

leled by the modified absolute rate theory predictions, but the formulation of the latter gives some insight into reasons for the deviations of the cyclohexane-based solvents from the normal paraffin results. Equations (4) and (6) indicate that the deviations of the parameter  $Y$  from unity depend upon the value of  $f$  which characterizes the particular solute-solvent combination. The fraction  $f$  utilized in the line representing the binary data is an average value for a large number of systems but is not a true constant for all substances or mixtures. Values less than the average are expected for systems composed of spherical molecules (such as cyclohexane and toluene) because the enhanced ability of the solute molecule to move freely in its equilibrium position reduces the contribution of the kinetic step. By Equations (4) and (6) low values of  $f$  would tend to move the ordinates toward unity; the spherical shape of cyclohexane (compared with normal paraffins) is thus a reasonable explanation for its anomalous behavior relative to  $n$ -hexane,  $n$ -decane, and  $n$ -tetradecane.

#### ACKNOWLEDGMENT

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#### NOTATION

$a$  = solute activity  
 $\Delta C_i$  = concentration difference be-

tween the two compartments of the diffusion cell at the beginning of an experiment, g.-moles/liter  
 $\Delta C_i$  = concentration difference between the two compartments of the diffusion cell at the end of an experiment, g.-moles/liter  
 $D$  = diffusion coefficient, sq. cm./sec.  
 $D_{SA}, D_{SB}$  = binary diffusivities of toluene (designated as  $S$ ) in the components of the solvent mixture (designated by  $A$  and  $B$ ), sq. cm./sec.  
 $f$  = fraction of the total free energy of activation required for the kinetic or bond-breaking step  
 $\Delta F^*$  = free energy of activation, cal./mole  
 $h$  = Planck's constant,  $6.624 \times 10^{-27}$  erg.-sec.  
 $k$  = Boltzmann's constant,  $1.38 \times 10^{-16}$  erg./°K.  
 $\bar{M}$  = mole fraction-average molecular weight of solvent  
 $N_{AV}$  = Avogadro's number,  $6.023 \times 10^{23}$   
 $t$  = time, sec.  
 $T$  = temperature, °K.  
 $V$  = molar volume of solution, cc./g.-mole  
 $x$  = mole fraction  
 $Y$  = defined by Equation (4)

#### Greek Letters

$\beta$  = cell constant  
 $\delta$  = parameter defined by Equation (7)  
 $\rho$  = solution density, g./cc.  
 $\mu$  = solution viscosity, poise  
 $\xi$  = parameter in Eyring theory

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# A Diffusion Model for Rinsing

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The removal, by immersion in water, of solute from a solution adhering to a 14.7-cm. wide flat plate has been experimentally investigated at about 80°F. over a 3.5 to 1,000 sec. range of contact time. Diffusivity was varied over a sixfold range (from 0.5 to 3.0 by  $10^{-5}$  sq.cm./sec.) by the use of two dilute solutions, pontamine blue dye and 0.09 N nitric acid. Equations relating the effects of film thickness, contact time, and diffusivity on the mass fraction of solute which was not removed during rinsing were developed from a diffusion model, under the assumption that the adhering solution was present throughout as a stagnant film of uniform thickness.

The experimentally determined effects of time and diffusivity agreed with those indicated by the idealized model. The agreement of these effects and the magnitude of unremoved solute gave strong indication that diffusion may be considered the controlling mechanism. The experimental dip and rinse method used offers potential as a technique for studying natural convection at transient conditions in the region where diffusion is also important, because it offers the advantage of allowing independent selection of initial fluid densities.

It might be thought that the removal of a contaminant-containing

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solution from a solid body by dipping the solid in a tank of water is due to the agitation resulting from the dipping motion. It is the purpose of this paper to show that under certain con-

ditions the effect of time and diffusivity on rinse removal is described by molecular diffusion.

The need to determine the controlling mechanism arose in the design of

rinsing processes in the metal finishing industries but will not be explored here as both the need and design applications have been discussed elsewhere (9, 10).

## STATEMENT OF THE MODEL

The rinsing condition examined is the rinsing of a flat plate, to which a solution is adhering, by immersion of the plate in a water rinse for a specified time. To describe the mass transfer in rinsing solely in terms of molecular diffusion the following idealized model is proposed.

The plate is entirely coated with a film of uniform thickness, and this film is not in fluid motion while the plate is in the rinse tank or while it is being inserted or removed. This supposition also implies that the film thicknesses before and after immersion are equal. In terms used in rinsing, where carry-over is the solution volume adhering to the plate before immersion and dragout is the solution volume adhering to the plate after it is withdrawn, constant film thickness implies that carry-over and dragout volumes are equal. The model is shown in Figure 1, where  $b$  is the film thickness and  $L$  is the distance between the plate and the tank wall.

This model is simply one-directional, unsteady state molecular diffusion of one component (the contaminant) through a second component (the rinse water). This phenomenon is described by Bird et al. (2) as follows:

$$N_A = X_A (N_A + N_B) - C_T D_{AB} \nabla X_A \quad (1)$$

## MATHEMATICAL DEVELOPMENT

In the case where density is constant and where the concentration of  $A$  is very small compared with the concentration of  $B$ , Equation (1), when combined with a mass balance, may be approximated by Fick's second law as follows:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (2)$$

Initially the concentration distribution in the tank is

$$C(x, 0) = f(x) \quad \text{at } t = 0 \quad (3)$$

$$\text{where } f(x) = C_o \quad \text{when } 0 \leq x < b$$

$$\text{and } f(x) = 0 \quad \text{when } b < x \leq L$$

Since there is no mass transfer across the solid boundaries at  $x = 0$  and  $x = L$ , the concentration gradient at these positions is zero for all times. Thus one obtains

$$\frac{\partial C(0, t)}{\partial x} = 0 \quad (4)$$

$$\frac{\partial C(L, t)}{\partial x} = 0 \quad (5)$$

An alternate solution may be obtained by considering a tank of infinite size so that the boundary condition given by Equation (5) would be replaced by Equation (6):

$$\lim_{x \rightarrow \infty} C(x, t) = 0 \quad (6)$$

This alternate solution, which yields the same result in the region of interest in this application, is discussed in the Appendix.

The solution of Equation (2), subject to the initial and boundary conditions of Equations (3) to (5), has been applied to rinsing by Buffham (3) as follows. By means of the solution of this boundary-value problem as presented by Carslaw and Jaeger (4) for heat conduction and the substitution of the initial conditions of Equation (3), the solution to Equation (2) is, in this notation

$$C(x, t) = \frac{bC_o}{L} + \frac{2C_o}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin \left( \frac{n\pi b}{L} \right) \cos \left( \frac{n\pi x}{L} \right) \exp \left( -\frac{n^2 \pi^2 D t}{L^2} \right) \quad (7)$$

The parameter of interest in rinsing is the fraction of unremoved contaminant which remains in the thin film after a specified contact time. This fraction is equal to the mass of contaminant in the film at the specified contact time divided by the initial mass, or

$$U = \frac{\int_0^b C(x, t_e) dx}{C_o b} \quad (8)$$

The quantity of unremoved contaminant is determined by substitution of the concentration profile of Equation (7) into Equation (8) and integration. Thus the exact solution of Equation (2) for this model is

$$U = \frac{b}{L} + \frac{2L}{\pi^2 b} \sum_{n=1}^{\infty} \frac{1}{n^2} \sin^2 \left( \frac{n\pi b}{L} \right) \exp \left( -\frac{n^2 \pi^2 D t_e}{L^2} \right) \quad (9)$$

Equation (9) shows that the unremoved contaminant fraction is independent of initial contaminant concentration.

The average value of dimensionless film thickness  $b/L$  in the experimental test reported subsequently was about 0.0004, and the maximum value of the dimensionless contact time  $D t_e / L^2$  was about 0.0006. In the region where these dimensionless parameters are small the series in Equation (9) converges slowly. Therefore in the region of immediate interest a large number of terms in the series is required for the evaluation of the unremoved contaminant fraction to three significant figures. This unfortunate situation may be avoided however if one replaces the infinite series in Equation (9) by the corresponding integral. (The validity of this approximation is discussed in the Appendix.) Then

$$U \cong \frac{b}{L} + \frac{2L}{\pi^2 b} \int_0^{\infty} \frac{1}{n^2} \sin^2 \left( \frac{n\pi b}{L} \right) \exp \left( -\frac{n^2 \pi^2 D t_e}{L^2} \right) dn \quad (10)$$

Equation (10) may be simplified by replacing the sine term with an infinite series and transforming it into a series of Gamma function integrals. With Gamma function relationships it follows that

$$U \cong \frac{b}{L} + \frac{1}{\sqrt{\pi}} \sum_{m=1}^{\infty} \frac{(-1)^{m-1}}{(2m)!} \left( \frac{2b}{\sqrt{D t_e}} \right)^{2m-1} (m-3/2) (m-5) \dots (1/2) \quad (11a)$$

which may also be written as

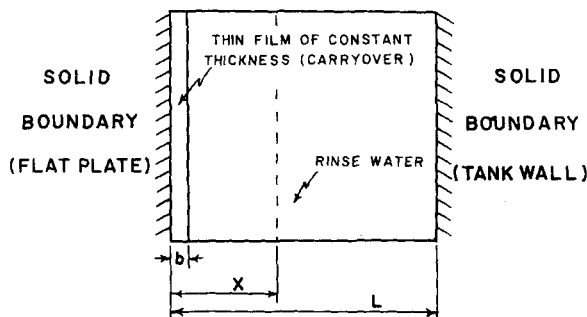


Fig. 1. Diffusion model.

$$U \cong \frac{b}{L} + \frac{1}{\sqrt{\pi}} \left[ \frac{b}{\sqrt{Dt_c}} - \frac{1}{6} \left( \frac{b}{\sqrt{Dt_c}} \right)^3 + \frac{1}{30} \left( \frac{b}{\sqrt{Dt_c}} \right)^5 \dots \right] \quad (11b)$$

Equation (11) then is the approximate solution of Equation (2) for the model proposed.

### SIMPLIFIED EQUATIONS FOR RINSE TESTS

As the film thickness parameter  $b/L$  was only about 0.0004 under conditions tested experimentally, Equation (11) may be further simplified to three significant figure accuracy by neglecting this parameter. Thus

$$U \cong \frac{1}{\sqrt{\pi}} \left[ \frac{b}{\sqrt{Dt_c}} - \frac{1}{6} \left( \frac{b}{\sqrt{Dt_c}} \right)^3 + \frac{1}{30} \left( \frac{b}{\sqrt{Dt_c}} \right)^5 \dots \right] \quad (12)$$

The maximum error in dropping the second and subsequent terms in the series depends on experimental conditions. This error is no more than the ratio of the second term divided by the first term, or

$$E \leq b^2/6Dt_c \quad (13)$$

Since, for the test conditions used the largest film thickness was 0.00239 cm. and the smallest diffusivity was  $0.5 \times 10^{-5}$  sq. cm./sec., the maximum error is

$$E \leq 0.186/t_c \quad (14)$$

Therefore for contact times of 100 sec. or greater Equation (12) may be simplified to about three significant figures by dropping the second and subsequent terms. Thus

$$U \cong \frac{b}{\sqrt{\pi Dt_c}} \quad (15)$$

For contact times of 10 to 60 sec. Equation (15) holds to two significant figures.

### EXPERIMENTAL CONDITIONS AND PROCEDURE

By means of a previously described, motor-driven, dipping apparatus (9) Barbolini (1) tested the applicability of Equation (15) over a 300-fold range of mean contact time and a sixfold range of diffusivity. The calculated film thickness was constant in the contact time tests and varied slightly in the diffusivity tests.

The thin, 14.7 cm. wide stainless steel plate used was immersed to a depth of 12.6 cm. in all tests. This resulted in an immersion area of 370 sq. cm. In rinsing the clean, dry plate was dipped into the contaminant solution to apply the solu-

tion, removed, dipped into a 15.4 cm. diam. rinse tank for a specified contact time, and removed for analysis. As the plate was always dipped and withdrawn at 1.9 cm./sec., the time of exposure during both dipping and withdrawing was constant at 7 sec. each.

Two contaminant solutions were used: a 3 g./ml. pontamine blue dye solution and a 0.09 N nitric acid solution. The concentrations of each solution was determined to three significant figures. Both solutions had densities and viscosities within 0.5% of those of water. Solution temperatures for the dye and acid tests were 81° and 78°F. respectively. Diffusivities, based on literature values, were  $0.5 \times 10^{-5}$  sq. cm./sec. (5) for the dye and  $3.0 \times 10^{-5}$  sq. cm./sec. for the acid. The acid value of  $2.62 \times 10^{-5}$ , for 0.05 N at 68°F. (6), was extrapolated to 78°F. under the assumption that diffusivity is directly proportional to the absolute temperature and inversely proportional to the solution viscosity.

The unremoved contaminant fraction due to rinsing was calculated from the measured mass of contaminant in the adhering film after rinsing as well as from independent measurements of carry-over volume. The mass of contaminant held on the plate after leaving either the contaminant bath (for carry-over measurements) or the rinse tank (for rinse tests) was determined by washing all the adhering liquid off the metal, diluting the collection solution to a known volume, and analyzing this dilute solution. The concentration of dilute dye solutions was measured at 660  $\mu$  with a colorimeter calibrated for solutions between 0.5 and 5 p.p.m. The concentration of dilute acid solutions was determined by adding a measured volume of 0.0014 N sodium hydroxide and back titrating with 0.00173 N nitric acid with phenolphthalein indicator. In the acid titrations it was necessary to use distilled water blanks and to take precautions to minimize absorption of carbon dioxide from air by the basic solution.

Carry-over volumes were determined by dividing the mass in the adhering film after it had been removed from the contaminant bath by the contaminant bath concentration. In six tests (CP 16 to 21) the carry-over from the dye solution was  $0.886 \pm 0.018$  ml.; in four tests (CP 41

to 42) the carry-over from the acid solution was  $0.667 \pm 0.008$  ml. Film thicknesses, determined by dividing carry-over volume by the immersion area, were 0.00239 and 0.00180 cm. for the dye and acid solutions respectively.

### ASSUMPTION OF ONE-DIMENSIONAL GRADIENT

During dipping (and withdrawing) a concentration gradient is established in the film in the direction of the plate motion, so that, strictly speaking, Equation (2) does not apply to the physical conditions tested. To be general a two-dimensional equation which includes plate velocity is required.

Nissan and Hansen (8) have solved this two-dimensional problem using temperature profiles. They found that in comparison with Equation (7) the solution considering the second dimension contained an additional term. They developed a criterion for deciding when the additional term may be neglected, which is, in the notation of this work, expressed by Equation (16):

$$(D^2 n^2 \pi^2 / L^2 V^2) \ll 1 \quad (16)$$

For the conditions of this work ( $D = 3.0 \times 10^{-5}$  sq. cm./sec.,  $L = 7$  cm., and  $V = 1.9$  cm./sec.), even up the thousandth term of the series ( $n = 1,000$ ), the criterion of Equation (16) was satisfied as shown below:

$$(D^2 n^2 \pi^2 / L^2 V^2) = 0.005 \quad (17)$$

This criterion was satisfied because the plate velocity was large in comparison with the molecular diffusion rate.

Since Equation (16) was satisfied, the one-dimensional gradient expressed by Equation (2) was sufficient for this work. Furthermore since the additional term arising from consideration of the second dimension was held constant, the additional term would not influence the comparison of the experimental effect of contact time in rinsing with that indicated by the model.

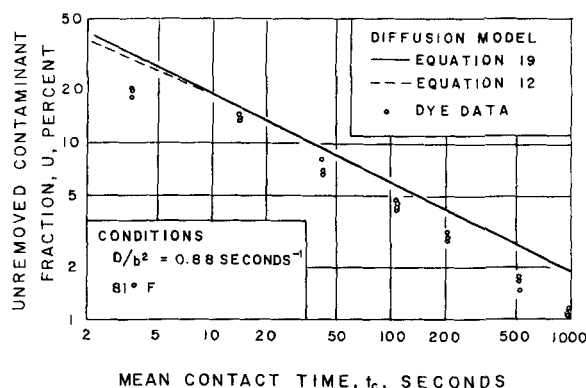


Fig. 2. Effect of contact time on unremoved contaminant.

## MEAN CONTACT TIME

Since the entire wetted area of the plate was not completely immersed during dipping and withdrawing, the effective or mean contact time is not simply the sum of dipping time, time at rest, and withdrawing time. The mean contact time has been given by Nissan (7) as Equation (18):

$$t_c = \left[ \frac{t_r^{0.5} + (t_d + t_r + t_w)^{0.5}}{2} \right]^2 \quad (18)$$

When the dipping time is equal to the withdrawing time, as was the case here, Equation (18) reduces to simpler relationships. At zero rest time the mean contact time equals one half the dipping time. When there are long rest times or when the dipping time is small compared with the rest time, the mean contact time equals the sum of the rest and dipping times. The latter approximation holds within 1% for this work for rest times of 34 sec. and longer.

## EFFECT OF CONTACT TIME

The effect of contact time on unremoved contaminant fraction during rinsing was studied with only the dye contaminant solution. Three runs were made for each of the following rest times: 0, 8, 34, 100, 200, 500, and 1,000 sec. The averaged unremoved contaminant (Runs RP 1 to 22) were 19.2, 14.2, 7.2, 4.5, 3.0, 1.7, and 1.1% for mean contact times of 3.5, 14, 41, 107, 207, 507, and 1,007 sec. respectively.

The volume of the rinse tank was such that the unremoved contaminant fraction at infinite time, when complete mixing would occur, would have been less than 0.04%.

Rinse values may be predicted from the diffusion model by means of Equation (15) which, for the diffusivity and film thickness of the dye contaminant, reduces to

$$U = 0.60/t_c^{0.50} \quad (19)$$

where  $t_c$  has units of seconds.

Experimental results for these dye rinse runs are compared with those predicted from Equation (19) in Figure 2. Experimental reproducibility, as shown by run to run variations, is indicated by the three data points at each contact time. A line drawn through the experimental data has a slope of about  $-0.6$  or  $-0.55$  depending on whether the data at 3.5 mean contact times is considered. Based on the similarity of slopes it was concluded that the effect of time on rinsing was very similar to that indicated by the diffusion model.

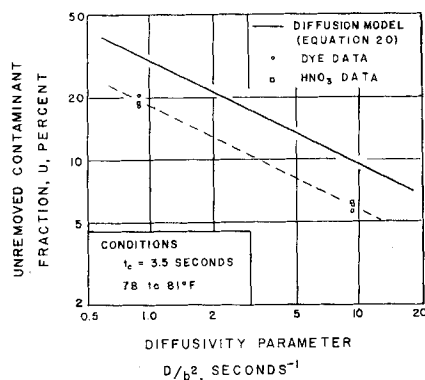


Fig. 3. Effect of diffusivity on unremoved contaminant.

## MAGNITUDE COMPARISON

Comparison of the magnitude of the results with model values may be approached from two bases: use of the unremoved contaminant fraction  $U$  or use of the contaminant fraction which was removed,  $1 - U$ .

Consider first the removed fraction  $1 - U$ . At 3.5 sec. mean contact time 81% of the contaminant was found to be removed, whereas the model [Equation (12)] indicated 71% removal. (Removal at complete mixing would be over 99.9%.) In this 3.5 sec. case the value indicated by the model was 87% of the actual removal; that is the model accounted for all but 13% of the removal. For all other contact times the model accounted for all but 1 or 2% of the mass actually removed. This agreement within 1 to 13% is an indication that most of the removal, especially at times longer than a few seconds, is probably due to molecular diffusion. While this comparison provides data necessary to indicate that diffusion may be considered the controlling mechanism, it is recognized that this data is not sufficient to ascertain proof.

Comparison on the basis of the unremoved contaminant, as shown in Figure 2, is a more critical evaluation since small differences are much larger on this basis than that of the removed fraction basis. The magnitudes of unremoved contaminant for the model values [Equation (12)] were 20 to 60% higher than experimental values for two-thirds of the twenty-two runs. The median difference was 40% higher, and the extreme ranges were 10 to 90% higher. It is believed that one of the major reasons for this 40% difference in magnitude was due to the presence of one or more other nonnegligible removal mechanisms. Such mechanisms acting simultaneously would tend to produce experimental values of unremoved contaminant lower than that of the model, that is in the same direction as that found in Figure 2. Among other sec-

ondary mass transfer mechanisms which have been noted (9) the one which is probably next in importance to diffusion is the dispersal of part of the carry-over across the rinse water surface at the time of entry. In any case precise agreement in magnitude of the experimental values with those of the diffusion model would probably require either elimination or quantitative description of any important secondary mechanisms.

On the basis of unremoved contaminant there is some indication of a trend of the difference between model and experiment as a function of time (see Figure 2). Except for the shortest mean contact time (at which model values were about 50% greater than experimental ones) the differences increased with time from about 10% at 14 sec. to about 80% at 1,007 sec. If this trend were significant, it might be due to some small effect of natural convection which becomes more noticeable at long times. However in view of the irregularity of the trend at short times (which may be due to some uncontrolled parameter) the trend is not, at this time, considered significant.

## EFFECT OF DIFFUSIVITY

The influence of diffusivity was studied with both the dye and acid solutions. In order to minimize any natural convection effects these rinse tests were conducted at the shortest possible contact time: zero rest time or 3.5 sec. mean contact time. The unremoved contaminant fraction was found to be  $19.2 \pm 0.9\%$  for the dye solution (Runs RP 1 to 3) and  $5.9 \pm 0.2\%$  for the acid solution (Runs RP 40 to 42).

Since the film thickness for the acid system was slightly different from that of the dye system, a graphical comparison of the rinse results with model values requires adjustment for film thickness. For the mean contact time used Equation (15) reduces to

$$U = 0.30 (D/b^2)^{0.50} \quad (20)$$

where  $D/b^2$  = diffusion parameter,  $1/\text{sec}$ . This diffusion parameter accounts for the difference in film thickness. As a parameter had values of 0.88 and 9.2 reciprocal sec. for the dye and acid systems respectively, the parameter was varied over a tenfold range.

Experimental results are compared with those indicated by Equation (20) in Figure 3. A line drawn through the experimental data has a slope of  $-0.5$ . Based on the similarity of slopes it was concluded that the effect of diffusivity on rinsing was very similar to that indicated by the diffusion model.

## FURTHER DISCUSSION

Experimental evidence indicates that the diffusion model presented here qualitatively describes the magnitude of rinse performance and quantitatively describes the effect of important variables. This agreement indicates that if tests were designed to minimize or correct for other modes of mass transfer, this dip method might be a useful experimental technique for studying unsteady state mass transfer by diffusion and, more important, simultaneous diffusion and natural convection under transient conditions. The use of this dip technique for studying transient mass transfer by natural convection has the advantage over most convective techniques of allowing independent variation of initial fluid densities.

## CONCLUSIONS

1. A constant-film-thickness diffusion model qualitatively describes the transient mass transfer which occurs in rinsing a solution of waterlike density from a flat plate. In view of the fact that other mechanisms are reportedly present the model represents the effect of contact time and diffusivity very well.

2. Results expressed as the unremoved contaminant fraction, for which model values were generally 20 to 60% higher than those found experimentally, indicated that secondary modes of mass transfer were present. Results expressed as the removed contaminant fraction, for which model values were generally only 1 to 2% lower than those found experimentally, provided necessary but not sufficient indication that molecular diffusion may be considered the controlling mechanism.

3. The dip and rinse method is a possible technique for measuring mass transfer by simultaneous diffusion and natural convection at transient conditions.

## ACKNOWLEDGMENT

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## NOTATION

$b$  = film thickness, cm.  
 $C$  = contaminant concentration  
 $C_0$  = initial contaminant concentration in the film  
 $C_T$  = total molal concentration of the solution  
 $D$  =  $D_{AB}$  = equi molal diffusivity of mass of A-B binary, sq. cm./sec.  
 $E$  = maximum absolute error due to dropping high-order terms

$L$  = tank size, distance from plate to tank wall, cm.  
 $N_A$  = molal flux of A relative to stationary coordinates, a vector  
 $N_B$  = molal flux of B relative to stationary coordinates, a vector  
 $t$  = time, sec.  
 $t_c$  = contact time or mean contact time, sec.  
 $t_d$  = time for dipping, sec.  
 $t_r$  = time at rest, sec.  
 $t_w$  = time for withdrawing, sec.  
 $x$  = rectangular coordinate  
 $X_A$  = mole fraction of A  
 $U$  = unremoved contaminant fraction during one rinse cycle, dimensionless  
 $V$  = flat plate velocity, cm./sec.  
 $\pi$  = 3.14159

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## APPENDIX—VALIDITY OF THE INTEGRAL APPROXIMATION

The error which results from replacing the infinite series of Equation (9) with the integral of Equation (10) may be estimated by a comparison of the value of  $U$  based on the integral with the physical situation at both very long and very short times.

At long times, that is as contact time approaches infinity in the limit, the integral of Equation (10) equals zero; thus  $U$  [Equation (10)] =  $b/L$  at infinite time. As complete mixing occurs at infinite time in the actual physical situation,  $U$  [Equation (9)] =  $b/L$ . At very long times therefore Equations (9) and (10) are in exact agreement.

At very short times, that is as contact times approaches zero in the limit, the

integral of Equation (10) equals  $(\pi^2 b/2L)$ ; thus  $U$  [Equation (10)] =  $1 + (b/L)$  at zero time. As no mixing occurs at zero time in the actual physical situation,  $U$  [Equation (9)] = 1. At very short times therefore Equations (9) and (10) differ by the quantity  $b/L$ . However under the conditions tested experimentally the ratio  $b/L$  was negligible in comparison with the unremoved contaminant.

Therefore for the conditions tested the error made in replacing the series by an integral is negligible at zero time and zero at infinite time.

The question of whether the error passes through a maximum or maxima may be examined with the solution to Fick's second law for a tank of infinite size, that is with boundary condition of Equation (6) instead of Equation (5). This solution would not be rigorous when the concentration at the tank wall increases above zero, but it will be exact for the short times used in this work. By considering two separate regions and joining these regions by setting concentrations and their derivatives equal at  $x = b$  the concentration profiles are

$$\text{for } x < b \quad \frac{C}{C_0} = \frac{1}{2} \left[ \operatorname{erf} \left( \frac{b+x}{\sqrt{Dt_c}} \right) + \operatorname{erf} \left( \frac{b-x}{\sqrt{Dt_c}} \right) \right] \quad (21)$$

$$\text{for } x > b \quad \frac{C}{C_0} = \frac{1}{2} \left[ \operatorname{erf} \left( \frac{b+x}{\sqrt{Dt_c}} \right) - \operatorname{erf} \left( \frac{b-x}{\sqrt{Dt_c}} \right) \right] \quad (22)$$

If one uses the concentration profile for the  $0 \leq x \leq b$  region [Equation (21)], the unremoved contaminant fraction is

$$U = \frac{1}{2b} \sqrt{\frac{D}{\pi}} \int_{t_c}^{\infty} \frac{1}{\sqrt{t_c}} \left[ 1 - \exp \left( \frac{-b^2}{Dt_c} \right) \right] dt \quad (23)$$

With the expansion of the exponential term into a series Equation (23) can be shown to be exactly equal to Equation (12). An examination of Equation (23) at zero and infinite times shows that it may have errors of the same magnitude of that of Equation (12), except that Equation (23) has zero error at short times and an error of  $b/L$  at long times. The nature of Equation (23) indicates that the error does not pass through a maximum.

Equation (23) also indicates that the error in replacing the series of Equation (9) with the integral of Equation (10) should be constant at  $b/L$  for all the times studied in this work if these times are short times. To test the constancy of this error the series of Equation (9) was evaluated numerically with the diffusivity and film thickness of the dye solution and the eight figure accuracy necessary for comparison of the difference with Equation (11). The error at both 225 sec. (requiring 300 terms for convergence) and at 900 sec. (requiring 150 terms) was found to be equal to  $b/L$ .