1.0904	1.1510	1.1858	0.8654
0.80	0.007	1.2759	2.100	1.2689	2.4376	2.2988	2.7129	1.8774
1.00	0.005	∞		∞	∞	76.5306		629.2271

TABLE 5. THE DERIVATIVE $(\partial X/\partial T)_\phi$

Results for apples at 30°C

		Correlation		
ϕ	Experimental	Henderson	Filonenko and Chuprin	$\phi = \gamma_w x_w$
0.989		−0.02668	+0.02767	−0.00114
0.857	−0.00120	−0.00213	+0.00047	−0.00076
0.800	−0.00015	−0.00153	−0.00011	−0.00067
0.7	−0.00155	−0.00097	−0.00043	−0.00057
0.6	−0.00105	−0.00071	−0.00051	−0.00047
0.5	−0.00040	−0.00052	−0.00053	−0.00041
0.4	−0.00065	−0.00039	−0.00053	−0.00035
0.3	−0.00046	−0.00029	−0.00052	−0.00030
0.2	−0.00035	−0.00019	−0.00051	−0.00025
0.1	−0.00028	−0.00011	−0.00050	−0.00019

TABLE 6. TYPICAL COMPOSITION OF FRESH APPLE
(Basis: 1 kg dry matter)

Water	6.50-7.00 kg/kg
Glucose and fructose	0.58 kg/kg
Sucrose	0.18 kg/kg

matric forces roughly corresponds to bound water (Wilson and Rose, 1967). Wiebe and Al-Saadi (1976) measured matric water contents for tissues of several vegetable foodstuffs. From their data it can be seen that the matric water content is only of importance when the total content is very low.

If the cell is regarded as being enclosed within ideally elastic walls, a linear relationship can be established between gauge pressure and relative change of volume from full turgor to zero gauge pressure (Noy-Meir and Ginzburg, 1967):

$$\bar{V}_w(P - P_o) = \bar{V}_{w}X\left(\frac{X - X^o}{X^o}\right) \quad (8)$$

SORPTION EQUILIBRIUM PREDICTION

A full description of the equilibrium relationships for apples should be for the full moisture content range, $0 \leq X \leq 7$ kg/kg rather than for the restricted ranges covered by the existing equations. For the purposes of design or simulation of conventional drying processes, the process starts at full turgor. Fresh fruits are usually packaged and stored under conditions close to those of full turgor. Commercial hot air drying terminates at a standard moisture content $X = 0.32$ kg/kg, while freeze drying or air drying followed by vacuum drying extends to a moisture content of almost zero.

SOLUBILITY

In the case of apples, a representative composition is shown in Table 15 (Rotstein et al., 1969; Voho and Varo, 1975). The vacuolar solution is a sugar solution made primarily of glucose and fructose, with some sucrose. Studies made on honeys by Bates et al. (1972) showed that sucrose could be treated as if it were fructose, from the standpoint of the solubility properties of the system. A characteristic feature of these solutions is their ability to remain in an oversaturated condition for a long period of time. Figure 7 is a plot of the solubility relationships for the system water-sucrose-invert sugar. If the glucose and fructose mixture is considered as if it were invert sugar, the line WP shows the evolution of a typical apple as its moisture content changes.

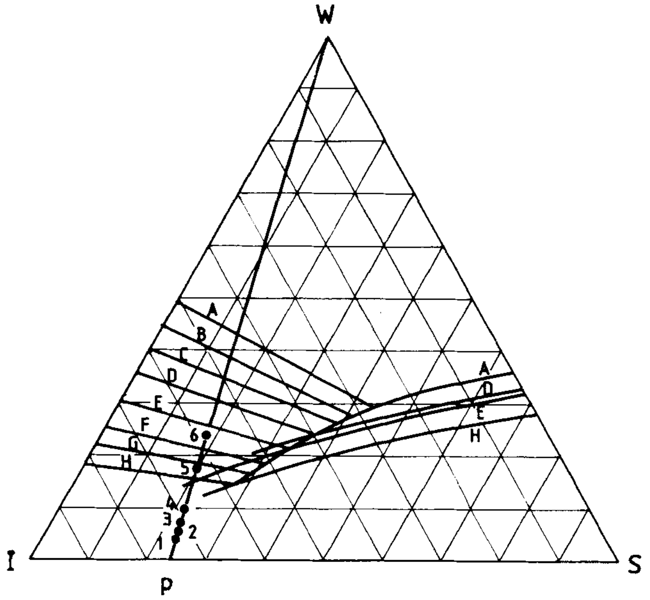

Fig. 7. Solubility of the sucrose-invert sugar-water system. Points 1, 2, 3, 4, 5, 6 represent moisture contents 0.03, 0.06, 0.08, 0.16, and 0.24 kg/kg, respectively. A, B, C, D, E, F, G, H are 0°, 10°, 15°, 23.15°, 30°, 40°, 45°, and 50°C isotherms, respectively. W, I, S are 100% water, invert sugar, and sucrose vertexes, respectively.

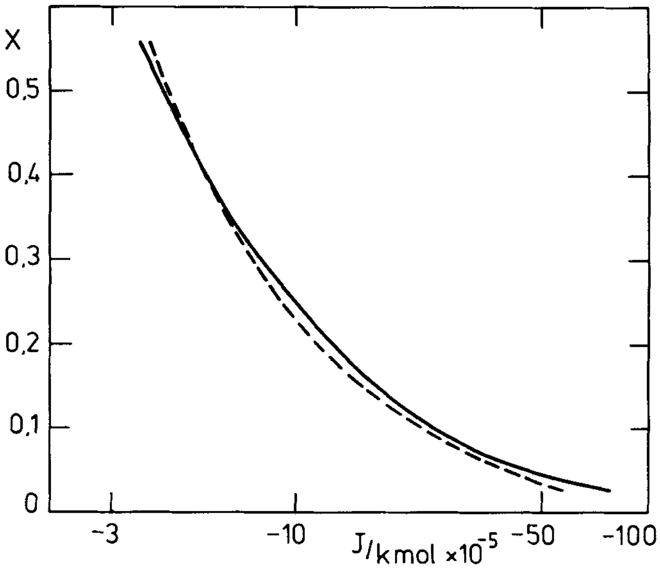

Fig. 8. Total and osmotic chemical potential. --- $RT \ln \phi$, ——— $RT \ln a_w$.

THE ACTIVITY COEFFICIENT OF GLUCOSE SOLUTIONS

Taylor and Rowlinson (1955) correlated the activity coefficient of water in glucose solutions as follows:

$$\gamma_w = 10^{A(1-x_w)^2} \quad (9)$$

Changes from one temperature to another can be made using the following equation:

$$\left(\frac{\partial \ln \gamma_w}{\partial T}\right)_{P,x} = -\frac{\overline{\Delta H}_w}{RT^2} \quad (10)$$

If the partial molar enthalpy change of mixing of water is regarded as being practically constant within the temperature range under consideration, then $\gamma_w(T)$ can be represented by

$$\ln \gamma_w = l + p/T \quad (11)$$

where $l = 1.274$, and $p = -635.840$ for $r^2 = 0.992$.

RELATIVE CONTRIBUTIONS OF THE CHEMICAL POTENTIAL TERMS

Figure 8 allows a comparison to be made of the values of the water vapor and osmotic chemical potential terms at successive sets of moisture content and activity values. The calculations were made on the assumption that the solutions reached oversaturation and that the thermodynamic relationships for the solution could be extrapolated into the oversaturated region. The test of the validity of this and other assumptions will be the ability of the method to predict equilibrium relationships. The water mole fraction was calculated from

$$x_w = \frac{X}{X + \sum_j \left(\frac{m_j}{d + \Sigma m_j} \cdot \frac{M_w}{M_j} \right)} \qquad (12)$$

It can be seen that through most of the range of moisture contents under consideration, the contribution of the osmotic term is a close approximation to the total chemical potential of the system. Departures from this statement are noted mainly at extreme moisture contents both high and low. As bound, or matric, water is the last to leave the solid, it seems reasonable to conjecture that as water content is reduced, it eventually becomes equal to the amount of bound water located mainly at the cell wall and cellular membrane. Throughout this process, the water apportioned to the osmotic term decreases, and the matric chemical potential becomes the dominant term. Obviously, the point at which all of the remaining water is bound water is ill defined.

At high moisture content, it is to be noted that the difference between water vapor chemical potential and osmotic potential is not as large as it is at low moisture contents. At full turgor, the difference for apples is about −25 100 J/kmole. As an approximation, it seems reasonable to consider that at full turgor the water accountability can be restricted to the vacuole. In that case, the significant contributions in Equation (7) are the swelling pressure and osmotic terms. The difference between the osmotic term and the water vapor chemical potential is due to the pressure term. This is consistent with the pressure term being positive.

REGIONS IN THE EQUILIBRIUM ISOTHERM

Three regions can be identified: the high moisture region, the low moisture region, and the intermediate water region.

The high moisture region

This region can be considered as extending from full turgor down to the moisture content at which the vacuolar pressure is equal to the external pressure. In terms of the foregoing analysis of the chemical potential, when attention is focused on the vacuole and matric potential is neglected, the moisture content at the lower limit of the high moisture region is located at the intersection of the curves $RT \ln \phi$ and $RT \ln \hat{a}_w$ (Figure 8).

A simple correlation can be presented for the pressure term by making use of Equation (8) and by noting that at full turgor the fruit can be considered to be in equilibrium with saturated moist air. Then, from Equations (7) and (8)

$$0 = \overline{V}_w \chi \left(\frac{X - X^o}{X} \right) + RT \ln (\hat{a}_w)_1 \qquad (13)$$

For the case of apples at 20°C, this results in

$$\chi = 1.54912 \times 10^6 \frac{J}{m^3}$$

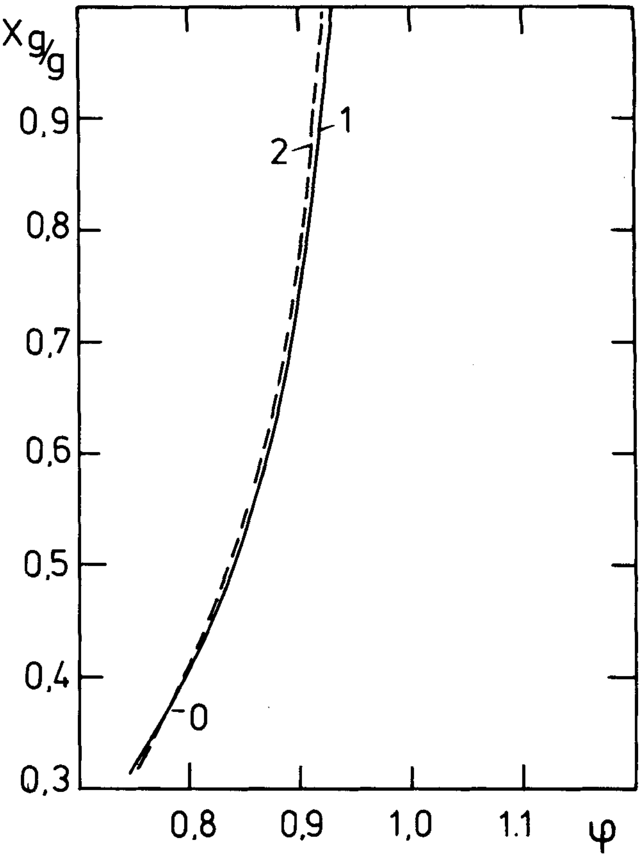

Fig. 9. Hydrostatic pressure contribution. 1—Equation (14), 2—Equation (15).

The equilibrium relationship for the high moisture region then results:

$$RT \ln \phi = \overline{V}_w \chi \left(\frac{X - X^o}{X} \right) + RT \ln \hat{a}_w \qquad (14)$$

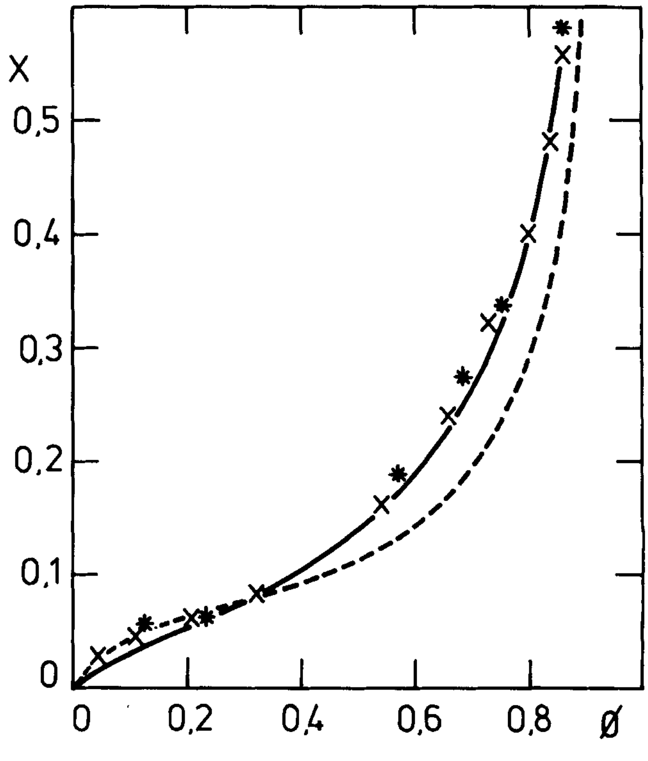

Fig. 10. Predicted equilibrium data (apples, 293°K). ——— Equation (15), * experimental data, – – – BET equation, × Filonenko and Chuprin (1967).

The actual significance of the pressure term is low, from the standpoint of the order of magnitude of its contribution to the moisture equilibrium content prediction. Figure 9 shows that there is little change in the predicted value if the pressure term in Equation (14) is dropped. In the case under consideration, this results in a maximum difference of 1% for moisture contents in the range $2 < X < 7$ kg/kg dry matter and progressively even less as the moisture content decreases further.

The Low Moisture Region

The low moisture region refers to the bound water content of the foodstuff. It has been seen that at low moisture contents, the BET equation predicts accurately the equilibrium values, probably because the actual situation is close to the concepts on which the Brunauer, Emmet and Teller theory is based.

The lower bound of this region is the zero moisture content point. The upper bound is defined as the intersection of the BET line and the line drawn for the intermediate moisture region.

The Intermediate Moisture Region

As stated earlier, this region and that of low moisture content are the regions usually described in the literature. The upper bound of this region is the point of zero gauge vacuolar pressure. It is to be noted that the literature is conflicting as to whether or not negative pressures exist inside the cell (Slatyer, 1960). The ability of a cell to retain a vacuum has been related to the cell wall capillaries, which it has been suggested (Nobel, 1974) operate as hydraulic seals. If the predictions of Figure 9 are correct, by the time the vacuolar gauge pressure becomes zero, a substantial amount of water has left the cell. If it were to keep its volume constant, this would mean that only about 10% of this volume would be liquid. Under these circumstances it is hard to visualize the build up of a substantial vacuum.

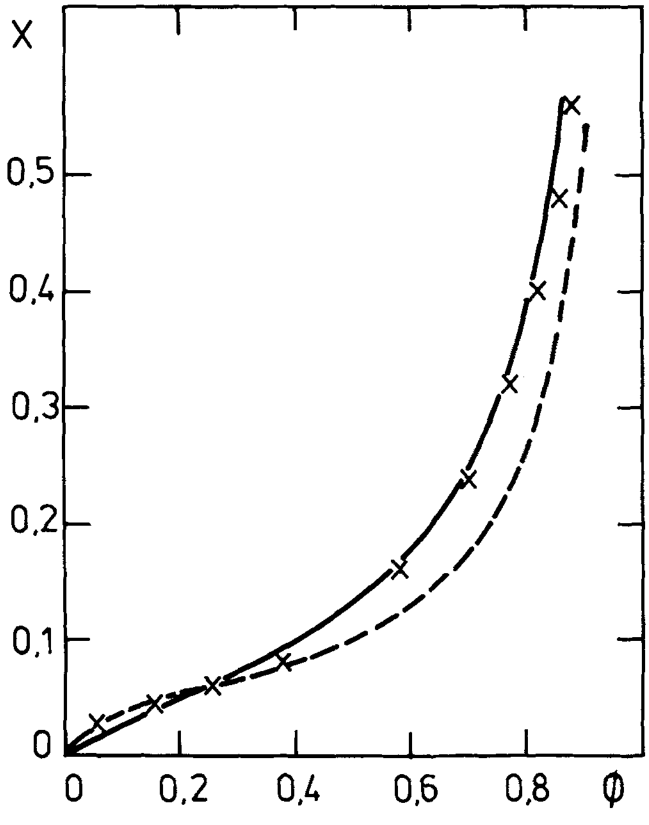

Fig. 11. Predicted equilibrium data (apples, 313°K). ——— Equations (10) and (15), - - - BET equation, × Filonenko and Chuprin (1967).

It is possible that depending on the vegetable under consideration, partial vacuum could be built up, which would then collapse.

On the other hand, and from a practical standpoint, it has been pointed out that the pressure term contribution can be neglected for the purposes of equilibrium moisture content prediction.

Thus the equilibrium relationship for the intermediate region is

$$\phi = \hat{a}_w \tag{15}$$

In practice, the use of this equation can be extended to the high moisture region. Figure 10 indicates the equilibrium values predicted by the above expression for apples at 20°C.

THE $(\partial X/\partial \phi)_T$ DERIVATIVE

For the intermediate and high moisture content regions, the derivative $(\partial X/\partial \phi)_T$ can be calculated using the following expression obtained from Equations (9), (12), and (15):

$$\left(\frac{\partial X}{\partial \phi}\right)_T = \frac{\alpha}{(1 - x_w)^2 \phi \left[\dfrac{1}{x_w} - 2\beta A(1 - x_w) \right]} \tag{16}$$

where

$$\alpha = \sum_j \frac{m_j}{\left(\sum_j m_j + d \right)} \cdot \frac{M_w}{M_j} \tag{17}$$

and $\beta = 2.30258\ldots$.

The results for apples at 20°C using the above equations are shown in Table 4 together with values calculated from several of the correlations described previously. It can be seen that several of the correlations yield good predictions for the intermediate moisture region. As moisture content increases, the best predictions are provided by the Filonenko and the Halsey correlations as well as by Equation (16). The Filonenko and Halsey correlations tend to overestimate the effect of a change in water vapor activity, whereas Equation (16) tends to underestimate it.

THE PREDICTION OF ISOTHERMS AT DIFFERENT TEMPERATURES

Equations (9) and (15) enable sorptional equilibrium values to be predicted at any temperature. As an example, values have been predicted for apples at 40°C (Figure 11).

THE DERIVATIVE $(\partial X/\partial T)_\phi$ IN THE PROPOSED CORRELATION

If we use Equation (15) to describe the whole range of moisture contents, the derivative is

$$\left(\frac{\partial X}{\partial T}\right)_\phi = - \frac{\alpha \beta p (1 - x_w)}{T^2 \left\{ 2 \ln\left(\dfrac{\phi}{x_w}\right) - \dfrac{(1 - x_w)}{x_w} \right\}} \tag{18}$$

Representative values were calculated for apples at 30°C and are shown in Table 5. It can be seen that the predicted values are a reasonable representation of the measured values and that they extend into the high moisture content region in a satisfactory manner.

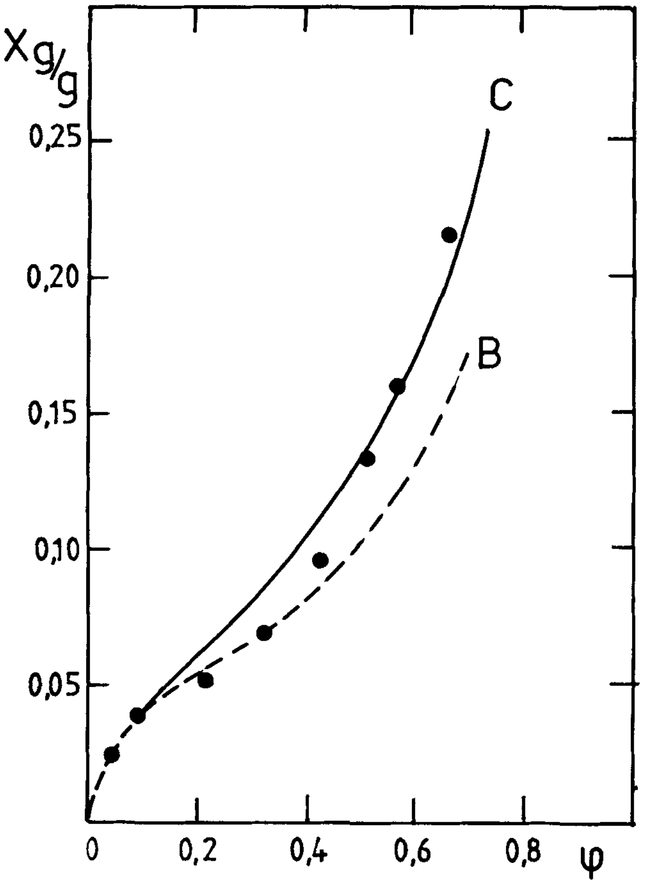

Fig. 12. Beetroot, 298°K. C, Equation (15); B, BET equation; ● Iglesias et al. (1975).

APPLICATION OF THE PROPOSED CORRELATION TO OTHER FOODSTUFFS

The proposed correlation procedure was applied to other foods and the results compared with experimental data. Typical compositional data were used to predict equilibrium data for all but the low moisture content region, where a BET equation was used, as described earlier. As some of the foodstuffs to be considered are sucrose based instead of glucose based, there is need for data on the water activity of sucrose solutions.

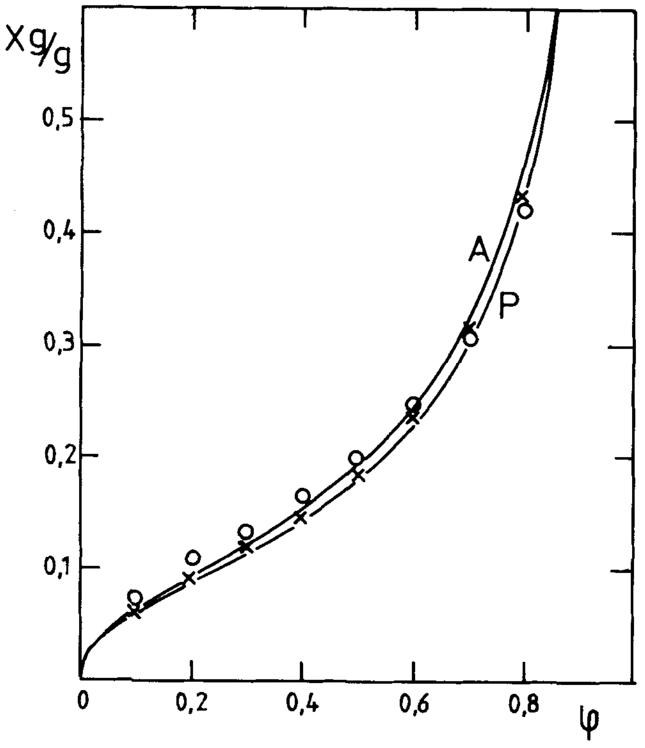

Fig. 13. Apricots (A) and plums (P), 293°K. ○ apricots data (Filonenko and Chuprin, 1967), × plums data (Filonenko and Chuprin, 1967).

THE ACTIVITY COEFFICIENT OF SUCROSE SOLUTIONS

Stokes and Robinson (1966) presented experimental data for the activity of sucrose solutions as well as a correlation which relates molalities to the activity coefficient of water. The use of their correlation presents difficulties when carried beyond the scope for which it was developed ($m < 6$), and at high sugar concentrations it is not adequate. Instead, the experimental data obtained by the above authors, together with data obtained by Scatchard et al. (1932), were fitted by a least-square linear regression procedure in the form of Equation (9). As a result, the following value was obtained

$$A = -2.789326$$

which fits the experimental data to within 0.8%. Norrish (1966) suggested a value of $A = -2.60$, which results in maximum errors of 3.6%.

BEETROOT

Cerny (1941), Dahlberg (1952), and Owens et al. (1955) have published data on typical compositions of beetroots from several origins. It is interesting to note that the sugar content of beetroot corresponds mainly to sucrose, instead of glucose. Equation (15) was used to predict the sorption equilibrium data in the intermediate moisture region, for beetroot at 25°C, using a representative value of α of 0.8061.

A least-square linear regression procedure yielded $X_m = 0.0518$ and $c = 16.16$ for the BET equation [Equation (l)]. The results are plotted in Figure 12 and compared with experimental data (Iglesias et al., 1975). It can be seen that the predicted values fit the experimental results adequately.

PRUNES

The chemical composition of prunes has been thoroughly reviewed by Strachan et al. (1951). Further reports were made by Kalasek and Blaha (1963) and by Chernovalova and Avetisyan (1969). It is concluded that about 70% of the sugar is sucrose. Figure 13 shows a prediction curve obtained by plotting the BET expression up to X_m and then continuing with Equation (15). In this case, $X_m = 0.0977$ g/g dry matter, $c = 11.7476$ as obtained by a least-squares regression procedure, and $\alpha = 0.59$. It is interesting to note that the values predicted by Equation (15) for $X < X_m$ are almost the same as those predicted by Equation (l). The results are compared with experimental data obtained by Filonenko and Chuprin (1967), and, as shown in Figure 13, the theoretical prediction is satisfactory.

APRICOTS

The composition of apricots was reviewed thoroughly by Strachan et al. (1951). Additional data were reported by Minicone (1962-3). Figure 13 shows a prediction curve obtained by matching the BET line up to X_m with Equation (15) from X_m upwards.

Again, the values predicted by the BET equation up to X_m ($X_m = 0.1092$ g/g, $c = 0.1092$) are almost identical with those predicted by Equation (15). The predicted values compare well with the experimental data obtained by Filonenko and Chupin (1967).

ACKNOWLEDGMENT

The authors wish to thank CONICET for the award of a fellowship to Enrique Rotstein.

NOTATION

A = constant, Equation (9)
a_w = activity of water in solution
a_1, a_2 = constants, Equations (h) and (g)
B, B_1, B_2, b = constants, Equations (i), (c), (f), and (i)
C, C_1, c = constants, Equations (c), (d), and (b)
c_s = solute concentration, Kg/m^3
D = constant, Equation (d)
d = mass of dry matter, kg
H = enthalpy, J
k, k_1, k_2 = constants, Equations (e), (a), and (h)
l = constant, Equation (11)
M_j = sugar component molecular weight, kg/mole
M_w = water molecular weight, kg/mole
m_j = sugar component weight, kg
n = constant, Equation (e)
n_m = number of moles of insoluble material
n_s = number of moles of solute
o = reference state
P = pressure, N/m^2
p = constant, Equation (11)
q = constant, Equation (c)
R = universal gas constant, J/mole °K
r_1 = constant, Equation (g)
r^2 = square or regression coefficient
$\overline{S}_w$ = partial molar entropy of water, J/k mole
T = temperature, °K
T_c = temperature, °C
T_R = temperature, °R
$\overline{V}_w$ = partial molar volume of water, m^3/k mole
X = moisture content, kg/kg
X_I, X_{II} = moisture content in lineal and nonlineal region, respectively, kg/kg, Equations (h) and (i)
X_l, X_m = constants, Equations (i) and (b)
x_w = water mole fraction

Greek Letters

α = constant, Equation (17)
β = constant, Equation (18)
γ_w = water activity coefficient
$\Delta\phi$ = $\phi - \phi_l$
θ = water volumetric content, m^3/m^3
κ = constant, Equation (f)
μ_w = water chemical potential, J/mole
ξ = constant, Equation (f)
π = osmotic pressure, N/m
ϕ = water vapor activity
χ = constant, Equation (8)
ψ_m = matric potential, N/m

LITERATURE CITED

Babcock, K. L., "Theory of the Chemical Properties of Soil Colloidal Systems at Equilibrium," *Hilgardia*, 34, 417 (1963).

Bates, F. R., et al., "Polarimetry, Saccharimetry and the Sugars," *Circular C440*, U.S. Dept. of Commerce, N.B.S. (1972).

Brunauer, S., P. H. Emmet, and E. Teller, "Adsorption of Gases in Multimolecular Layers," *J. Am. Chem. Soc.*, **60**, 309 (1938).

Cerny, M., "Studies of the Components of Beet Pulp," *Listy Cukrovar*, **60**, 103 (1941).

Chernovalova, V. D., and S. N. Avetisyan, "Chemical Composition of the Mazard, Cherry and Plum in the Smarkand Region," *Konserv. Ovoshchesush. Prom.*, **24**, 27 (1969).

Dahlberg, H. W., "Composition of Beets from Widely Separated Areas," *Sugar*, **47**, No. 10, 46 (1952).

Filonenko, G. K., and A. E. Chuprin, "Equilibrium Moisture Content of Foodstuffs," *J. Eng. Phys.*, Tr. from *Inzh.-Fiz. Zh.*, 13, 98 (1967).

Gane, R., "The Water Relations of Some Dried Foods," *J.S.F.A.*, 1, 42 (1950).

Halsey, G., "Physical Adsorption on Non-Uniform Surfaces," *J. Chem. Phys.*, **16**, 931 (1948).

Harkins, W. D., and G. Jura, "An Adsorption Method for the Determination of the Area of a Solid Without the Assumption of a Molecular Area, and the Area Occupied by Nitrogen Molecules on the Surfaces of Solids," *ibid.*, **11**, 431 (1947).

Hellkvist, J., G. P. Richards, and G. Jarvis, "Vertical Gradients of Water Potential and Tissue Water Relation in Sitka Spruce Trees Measured with the Pressure Chamber," *J. Appl. Ecol.*, **11**, 637 (1974).

Henderson, S. M., "A Basic Concept of Equilibrium Moisture," *Agr. Eng.*, **33**, 92 (1952).

Iglesias, H. A., J. Chirife, and J. L. Lombardi, "Water Sorption Isotherms in Sugar Beet Root," *J. Fd. Technol.*, **10**, 229 (1975).

Kalasek, J., and J. Blaha, "Chemical Composition and Quality of the Domestic Plums," *Prumysl Potravin*, **14**, 457 (1963).

Kuhn, I., "A New Theoretical Analysis of Adsorption Phenomena," *J. Colloid Sci.*, **19**, 685 (1964).

Labuza, T. P., "Sorptional Phenomena in Foods: Theoretical and Practical Aspects," in *Theory, Determination and Control of Physical Properties of Food Materials*, Chokyun Rha, ed., D. Reidel, Dordrecht-Holland (1974).

Langmuir, I., "The Constitution and Fundamental Properties of Solids and Liquids," *J. Am. Chem. Soc.*, 38, 2221 (1916).

———, "The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum," *ibid.*, **40**, 1361 (1918).

Minicone, B., "Chemical Composition of Some Varieties of Apricots Produced in Campania," *Ann. Fac. Sci. Agrar. Univ. Studi Napoli Portici*, **28**, 287 (1962-3).

Nobel, P. S., *Introduction to Biophysical Plant Physiology*, W. H. Freeman and Co., San Francisco, Calif. (1974).

Norrish, R. S., "An Equation for the Activity Coefficients and Equilibrium Relative Humidities of Water in Confectionary Syrups," *J. Fd. Technol.*, **1**, 25 (1966).

Noy-Meir, I., and B. Z. Ginzburg, "An Analysis of the Water Potential Isotherms in Plant Tissue I. The Theory," *Aust. J. Biol. Sci.*, **20**, 695 (1967).

Owens, H. S., J. D. Stark, A. E. Goodban, and H. G. Walker, "Application of Compositional Knowledge to Beet Sugar Technology," *J. Agr. Food Chem.*, **3**, 350 (1955).

Reeve, R. M., "Histological Investigations of Texture in Apples," *Food Res.*, **18**, 604 (1953).

Rotstein, E., M. Namor, A. M. Sica, and J. Aruanno, "Apples from Argentina: Chemical and Physical Characteristics useful for Technology," *J. Milk Food Technol.*, **32**, 79 (1969).

Rounsley, R. R., "Multimolecular Adsorption Equation," *AIChE J.*, **1**, 308 (1961).

Saravacos, G. D., "Effect of Drying Method on the Water Sorption of Dehydrated Apple and Potatoes," *J. Food Sci.*, **32**, 81 (1967).

Scatchard, G., W. J. Hamer, and S. E. Wood, "Isotonic Solutions. I. The Chemical Potential of Water in Aqueous Solutions of Sodium Chloride, Potassium Chloride, Sulphuric Acid, Sucrose Urea and Glycerol at 25°C.," *J. Am. Chem. Soc.*, **60**, 3061 (1938).

Shepherd, W., "Matric Water Potential of Leaf Tissue. Measurement and Significance," *J. Exp. Bot.*, **26**, No. 92, 465 (1975).

Slatyer, R. O., "Aspects of the Tissue-Water Relationships of an Important Arid Zone Species (Arcacia Aneura F. Muell) in Comparison with Two Mesophytes," *Bull. Res. Conc. of Israel*, 8D, 159 (1960).

Stokes, R. H., and R. A. Robinson, "Interactions in Aqueous Nonelectrolyte Solutions. I. Solute-solvent Equilibria," *J. Phys. Chem.*, 7, 2126 (1966).

Stocking, C. R., "Hydration and cell physiology," in *Encyclopedia of Plant Physiology*, W. Ruhland, ed., Vol. 2, Springer-Verlag, Berlin, Germany (1956).

Strachan, C. C., A. W. Moyls, F. E. Atkinson, and J. E. Britton, "Chemical Composition and Nutritive Value of British Columbia Tree Fruits," *Pub. No. 862*. Dept. of Agriculture, Ottawa, Canada (1951).

Taylor, A. A., "Determination of Moisture Equilibrium in Dehydrated Foods," *Food Technol.*, **15**, 536 (1961).

Taylor, J. B., and J. S. Rowlinson, "The Thermodynamics of

Solutions of Glucose," *Trans. Faraday Soc.*, 51, 1186 (1955).
Voho, K., and P. Varo, "Chemical and Organoleptic Evaluation of Some Finnish Apple Varieties," *J. Sci. Agr. Soc. Finland*, 47, 445 (1975).
Wiebe, H. H., and H. A. Al-Saadi, "Matric Bound Water of Water Tissue from Succulents," *Physiol Plant.*, 36, 47 (1976).
Wilson, J. W., and C. W. Rose, "The Components of Leaf Water Potential. I. Osmotic and Matric Potentials," *Aust. J. Bio. Sci.*, 20, 239 (1967).
Wolf, M., J. E. Walker, and J. G. Kapsalis, "Water Vapor Sorption Hysteresis in Dehydrated Food," *J. Agr. Food Chem.*, 20, 1073 (1972).

Manuscript received July 22, 1977; revision received May 10, and accepted June 21, 1978.

Vapor-Liquid Equilibria in Multicomponent Aqueous Solutions of Volatile Weak Electrolytes

T. J. EDWARDS
GERD MAURER
JOHN NEWMAN
and
J. M. PRAUSNITZ

Chemical Engineering Department
University of California
Berkeley, California 94720

A molecular-thermodynamic correlation is established for calculating vapor-liquid equilibria in aqueous solutions containing one or more volatile electrolytes: ammonia, carbon dioxide, hydrogen sulfide, sulfur dioxide, and hydrogen cyanide. The correlation is similar to that presented in 1975, but the domain of application has been increased. The present correlation holds from about 0° to 170°C and for ionic strengths of about 6 molal; for the weak electrolytes considered here, this corresponds to total concentrations between 10 and 20 molal. To represent activities at these high concentrations, activity coefficients are expressed as a function of molality by Pitzer's equation. Required parameters are estimated from data reduction or from correlations.

Special attention is given to the ternary systems ammonia-carbon dioxide-water and ammonia-hydrogen sulfide-water. Calculated equilibria are in satisfactory agreement with the severely limited experimental data now available.

SCOPE

In response to ecological, economic, and political developments, the chemical and petroleum industries must more effectively recover weak electrolytes from plant effluent streams. Towards that end, it is necessary to examine the vapor-liquid equilibria of aqueous, volatile weak electrolytes.

The volatile weak electrolytes of greatest industrial importance are ammonia, carbon dioxide, and hydrogen sulfide, although sulfur dioxide and hydrogen cyanide are also of interest. Literature for the most commonly encountered industrial case (aqueous solutions containing two or more volatile weak electrolytes) is seriously limited. Most of the few available experimental data pertain to dilute solutions and to ambient temperatures.

In contrast to the large body of work published on nonelectrolyte and strong electrolyte solutions, theoretical or correlational work is sparse for aqueous, volatile weak electrolytes. Van Krevelen's (1949) studies apply only to ammonia rich systems; further, they are limited to restricted ranges of ammonia/acid ratios and, for some cases, require experimental information which is not available. The more recent work of Edwards et al. (1975) is limited to low concentrations of weak electrolytes and to temperatures below (about) 80°C. The present work extends Edwards' earlier efforts to higher concentrations and higher temperatures.

The purpose of this work is to extend a previously presented thermodynamic framework for calculating vapor-liquid equilibria for solutions containing volatile weak electrolytes as commonly encountered in the chemical and related industries. The electrolytes examined are ammonia, carbon dioxide, hydrogen sulfide, and sulfur dioxide for the temperature range 0° to 170°C; the composition range, depending on extent of ionization, may be as high as 10 to 20 molal. Limited information is also given for hydrogen cyanide.

T. J. Edwards is with Air Products and Chemicals, Allentown, Pennsylvania 18105. Gerd Maurer is on leave from Institut für Thermodynamik und Kältetechnik, Universität Karlsruhe, Germany.

0001-1541-78-9488-0966-$01.35.