THE BATCHWISE TRANSFER OF ACETIC ACID FROM CHLOROFORM TO WATER

(DETERMINATION OF INDIVIDUAL FILM COEFFICIENTS)

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Abstract—The theory of the batchwise transfer of a solute from one immiscible phase to another has been examined. For systems of constant partition coefficient, the decay of solute concentration in the one phase and the complementary growth in the other are shown to be exponential under all conditions. For systems of varying partition coefficient, this decay is only exponential when the mole ratio of the two pure solvents equals the ratio of the individual film coefficients.

Two methods are suggested for evaluating the film coefficients for such systems. The first method is only feasible in practice if concentration measurements can be made with extreme precision. The second method, involving trial and error graphical integration of the rate equation leads to the successful determination of the two coefficients.

NOMENCLATURE

A, interfacial area available for mass transfer;

C_{xn}, integrated coefficient based on the X phase defined by

$$C_{xn} = \frac{X_n}{t_{n+1} - t_n} \int_{x_n}^{x_{n-1}} \frac{dx}{x_i - x};$$

C_{yn}, integrated coefficient based on the Y phase defined by

$$C_{yn} = \frac{Y_n}{t_{n+1} - t_n} \int_{y_{n+1}}^{y_n} \frac{dy}{y - y_i};$$

D, root mean square deviation of the various C_{xn} and C_{yn};

k_x, film coefficient of mass transfer for the X phase, moles/cm²/s;

k_y, film coefficient of mass transfer for the Y phase, moles/cm²/s;

K, k_x/k_y;

L, X/Y;

M, $(y_e - y_i)/(x_e - x_i)$;

N, rate of diffusion of solute from phase Y to phase X, moles/cm²/s;

t, time in seconds, unless otherwise stated;

V, volume of acetic acid added to the Y phase, ml;

X, moles of pure solvent (water) in the X phase;

Y, moles of pure solvent (chloroform) in the Y phase.

x, mole ratio of the solute (acetic acid) in the X phase, moles acid/moles water;

y, mole ratio of the solute (acetic acid) in the Y phase, moles acid/moles chloroform.

Subscripts

i, interfacial value;

e, final equilibrium value;

n, nth observation at time t_n;

o, initial observation.

INTRODUCTION

THE current theories of mass transfer, [1, 2, 3] when applied to the diffusion of a third component from one phase to another, lead to the concept of the resistance to transfer being made up of two individual resistances, one due to each phase. The individual resistances are additive to give the total resistance, but their use in rate calculations is limited to those cases where interfacial concentrations are known.

Generally speaking, film coefficients are only obtainable for two component systems, and rate

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calculations for multi-component systems are usually performed using overall driving forces and overall mass-transfer coefficients. The present paper is an attempt to determine the two individual coefficients for the transfer of acetic acid from chloroform to water, using a stirred cell technique similar to that used by Lewis [4] and Mayers [5]. Experiments have been performed at a sufficiently low acid concentration for the mutual solubilities of the two solvents to remain virtually the same as in the acid free system. The process could therefore be considered as being that of the transfer of a solute from one completely immiscible phase to another.

THEORETICAL CONSIDERATIONS

Consider the transfer of a solute from phase Y to phase X across the X–Y interface. For the batch process the rates of transfer may be written as

$$N = -\frac{Y}{A}\frac{dy}{dt} = k_y(y - y_i)$$

$$= \frac{X}{A}\frac{dx}{dt} = k_x(x_i - x). \qquad (1)$$

The two transfer coefficients in this equation cannot be determined as the interfacial concentrations are not known.

A material balance on the diffusing solute gives

$$Y(y - y_e) = X(x_e - x). \qquad (2)$$

Defining M by the following equation,

$$M = (y_e - y_i)/(x_e - x_i). \qquad (3)$$

and eliminating x, x_i and x_e from (1), (2) and (3), it follows that

$$-\frac{Y}{A}\frac{dy}{dt} = \left(\frac{1 + M/L}{1 + M/K}\right)(y - y_e)k_y \qquad (4)$$

where $L = X/Y$ and $K = k_x/k_y$. By eliminating the terms in y between the same equations, the analogous equation in x can be derived.

Equations (1), (2) and (3) are shown graphically on the equilibrium diagram of Fig. 1. A_o, (x_o, y_o) and C, (x_e, y_e) are the initial and final (equilibrium) concentrations respectively, and
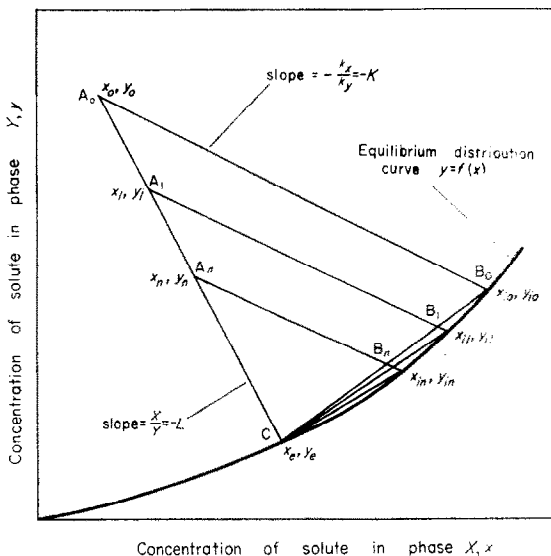

FIG. 1. Graphical illustration of the implications of the two film theory.

the points A_1 and A_n conditions at some intermediate times during the process. The instantaneous interfacial concentrations are related to the corresponding bulk values by (1) and provided that the ratio k_x/k_y is constant throughout the experiment, are located at points B_o to B_n on the equilibrium curve. As the bulk concentrations change from A_o to C during the process, so the interfacial concentrations move along the equilibrium curve from B_o to C. Thus, at equilibrium, the bulk and interfacial concentrations are equal.

The factor M defined above is the slope of the family of chords CB_n, and except for the case where the solute partition coefficient is constant and the equilibrium curve is therefore linear, M will vary throughout the experiment. It is on this variation in M that the determination of the individual film coefficients depends.

Integration of (4) leads to an exponential expression under two sets of conditions only.

(a) If M is constant, no matter what the values of L and K, integration between the limits of $y = y_n$ at $t = t_n$ and $y = y_{n+1}$ at $t = t_{n+1}$ gives

$$\frac{Y_n}{t_{n+1} - t_n} \cdot \ln\frac{y_n - y_e}{y_{n+1} - y_e} = \left(\frac{1 + M/L}{1 + M/K}\right)Ak_y \qquad (5)$$

where Y_n is the solvent content of the Y phase (moles), during the time interval t_n-t_{n+1}. Since $(1 + M/L)/(1 + M/K)$ is constant, (5) represents a truly exponential decay of the concentration y_n with time. k_y cannot be determined by measuring values of y_n at times t_n, as evaluation of the L.H.S. of (5) always yields the product of Ak_y and the indeterminate term $(1 + M/L)/(1 + M/K)$.

(b) If $L = K$, whatever the value of M, constant or otherwise, $(1 + M/L) = (1 + M/K)$ and integration between the same limits as above gives

$$\frac{Y_n}{t_{n+1} - t_n} \ln \frac{y_n - y_e}{y_{n+1} - y_e} = Ak_y \qquad (6)$$

which again represents an exponential decay.

Reference to Fig. 1 shows that when $L = K$ the operating line, A_oC, and the lines A_nB_n become coincident, so that the interfacial concentrations remain equal to the final bulk equilibrium concentrations throughout the process.

When L is equal to K, and M is not constant, the decay will no longer be strictly exponential, since under these conditions (4) cannot be integrated to either of the forms (5) or (6). It is on the ability to distinguish the actual decay of the concentration from the strictly exponential that the determination of the film coefficients depends, and accordingly these may only be obtained for systems of varying partition coefficient.

METHOD OF APPROACH

In theory there are two possible ways of determining the film coefficients, both involving the same experimental technique. Either the ratio X/Y giving rise to the strictly exponential decay of (6) may be determined by trial and error experimentally and the film coefficients calculated from (6), (Null method), or, from the results of a single experiment, the values of x_i and y_i corresponding to each of the measured bulk concentrations can be estimated from an equilibrium diagram, and (1) integrated graphically (Integration method).

(a) *The Null method*

From the results of a batch diffusion experiment at a given value of X/Y, the values of Ak_y are calculated from (6). These will only be constant when the correct ratio of X/Y leading to the exponential decay has been used. Experiments are therefore performed using different values of the X/Y ratio until a constant series of coefficients is obtained for Ak_y from (6). k_x may then be calculated from the equation in x analagous to (6), or from the relationship $X/Y = k_x/k_y$.

(b) *The Integration method*

Equation (1) may be rewritten as

$$Ak_y = \frac{Y_n}{t_{n+1} - t_n} \int_{y_{n+1}}^{y_n} \frac{dy}{y - y_i}. \qquad (7)$$

By plotting y_n against x_n on an equilibrium diagram, the operating line, (2) is obtained. The interfacial concentrations corresponding to each of the bulk conditions are now estimated from the diagram for a guessed value of K. This is shown in Fig. 1. Lines of slope $-K$ have been drawn through each of the points A_n in turn, and the interfacial values corresponding to each of these bulk concentrations located at points B_n on the equilibrium curve. Equation (7) is then integrated graphically by plotting $1/(y_n - y_{in})$ against y_n, and evaluating the areas enclosed by the curve and the ordinates y_{n-1} and y_n, and y_n and y_{n+1} etc. A series of values of Ak_y can then be calculated from (7), but these will only be constant if the correct values of the interfacial concentrations have been used in the integration. The procedure is now repeated using different values of K, a series of coefficients being calculated from (7) in each case. If the assumption of interfacial equilibrium is correct, this procedure should lead to a single constant series for Ak_y. The inconstant series obtained in all other cases will be referred to as the "integrated coefficients, C_{yn}". The coefficients calculated form the analagous equation in x will be designated C_{xn}.

That this method also depends on the variation of partition coefficient may be shown in the following way. If y_i is the true value of the interfacial concentration, and y_i^* is the value corresponding to a guessed value of $K = K^*$, then we may write

$$y - y_i = \left(\frac{1 - M/L}{1 - M/K}\right)(y - y_e)$$

and

$$y - y_i^* = \left(\frac{1 - M/L}{1 - M/K^*}\right)(y - y_e).$$

Thus if M is constant, substitution in (7) gives

$$Ak_y = \frac{1 + M/K}{1 + M/L} \cdot \frac{Y_n}{t_{n-1} - t_n} \cdot \int_{y_{n-1}}^{y_n} \frac{dy}{y - y_e}$$

and

$$C_{yn} = \frac{1 + M/K^*}{1 + M/L} \cdot \frac{Y_n}{t_{n-1} - t_n} \cdot \int_{y_{n-1}}^{y_n} \frac{dy}{y - y_e}$$

whence it follows that $C_{yn} = (1 + M/K^*)Ak_y/(1 + M/K)$. Thus when M is constant the integrated coefficient is always a constant unknown multiple of the true film coefficient. Analogous arguments apply to x.

CHOICE OF SYSTEM

The success of the methods depends on choosing a system exhibiting as large a variation in partition coefficient as possible. The chloroform–water–acetic acid system was chosen for the following reasons.

(1) No other common system exhibits partition coefficient variation to such a pronounced degree.

(2) The acid is readily determinable by titration.

(3) The low viscosity of both solvents makes for easy and efficient stirring.

(4) Below about 10 per cent w/w acid in either phase, the mutual solubilities of the two solvents remains almost the same as in the acid free system, so that the diffusion may be considered as being that of a solute between two completely immiscible phases.

Lewis [4] made measurements of the film coefficients for a number of two component systems using a stirred cell technique and showed that the film coefficient was dependent on conditions in both phases, being related to the Reynolds number of each phase, but Mayers [5] later showed that the transfer rate became independent of the fluid dynamics of the cell in the presence of certain surface active agents. By making the aqueous phase of the water–isopropanol benzene system 0·0001M with

respect to sodium lauryl sulphate (S.L.S.) the rate of transfer of the isopropanol from the water to the benzene was reduced to 20 per cent of its former value in the unadulterated system and became independent of the stirring rates. For this reason it was decided to add S.L.S. to the aqueous phase to produce conditions giving rise to constant transfer coefficients.

APPARATUS

Fig. 2 shows a labelled sketch of the apparatus, which consisted of a simple stirred cell similar to those used by the previous workers. Provision was made for the sampling of each phase through the base of the cell by means of stainless cannulae fitted through the holes A. The cannulae were sealed into the holes by means of neoprene washers, these being held in place by means of drilled brass plugs which screwed into the tapped portion of the holes. A further hole, B, was drilled and fitted with a stainless steel tube to allow for the injection of mercury to take the place of the chloroform sample removed and thus maintain the level of the interface constant. The stirrers were arranged to be contrarotating at 280 r.p.m. by means of a pulley belt system powered by a small electric motor. Apart from these points the cell and stirrers are self explanatory.

EXPERIMENTAL

The clean dry cell was mounted beneath the stirrers and connection made to the mercury reservoir. The sampling cannulae, fitted with small taps at their lower ends, were inserted into the cell and mercury was then run into the cell to a depth of about $\frac{1}{4}$ in. The required volume of Analar chloroform was run into the cell by means of a long funnel. By running more mercury into the cell the level of the chloroform was made to coincide with the bottom edge of the interface stabilizer. The previously decided upon volume of 0·0001M S.L.S. solution was then poured slowly down the funnel on to the top of the interface stabilizer, in this way avoiding the entrainment of one phase in the other.

Water at 25°C from a thermostat was circulated round the water jacket of the cell, the stirrers were started and the system allowed to stand for 2 h to allow the phases to reach thermal
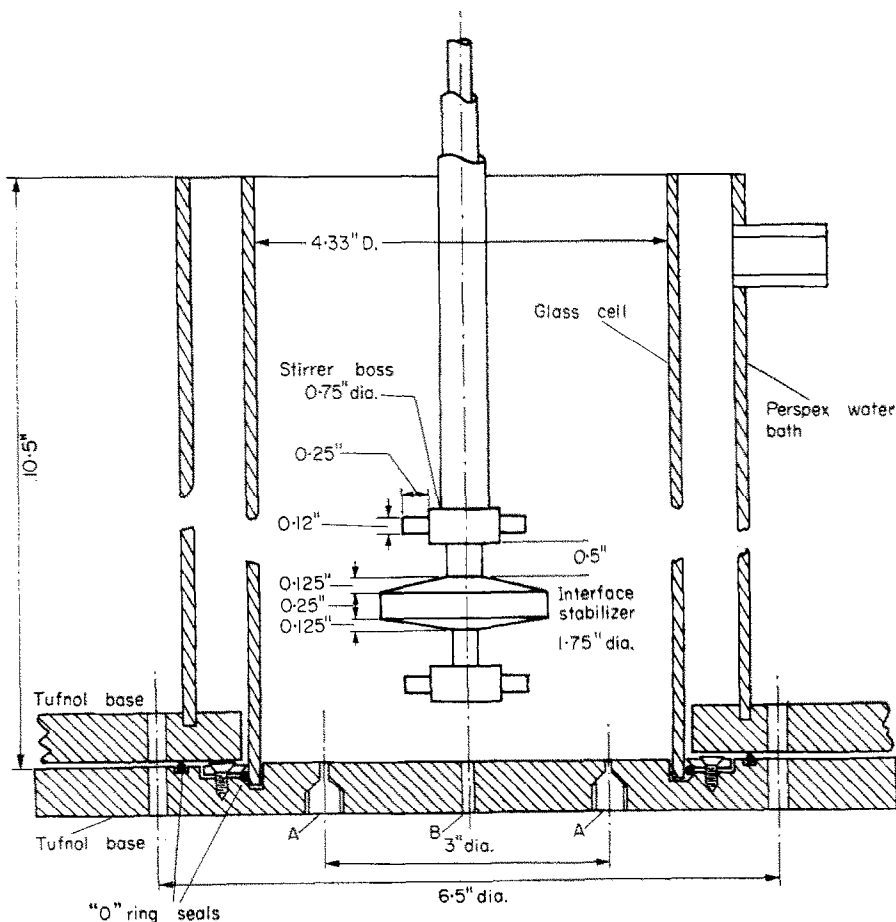
FIG. 2. The cell and stirrers.

equilibrium and become mutually saturated. The desired amount of acetic acid thermostated at 25°C was then added to the lower chloroform layer by means of a syringe. The level of the interface was adjusted to coincide with the centre of the vertical side of the interface stabilizer by running in more mercury.

Samples were withdrawn from each phase at suitable time intervals, the level of the interface being kept constant. The samples were analysed by potentiometric titration against barium hydroxide, the chloroform sample being titrated under water.

TREATMENT OF RESULTS

The experimental procedure outlined above yielded a series of values of the concentrations x_n and y_n at time t_n. Since the volumes of the samples removed were known, Y_n and X_n, the moles of solvent in each phase at times t_n could be calculated. These data are shown in Table 1, where the results of Run 4 have been chosen for the purposes of illustration. Equation (5) shows that the factor determining the nearness to the strictly exponential decay is $(1 + M/L)/(1 + M/K)$. A calculation was performed with the aid of a diagram similar to Fig. 1 to determine the maximum change which might be expected in the null coefficients. For the hypothetical case of $K = 0.5$ and $L = 1$, a situation well away from null conditions, it was found that the total variation in the null coefficients would be about 4 per cent. Since an error of 0.5 per cent in the acid concentration leads to

Table 1. Numerical illustration of the integration method—Run 4

t_n (min)	y_n	Y_n	$\dfrac{Y_n}{t_{n+1}-t_n}$	$y_{in}(K=1.5)$	$\dfrac{1}{y_n-y_{in}}$	$\displaystyle\int_{n-1}^{n}\dfrac{dy}{y_u-y_{in}}$	C_{yn}
0	0·07965	4·954		0·02450	18·13		
10	0·06220	4·837	0·4837	0·01876	23·02	0·3547	0·1716
20	0·04730	4·718	0·4718	0·01415	30·17	0·3938	0·1858
35	0·03095	4·598	0·3065	0·00923	46·04	0·6088	0·1866
55	0·01743	4·477	0·2239	0·00565	84·88	0·8274	0·1853
75	0·00998	4·355	0·2178	0·00390	164·47	0·8780	0·1912

t_n (min)	x_n	X_n	$\dfrac{X_n}{t_{n+1}-t_n}$	$x_{in}(K=1.5)$	$\dfrac{1}{x_{in}-x_n}$	$\displaystyle\int_{n}^{n+1}\dfrac{dx}{x_{in}-x_n}$	C_{xn}
0	0·00102	44·45		0·03775	27·23		
10	0·00296	43·31	4·331	0·03195	34·49	0·05911	0·2560
20	0·00452	42·22	4·222	0·02674	45·00	0·06152	0·2597
35	0·00622	41·12	2·741	0·02075	68·82	0·09271	0·2541
55	0·00762	40·03	2·002	0·01549	127·06	0·1305	0·2612
75	0·00842	38·95	1·948	0·01245	248·14	0·1380	0·2688

Table 2

$Y = 6·192$ moles, $X = 55·56$ moles, $V = 30$ ml

Run 1	Values of C_{yn}				
t(min)	$K=2.0$	$K=1.3$	$K=1.0$	$K=0.7$	$K=0.5$
0					
12	0·1538	0·1792	0·2025	0·2468	0·3121
20	0·1576	0·1828	0·2056	0·2496	0·3123
35	0·1551	0·1817	0·2045	0·2456	0·3056
55	0·1630	0·1865	0·2065	0·2496	0·3019
85	0·1605	0·1877	0·2084	0·2424	0·2913
D	3.39×10^{-3}	3.13×10^{-3}	1.97×10^{-3}	2.70×10^{-3}	7.75×10^{-4}

Run 1	Values of C_{xn}				
t(min)	$K=2.0$	$K=1.3$	$K=1.0$	$K=0.7$	$K=0.5$
0					
12	0·2884		0·1907	0·1633	0·1481
20	0·2883	not	0·1880	0·1581	0·1411
35	0·3032	evaluated	0·1948	0·1653	0·1458
55	0·3054		0·1943	0·1622	0·1413
85	0·3016		0·1827	0·1516	0·1307
D	7.47×10^{-3}		4.46×10^{-3}	5.37×10^{-3}	5.98×10^{-3}

Run 2	Values of C_{yn}				
t(min)	$K=2.0$	$K=1.38$	$K=1.0$	$K=0.7$	$K=0.6$
0					
10	0·1393	0·1642	0·1899	0·2248	0·2654
20	0·1573	0·1815	0·2063	0·2502	0·3019
35	0·1586	0·1813	0·2114	0·2417	0·2877
55	0·1639	0·1856	0·2107	0·2419	0·2880
75	0·1668	0·1877	0·2073	0·2434	0·2790
D	9.59×10^{-3}	8.27×10^{-3}	7.85×10^{-3}	8.39×10^{-3}	12.01×10^{-3}

Table 2.—continued

Run 2 t(min)	$K = 2\cdot0$	$K = 1\cdot38$	Values of C_{xn} $K = 1\cdot0$	$K = 0\cdot7$	$K = 0\cdot6$
0					
10	0·3163		0·2101	0·1801	0·1609
20	0·3004	not	0·1967	0·1674	0·1491
35	0·3113	evaluated	0·1999	0·1682	0·1485
55	0·3104		0·1974	0·1639	0·1432
75	0·3214		0·1990	0·1637	0·1393
D	$6\cdot99 \times 10^{-3}$		$4\cdot87 \times 10^{-3}$	$6\cdot0 \times 10^{-3}$	$7\cdot30 \times 10^{-3}$

Run 3 t(min)	$K = 2\cdot0$	$K = 1\cdot0$	Values of C_{yn} $K = 0\cdot7$	$K = 0\cdot5$	$K = 0\cdot3$
0					
10	0·1576	0·2033	0·2507	0·3380	
20	0·1681	0·2128	0·2607	0·3266	not
35	0·1689	0·2119	0·2575	0·3171	evaluated
55	0·1734	0·2138	0·2555	0·3163	
75	0·1755	0·2101	0·2484	0·2935	
D	$6\cdot19 \times 10^{-3}$	$3\cdot74 \times 10^{-3}$	$4\cdot47 \times 10^{-3}$	$14\cdot68 \times 10^{-3}$	

Run 3 t(min)	$K = 2\cdot0$	$K = 1\cdot0$	Values of C_{xn} $K = 0\cdot7$	$K = 0\cdot5$	$K = 0\cdot3$
0					
10	0·2876	0·2073	0·1772	0·1591	0·1408
20	0·3039	0·2150	0·1822	0·1616	0·1428
35	0·2926	0·2034	0·1717	0·1496	0·1312
55	0·2870	0·1979	0·1649	0·1431	0·1239
75	0·2979	0·1962	0·1619	0·1395	0·1173
D	$6\cdot40 \times 10^{-3}$	$6\cdot79 \times 10^{-3}$	$7\cdot52 \times 10^{-3}$	$8\cdot65 \times 10^{-3}$	$9\cdot73 \times 10^{-3}$

$$Y = 4\cdot954 \text{ moles}, \quad X = 44\cdot45 \text{ moles}, \quad V = 25 \text{ ml}$$

Run 4 t(min)	$K = 2\cdot0$	$K = 1\cdot0$	Values of C_{yn} $K = 0\cdot7$	$K = 0\cdot5$
0				
10	0·1552	0·2052	0·2508	0·3200
20	0·1681	0·2199	0·2667	0·3344
35	0·1694	0·2186	0·2618	0·3260
55	0·1715	0·2162	0·2579	0·3168
75	0·1776	0·2217	0·2546	0·3051
D	$9\cdot75 \times 10^{-3}$	$5\cdot84 \times 10^{-3}$	$5\cdot91 \times 10^{-3}$	$6\cdot35 \times 10^{-3}$

Run 4 t(min)	$K = 2\cdot0$	$K = 1\cdot0$	Values of C_{xn} $K = 0\cdot7$	$K = 0\cdot5$
0				
10	0·2808	0·2072	0·1793	0·1582
20	0·3112	0·2048	0·1751	0·1564
35	0·3126	0·2002	0·1691	0·1484
55	0·3204	0·2018	0·1683	0·1454
75	0·3363	0·2047	0·1662	0·1430
D	$18\cdot08 \times 10^{-3}$	$2\cdot46 \times 10^{-3}$	$4\cdot86 \times 10^{-3}$	$6\cdot01 \times 10^{-3}$

an uncertainty of about 5 per cent in the null coefficient this method was thought to be unsuitable. This was borne out by experiment, and the method was not pursued further.

The values of x_n and y_n were plotted on an equilibrium diagram similar to Fig. 1 and the values of x_{in} and y_{in} corresponding to a guessed value of $K = 1.5$ were obtained from the diagram as explained earlier. Values of the integral in equation (7) are tabulated in column 7 of Table 1 and the various C_{yn} and C_{xn}, obtained as the product of the data in columns 4 and 7 reported in the end column.

This trial and error procedure was then repeated for various values of K, and the results of these calculations together with similar calculations performed for Runs 1, 2 and 3 are shown in Table 2. Runs 1, 2 and 3 were identical having been carried out using 500 ml of chloroform, 1000 ml of 0·0001M S.L.S. solution and 30 ml of acetic acid. The integrated coefficients show the behaviour predicted by the theory, for at large values of K the coefficients increase with time, but as K decreases, the magnitude of the increase with time also diminishes, until at some value of K between 0·7 and 1·0 the coefficients show a decrease with time. At values of K less than 0·7 this decrease becomes more pronounced.

All the results show some degree of scatter due to experimental errors and inaccuracies introduced in the graphical integrations, but the agreement between the various coefficients calculated for each run at the same value of K is reasonable.

Run 4 was performed using 800 ml of S.L.S. solution and 400 ml of chloroform. The results of this run indicate that the coefficients are independent of volume.

Calculation of the film coefficients now depends on the selection of the values of K giving rise to the most constant series of integrated coefficients. For each run the root mean square deviation, D, of the integrated coefficients at each value of K have been calculated. These values have been plotted against $\log K$ (to avoid crowding of the points) in Figs. 3 and 4. This procedure assumes that the errors superimposed on the integrated coefficients are the same as in any experiment, so that D_{min} should occur at the value of K giving rise to the most constant
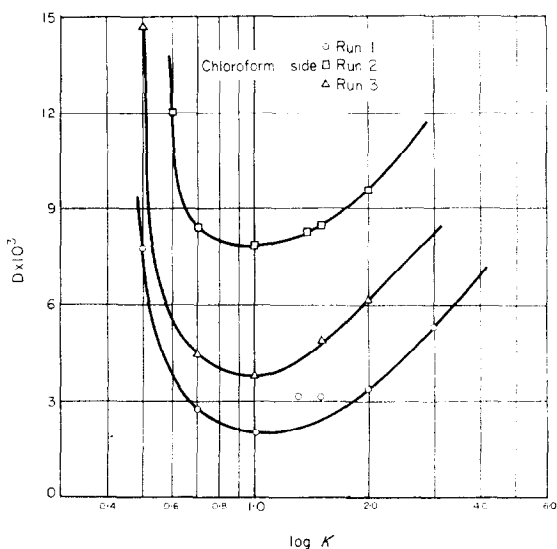

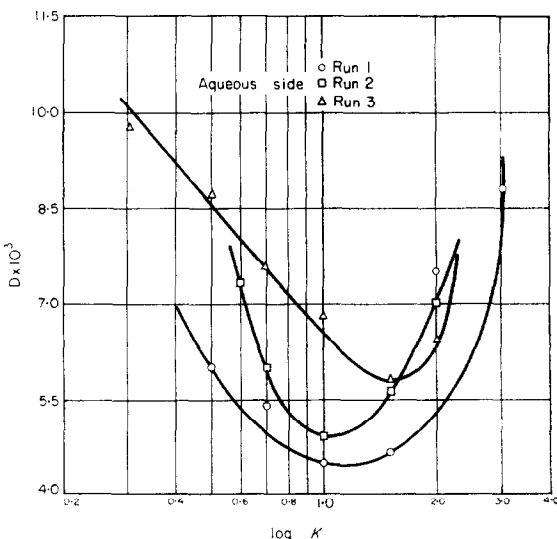FIG. 3. Selection of the optimum value for K-chloroform side.

FIG. 4. Selection of the optimum value for K-aqueous side.

set of coefficients. This value of D_{min} will then be a measure of the total error of the method.

The results of the chloroform phase are shown in Fig. 3 and indicate that the minimum deviation occurs at $K = 1$. The results based on the aqueous phase confirm this with one exception (Fig. 4).

CALCULATION OF THE FILM COEFFICIENTS

The average value of C_{yn} at $K = 1 \cdot 0$ is $0 \cdot 206$ for Run 1 and for this case $C_{yn} = A k_y$.

Cell interfacial area $= 79 \cdot 5$ cm².

Hence $k = 4 \cdot 3 \times 10^{-5}$ mole/cm²/s.

Similarly, $k_x = 4 \cdot 0 \times 10^{-5}$ mole/cm²/s.

The film coefficients for each run are summarized in Table 3. It should be noted that in

Table 3

Run 1	k_y	$4 \cdot 3 \times 10^{-5}$
	k_x	$4 \cdot 0 \times 10^{-5}$
Run 2	k_y	$4 \cdot 6 \times 10^{-5}$
	k_x	$4 \cdot 2 \times 10^{-5}$
Run 3	k_y	$4 \cdot 4 \times 10^{-5}$
	k_x	$4 \cdot 3 \times 10^{-5}$
Run 4	k_y	$4 \cdot 5 \times 10^{-5}$
	k_x	$4 \cdot 3 \times 10^{-5}$

averaging the values of C_{yn} and C_{xn} for Run 2, the first value has in each case been omitted as it disagrees greatly with the others.

Since $K = 1$ has been taken as the correct ratio of the film coefficients, all the results in Table 3 should be identical. Taking the mean as the best estimate of the film coefficients gives:

$$k_x = k_y = 4 \cdot 3 \pm 0 \cdot 6 \times 10^{-5} \text{ mole/cm}^2/\text{s}.$$

That the value $K = 1$ is not the precise ratio of the coefficients is demonstrated by the fact that k_x and k_y in Table 3 are not exactly equal, for in general, $k_y = 1 \cdot 06 k_x$. However the value of K required to accommodate this discrepancy cannot be distinguished from unity within the limits of the method and accordingly coefficients have been evaluated at this value of K.

The main sources of error in the experimental and calculation procedures are:

(a) in the measurement of the acid concentrations. Determination of the acid concentration by titration was performed with considerable accuracy and even in the most dilute solutions the error was not more than 0·5 per cent.

(b) In the measurement of the solvent content of each phase. Since a small volume of each phase was used to purge the cannulae before withdrawing the measured sample for analysis, it was estimated that the solvent content of either phase was not known to better than about ±2 per cent towards the end of an experiment.

(c) In the location of the curve and then subsequently in the determination of the areas under the curve when performing the graphical integration. The error here is unlikely to be more than 2·5 per cent even when allowance has been made for the inaccuracies in the concentrations.

Cumulatively, these errors lead, in the worst case, to an uncertainty of not more than 15 per cent in the film coefficients and accordingly, these have been reported to this degree of accuracy in Table 3.

CONCLUSIONS

A method has been proposed whereby the individual film coefficients of mass transfer can be determined for the transfer of a third component from one immiscible liquid phase to another. The feasibility of the method has been demonstrated by determining the two film coefficients for the transfer of acetic acid from chloroform to water.

The success of the method is dependent upon the two following conditions.

(a) There must be considerable variation of the solute partition coefficient with concentration, since use of the method depends upon the non-linearity of the solute equilibrium distribution curve—the greater the curvature, the better.

(b) Since the process has been considered as being that of the distribution of a solute between two completely immiscible solvents, it is essential that the presence of the solute does not appreciably affect the mutual solubility of the two solvents over the range of concentration being considered.

Both these conditions must be satisfied by the chosen system.

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Résumé—On examine la théorie du transfert en discontinu d'un soluté d'une phase à une autre non miscible. Dans les systèmes à coefficient de partage constant, on montre que les variations de la concentration du soluté (croissants dans une phase, décroissantes dans l'autre) sont exponentielles dans toutes les conditions. Quand le coefficient de partage varie, la décroissance de la concentration du soluté n'est exponentielle que dans le cas où le rapport molaire des deux solvants purs est égal au rapport des coefficients individuels de transfert interfaciaux.

On propose deux méthodes pour évaluer les coefficients de transfert interfaciaux pour de tels systèmes. La première n'est applicable que si les mesures de concentration peuvent être faites avec une très grande précision. La seconde méthode, qui consiste à intégrer graphiquement l'équation de transfert, conduit à une détermination correcte des deux coefficients.

Zusammenfassung—Die Theorie eines chargenweisen Transportes eines gelösten Stoffes von einer unmischbaren Phase in eine andere wurde untersucht. Bei Systemen konstanter Verteilungskoeffizienten zeigt sich, dass der Abfall der Konzentration des gelösten Stoffes in der einen Phase und die entsprechende Zunahme in der anderen unter allen Bedingungen exponentiell verlaufen. Für Systeme veränderlicher Verteilungskoeffizienten verläuft diese Abnahme nur exponentiell, wenn das Molverhältnis der beiden reinen Lösungsmittel gleich dem Verhältnis der einzelnen Filmkoeffizienten ist.

Zur Berechnung der Filmkoeffizienten solcher Systeme werden zwei Methoden vorgeschlagen. Die erste Methode ist nur mit äusserst genauen Konzentrationsmessungen durchführbar. Die zweite Methode ermöglicht mit einem grafischen Iterationsverfahren für die Austauschgleichung die Bestimmung der beiden Koeffizienten.

Аннотация—Рассмотрена теория вопроса периодического переноса растворенного вещества из одной несмешивающейся фазы в другую. Показано, что для систем с постоянным коэффициентом распределения уменьшение концентрации растворенного вещества в одной фазе и увеличение ее в другой происходит при всех условиях по экспоненциальному закону. Для систем с изменяющимся коэффициентом распределения это уменьшение происходит по экспоненте в тех случаях, когда молярное отношение двух чистых растворенных веществ равно отношению их пленочных коэффициентов.

Предложены два метода вычисления пленочных коэффициентов для таких систем. Первый метод осуществим на практике только в случае, если измерения концентраций выполнены с большой точностью. Второй метод, включающий графическое решение уравнения скорости переноса, дает возможность успешно определить эти два коэффициента.