Equilibration of Solutes in Nonfermenting, Brined Pickling Cucumbers

E. A. POTTS, H. P. FLEMING, R. F. McFEETERS, and D. E. GUINNUP

ABSTRACT

The equilibration of solutes between whole cucumbers and the brine in which they were held was found to be consistent with a diffusion-controlled first-order rate process. First-order rate coefficients for attainment of equilibrium (K_D) for sugar and malic acid (initially in cucumbers) and NaCl and lactic, tartaric, acetic and formic acids (initially in brine) varied up to threefold among four cucumber lots. However, the ratios of K_D values among solutes were not significantly different ($P>0.05$). K_D values increased as cucumber size decreased. Peeling increased K_D values 3.7- to 11.1-fold. Temperature dependency was greater for solute movement out of [apparent activation energies (E_a) of 6.5 and 6.3 kcal/mole for malic acid and sugar] than into (apparent E_a of 4.5 and 4.2 kcal/mole for NaCl and lactic acid) cucumbers. The equilibration-prediction model used may be helpful in studying rate limiting factors in the fermentation of brined vegetables and in other food preservation processes where solute movement is important.

INTRODUCTION

THE FERMENTATION of cucumbers has been viewed traditionally as a process where sugar and other nutrients diffuse from the cucumbers into the brine, with fermentation by lactic acid bacteria and yeast occurring exclusively in the brine (Etchells et al., 1968). In the controlled fermentation process recommended by Etchells et al. (1973), cucumbers are held in acidified brines for 18 to 24 hr to allow nutrients to diffuse into the brine and NaCl and acetic acid to diffuse into the cucumbers. The brine is then adjusted to about pH 4.5 and inoculated with lactic acid bacteria.

Recently, lactic acid bacteria were found to enter and multiply inside brined cucumbers (Daeschel and Fleming, 1981). The internal gas composition of the cucumbers at brining and the time of brine inoculation influenced the amount and extent of bacterial colonization of the brined cucumbers (Daeschel et al., 1982). Degradation of malic acid, a natural cucumber constituent, into lactic acid and CO_2 has been shown to be a major source of microbially produced CO_2 (McFeeters et al., 1982). Thus, growth of lactic acid bacteria inside brined cucumbers was implicated as a cause of bloater damage (hollow cucumbers). Equilibration of malic acid, reducing sugar, NaCl, acetic acid, lactic acid and other solutes may affect fermentation rate, fermentation site and quality of fermented brine stock.

Researchers have used various methods to describe solute movements in brined cucumbers. Pflug et al. (1967) modeled the desalting of brine stock in a flowing water system with a logarithmic equation and used a method developed for heat penetration in canning processes (Olson and Jackson, 1942) to convert slopes into diffusion coefficients. However, when cucumbers were desalted by equilibration with water in a batch process, diffusion coefficients were determined from a graphical correlation developed by Crank (1956). Eder (1970) used an iterative procedure to express movement of glucose through fresh and fermented cucumber tissue as diffusion coefficients and through cucumber skin as permeability coefficients. Bell et al. (1972), Bomben et al. (1974), Fabian and Fulde (1950a, b), Schwartzberg and Chao (1982), and Switzer et al. (1939) reported data relating to diffusion of solutes in cucumbers.

Herein, equilibration of solutes in nonfermenting, brined cucumbers was modeled by a logarithmic equation and the rate of equilibration expressed as a first-order rate coefficient (K_D). This method of expressing solute movement was chosen because of its simplicity and application to our experimental system. The effects of temperature, cucumber size, cucumber lot, and peeling of cucumbers on equilibration of solutes were studied.

Authors Potts, Fleming, and McFeeters are with the Food Fermentation Laboratory, U.S. Dept. of Agriculture, ARS, and North Carolina Agricultural Research Service, Dept. of Food Science, North Carolina State Univ., Raleigh, NC 27695-7624. Author Guinnup is with the Dept. of Chemical Engineering, North Carolina State Univ., Raleigh, NC 27695-7905.

MATERIALS & METHODS

Experimental protocol

Pickling cucumbers were obtained from local growers or pickle companies. Cucumber variety and harvest conditions were unknown. Cucumbers were graded into the following sizes based on cucumber diameter (maximum): no. 1 (1.9–2.7 cm); no. 2 (2.7–3.8 cm); no. 3 (3.8–5.1 cm); and no. 4 (5.1–6.4 cm). Number 3 size cucumbers were used in all experiments except those concerning the effect of fruit size. In experiments concerning the effect of peeling, a kitchen potato peeler was used to remove about 2 mm of skin from the cucumbers. Cucumber surface area (A) was estimated from length (L) and diameter (D) measurements of each fruit, assuming the cucumber to be a cylinder with hemispherical ends, using the formula: $A = \pi DL$.

Cucumbers were brined in 1-gal (3.8-liter) glass jars containing 50% cucumbers and 50% brine by weight. Cover brines contained 10% NaCl and 0.8% of one of the following acids: tartaric, lactic, acetic, or formic. Microbial growth was prevented by adding 1,000 ppm sodium benzoate and 3 ppm Merthiolate (Eli Lilly and Company, Indianapolis, IN) to the cover brines. By preventing microbial growth, changes in fermentable solutes due to diffusion could be followed until equilibrium between the cucumbers and the brine was approached.

Brined cucumbers were held at room temperature (about 25°C), except in experiments concerning the effect of temperature. In such experiments the brine and cucumbers were adjusted to the appropriate temperature before brining and storage.

Equilibration of solutes was followed by taking periodic (6–48 hr) 5-mL brine samples. Surplus cover brine, diluted 1:1 with water, was added as needed to containers to maintain an approximately equal cucumber-to-brine ratio and to keep all cucumbers completely submerged under brine. Total brine removed by sampling was 2.5% of the volume of brine and cucumbers. Capped jars were shaken to insure brine uniformity before each sampling. For comparative purposes, brines in representative containers of cucumbers were continually mixed by a continuous flow of nitrogen [about 10 mL/min/gal (2.64 mL/min/L) of brined cucumbers] through fritted glass spargers. No significant differences ($P > 0.05$ by ANOVA) were found between K_D values obtained from jars that were shaken, compared to jars that were continually mixed by nitrogen flow.

The concentration of tartaric, lactic, acetic or formic acid in brines was determined by titration with standard NaOH to a pH 8.3 endpoint. NaCl was determined by titration with standard $AgNO_3$ using dichlorofluorescein as an indicator. Total reducing sugar was determined spectrophotometrically using dinitrosalicylic acid reagent by the method of Sumner and Sisler (1944). Handley et al. (1983) found that glucose and fructose (both reducing sugars) comprised about 95% of the naturally occurring sugars in cucumber fruit. Malic acid (naturally present in cucumbers) was determined with high pressure liquid

chromatography (HPLC) using a C_{18}, reverse-phase column with 0.05*M* H_3PO_4 buffer (adjusted to pH 2.5 with NH_4OH) as the mobile phase (McFeeters et al., 1984). Sample size was 10 μL and solute peaks were detected with a differential refractometer. Peak area was related to solute concentration with a computing integrator.

Theoretical development

The diffusive flux of a solute in the X-direction is given by Fick's first law, Eq. 1:

$$J = -K\,(dC/dX) \quad (1)$$

where J is the diffusive flux, K is the effective diffusion coefficient, and dC/dX is the concentration gradient. Movement of solute molecules into and out of brined cucumbers was modeled using the mass transfer approach of Coulson and Richardson (1956). This model neglects any effect due to bulk flow of solute molecules and assumes that the major resistance to mass transfer exists in the stagnant liquid film which surrounds the cucumbers. While this represents a rather simplistic view of a very complex process, it does provide us with a basis for comparison of experimental results. Based on this approach, Eq. 1 could be approximated by:

$$J = -K\frac{(C - C_c)}{B} \quad (2)$$

A mass balance on the total solute in the system can be used to calculate the concentration at equilibrium:

$$Ceq = CF + C_c\,(1 - F) \quad (3)$$

Solving for the solute concentration in the cucumbers, one obtains:

$$C_c = \frac{Ceq - CF}{(1 - F)} \quad (4)$$

This may be substituted into Eq. (2) to yield:

$$J = \frac{-K\left(\frac{C - Ceq}{1 - F}\right)}{B} \quad (5)$$

Since our system contained 50% brine and 50% cucumbers by volume, (1 − F) = 0.5. Thus:

$$J = \frac{-2K\,(C - Ceq)}{B} \quad (6)$$

J = dM/AdT, substituting and rearranging yields:

$$\frac{dM}{dT} = \frac{2KA\,(Ceq - C)}{B} \quad (7)$$

Considering a batch process with constant volume, then dM = VdC. Following substitution and rearrangement, Eq. (7) becomes:

$$\frac{dC}{dT} = \frac{2KA\,(Ceq - C)}{BV} \quad (8)$$

Assuming that K, A, B, and V are constant throughout the diffusion process, rearrangement and integration gives Eq. (9), where 2KA/BV equals K_D:

$$\int_{Co}^{C}\frac{dC}{(Ceq - C)} = \frac{2KA}{BV}\int_{To}^{T} dT$$

integrating,

$$Ln\left(\frac{Ceq - Co}{Ceq - C}\right) = K_D\,(T - To) \quad (9)$$

To obtain values of K_D for each solute, experimental values of the left side of Eq. (9) were plotted versus (T − To), and slopes (equal to K_D) were determined using the method of least squares. Since variance is magnified exponentially as C approaches Ceq in Eq. (9), only experimental values of C that were 85% or less of Ceq were used to determine K_D values by the method of least squares. Eq. (9) may be expressed in exponential form and rearranged to give:

$$C = Ceq - (Ceq - Co)\,e^{-K_D(T - To)} \quad (10)$$

Following determination of K_D values, Eq. (10) was used to draw calculated equilibrium curves for comparison to experimental data points. Logarithmic progressions of the form of Eq. (9) approach Ceq by a constant percentage each day based on the magnitude of K_D. The percentage can be calculated by setting T − To in Eq. (9) equal to 1.0 and solving for [(C − Co)/Ceq − Co)] × 100:

% attainment of equilibrium per day

$$= \left(\frac{C - Co}{Ceq - Co}\right) \times 100 = \left(1 - \frac{1}{e^{K_D}}\right) \times 100 \quad (11)$$

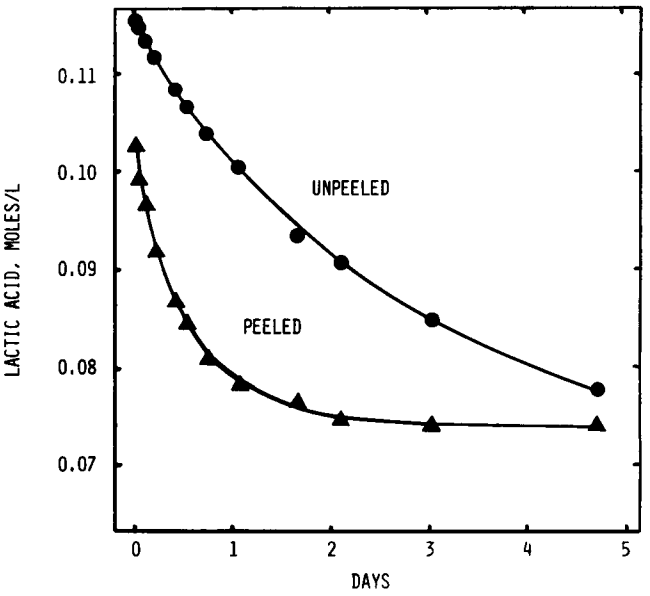

Fig. 1—Changes in brine lactic acid concentration for peeled (▲) and unpeeled (●) no. 3 cucumbers. Symbols mark data points. Solid lines are the calculated equilibrium curves using Eq. (6) and the slopes of the Ln plots shown in Fig. 2.

RESULTS & DISCUSSION

EQUILIBRATION of solutes initially in cover brines (lactic acid, NaCl, tartaric acid, acetic acid and formic acid) resulted in brine concentration curves as typified by lactic acid in Fig. 1. Linear relationships ($r^2 > 0.99$) were found when experimental points were plotted according to Eq. (9) (Fig. 2). Following determination of K_D values (slopes), Eq. (10) was used to draw calculated equilibrium curves, which compared favorably to experimental points (Fig. 1). Similar results were found for the other solutes initially in cover brines. The rate of attainment of equilibrium was related to K_D as shown in Eq. (11): the greater the value of K_D, the more rapidly equilibrium was approached.

Due to the form of Eq. (9), the y-intercepts (I) of the least squares regression lines in Fig. 2 should be approximately zero. This was true for unpeeled cucumbers but not for peeled cucumbers. The positive y-intercepts of the logarithmic plots of solutes diffusing into peeled cucumbers indicated that the initial concentration of brine solutes decreased very rapidly, perhaps by a second mechanism, immediately (2 hr or less) following brining. This rapid decrease in solute concentration was followed by equilibration as shown in Fig. 1. Possibly, osmotic differences between the brine (about 10% NaCl) and the cucumbers resulted in water being drawn rapidly from the cucumbers for a short time, which would have the effect of

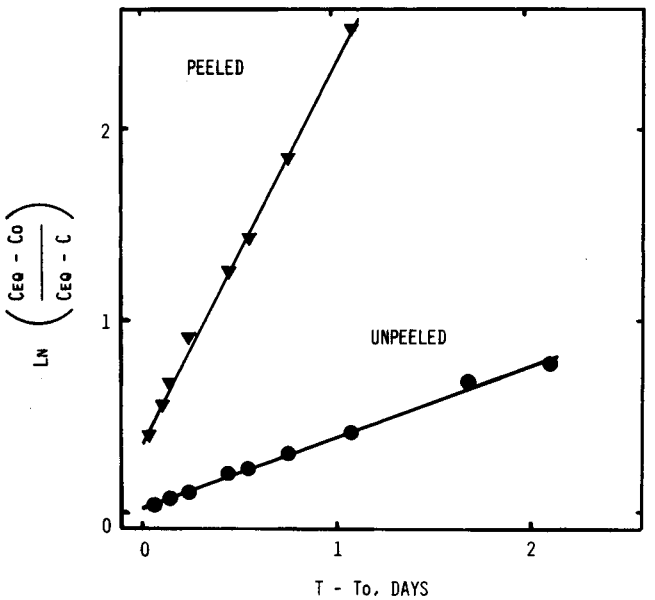

Fig. 2—Ln plots of lactic acid equilibration data shown in Fig. 1. For the peeled cucumbers (▲): S = 1.945 day⁻¹, I = 0.359, Co = 0.1165M, Ceq = 0.074M, To = 0, and r² = 0.997. For the unpeeled cucumbers (●): S = 0.359 day⁻¹, I = 0.016, Co = 0.1165M, Ceq = 0.068M, To = 0, r² = 0.997.

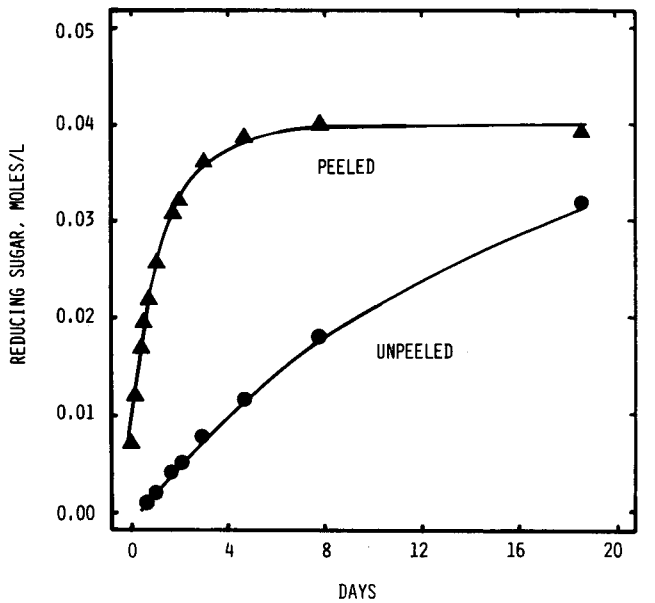

Fig. 3—Changes in brine reducing sugar concentration for peeled (▲) and unpeeled (●) no. 3 cucumbers. Symbols mark data points. Solid lines are the calculated equilibrium curves using Eq. (6) and the slopes of the Ln plots shown in Fig. 4.

reducing the initial concentration of solutes in the brines. Alternatively, the mathematical treatment of Crank (1956) suggests the possibility that such nonzero y-intercepts are the result of large internal resistances to diffusion.

Equilibration of solutes initially inside the cucumbers (reducing sugar and malic acid) produced typical brine concentration curves as shown for reducing sugar in Fig. 3. Logarithmic plots of experimental points produced linear relationships ($r^2 > 0.92$) as shown in Fig. 4. Calculated equilibrium curves compared favorably to experimental points (Fig. 3). Eq. (9) was an excellent model for describing equilibration of solutes diffusing both into and out of brined cucumbers.

The regression lines for reducing sugar and malic acid equil-

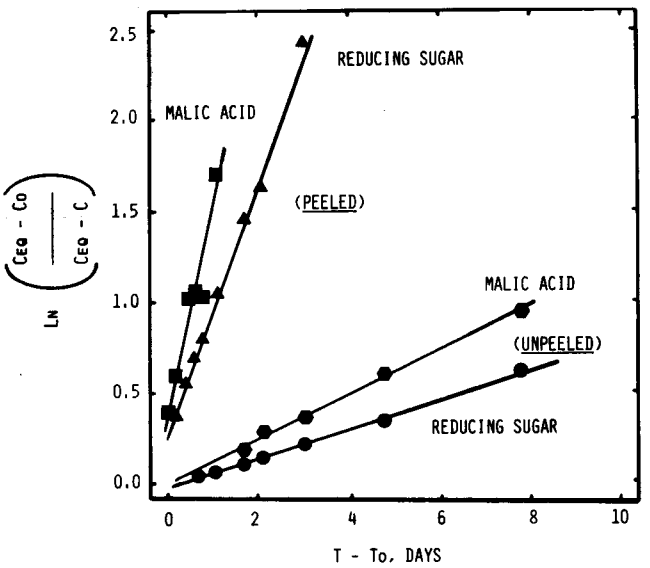

Fig. 4—Ln plots of reducing sugar and malic acid equilbration. Data for reducing sugar are shown in Fig. 3. For the peeled cucumbers (▲, reducing sugar): S = 0.699 day⁻¹, I = 0.249, Co = 0M, Ceq = 0.040M, To = 0, and r² = 0.994; (■, malic acid): S = 1.169 day⁻¹, I = 0.372, Co = 0 mM, Ceq = 7.39 mM, To = 0, and r² = 0.929. For the unpeeled cucumbers, (●, reducing sugar): S = 0.081 day⁻¹, I = 0.032, Co = 0M, Ceq = 0.040M, To = 0, and r² = 0.999; (●,malic acid): S = 0.125 day⁻¹, I = 0.001, Co = 0 mM, Ceq = 8.02 mM, To = 0, and r² = 0.995.

ibration had y-intercepts near zero for unpeeled cucumbers and relatively large y-intercepts for peeled cucumbers (Fig. 4). The large positive y-intercepts indicated that the initial brine concentrations of reducing sugar and malic acid were greater than zero for peeled cucumbers. Fluids from cells ruptured by peeling may have mixed with the brine on contact; or alternatively, a rapid exit of water from peeled cucumbers, as previously mentioned, may have carried along cucumber solutes. Again, large internal resistances to diffusion may account for this phenomenon.

Peeling of cucumbers increased K_D values 6.9- to 11.1-fold for reducing sugar, 10.6-fold for malic acid (only size no. 3 cucumbers were studied), 3.7- to 7.3-fold for NaCl, and 3.5- to 8.1-fold for lactic acid equilibration (Table 1). Thus, peeling had a greater influence on solutes diffusing out of the cucumbers (reducing sugar and malic acid) than on solutes diffusing into the cucumbers (NaCl and lactic acid). The effect of peeling on K_D values increased as the size (diameter) of the cucumbers increased.

K_D values decreased as cucumber diameter increased. Linear relationships were found between the K_D values of reducing sugar and total surface area of size no. 2, 3 and 4 peeled and unpeeled cucumbers (Fig. 5). However, in the smallest cucumbers (size no. 1), K_D values were greater than predicted by increased surface area. Similar relationships with surface area were found for the K_D values of both lactic acid and NaCl in peeled and unpeeled cucumbers.

Smith et al. (1979) found that the stomatal index [stomatal frequency/(stomatal frequency + epidermal cell frequency)] was the same for small size no. 1 cucumbers as for larger size no. 3 cucumbers. This implied that the total number of stomata per fruit did not change with increasing size. Further observations from their work indicated that the size of the stomatal pore changed very little with increasing fruit size. At this point, we hypothesized that since the stomatal surface area of small cucumbers was roughly equal to that of large cucumbers, and since equal weights of small and large cucumbers were used for the experiments, then the differences in mass-transfer between small and large cucumbers should be proportional to the

Table 1—Effect of cucumber size and peeling on K_D

Grade size	Diameter (cm)	K_D (day^{-1})[a] Reducing sugar	Malic acid	NaCl	Lactic acid
Unpeeled					
1	1.9-2.7	0.472 (37.6)[b]	ND[c]	1.673 (81.2)	1.973 (86.1)
2	2.7-3.8	0.146 (13.6)	ND	0.679 (49.3)	0.720 (51.3)
3	3.8-5.1	0.077 (7.4)	0.107 (10.1)	0.301 (26.1)	0.356 (30.0)
4	5.1-6.4	0.045 (4.4)	ND	0.170 (15.6)	0.189 (17.2)
Peeled					
1	1.9-2.7	ND	ND	ND	ND
2	2.7-3.8	1.014 (63.7)	ND	2.487 (91.7)	2.507 (91.8)
3	3.8-5.1	0.709 (50.8)	1.139 (68.0)	1.810 (83.6)	1.872 (84.6)
4	5.1-6.4	0.499 (39.3)	ND	1.237 (70.8)	1.533 (78.4)

[a] Values are the means of duplicates; mean coefficient of variation for the duplicates was 5.7%.
[b] Numbers in parentheses are the percentages attainment of equilibrium per day.
[c] Not determined.

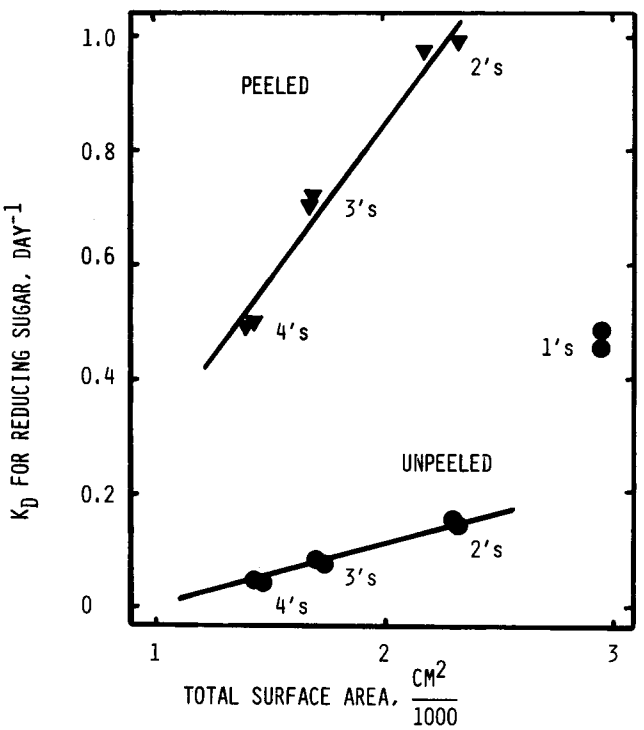

Fig. 5—Reducing sugar (K_D) vs total surface area of nos. 2, 3 and 4 peeled (▲) and for nos. 1, 2, 3, and 4 unpeeled (●) cucumbers. For peeled cucumbers, S = 546 day^{-1}cm^{-2}, I = 0.250 day^{-1}, and r^2 = 0.970. For unpeeled cucumbers (only size nos. 2, 3, and 4 included in the least squares regression line), S = 110 day^{-1}cm^{-2}, I = 0.111 day^{-1}, and r^2 = 0.968. There were 6, 10, and 21 cucumbers per 3.8-liter jar for no. 4, 3, and 2 cucumbers, respectively. Duplicate 3.8-liter jars of no. 1 cucumbers contained 43 and 46 cucumbers.

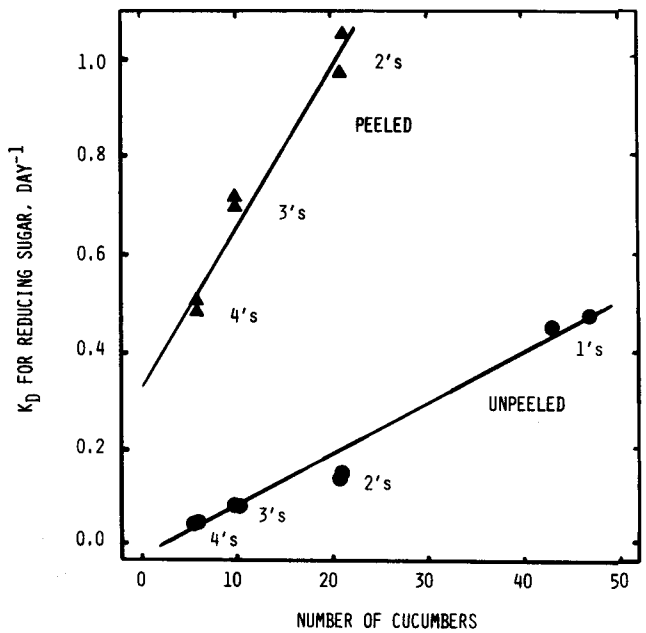

Fig. 6—Reducing sugar (K_D) vs number of cucumbers per 3.8-liter jar for nos. 2, 3, and 4 peeled (▲) and for nos. 1, 2, 3, and 4 unpeeled (●) cucumbers. For peeled cucumbers, S = 0.039 day^{-1}, I = 0.335 day^{-1}, r^2 = 0.960. For unpeeled cucumbers (size nos. 1, 2, 3, and 4 included in the least squares regression line), S = 0.011 day^{-1} cucumber^{-1}, I = −0.043 day^{-1}, r^2 = 0.974.

number of cucumbers per jar. Fig. 6 suggests that such a linear relationship does indeed exist and that solute transport in unpeeled cucumbers occurs mainly through the stomata.

Increasing the temperature of brining and storage increased the K_D values of the solutes (Table 2). Arrhenius plots of K_D vs the reciprocal of the absolute temperature were used to determine an apparent energy of activation (E_a) for the equilibration process. E_a values for reducing sugar and malic acid (solutes initially inside the cucumbers) equilibration were significantly ($P<0.05$) higher than E_a values for NaCl and lactic acid (solutes initially in the brine) equilibration. The E_a values found for equilibration of solutes were of the magnitude expected for diffusion processes (Schuler et al., 1948; Boyd and Soldano, 1953; Soldano and Boyd, 1953).

A comparison of solutes initially inside the cucumbers showed that malic acid (molecular weight = 134) approached equilibrium faster than reducing sugar (molecular weight = 180) (Table 3). Similarly, for solutes initially in the brine, the smaller was the molecular weight, the larger was the K_D value with the exception of NaCl. Equilibration proceeded more slowly than expected for NaCl, based on molecular weight. This may be because NaCl has two ionic particles of comparable size, which must diffuse together to maintain charge balance. In

Table 2—Effect of temperature on K_D[a]

Temp (°C)	K_D (day^{-1}) Reducing sugar	Malic acid	NaCl	Lactic acid
4	0.113	0.133	0.502	0.559
11	0.126	0.178	0.552	0.858
23	0.234	0.315	0.854	0.970
39	0.369	0.453	1.144	1.297
48	0.533	0.742	1.541	1.877
LSD 0.05[b]	Apparent activation energy (kcal/mole)			
1.4	6.5	6.3	4.5	4.2

[a] Size no. 3 cucumbers.
[b] Least significant difference at $P<0.05$ level.

Table 3—Effect of solute molecular weight on K_D[a]

Solute	Molecular weight	K_D (day^{-1})	Normalized diffusion coefficients[c]
Initially inside cucumbers			
Reducing sugar	180	0.234 (20.9)[b]	0.63
Malic acid	134	0.315 (27.0)	0.79
Initially in the brine			
Tartaric acid	150	0.790 (54.6)	0.78
Lactic acid	90	0.970 (62.1)	0.97
Acetic acid	60	1.286 (72.4)	1.20
Formic acid	46	1.420 (75.8)	1.33
NaCl	58.5	0.854 (57.4)	1.31

[a] Size no. 3 cucumber, ca 25°C.
[b] Numbers in parentheses are the percentage attainment of equilibrium per day.
[c] Diffusion coefficients at 25°C, taken from Perry and Chilton (1973); normalized to diffusion coefficient for lactic acid equal to 0.97.

comparison, organic acid anions are balanced by a hydrogen cation, while reducing sugars are nonionic. Additionally, since brines had pH values of 2.2–3.1, most organic acid molecules would be in the undissociated form. However, the K_D for tartaric acid, which was initially in the brine, was about 2.5 times larger than the K_D of malic acid, which was initially inside the cucumbers. Tartaric acid and malic acid are both 4-carbon, straight-chained, dicarboxylic acids which differ in that malic acid has one less hydroxyl group. This suggests that equilibration may have occurred more rapidly when the net movement of solute molecules was from the brine into the cucumbers, rather than vice versa.

Since the K_D values reported in Table 3 were all taken from the same experiment, the differences in K_D values among chemical compounds should be directly due to differences in their diffusion coefficients. A comparison of differences in diffusion coefficients among these compounds (Perry and Chilton, 1973) is made in the right hand column of Table 3. Here, reported values for diffusion coefficients of the individual molecular species in water have been normalized such that the value for lactic acid is equivalent to our measured value of K_D for lactic acid. The remaining diffusion coefficient values can thus be compared directly to our reported K_D values. Several important observations can be made by direct comparison:

(1) the transport of all acids into the cucumbers showed differences in K_D values which are consistent with the differences among reported diffusion coefficients; (2) the transport of NaCl into the cucumbers was significantly slower than that which might be expected on a strictly diffusional basis, and this may be due to charge-related steric effects; (3) the transport of solutes *out of* the cucumbers was significantly slower than one might predict on a diffusional basis using data from transport *into* the cucumbers. This may be an indication that outward transport was more affected by membrane permeation than inward transport. It was interesting to note that the K_D values of the two outward-transported species were self-consistent on a diffusional basis (as can be seen by comparing the ratios of K_D values and diffusion coefficients for reducing sugar and malic acid).

The comparisons in the previous paragraph coupled with the agreement of experimental data with a first-order model suggest that a simple refinement of the model should allow the quantitative prediction of solute transport into and out of cucumbers. This refinement would entail the use of an "effective" K_D which would include a factor to account for reduced transport in the case of solutes initially in the cucumber (60–65% reduction in this case) and in the case of diffusing ionic species (35% reduction for NaCl in this case). While such a model may be rather simple minded in terms of the complexity of biological processes, its applicability here may prove very useful in the quantitative estimation of fermentation periods for the pickling industry.

Up to three-fold differences were found among four cucumber lots in the rates at which solutes approached equilibrium (Table 4). However, the K_D values of the four solutes increased or decreased in a similar manner. When the K_D for reducing sugar was divided into the K_D values of the remaining three solutes within lots, and when these ratios were compared by ANOVA, differences among lots were not significant ($P>0.05$) (Table 5). Similar results were found when the K_D of malic acid, NaCl, or lactic acid was used as the divisor for determination of the ratios. Therefore, we concluded that differences in resistance to solute movement among cucumber lots affected the solutes studied in a like manner, without apparent discrimination among solutes.

First-order rate coefficients have the advantage of being concentration independent. This, coupled with the apparent constancy of K_D ratios, suggests that solute movements of reducing sugar and malic acid (which are metabolized during fermentation) can be predicted in fermenting cucumbers by measuring the K_D of nonmetabolizable solute such as NaCl. Olson and Schultz (1942) reported a method of using first-order rate coefficients for heat transfer to predict the temperature at any time in the center of a can during heat processing. By analogy, the same method may be of value in predicting the acid concentration in the center of acidified vegetables. K_D values and the logarithmic model used in this study may be useful in studying the effect of solute movements on the fermentation and processing of brined cucumbers and other processed food products.

NOMENCLATURE

A	=	surface area of the cucumber-brine interface, cm.
ANOVA	=	analysis of variance.
B	=	effective thickness of the diffusion barrier at the cucumber-brine interface, cm.
C	=	solute concentration in the brine at time = T, moles/liter.
C_c	=	solute concentration in the cucumbers at time = T, moles/liter.
Ceq	=	solute concentration in the brine after equilibrium between the cucumbers and brine, determined by estimation of the asymptote of the equilibration curve. Ceq also may be obtained by a mass balance, when the initial concentration of the solute in the cucumbers and brine is known, moles/liter.
Co	=	initial solute concentration in the brine at time = To, moles/liter.
d	=	infinitesimal change.
D	=	diameter at cucumber mid-section, cm.
e	=	base of Napierian logarithms, 2.71828 . . .
E_a	=	apparent energy of activation, kcal/mole.
F	=	volume of brine expressed as a fraction of the total volume of cucumbers and brine, unitless.
(1 − F)	=	volume of cucumbers expressed as a fraction of the total volume of cucumbers and brine, unitless.
I	=	y-intercept.
J	=	dM/AdT = diffusive flux, moles/(cm^2) (day).
K	=	diffusion coefficient, cm^2/day.
K_D	=	first-order rate coefficient for attainment of diffusional equilibrium, day^{-1}.
L	=	length of cucumber, cm.
Ln	=	Napierian or natural logarithm.
M	=	mass of solute, moles.
P	=	statistical probability based on ANOVA.
π	=	pi = 3.1416 . . .
r^2	=	coefficient of determination.
S	=	slope of least squares regression line.
T	=	time, days.
To	=	initial time = time of first brine sample (0-6 hr after brining), days.

Table 4—Differences in K_D among cucumber lots[a]

Lot	K_D (day^{-1})[b]			
	Reducing sugar	Malic acid	NaCl	Lactic acid
1	0.234 (0.021)[c]	0.315 (0.020)	0.854 (0.175)	0.970 (0.074)
2	0.140 (0.007)	0.168 (0.006)	0.461 (0.011)	0.551 (0.051)
3	0.077 (0.005)	0.107 (0.024)	0.301 (0.027)	0.356 (0.004)
4	0.083 (0.007)	0.100 (0.009)	0.263 (0.011)	0.329 (0.029)

[a] Size no. 3 cucumbers, ca. 25°C.
[b] Diffusion rates of lots 1-4 were the means of 6, 2, 2, and 4 replicates, respectively.
[c] Standard deviations in parentheses.

Table 5 — Ratios of K_D for malic acid, NaCl, and lactic acid to the K_D of reducing sugar within lots[a]

Lot[b]	Malic acid	NaCl	Lactic acid
1	1.349 (0.122)[c]	3.618 (0.428)	4.145 (0.268)
2	1.197 (0.023)	3.292 (0.099)	3.927 (0.154)
3	1.378 (0.220)	3.908 (0.618)	4.611 (0.272)
4	1.213 (0.113)	3.203 (0.321)	3.998 (0.429)
Mean	1.284	3.505	4.170

[a] Size no. 3 cucumbers, ca. 25°C.
[b] Reported values of lots 1-4 were the means fo 6, 2, 2, and 4 replicates, respectively.
[c] Standard deviations in parentheses.

V = volume of brine, liters or cm^3.
X = linear distance, cm.

REFERENCES

Bell, T.A., Turney, L.J., and Etchells, J.L. 1972. Influence of different organic acids on the firmness of fresh-pack pickles. J. Food Sci. 37: 446.
Bomben, J.L., Durkee, E.L., Lowe, L., and Secor, G.E. 1974. A laboratory study on countercurrent desalting of pickles. J. Food Sci. 39: 260.
Boyd, G.E. and Soldano, B.A. 1953. Self-diffusion of cations in and through sulfonated polystyrene cation-exchange polymers. J. Am.Chem. Soc. 75: 6091.
Coulson, J.M. and Richardson, J.F. 1956. "Chemical Engineering, Vol. 2," p. 570. Pergamon Press Ltd., London, England, UK.
Crank, J. 1956. "The Mathematics of Diffusion," p. 72, Oxford University Press, London, England, UK.
Daeschel, M.A. and Fleming, H.P. 1981. Entrance and growth of lactic acid bacteria in gas-exchanged, brined cucumbers. Appl. Environ. Microbiol. 42: 1111.
Daeschel, M.A., Fleming, H.P., and Potts, E.A. 1985. Compartmentalization of lactic acid bacteria and yeasts in the fermentation of brined cucumbers. Food Microbiol. 2: 77.
Eder, B.D. 1970. Diffusion of sugar in cucumbers and pickles. Ph.D. thesis, Michigan State Univ., East Lansing, MI.
Etchells, J.L., Bell, T.A., Fleming, H.P., Kelling, R.E., and Thompson, R.L. 1973. Suggested procedure for the controlled fermentation of commercially brined pickling cucumbers — the use of starter cultures and reduction of carbon dioxide accumulation. Pickle Pak Sci. 3: 4.
Etchells, J.L., Borg, A.F., and Bell, T.A. 1968. Bloater formation by gas-forming lactic acid bacteria in cucumber fermentations. Appl. Microbiol. 16: 1029.
Fabian, F.W. and Fulde, F.C. 1950a. Rate of salt penetration into pickles charted, size by size. Part 1. Food Packer 31: 23.
Fabian, F.W. and Fulde, F.C. 1950b. Rate of salt penetration into pickles charted, size by size. Part 2. Food Packer 31: 28.
Handley, L.W., Pharr, D.M., and McFeeters, R.F. 1983. Carbohydrate changes during maturation of cucumber fruit. Plant Physiol. 72: 498.
McFeeters, R.F., Fleming, H.P., and Thompson, R.L. 1982. Malic acid as a source of carbon dioxide in cucumber juice fermentations. J. Food Sci. 47: 1862.
McFeeters, R.F., Thompson, R.L., and Fleming, H.P. 1984. Liquid chromatographic analysis of sugars, acids, and ethanol in lactic acid vegetable fermentations. J. Assoc. Off. Anal. Chem. 67: 710.
Olson, F.C.W. and Jackson, J.M. 1942. Heating curves: theory and practical application. Ind. Eng. Chem. 34: 337.
Olson, F.C.W. and Schultz, O.T. 1942. Temperatures in solids during heating or cooling. Ind. Eng. Chem. 34: 874.
Perry, R.H. and Chilton, C.E. 1973. "Chemical Engineers' Handbook," 5th ed. McGraw-Hill Book Co., New York, NY.
Pflug, I.J., Fellers, P.J., and Gurevitz, D. 1967. Diffusion rates in the desalting of pickles. Food Technol. 21: 1634.
Schuler, K.E., Dames, C.A., and Laider, K.J. 1948. Kinetics of membrane processes. III. The diffusion of various nonelectrolytes through collodion membranes. J. Chem. Phys. 17: 860.
Schwartzberg, H.G. and Chao, R.Y. 1982. Solute diffusivities in leaching processes. Food Technol. 36: 73.
Smith, K.R., Fleming, H.P., Van Dyke, C.G., and Lower, R.L. 1979. Scanning electron microscopy of the surface of pickling cucumber fruit. J. Amer. Soc. Hort. Sci. 104: 528.
Soldano, B.A. and Boyd, G.E. 1953. Self-diffusion of anions in strong-base anion exchangers. J. Am. Chem. Soc. 75: 6099.
Sumner, J.B. and Sisler, E.B. 1944. A simple method of blood sugar. Arch. Biochem. 4: 333.
Switzer, R.G., Richardson, D.E., and Fabian, F.W. 1939. Experimental work on processing and finishing pickles. Fruit Prods. J. 18: 260.

Ms received 4/19/85; revised 9/26/85; accepted 10/19/85.

Paper no. 9780 of the Journal Series of the North Carolina Agricultural Research Service, Raleigh, NC 27695-7601. Mention of a trademark or proprietary product does not constitute a guarantee or warranty of the product by the U.S. Dept. of Agriculture or North Carolina Agricultural Research Service, nor does it imply approval to the exclusion of other products that may be suitable.

This investigation was supported in part by a research grant from Pickle Packers International, Inc., St. Charles, IL.

We thank Dr. R.J. Monroe for statistical advice. We thank Dr. H.G. Schwartzberg for constructive criticism in review of the manuscript, particularly in regard to derivation of working equations for studying mass transfer of solutes.