$N_{A'}$ = mass transfer flux in lb. mol./hr. sq.ft.
P = vapor pressure of water, in. Hg.
P_{Blm} = log-mean partial pressure of stagnant components
$P_{Bavg.}$ = total pressure minus average of P_s and P_w assumed approximately equal to P_{Blm}
P_s = vapor pressure on solution side, in. Hg. = $a\, P_{ws}$
P_w = vapor pressure on water condensate side, in. Hg.
P_{ws} = vapor pressure of pure water at T_s, in. Hg.
P_1, P_2 = vapor pressures at membrane interfaces, solution and coolant sides
q_c = heat conducted through membrane, B.t.u./hr. sq.ft.
q_v = heat transferred through membrane with vapor as latent heat, B.t.u./hr. sq.ft.
q_t = total heat transferred = $q_c + q_v$
R = gas constant
T_w = coolant-condensate bulk temperature, °F.
T_s = solution bulk temperature, °F.
T_1 = solution-membrane interface temperature, °F.
T_2 = coolant-condensate (water)-membrane interface temperature, °F.
$\overline{T}$ = average of T_s and T_w converted to °R.
Wg = weight of glass fiber in g. per sq.ft. of membrane
X = wt. of glass fiber in g. per 111 sq.cm. of membrane or wt. glass fiber, g./12 sq.ft., used as a measure of thickness
X' = membrane thickness in ft.
ΔT = $T_s - T_w$
λ = latent heat of vaporization, B.t.u./lb.
π = total pressure in in. Hg. (Atmospheric throughout this study)

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Cyclic Steady State Diffusion

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Analytic equations describing cyclic steady state diffusion in which the diffusivity depends on the direction of transfer, as well as on the system, have been obtained.

By imposing the cyclic steady state constraint, of periodically repetitive concentration profiles, simultaneous solution of separate Fick's diffusion equations for the on-off segments of the cycle results in the desired equations. The method of solution can be extended to more complex diffusion problems, such as coupled diffusion processes. Shallow bed experiments have been performed on particle-diffusion controlled, cyclic steady state ion exchange. Agreement between the predicted and experimental transfer was obtained. Variables and parameters affecting cyclic steady state diffusion are discussed.

Many unit processes, operated in a cyclic steady state* have been shown to be superior to the noncyclic analogues. Steady state operations such as distillation and extraction have been made cyclic, leading to improved throughputs and efficiencies (*2, 5, 14, 18, 19, 23*). These controlled cyclic operations have generally been treated mathematically in a similar manner to their noncyclic analogues (*1, 12, 15, 17*), and analysis has shown that the noncyclic steady state operation is a special case of the cyclic operation.

Even a process, such as ion exchange, commonly operated in a transient state, has been operated at a cyclic steady state resulting in improved performance (*13, 20, 21*). The mathematical problems involved in the latter case are complex, due, not only to the column dynamics, but also to the diffusional process within the ion exchange material (*9*).

Since many processes are diffusion controlled (for example cyclic steady state ion exchange), a fundamental examination of cyclic steady state diffusion was felt to be necessary for a complete understanding of such processes.

THEORETICAL ANALYSIS

Diffusion Controlled Processes

Processes which have diffusion controlled steps (for example ion exchange, adsorptions) may have diffusivities which are functions of the dependent and/or independent variables. In the analysis of such operations, nonlinear partial differential equations, which have not admittted to analytic solutions, are frequently encountered (*3a, 4*). To overcome this problem, numerical or approximate solutions are necessary. A striking example is the numerical solution of the nonlinear partial differential equation describing ion exchange diffusion (*10, 11*).

An approximate analytic solution can sometimes be obtained for such systems by assuming a constant effective diffusivity which will be dependent upon the direction of transfer as well as on the system (*3b, 4*).

Cyclic Steady State Diffusion

If the diffusivity is constant, but not dependent on the direction of transfer, a cyclic steady state diffusion equation is readily solved (*3c*). The method of solution involves one partial differential equation, with a specified time varying boundary condition. In order to solve the cyclic steady state diffusion problem with different diffusivities for the on and off portions of the cycle, a different approach is necessary.

The following method of solution is similar to that used

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* Definition: If a periodic boundary condition is imposed on a body, with a given initial condition, the cyclic steady state is the condition existing after the transient involving the initial conditions has died away. In the cyclic steady state, the dependent variable is periodically repetitive with time.

by Hausen (7) for regenerative heat exchangers with complex boundary conditions.

Consider a spherical particle subjected to cyclic steady state diffusion under the following assumptions:

1. The particle is a quasihomogeneous phase.
2. The particle volume remains constant.
3. Only radial diffusion is considered.
4. The diffusivity, which is a function of the dependent and/or independent variables, can be approximated by an effective diffusivity.
5. Many cycles have passed, in order that the cyclic steady state is attained.
6. Diffusion through the particle is the rate determining step.
7. The surface condition is;

on portion of cycle, $0 < t \leqq t_f$;
surface is a constant value (V_F^*); off portion of cycle, $0 < \theta \leqq \theta_f$;
surface is a constant value (V_R^*) where, $(t_f + \theta_f)$ = total cycle time.

Each portion of the cycle can be described by an independent equation with the appropriate boundary conditions, thus

on portion:

$$\frac{\partial V_F}{\partial \tau} = \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left(\rho^2 \frac{\partial V_F}{\partial \rho} \right) \tag{1}$$

Boundary conditions;

$$\rho = 0,\ \tau \geqq 0,\ V_F = \text{finite}$$

$$\rho = 1,\ \tau > 0,\ V_F = V_F^*$$

$$0 \leqq \rho \leqq 1,\ \tau = 0,\ V_F = h(\rho)$$

where,

$$V_F = \frac{v_F(r, t)}{v_0},\ \tau = \frac{\overline{D}_F t}{r_0^2},\ \rho = \frac{r}{r_0}$$

off portion;

$$\frac{\partial V_R}{\partial \phi} = \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left(\rho^2 \frac{\partial V_R}{\partial \rho} \right) \tag{2}$$

Boundary conditions;

$$\rho = 0,\ \phi \geqq 0,\ V_R = \text{finite}$$

$$\rho = 1,\ \phi > 0,\ V_R = V_R^*$$

$$0 \leqq \rho \leqq 1,\ \phi = 0,\ V_R = g(\rho)$$

where,

$$V_R = \frac{v_R(r, \theta)}{v_0},\ \phi = \frac{\overline{D}_R \theta}{r_0^2},\ \rho = \frac{r}{r_0}$$

The solutions to these equations are (3*d*);

$$V_F = V_F^* + 2 \sum_{n=1}^{\infty} \frac{\sin(n \pi \rho)}{\rho} e^{-n^2\pi^2\tau} \left(\frac{(-1)^n V_F^*}{n\pi} + h(n) \right) \tag{3}$$

$$V_R = V_R^* + 2 \sum_{n=1}^{\infty} \frac{\sin(n \pi \rho)}{\rho} e^{-n^2\pi^2\phi} \left(\frac{(-1)^n V_R^*}{n\pi} + g(n) \right) \tag{4}$$

where,

$$h(n) = \int_0^1 \rho' \ h(\rho') \ \sin(n \pi \rho') \ d\rho'$$

$$g(n) = \int_0^1 \rho' \ g(\rho') \ \sin(n \pi \rho') \ d\rho'$$

At the cyclic steady state, a physical constraint on the dependent variables V_F and V_R exists, such that the profiles within the particle are periodically repetitive. Thus, at the end of the on portion (that is $\tau = \tau_f$) $V_F = g(\rho)$, and at the end of the off portion (that is $\phi = \phi_f$), $V_R = h(\rho)$.

Apply this condition to Equations (3) and (4);

$$g(\rho) = V_F^* + 2 \sum_{n=1}^{\infty} \frac{\sin(n \pi \rho)}{\rho} e^{-n^2\pi^2\tau_f} \left(\frac{(-1)^n V_F^*}{n\pi} + h(n) \right) \tag{5}$$

$$h(\rho) = V_R^* + 2 \sum_{n=1}^{\infty} \frac{\sin(n \pi \rho)}{\rho} e^{-n^2\pi^2\phi_f} \left(\frac{(-1)^n V_R^*}{n\pi} + g(n) \right) \tag{6}$$

Multiply Equations (5) and (6) by ρ and apply the finite Fourier sine transform to each of the resulting equations;

$$V_F^* \frac{(-1)^n}{n\pi} (e^{-n^2\pi^2\tau_f} - 1) + h(n) \ e^{-n^2\pi^2\tau_f} = \int_0^1 \rho' \ g(\rho') \sin(n \pi \rho') \ d\rho' = g(n) \tag{7}$$

$$V_R^* \frac{(-1)^n}{n\pi} (e^{-n^2\pi^2\phi_f} - 1) + g(n) \ e^{-n^2\pi^2\phi_f} = \int_0^1 \rho' \ h(\rho') \sin(n \pi \rho') \ d\rho' = h(n) \tag{8}$$

Solving (7) and (8) simultaneously for $g(n)$ and $h(n)$; and substitute in (3) and (4) to obtain the cyclic steady state diffusion equations;

on portion;

$$V_F = V_F^* + 2(V_F^* - V_R^*) \sum_{n=1}^{\infty} \frac{(-1)^n}{n\pi} \frac{\sin(n \pi \rho)}{\rho} e^{-n^2\pi^2\tau} \left[\frac{1 - e^{-n^2\pi^2\phi_f}}{1 - e^{-n^2\pi^2(\tau_f - \phi_f)}} \right] \tag{9}$$

off portion;

$$V_R = V_R^* + 2(V_R^* - V_F^*) \sum_{n=1}^{\infty} \frac{(-1)^n}{n\pi} \frac{\sin(n \pi \rho)}{\rho} e^{-n^2\pi^2\phi} \left[\frac{1 - e^{-n^2\pi^2\tau_f}}{1 - e^{-n^2\pi^2(\tau_f - \phi_f)}} \right] \tag{10}$$

The equations for the dependent variable averaged over the radius of the sphere are given by;

on portion;

$$\overline{V}_F = 3 \int_0^1 \rho'^2 V_F \ d\rho' = \overline{V}_F^* - \frac{6}{\pi^2} (\overline{V}_F^* - \overline{V}_R^*) \sum_{n=1}^{\infty} \frac{e^{-n^2\pi^2\tau}}{n^2} \left[\frac{1 - e^{-n^2\pi^2\phi_f}}{1 - e^{-n^2\pi^2(\tau_f + \phi_f)}} \right] \tag{11}$$

off portion;

$$\overline{V}_R = 3 \int_0^1 \rho'^2 \ V_R \ d\rho' = \overline{V}_R^* - \frac{6}{\pi^2} (\overline{V}_R^* - \overline{V}_F^*) \sum_{n=1}^{\infty} \frac{e^{-n^2\pi^2\phi}}{n^2} \left[\frac{1 - e^{-n^2\pi^2\tau_f}}{1 - e^{-n^2\pi^2(\tau_f + \phi_f)}} \right] \tag{12}$$

ANALYSIS OF THE CYCLIC STEADY STATE EQUATIONS

If $\overline{D}_F = \overline{D}_R = \overline{D}$, the cyclic steady state Equations (9) and (10) reduce to those outlined in Carslaw and Jaeger (*3c*). The equations given by Carslaw and Jaeger were obtained from one differential equation, with a specified time-varying surface condition. These equations also enable the prediction of the approach to the cyclic steady state. In the present equations, the approach to the cyclic steady state has been sacrificed in order that different diffusivities, dependent on the direction of transfer, may be used.

The profiles, as given by Equations (9) and (10) are shown in Figure 1. The profiles are only approximations to those which would be found if the diffusivity was a function of the dependent and/or independent variable.

The method of solution may be extended to other cyclic steady state problems, such as variable surface conditions on one or both portions of the cycle, combined film-particle diffusion operations, small time approximations and other geometries. These problems, and the application of the equations to unit processes, is under investigation.

TEST OF THE MODEL

In order to test the cyclic steady state model, a mass transfer process, cyclic steady state ion exchange was chosen (*21, 13*). The diffusivity, in ion exchange, is a strong function of the composition of the ion exchanger as well as being dependent on the system. The most rigorous treatment (*10, 11*) of the ion exchange process gives the diffusivity as a function of composition, valence ratio, and individual ionic diffusivities, that is,

$$D = D_{AB} = D_A \left(\frac{a\overline{X}_A + 1}{b\overline{X}_A + 1} \right) \qquad (13)$$

where,

$$a = Z_A/Z_B - 1$$

$$b = (D_A/D_B)(Z_A/Z_B) - 1 \qquad (14)$$

Substitution in the general diffusion equation, results in a nonlinear, partial differential equation. This equation has not admitted to an analytic solution, but has been successfully solved numerically (*8* to *10*).

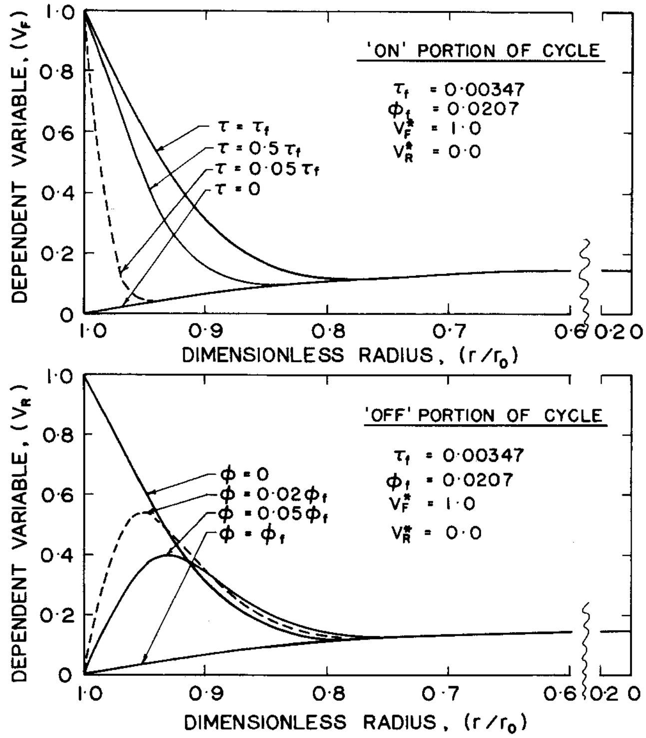

Fig. 1. Typical cyclic steady state profiles, Equations (9) and (10).

Usually, an effective diffusivity which depends on the direction of transfer as well as on the system can be used to approximate the ion exchange process (*6, 9*).

Since composition profiles cannot, at present, be measured in an ion exchange particle, the average composition is measured as a function of time. The average composition is given by Equations (11) and (12), with the substitutions of $\overline{\overline{X}}_{AF}$ for $\overline{V}_F$ and $\overline{\overline{X}}_{AR}$ for $\overline{V}_R$, and the imposition of the usual assumptions applied in ion exchange processes (*9*).

For convenience in interpretation of experimental data, t/t_f will be used for τ/τ_f, and similarly, θ/θ_f for ϕ/ϕ_f.

The system, which has been chosen, is the exchange between H^+ ions and Ca^{++} ions. This system is particularly suitable for the test of the model, since the individual diffusivities of H^+ and Ca^{++} in an ion exchange particle may differ by two orders of magnitude. The differences in the individual diffusivities result in effective diffusivities, which may differ by an order of magnitude, the effective diffusivity for the exchange, $2H^+ + Ca(Ex)_2{}^{\dagger} \rightarrow$, being less than for the exchange, $Ca^{++} + 2H(Ex) \rightarrow$ (*22*).

EXPERIMENTAL DETAILS

Equipment

The experimental apparatus and associated electrical system are shown in Figure 2.

Operation

Timers 1 and 2 are connected in tandem, causing a repetitive on/off sequence, with the ability to independently adjust the on/off portions of the cycle. The interruption timer allows the termination of either portion of the cycle at a preset fraction of the portion time. Exchange is immediately stopped by rapid washing with distilled water.

On Portion. (solution 2 on stream)

B and C are energized, D and A are de-energized. E is de-energized for 5 sec., splitting the exhaust solution, discarding the first slightly contaminated portion to waste. Then E is energized, sending the rest of the solution through the ion exchanger (I_2) for purification, finally to the recovery reservoir 2. At the end of the preset time for the on portion, the off portion begins.

Off Portion. (solution 1 on stream)

D and C are energized, B and E are de-energized, and A is de-energized for 5 sec. and then energized (exhaust stream splitting). At the end of the off portion preset time, the on portion begins and the cycle is repeated.

All flowrates were maintained at 20 cc./sec., and temperatures were maintained at 23 ± 2°C.

Interruption Timer

The interruption timer is preset to the desired fraction of the time for either the on or off portion. If the on portion is to be interrupted, the interruption switch is set to the on timer during the off portion. The on portion and interruption timers start simultaneously, and the pump (P_3) is switched on manually. At the preset interruption time, all valves de-energize allowing distilled water to wash the particles, stopping the exchange.

System

Solution 1; 0.40 ± 0.05 N $Ca(NO_3)_2$
Solution 2; 0.40 ± 0.05 N HCl

The ion exchange particles used were Dowex 50 W-X8, classified with respect to size by the fluidized elution technique of Reichenberg (*16*). The diameters of the particles were measured under a microscope. The mean diameter, of each form in different media, are given in Table 1.

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† Ex = the unchanged polymer backbone and functional groups of the ion exchanger.

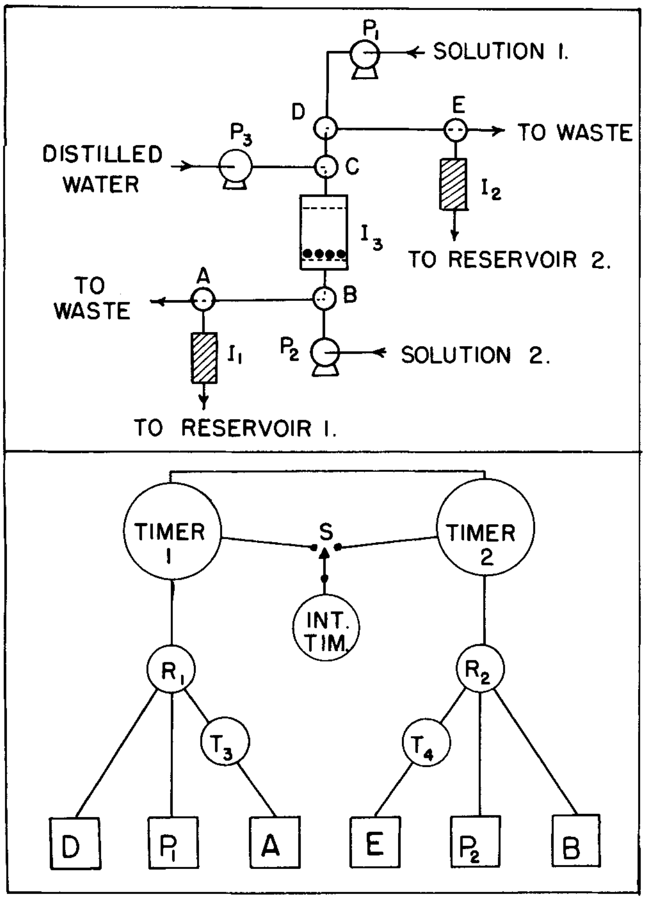

Fig. 2. Experimental equipment. A, B, C, D, E = stainless steel, three-way solenoid valves, shown in de-energized position; I_1 = ion exchange column, 1¼ in. I.D. × 5 in. containing Dowex 50 W-X8, 50 to 100 mesh, cation form of solution 1; I_2 = ion exchange column, 1¼ in. I.D. × 5 in. containing Dowex 50 W-X8, 50 to 100 mesh, cation form of solution 2; I_3 = lucite column, 0.9 cm. I.D. × 1.2 cm., each end screened with 423μ nylon mesh. Column is removable from system. Contains 1 to 2 layers of ion exchange particles; P_1, P_2, P_3 = centrifugal pumps, monel, 1/100 hp. Electrical system (110v., 60 cycle): Timer 1, timer 2, int. tim. (interruption timer) = Metrix crystal timers, 0 to 60 sec. range; T_4, T_5 = delay timers, 0 to 15 sec. range; R_1, R_2 = contact switches for protection of timers 1 and 2.

TABLE 1.

Resin Form	External Solution	Mean Diameter** (mm.)	Standard deviation of particle diameter**
H^+	distilled water	1.05	0.087
H^+	0.4N HCl	1.04	0.089
Ca^{++}	distilled water	1.01	0.088
Ca^{++}	0.4N $Ca(NO_3)_2$	1.00	0.088

** based on approximately 400 particles.

The diameter used in all calculations was that of H^+ form in distilled water.

Broken and shattered beads were removed before use. The usual sample consisted of approximately 175 particles with a capacity of approximately 0.3 mequiv.

Analysis

After washing of the exchanger particles, the column containing the particles was removed from the equipment. The particles were eluted with 30 cc. of 2N $Ca(NO_3)_2$, washed with distilled water, and the eluant (+ wash) titrated for H^+, under a N_2 atmosphere, using approximately 0.01 N KOH with bromothymol blue indicator.

Particle Diffusion Control Tests

To test for particle diffusion control, interruption tests were performed by Stevens (22) on the same system with the same particles. The flow velocities used in the present work were double those used by Stevens in order to diminish the effect of the film diffusion lag on the on portion (H^+ on).

Reproducibility

The reproducibility of the experimental data was within 2%. The use of different random samples of particles, from the overall classified sample, gave results which agreed within the above experimental error.

Cyclic Steady State Test

Reproducible results were obtained after successive cycles indicating cycle steady state had been attained. Usually, 12 cycles were sufficient.

DISCUSSION OF RESULTS

Qualitative Analysis of Data

Examination of the experimental results (Figures 3 and 4), indicates a number of interesting features of the cyclic steady state. Since, for the on portion of the cycle (H^+ on), the effective diffusivity may be an order of magnitude less than that of the off portion (H^+ off) (22), the average composition would be expected to be near the low H^+ end of the composition scale (low $\overline{\overline{X}}_{H^+}$). The results substantiate this expectation, even at time ratios (on time/off time) greater than 3 to 1, and at large cycle times (for example 120 sec.).

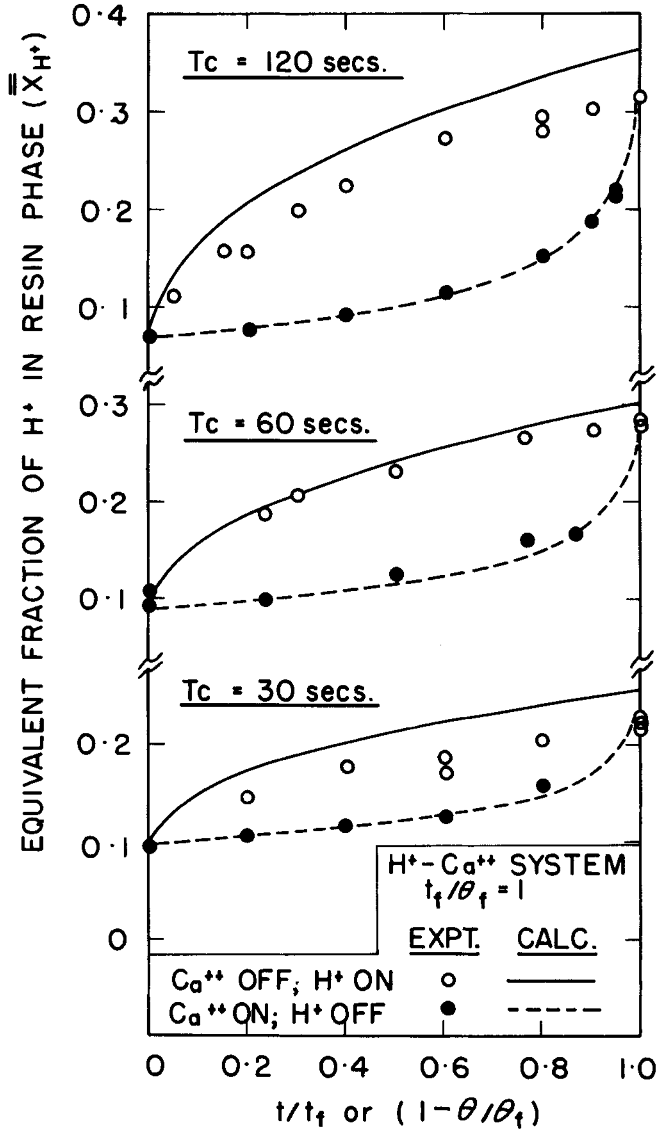

Fig. 3. Effect of total cycle time on composition.

Since the off portion diffusivity must be greater than the on portion diffusivity, the off portion should control the level of the composition range. A comparison of the data for the effect of variation of the time ratios at constant cycle time (Figure 4), confirms the off portion control. Thus a ratio of 11 to 1, is required to raise the mean composition, with respect to the total range, to a value above 0.5.

Variation of the total cycle time at a constant time ratio, (Figure 3) shows, as expected, that as the total cycle time increases, the mass exchange increases. In general, the composition range tends towards the low $\overline{\overline{X}}_{H^+}$, due to the controlling off portion diffusivity.

Estimation of Diffusivities

An independent estimation of the effective diffusivities for the on and off portions of the cycle is desirable. Since in ion exchange, the diffusivity is a strong function of composition [Equation (13)], the estimation of the effective diffusivity from a mathematical viewpoint would be difficult due to the complexity of the nonlinear problem.

Examination of the cyclic steady state profiles as given by Equations (9) and (10) (Figure 1) suggests the possibility of estimating the effective diffusivities from rate data obtained from experiments in which the initial profile is uniformly distributed throughout the exchanger. The initial exchange rate for the on portion of the cyclic steady state would be similar to the corresponding initial exchange rate in an experiment in which the initial profile is zero composition in H^+ (that is $2H^+ + Ca(Ex)_2 \rightarrow$), which corresponds to the off portion surface composition during the cyclic steady state experiments. Similarly, the initial exchange of the off portion, of the cyclic steady state, would correspond to the initial exchange rate, when the exchanger is uniformly saturated in H^+ (i.e. $Ca^{++} + 2H(Ex) \rightarrow$). Thus, diffusion experiments, for exchange with an initial uniform composition (corresponding to the cyclic steady state surface composition for the previous portion of the cycle), should yield a first approximation to the cyclic steady state effective diffusivities.

From the appropriate rate data of Stevens (*22*), on the same system, the following estimates for the effective diffusivities (with 95% confidence limits) were obtained.

$$\overline{D}_F \approx \overline{D}(2H^+ + Ca(Ex)_2 \rightarrow)$$

$$= (0.447 \pm 0.080) \times 10^{-6} \text{ sq. cm./sec.}$$

$$\overline{D}_R \approx \overline{D}(Ca^{++} + 2H(Ex) \rightarrow)$$

$$= (2.74 \pm 0.133) \times 10^{-6} \text{ sq. cm./sec.}$$

In the case of certain ion pairs, for which the individual diffusivities are known but where the ratio $D_A/D_B \leqq 20$, it may not be necessary to perform any experiments to estimate effective diffusivities. It has been shown by Gopala Rao and David (*6*) that effective diffusivities, for the initial exchange starting with zero composition (in the ion going onto the exchanger) and the surface maintained at the saturation value (of the ion going onto the exchanger), may be estimated from individual diffusivities. The correlation used was based on an empirical fit to data, generated from the effective diffusivity and variable diffusivity models. Unfortunately, the variable diffusivity model has not been applied to individual diffusivity rations greater than 20 (*11*) and thus the correlation method can not be presently applied to the $H^+ - Ca^{++}$ system.

Comparison of Predicted and Experimental Results

A comparison of the predicted and experimental results (Figures 3 and 4), shows that the agreement in all cases (except at a time ratio of 11 to 1) is satisfactory. At a time ratio of 11 to 1 the model (with the estimated effective diffusivities) does not adequately describe the data and deviations in predicted values of 20% are encountered. It should be noted, that the time ratio is unlikely to exceed 5 to 1 in cyclic ion exchange processes (*13*, *20*, *21*), thus the result at a time ratio of 11 to 1 is far outside the normal operating range.

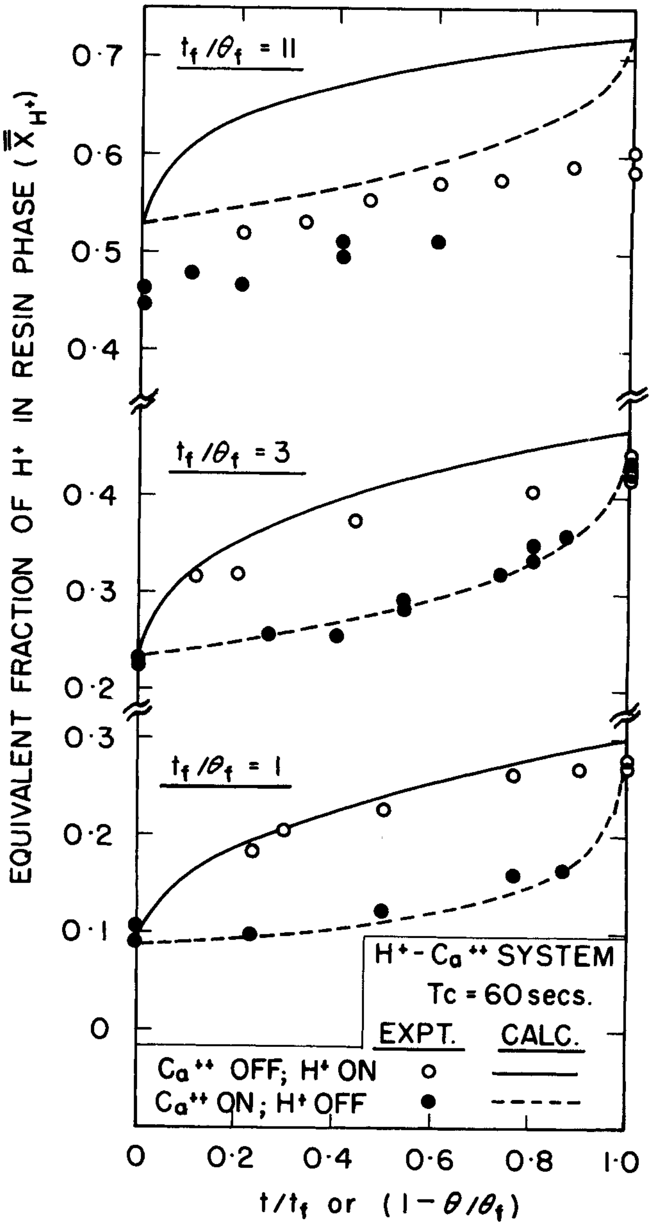

Fig. 4. Effect of time ratio on composition.

It is immediately obvious, that a model such as outlined in Carslaw and Jaeger (*3c*) based on equal effective diffusivities, could not represent the data.

The deviations between the predicted and experimental results can be attributed to the use of an effective diffusivity to describe a variable diffusivity situation, and/or the fact that the surface liquid film transfer is neglected in the derivation of the cyclic steady state equations.

The adequacy of the effective diffusivity model, in representing the data, depends upon precise independent estimation of effective diffusivities. Since the agreement between the predicted and experimental results is satisfactory (excluding data at a time ratio of 11 to 1), it appears that the suggested method for estimation of effective diffusivities is reasonable. In a system such as the $H^+ - Na^+$ system a more precise prediction of effective diffusivities [from experimental data or by the correlation of Gopala Rao and David (6)] could be obtained. Since the individual diffusivity ratio for the $H^+ - Na^+$ system is only about 5/1 to 10/1 (9, 10, 22) giving effective diffusivity ratios of approximately 2/1 to 3/1, this system does not offer as difficult a test of the model as the $H^+ - Ca^{++}$ system.

The neglect of the effect of transfer through the liquid, in the derivation of the cyclic steady state equations, would affect the predicted results. Film diffusion has a greater effect on the H^+ on exchange than on the H^+ off exchange (9, 22). For the H^+ on exchange, the effect can be substantial, whereas in the H^+ off exchange, the effect is probably negligible. Thus, the film diffusion effect could account for part of the on portion deviations, in particular for the exchange at a time ratio of 11 to 1. Of course, the model can be modified in an attempt to account for the film diffusion effect.

CONCLUSIONS

1. A cyclic steady state diffusion model incorporating effective diffusivities which depend upon the transfer direction as well as on the system, has been formulated. The model may be easily extended to account for time-dependent surface conditions and coupled diffusion problems.

2. The suggested model, requires the independent estimation of precise effective diffusivities for the on and off portions of the cycle. Unfortunately, the necessary information for the prediction of the effective diffusivities, in the ion exchange system tested, are presently only available for a narrow range of conditions. However, effective diffusivities can be estimated from independent noncyclic experiments.

3. Experimental verification of the model (over a practical operating range) was obtained using ion exchange diffusion, in which the effective diffusivity is dependent upon the direction of transfer as well as on the system.

ACKNOWLEDGMENT

The authors wish to express their appreciation to the National Research Council of Canada for financial assistance in this work and for the fellowship held by P. J. Simmons.

NOTATION

$\overline{D}$ = effective diffusivity, dependent on the direction of transfer and on the system (that is either thermal or mass diffusivity), (sq. cm./sec.)
D_A = individual diffusion coefficient of ion A in ion exchanger (sq. cm./sec.)
D_B = individual diffusion coefficient of ion B in ion exchanger (sq. cm./sec.)
D_{AB} = variable diffusion coefficient in ion exchanger for B replacing A (also written as D), (sq. cm./sec.)
$g(\rho)$ = function of dimensionless radius (ρ) for V_R at $\theta = 0$
$h(\rho)$ = function of dimensionless radius (ρ) for V_F at $t = 0$
r = radius coordinate in sphere (cm.)
r_o = outside radius of sphere (cm.)
t = time during on portion of cycle (forward transfer) (sec.)
T_c = total cycle time = $t_f + \theta_f$ (sec.)
$v(r,t)$ = dependent variable which is function of t and r (that is temperature or concentration)
v_o = reference value of dependent variable, used to make dependent variable dimensionless (that is datum temperature or total concentration of mass in particle)
V = normalized dependent variable = $v(r, t)/v_o$
$\overline{V}$ = average normalized dependent variable = $3 \int_0^1 V\rho^2 d\rho$
$\overline{X}_A$ = equivalent fraction of A in resin (function of r and t) = $1 - \overline{X}_B$
$\overline{\overline{X}}_A$ = average equivalent fraction of A in resin = $3 \int_0^1 \overline{X}_A \rho^2 d\rho$
Z_A = ionic charge of ion A
Z_B = ionic charge of ion B
θ = time during off portion of cycle (reverse transfer) (sec.)
ρ = dimensionless radius = r/r_o
τ = dimensionless time = $\overline{D}_F t/r_o^2$
ϕ = dimensionless time = $\overline{D}_R \theta/r_o^2$

Superscripts

$*$ = value of dependent variable on surface
$'$ = dummy variable

Subscripts

f = final value of independent variable
F = forward transfer (on portion)
R = reverse transfer (off portion)

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