

Measurement of Liquid-Liquid Interfacial Kinetics

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I. Introduction

Liquid-liquid interfacial kinetics has become an increasingly important subject over the last 15 years. Researchers from diverse fields such as nuclear engineering, hydrometallurgy, pharmaceutical chemistry, and biotechnology have realized the need to better understand interfacial mass transfer. Investigations of



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different systems have proliferated in the literature, and several authors have proposed general reaction schemes or models. In spite of the wealth of information which has been generated, there is still no general agreement on the mechanisms and the rate-determining role of interfacial reactions or on the experimental technique

most suitable to measure them. In this review, we will summarize the different measurement techniques which have been applied. The emphasis will be on the theory and application of the techniques rather than a detailed discussion of interfacial reaction mechanisms for different systems.

There are two distinct types of systems which are industrially important. The simplest system involves transfer of a mutually soluble solute from the oil phase to the aqueous phase or vice versa. These systems typically appear in biological applications such as drug transfer across a lipid membrane. Carboxylic acid transfer is another example of the "purely diffusive" systems. The second type of system is more complex. The solute is typically soluble only in the aqueous phase, and transfer to the oil phase is accomplished by an oil-soluble complexing agent. Metal-ion transfer is the most typical example of an "interfacial reaction" system. A hybrid of these two systems can occur if a complexing agent is present when a mutually soluble species is being transferred. An example of this process would be carboxylic acid transfer with an amine carrier present.

There are several problems with true interfacial kinetics measurement. In all real processes, the total mass-transfer rate is determined not only by the interfacial kinetics, but also by diffusion of the reactant to the interface and diffusion of the products away from the interface. In some cases, the process may be diffusion-limited and in others, kinetically limited. The most complicated situations arise when a system operates in a regime in which both diffusion and kinetics affect the transport rate. It is essential, therefore, to develop a measurement technique which can measure kinetics free from the influence of diffusion. Typically, the apparatus is designed to operate either in a kinetically limited regime, or to allow calculation of the diffusional component of the overall mass-transfer rate. The second problem is contamination of the interface by impurities which are more surface-active than the solute or the complexing agent. Special care must be exercised to insure that all equipment and reagents are free from any potential contaminants. Cleanliness is a particular problem when studies are done using complexing agents "as received" from the manufacturer. Accurate determination of the interfacial area is an additional problem. Direct liquid contact methods often have slightly rippled interfaces, and methods using membranes must account for the pore structure in calculating the contact area.

In this review, we will summarize the measurement techniques which have been applied to various interfacial systems. We will give special attention to the hydrodynamics and diffusional problems associated with each system. We will also review the available techniques for interfacial concentration measurement. Some attempts have been made to develop general models for equilibrium data and interfacial-reaction kinetics, and we will summarize these efforts.

Finally, where is interfacial-kinetics research heading? What advances can be made in understanding diffusion, interfacial kinetics, and surface contamination? Can a better measurement method for hydrodynamics and interfacial area be developed? Do existing models adequately describe interfacial transfer on a macro- and

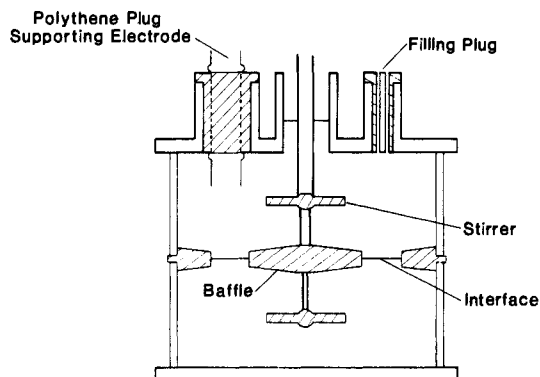


Figure 1. Original contacting cell developed by Lewis. Reprinted with permission from: Lewis, J. B. *Chem. Eng. Sci.* 1954, 3, 218-259. Copyright 1954 Pergamon Press.

microscale? We will examine these questions as we summarize the review. Although this review does not begin with literature from a certain year forward, most of the research has been published since 1975.

II. The Stirred Cell

A. History and Development

1. Invention by Lewis

Lewis^{1,2} was the first to recognize the need for better interfacial measurement systems and proposed an apparatus to address the problems. The Lewis cell apparatus provided direct liquid-liquid contact with a well-defined interfacial area and agitation of both phases without breakup of the interface. Figure 1 is a diagram of the original Lewis cell. The cell was completely full of liquid to prevent vortexing at the upper surface. The baffles were placed at the center to eliminate vortexing and at the edges to eliminate wall effects. The baffles were beveled to allow droplets of the opposite phase which were accidentally entrained to roll to the interface. Interfacial transfer took place in the annular region. The upper and lower phases were stirred in the same direction and at the same rate. The degree of interfacial turbulence varied from system to system, but the interfacial region generally remained flat.

Although the Lewis cell was a considerable step forward, the hydrodynamics were still poorly defined. Stirring the upper and lower phases at the same rates produced different Reynolds numbers (see Appendix) in each compartment. If the convective transfer in each compartment is different due to density or viscosity differences, then the diffusional contributions are different on each side. The design of the cell did not permit efficient stirring of the fluid near the interface, so large diffusion films were present in the cell. Lewis used a film-theory approach² coupled with a laborious graphical technique to evaluate the interfacial rate constants. Since Lewis first presented the design of his transfer cell, two significant modifications have greatly improved its utility.

2. Modifications To Improve Performance

The first major set of modifications was made by Nitsch and Hillekamp.³ The Nitsch cell is shown in Figure 2. The screens situated on either side of the interface are the most important addition to the Lewis

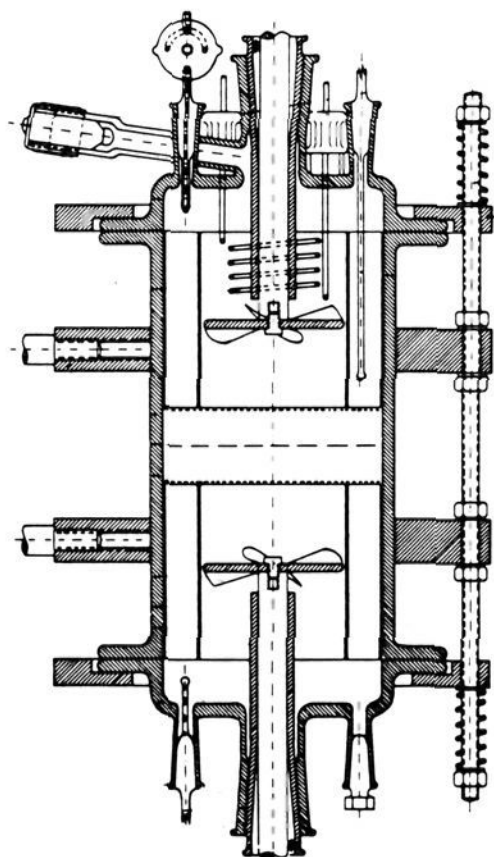


Figure 2. Contacting cell developed by Nitsch. Reprinted with permission from: Nitsch, W.; Kahni, G. *Ger. Chem. Eng. Engl. Trans.* 1980, 3, 96-103. Copyright 1980 VCH.

cell. Each phase was stirred separately and in the opposite direction, and the stirring rates were adjusted so that the Reynolds number in each phase was equal. The geometry of the system allowed a high degree of turbulence within each phase but maintained a quiescent interface. In previous Lewis cells, the stirrer blades were very low-pitch to avoid breakup at the interface. The low-pitch blades were not as efficient for bulk mixing as the higher-pitch which can be used with the Nitsch cell. Nitsch⁴ recently summarized some of the problems associated with studying interfacial kinetics for liquid-liquid systems. He then discussed this type of stirred cell and recommended calibration measurements to insure that stirred cells were operating in the proper regime.

A second major modification was made by Danesi et al.⁵ The ARMOLLEX (Argonne Modified Lewis cell for Liquid-liquid Extraction, Figure 3) was designed to accomplish efficient interfacial contact without requiring large volumes or intermittent sampling. The Nitsch cell has a capacity of approximately 1 L, but the ARMOLLEX requires only 100 mL. The ARMOLLEX allowed continuous sample analysis by incorporating a flow loop. The flow loop also eliminated problems associated with volume change due to sampling during a run.

An alternative mixing design for the stirred cell was demonstrated by Stowe and Shaiewitz⁶ who used rotating discs on each side of the interface instead of stirring paddles. They solved the equation of motion for flow far from the disc to characterize the flow field at the interface. They presented their data in terms of calculated vs. observed Sherwood numbers (see Appendix), and direct comparison to other studies is difficult. They recently reported some solubilization studies using this device,⁷ but the general utility of this contacting scheme has not yet been determined.

The mathematical analysis by Stowe and Shaiewitz⁶ is somewhat similar to that used for the rotating diffusion cell (section III). A simplified velocity profile

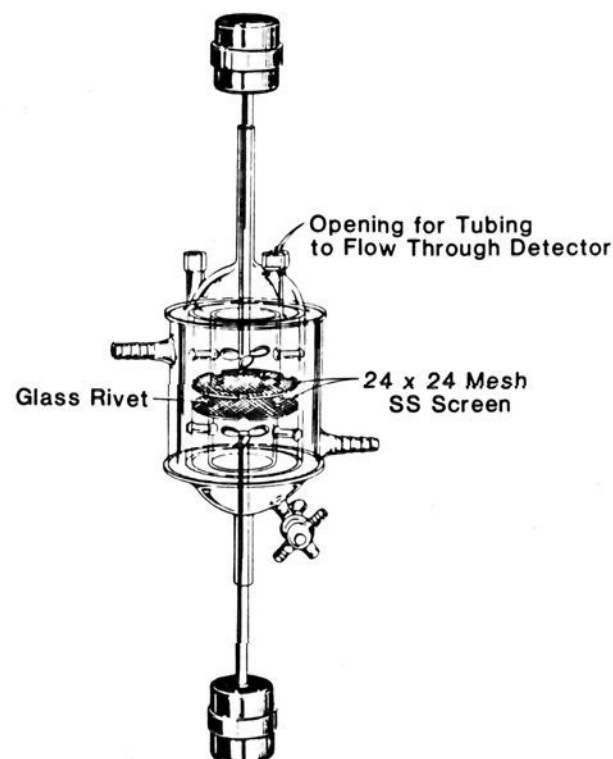


Figure 3. ARMOLLEX contacting cell. Reprinted with permission from: Danesi, P. R.; Cianetti, C.; Horowitz, E. P.; Diamond, H. *Sep. Sci. Technol.* 1982, 17 (7), 961-968. Copyright 1982 Marcel Dekker.

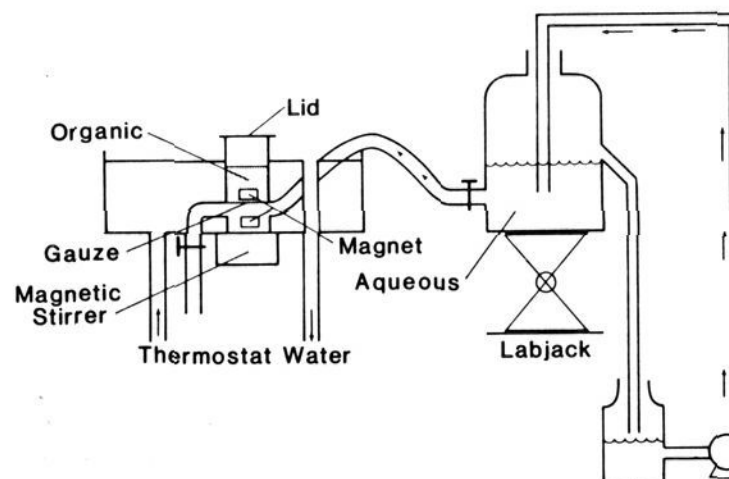


Figure 4. Gauze cell developed by Bhaduri et al. Reprinted with permission from: Bhaduri, M.; Hanson, C.; Hughes, M. A.; Whewell, R. J. *Int. Solvent Extr. Conf. [Proc.]* 1983, 293-294. Copyright 1983 International Solvent Extraction Conference.

based on a finite disc size arises from assuming a concentration boundary layer thickness which is much smaller than the hydrodynamic boundary layer thickness. The ratio of the disc diameter to the disc-interface distance and the disc to cell diameter ratio are important parameters in the calculations. Stowe and Shaiewitz calculated an interfacial resistance on each side of the interface and related it to the Sherwood number, but made no mention of any interfacial reaction.

Other investigators have used Lewis cells of different types,⁸⁻¹² but all the devices are either similar to Lewis's original model¹ or the Nitsch³ or Danesi⁵ modified types.

B. Other Contacting Cells

Bhaduri et al.,¹³ modified the conventional concept of the Lewis cell and produced the gauze cell (Figure 4). The cell was designed to provide kinetic data which would be more relevant to industrial process conditions, but comparative data for industrial contactors was not presented in the original publication. The cylindrical contacting chamber had a platinum gauze, which was approximately 40% porous, positioned at the interface. A magnetic stirrer rested on the gauze in the organic

phase and a second stirrer was located in the aqueous phase. The aqueous phase flowed through the cell from a large feed tank which kept the aqueous concentration nearly uniform during experiments. Although the authors suggested that the stirring of the interface by the upper magnetic bar eliminated any diffusional contributions to the measured rate, it is almost certain that boundary layers and/or stagnant films were present in and around the gauze. As with most of the stirred cells, the rate data were obtained in the plateau region of the rate vs. stirring speed curve.

1. The Kreevoy Contactor

Ulrick et al.,¹⁴ reported a modified dialysis cell which was patterned after a design by Brandlein.¹⁵ The cell consisted of a sandwich made up of a membrane between two static mixers and two silicone rubber gaskets. The static mixers promoted good contact of the aqueous phase with the membrane. An organic layer was contained in the pores of the membrane, and aqueous phases were pumped through the static mixers of each side of the cell.

The resistances of boundary layer diffusion, membrane diffusion, and interfacial reaction combined to produce the total resistance to mass transfer. The analysis of the transfer data was similar to that of the rotating diffusion cell (see section III), but the hydrodynamic contributions to the total rate of transfer did not have a theoretical basis. By measuring the mass-transfer coefficient under various conditions, the authors separated the resistances to mass transfer. The system they studied, however, did not show any appreciable interfacial reaction contribution. Therefore, the utility of this cell for interfacial kinetics measurement has not yet been demonstrated.

2. Highly Agitated Contactors

The AKUFVE apparatus has been reviewed previously^{16,17} and will only be summarized here. The name derives from a Swedish acronym which translates to "apparatus for continuous investigation of distribution factors in solvent extraction". As the name implies, the primary capability of the apparatus is to measure distribution coefficients. The system consisted of a highly agitated mixing chamber with supporting equipment to provide for rapid, continuous measurement of distribution coefficients. Because of the highly agitated contactor, the surface area for interfacial reactions was not known. The applicability of the method for determination of rates of reaction is therefore quite limited.

Carter and Freiser¹⁸ developed a highly stirred contacting cell for interfacial kinetics measurement. Two phases were intimately mixed at 5,000–20,000 rpm and samples were periodically withdrawn. The device was later automated,¹⁹ which removed errors introduced by sampling. Although many metal extraction systems were studied with this cell, the interfacial area was unknown and not necessarily reproducible. These discrepancies were generally discounted²⁰ by assuming that extraction reactions were not interfacial, but occurred in the aqueous phase. More recent publications by Watarai and Freiser²¹ and Freiser et al.,²² indicated that more attention needs to be focused on the role of the interface. The data obtained from this cell cannot

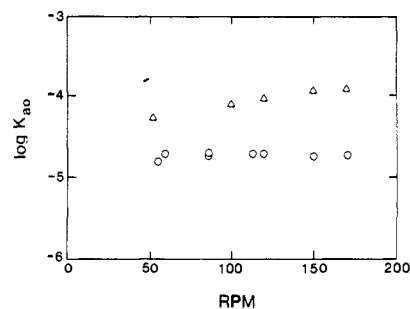


Figure 5. Typical plot of rate of mass transfer as a function of stirring speed in a stirred cell (ARMOLLEX). The plateau region extends over the entire range of stirring speeds. Reprinted with permission from: Danesi, P. R.; Cianetti, C. *Sep. Sci. Technol.* 1982, 17 (7), 969–984. Copyright 1980 Marcel Dekker.

be compared with cells which operate with known interfacial area.

C. Hydrodynamics and Diffusion

One of the goals of all interfacial kinetics measurements is to effectively separate the contributions of kinetics from those of diffusion. The stirred-cell approach to kinetics measurement relies on minimizing the contribution of diffusion to the overall transfer rate. The improvements in stirring the individual phases without breaking up the interface have extended the range and effectiveness of the stirred-cell approach. In practice, the rate of transfer between phases is measured as a function of stirring speed. A typical plot is given in Figure 5. The beginning of the "plateau region" indicates the transition between mass transfer limited by diffusion and mass transfer limited by chemical reaction. As the stirring rate is increased, the boundary layer thickness on each side of the interface decreases. If the mass-transfer rate is independent of the boundary layer thickness, then the process must be in a kinetically limited regime. Consequently, all stirred-cell data is collected at stirring rates in the "plateau region." The order of reaction and the rate constants are determined by varying the concentrations and other conditions, but the stirring rate must be maintained so that the data are collected in the "plateau region." The effects of diffusion are not eliminated (in a pure sense) but minimized and assumed to be negligible.

The stirred-cell technique is limited when fast-reaction kinetics are encountered because a plateau region is not obtained. That is, as the boundary layer thickness decreases from increased agitation, the mass-transfer rate continues to increase. If the transport rate is a linear function of stirring rate, then the process is completely limited by diffusion to the interface. If the transport rate is a nonlinear function of stirring rate, then diffusion and interfacial kinetics are both influencing the transport process.

Although one could argue that fast kinetics are not as important to measure because they do not generally limit the process with which they are associated, it is probably more realistic to acknowledge that the stirred-cell technique is only adequate for slower reaction rates. An alternative approach would be to try to measure or calculate the contribution from diffusion. Because the phases are in turbulent flow in a geometry which is not usually well defined, the calculation of the boundary layer thickness is very difficult. We are not aware of any empirical approaches to correlating the

concentration boundary layer thickness in stirred cells to measurable system parameters.

Danesi et al.,²³ pointed out a major problem which can arise when diffusional contributions cannot be accurately determined. They showed that diffusion combined with a simple one-step interfacial reaction can mimic an interfacial reaction which has two consecutive steps. Therefore, it is not always sufficient to minimize diffusion without an independent determination of the diffusion effect. Hughes and Rod²⁴ demonstrated that if a reaction occurs in the aqueous film, transport could be limited by diffusion and reaction but a plateau region would still be observed. Therefore, investigators must exercise caution in interpreting the plateau region for each system.

D. Summary of Systems Studied

Hydrometallurgy has been the primary emphasis of workers using the stirred-cell method. Danesi and Chiarizia²⁵ studied extraction of iron, europium, cerium, thulium, and gadolinium by dinonylnaphthalenesulfonic acid. Danesi et al.,²⁶ reported rate constants and proposed mechanisms for reaction of cupric and ferric ions with a β -hydroxy oxime. Danesi and Cianetti²⁷ studied extraction rates of europium with bis(ethylhexyl)-phosphate and Danesi et al.,²⁸ reported equilibrium constants for the same reaction. In a broader study, Cianetti and Danesi²⁹ examined extraction kinetics of nickel, iron, cobalt, zinc, americium, and europium with various organophosphorous extractants. Nitsch and van Schoor³⁰ studied the coextraction of uranyl nitrate and nitric acid by tributyl phosphate. In a slightly different application, Kondo et al.,⁸ used a stirred cell to study uptake of copper by an emulsion liquid membrane system with a benzoylacetone carrier.

Nitsch and Kruis³¹ used the zinc-dithizone system to evaluate the effects of flow and concentration on reaction mechanism. Nitsch and Roth³² also used the zinc-dithizone system to study the effect of adsorbed layers on mass-transfer rates. Nitsch and Sillah³³ studied complex formation at the interface for the dithizone complexes of cadmium, cobalt, and zinc.

The stirred cell has also been used for studying kinetics of nonmetals. McManamey et al.³¹ studied the transport of helium from water to *n*-butyl alcohol or toluene. Shanbag¹⁰ investigated protein diffusion between mutually insoluble aqueous phases with a slow-stirred Lewis cell. Byron et al.¹¹ used a similar cell to study barbiturate transfer into 1-octanol. Asai et al.⁹ collected data on thirty systems including transport of iodine, caproic acid, oxygen, and hydrogen into different solvents. They developed a general Sherwood number correlation for all the systems. Fyles et al.³⁵ studied complexation rates of potassium ions with crown ethers. The potassium chloride/water/*n*-butyl alcohol system has been used to determine if hydrodynamics or kinetics was a rate-limiting step,^{36,37} retardation of transfer by polymers¹² and effects of adsorption of macromolecules.

III. The Rotating Diffusion Cell

A. History and Development

1. Development from the Rotating Disc Electrode

The rotating-disc electrode has been used by electrochemists for many years, and the method has been

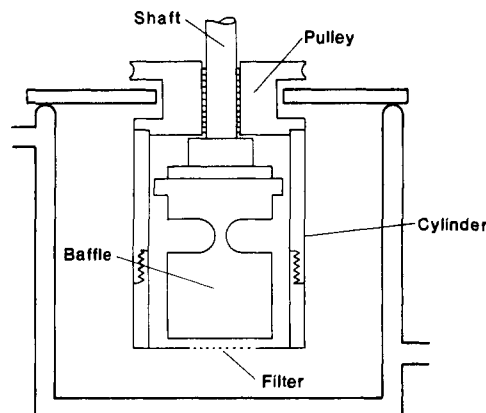


Figure 6. The rotating diffusion cell. Reprinted with permission from: Albery, W. J.; Burke, J. F.; Leffler, E. B.; Hadgraft, J. J. *Chem. Soc., Faraday Trans 1* 1976, 72 (7), 1618-1626. Copyright 1976 Royal Society of Chemistry.

thoroughly reviewed.³⁹ The rotating disc creates a laminar flow field which can be completely described mathematically. Von Karman⁴⁰ solved the original rotating-disc problem with an approximate solution. His solution was improved by Cochran,⁴¹ and then Levich⁴² obtained a solution for the diffusion boundary layer thickness as a function of rotational speed, kinematic viscosity, and diffusivity. Although studies involving electrochemical reactions at the disc surface have been conducted, the rotating-disc system was not applied to interfacial mass transfer until recently.

Following the successful adaptation of a Stokes diffusion cell for interfacial kinetics measurement,⁴³ Albery et al.⁴⁴ created the rotating-diffusion cell (RDC) and successfully combined the hydrodynamics of the rotating disc with interfacial mass transfer. A diagram of the RDC is given in Figure 6. A thin membrane attached to a hollow cylinder was rotated which created rotating-disc hydrodynamics on both sides of the filter. The interface was created on either side of the filter depending on the procedure and solutions used. Mass transfer occurred from the inner chamber, through the membrane, and into the outer chamber. The RDC can therefore be considered a type of immobilized liquid membrane cell with known hydrodynamics.

2. Theory of Operation

Several detailed accounts of rotating-disc hydrodynamics and diffusion are already available,^{39,42,45} so the results will be summarized here with a brief discussion on aspects which are subject to disagreement of interpretation. The Navier-Stokes equations for flow up to the surface of a rotating disc can be reduced and solved to give the velocity profiles. The momentum boundary layer thickness was determined by Levich⁴² at the point where v_r (radial) and v_ϕ (tangential) had reached 95% of their bulk value and v_y (axial) had reached 80% of its bulk value.

Once the velocity profiles are known, the diffusion problem can be formulated. If the concentration is only a function of distance from the disc and not a function of r or ϕ , then the convective-diffusion equation reduces to

$$v_y \frac{dc}{dy} = D \frac{d^2c}{dy^2} \quad (1)$$

Equation 1 also ignores any edge effects which may be

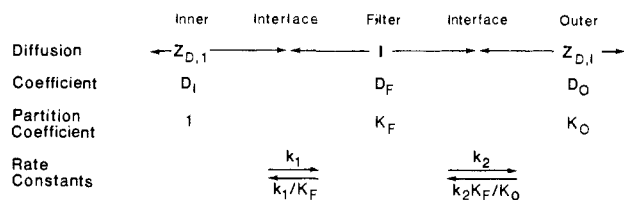


Figure 7. Resistance to mass transfer for the rotating diffusion cell system.

present. If only the first term in the expansion of velocity normal to the disc is considered, a Γ -function solution is obtained for the mass flux to the disc. Once the flux has been calculated, an equation describing the diffusional boundary layer thickness in the absence of chemical reaction can be developed. This result can be summarized as

$$Z_D = 0.643W^{-1/2}D^{1/3}\nu^{1/6} \quad (2)$$

The above equation is typically referred to as the Levich equation, where Z_D is the diffusive boundary layer thickness, W is the rotational speed of the disc in Hz, ν is the kinematic viscosity (cm^2/s), and D is the diffusivity of the species (cm^2/s). Gregory and Riddiford⁴⁶ have shown that a small correction is required to account for the error introduced by truncating the velocity expression to the first term. The correction is based on the Schmidt number (Sc , see Appendix) and alters the diffusive boundary layer thickness by about 3% for normal liquid systems. Newman⁴⁷ has solved the boundary layer thickness problem analytically by expanding the exponential term which appears in the integrand. He tabulates values for Levich's equation, for Gregory and Riddiford's graphical correction,⁴⁶ and for the analytical solution and compares them to a numerical solution. The analytical form matches the numerical solution to within 0.1%. The Levich equation incorporating the Newman solution is given by

$$Z_D = 0.643W^{-1/2}D^{1/3}\nu^{1/6}(1 + 0.2980Sc^{-1/3} + 0.14514Sc^{-2/3}) \quad (3)$$

A typical Schmidt number for liquid systems is 2000 which means the boundary layer thickness deviates by 2.5% from the Levich solution. All the investigations with the RDC have used Levich's original eq 2, presumably because the correction is relatively small.

In the rotating diffusion cell, the overall mass transfer can encounter up to five resistances in series (see Figure 7). On each side of the membrane, there is a diffusive boundary layer and an interfacial reaction. In addition to these resistances, the species must also diffuse through the liquid held in the membrane. The overall transfer rate will depend on all these resistances if the cell is set up in "sandwich" form with aqueous solutions on each side of the membrane and an organic liquid in the membrane. One of the interfacial reaction terms can be eliminated if the cell is set up with only two phases present rather than the "sandwich" configuration. If the solutions in the inner and outer chambers are identical, then the diffusive boundary layer contributions on each side are equal. If the reactions occurring on each side of the membrane are the same, then the kinetic contributions are equal. The exact mathematical formulation for the resistances depends on the system being studied. For example, consider the transfer to solute from an inner aqueous phase, through

an organic phase entrapped in the membrane, and into the outer aqueous phase. Assuming first-order kinetics at the interface, the overall mass-transfer coefficient can be expressed as

$$\frac{1}{\bar{k}} = \frac{2Z_{D,a}}{D_a} + \frac{2}{ak_{-1}} + \frac{lK}{aD_o} \quad (4)$$

where \bar{k} is the overall mass-transfer coefficient, Z_D is the aqueous boundary layer thickness, D is the diffusivity (subscript a for aqueous and o for organic), a is a factor representing the effective area of the membrane, k_{-1} is the rate constant for transfer from aqueous to organic; l is the path length through the pores of the membrane and K is the distribution coefficient (C_{aq}/C_{org}). From eq 4, the inverse mass transfer coefficient is proportional to the boundary layer thickness. From eq 2, the boundary layer thickness is proportional to rotational speed to the negative $1/2$ power. Experimentally, the inverse mass transfer coefficient is plotted against the rotational speed to the negative $1/2$ power which results in a straight line when the rotational speed is between approximately 50 and 500 rpm. Extrapolation of the line to infinite rotational speed ($w^{-1/2} = 0$) eliminates the boundary layer contribution to mass transfer. The resulting intercept is the mass-transfer coefficient representing diffusion through the membrane and interfacial reaction. The contribution from diffusion through the membrane is then calculated and subtracted from the mass-transfer coefficient which leaves only the contribution from the interfacial kinetics.

The above discussion points out one obvious difficulty with the RDC. The diffusion through the membrane and the area of the membrane available for reaction must be well characterized. Typically, manufacturers' values for pore-size distributions and available area have been used without verification for each membrane, although Albery and Fisk⁴⁸ reported a more detailed technique for analyzing the effective membrane area. The thickness of the membrane also determines the sensitivity of the technique to fast reactions. If diffusion through the membrane represents a large fraction of the resistance to mass transfer, then the inferred kinetics will be derived from the difference of two large numbers, which amplifies the potential for error.

The hydrodynamic considerations pose an additional difficulty in interpreting results obtained with the RDC. The inner chamber is baffled to promote rotating-disc hydrodynamics, but no studies have shown conclusively that the flow inside the cylinder is the same as flow outside the cylinder. Corrections for small membranes and edge effects are also possible contributors to errors in measurement. Smyrl and Newman⁴⁹ calculated the edge effect due to radial diffusion for large Schmidt numbers. They used a singular perturbation technique to determine a correction to the Levich result (eq 2). The radial position at which edge effects are no longer important can be determined using a "stretched" coordinate which is related to the difference between the radial position and the cylinder radius. To be free from influence, the radius of the active membrane area in the RDC must be smaller than the onset radius for radial diffusion effects.

Millsaps and Pohlhausen⁵⁰ solved the analogous problem of heat transfer from a rotating disc in laminar

flow conditions. They accounted for radial velocity effects and demonstrated the effect on the hydrodynamic boundary layer. They then calculated the radial and axial temperature variations. Their results are difficult to extrapolate to large Schmidt number conditions typically found in mass-transfer applications.

3. Alternative Designs

Most other investigators⁵¹⁻⁵³ have used RDC's which are nearly identical with the one reported by Albery et al.⁴⁴ Huang et al.⁵⁴ constructed a "spinning liquid disc" and made flux measurements as a function of Reynolds number. The liquid was contained in a cylindrical chamber with a membrane on the end, which was exposed to the other fluid. The resistances to mass transfer are the same for the liquid disc system and the RDC, and the data from the liquid disc produced conclusions similar to those which could be drawn from the RDC. Stowe and Shaewitz⁵ conducted experiments in a cell which resembles a Lewis cell, but the propeller stirrers were replaced with rotating discs. The results are summarized in section II.

B. Diffusion-Coefficient Measurement

The rotating diffusion cell has been used to estimate or measure diffusion coefficients in two different ways. Guy and Fleming⁵¹ estimated aqueous diffusion coefficients for methyl and ethyl nicotinate from the slope of the Levich plot (k^{-1} vs. $W^{-1/2}$). Equations 2 and 4 can be combined to show that the Levich plot has a slope of

$$\text{slope} = 1.286\nu^{1/6}D^{-2/3} \quad (5)$$

where ν is the kinematic viscosity in cm^2/s and D is the diffusivity in cm^2/s . The diffusion coefficient in the organic solution entrapped in the membrane pores is more difficult to measure directly without prior knowledge of the interfacial kinetics. The intercept which results from combination of eq 2 and 4 has terms which arise from kinetics and terms from diffusion through the pores of the membrane. Typically, the organic phase diffusion coefficient is obtained from another source.

Guy and Fleming⁵¹ calculated the kinetics for methyl nicotinate and then assumed that changes in the rate of transfer for different solvents in the membrane were due to changes in the organic phase diffusivity. They then estimated the diffusivity of methyl nicotinate in four other solvents. The method appears to work reasonably well if the organic solvents chosen are similar in their interaction with the solute. Comparative data were not available, so error limits could not be determined.

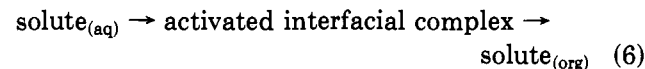
Guy and Fleming⁵⁵ presented an alternate method for diffusion-coefficient determination with the RDC. Their previous work used pseudo-steady-state fluxes to determine the diffusion coefficient. A transient method based on the lag-time between the initial contact of the donor phase with the membrane and the appearance of the solute in the receptor phase was used to compute the diffusivity of the solute in the organic phase in the membrane. The method is limited to cases where the interfacial reaction is fast compared to membrane diffusion and the times are on the order of 1000 s. Diffusion coefficients for methyl and ethyl nicotinate in

a phospholipid were reported. The results were presented as a range which covered an order of magnitude, which indicates that this method only produces estimates of diffusion coefficients.

Flynn et al.⁵⁶ reported interesting data on the effects of viscosity on diffusion coefficients and diffusional boundary layers in the RDC system. They measured solute-transfer rates for solutions whose viscosities were increased by addition of sucrose or by addition of small amounts of methylcellulose. The sucrose solutions varied from 5 to 60% sucrose, and the transfer rates showed that the diffusivity and the diffusion boundary layer thickness were altered significantly. When the viscosity was altered by addition of methylcellulose, the macroscopic viscosity (and consequently, the diffusion boundary layer thickness) increased as expected. The diffusivity, however, was largely unaffected because the microscopic viscosity was not changed significantly by the addition of the methylcellulose. The results indicate that adjustments for viscosity in the equations governing the RDC need to be carefully evaluated.

C. Determination of Thermodynamic Variables

If rate constants and partition coefficients are measured as functions of temperature, several interesting thermodynamic calculations can be made to yield free energies, enthalpies, and entropies associated with the interfacial transfer process. The partition coefficient yields thermodynamic properties which compare the state of the solute in the bulk aqueous and organic phases. If the kinetic mechanism follows the schematic pathway



then the rate constant can be used to determine thermodynamic properties for the activated complex. Comparison of the entropies, enthalpies, and free energies for the activated state can reveal information about the nature of the interfacial complex.

Albery et al.⁴⁴ reported thermodynamic properties for the systems they studied, and numerous other studies have added to the thermodynamic data for interfacial transfer.^{52,57-60} The most interesting result from the thermodynamic properties is probably the role of the entropic contribution to the interfacial complex. Large positive entropies are indicative of structural breakup at the interface (compared to the state where no solute is present), or of a much less ordered solvent sheath around the solute molecule. Large negative entropies are indicative of more order in the interfacial complex than the solute experienced in the bulk phase. (See section VII for an alternative interpretation of activated state thermodynamics.)

D. Diffusive vs. Reactive Systems

Until recently, all the systems investigated with the RDC could be classified as purely diffusive. The only reaction occurring at the interface is described by



Albery and Fisk⁴⁸ and Albery et al.⁶² reported an investigation of copper transfer studied with the RDC. Since the mechanism of an interfacial metal chelation is often complex and unknown, considerable effort is

required to modify the interfacial reaction contributions in the resistance model (see eq 4). Albery et al.⁶² developed a general model for copper transfer and determined the rate-limiting step and most probable reaction mechanism. Although the primary purpose of the study was to demonstrate the utility of the ring electrode in combination with the RDC, the investigation proved that a complex-chelation reaction could be addressed with the RDC.

E. Summary of Systems Studied

The majority of systems studied with the RDC involved either carboxylic acids or esters of nicotinic acid. Albery et al.⁴⁴ reported kinetic data for six different solutes in isopropyl myristate (IPM) or hexane. The solutes were acetic acid, hexanoic acid, *p*-methylbenzyl chloride, and methyl, *n*-butyl, and *n*-hexyl nicotinate. Salicylic acid kinetics were investigated in IPM⁵⁷ and in C₉–C₁₆ hydrocarbons.⁵⁸ Sagert et al.⁵² studied kinetics for five carboxylic acids in dodecane. The solutes were acetic, butanoic, 2-methylbutanoic, 2,2-dimethylpropanoic, and hexanoic acids. Sagert and Quinn⁶³ measured kinetics for di-*n*-butyl phosphate in dodecane.

Many studies have reported the kinetics of methyl or ethyl nicotinate under various experimental conditions. The nicotines are considered good representative systems for drug absorption in the human body. Guy and Fleming^{51,55} used IPM, tetradecane, linoleic acid, egg lecithin, and phospholipids as organic phases for nicotinate transfer measurements. In later studies, Guy et al.^{59,64} evaluated the effects of urea and PEG 400 on nicotinate transfer in IPM, nonane, dodecane, and pentadecane. The nicotinate kinetics in the C₉, C₁₂, and C₁₅ hydrocarbons were also reported by Guy,⁶⁰ and the temperature dependence of nicotinate systems was reported by Fleming et al.⁶¹

Other systems investigated with the RDC include transfer of KCl from *n*-butyl alcohol,⁶⁵ phenothiazine transfer with bile salts,⁶⁶ and phenothiazine transfer with different organic phases.⁶⁷ Amidon et al.⁵³ investigated progesterone transfer with micelles, and Flynn et al.⁵⁶ used the progesterone-transfer system to investigate the effects of viscosity on the boundary-layer thickness in the kinetic measurements.

Most systems mentioned to this point have not involved an interfacial complexation reaction. Until recently, the RDC had not been applied to hydrometallurgical systems where complexation reactions are more commonplace. Albery and Fisk⁴⁸ reported kinetic data for the forward and reverse extraction rates of cupric ion by the commercial oxime extractant Acorga P-50. In a subsequent publication, Albery et al.⁶² followed the reaction using a ring-disc electrode which was deposited on the surface of the rotating membrane, rather than the conventional approach of sampling the external phase at various time intervals. The flux was determined by measuring the current from the ring-disc electrode.

IV. Other Measurement Methods

A. Liquid-Jet Recycle Reactor

1. Theory of Operation

The liquid-jet recycle reactor (LJRR) was reported

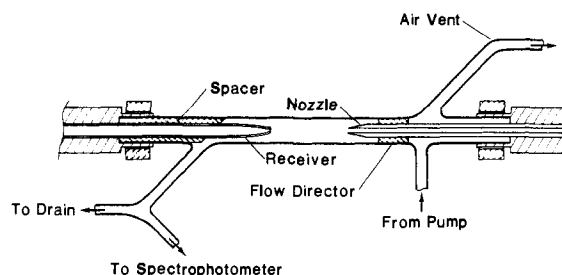


Figure 8. The inner portion of the Liquid-Jet Recycle Reactor. Reprinted with permission from: Freeman, R. W.; Tavlarides, L. L. *Chem. Eng. Sci.* 1980, 35, 559–566. Copyright 1980 Pergamon Press.

by Freeman and Tavlarides⁶⁸ and patented by Tavlarides et al.⁶⁹ The technique was proposed as a superior alternative for interfacial kinetics measurement because it allows direct liquid–liquid contact with known interfacial area and hydrodynamics. Figure 8 is a diagram of the jet system. An aqueous liquid jet flows downward through a cocurrent, coaxially flowing organic fluid. The contact time is short, and the organic phase is continuously recycled through a spectrophotometric loop.

The mathematical analysis of the LJRR is based on the following assumptions: isothermal operation; constant densities, viscosities, and diffusion coefficients; no ionization or homogeneous reaction; small penetration depth into the jet; negligible curvature and axial diffusion; steady state operation. By using penetration theory analysis, the solute flux can be expressed in terms of the system parameters and bulk phase concentrations.

The analysis is based on a fully relaxed jet; that is, the velocity profile does not change as a function of distance down the jet. For short jet lengths and large average jet velocities, Freeman and Tavlarides⁷⁰ note that the average surface velocity is less and the contact angle longer than that obtained by assuming a completely relaxed jet.

The LJRR suffers from several other drawbacks in addition to the problem of the fully relaxed jet. The apparatus is difficult to properly align and operate due to the sensitive nature of the jet and receiver. Surface active agents produce instabilities in the jet. Although this feature can detect surface impurities, it also renders the technique difficult to use for surface active complexing agents which may be present in the organic phase. The general applicability of the LJRR has not yet been proven, and the patent may make it difficult for other investigators to conveniently adopt this method.

2. Systems Studied

In their initial work, Freeman and Tavlarides⁶⁸ reported diffusivities for benzene and toluene in water. For systems with an interfacial reaction present, Freeman and Tavlarides^{70,71} modified the boundary conditions and used a numerical method to solve the resulting differential equations. They tested different interfacial reaction mechanisms for the extraction of copper, and found that several rate laws fit the data successfully. They concluded that more specific information, including surface adsorption of the complexing agent, was necessary before a more definitive reaction-rate expression could be formulated. Huang

and Freeman⁷² studied the effect of DC fields on copper extraction.

B. Single-Drop Method

Single-drop methods have been widely employed by chemical engineers to determine mass-transfer coefficients for solvent-extraction processes. Chemists have also used these methods but call the results solute-transfer kinetics. The experimental method (falling drop or rising drop) is straightforward enough to be implemented as a laboratory experiment for senior students. The analysis, unfortunately, is not as simple.

The methods for determining kinetics by single drops have been summarized recently¹⁷ and the details will not be repeated here. Drops of phase one are dropped or allowed to rise through phase two, and mass transfer can occur in either direction. Several assumptions are required for analysis.

(1) The change in concentration of the feed phase must be negligible.

(2) The drops must be spherical and uniform in size.

(3) The circulation pattern within the drops can be analyzed.

(4) Negligible mass transfer occurs during drop formation and in the stagnant pool of coalesced drops at the end of the column.

In practice, only assumption one can be routinely satisfied. The use of single-drop methods has particularly decreased because of problems with analyzing the circulation patterns in the drops (assumption 3).

Nitsch and Schuster⁷³ presented an experimental method designed to produce kinetic data applicable to liquid-liquid extraction columns. An array of capillaries at the bottom of the tank produced uniformly sized swarms of droplets which coalesced at the top of the tank on a teflon surface. Nitsch and Schuster applied single-drop analysis methods to this system to determine mass-transfer coefficients for the extraction of uranyl nitrate into dodecane. Although the method is still subject to the constraints imposed by single-drop techniques, the application appears to be useful for providing data which is directly applicable to industrial applications.

Bauer⁷⁴ developed a growing-drop method in which fresh interfacial area was constantly created. He studied copper extraction and stripping and produced a model which would predict rates of reaction for those systems. The mass-transfer process was analyzed using penetration theory. This method has not been widely applied.

C. Electrochemical Methods

1. Vibrating Capacitor

Kharkats et al.⁷⁵ studied charge transfer across an octane-water interface in a functioning enzyme-membrane system. During an enzyme reaction at an interface involving charge transfer, the initial potential changes due to the changes of the charge on the electric double layer. At steady state, the currents from forward and reverse charge transfer become equal and a new potential distribution is established. An experimental cell was constructed with an electrical configuration which can be described as gold/air/oil/water/salt bridge/reference. Vibrating the gold electrode changes

the capacitance between the gold and reference electrodes and produces a current. The voltage is measured by applying an external voltage to the capacitor until the current is driven to zero. The applied voltage is then equal and opposite to the voltage across the capacitor.

Kharkats et al.⁷⁵ studied proton transfer during the action of a mitochondrial enzyme absorbed at the interface. They related the reaction current to the rate constants and derived mechanistic information about the catalytic enzyme behavior. They also monitored electron transfer across the interface in the presence of chlorophyll. This method may have some utility in further application for biological systems and other systems involving charge transfer. The details of the experimental system were not described nor were error limits provided for the data.

2. Electrochemical Polarization Phenomena

Koryta⁷⁶ followed simple ion transfer across the interface of two immiscible-electrolyte solutions with cyclic voltammetry, chronopotentiometry, and polarography. No rate constants were evaluated because the transfer times corresponded with simple diffusion. Koryta also evaluated facilitated transfer of alkali metal ions but reported only that the transfer occurred rapidly. Although the application of analytical electrochemistry to interfacial transfer is a unique idea, the speed of the measurement system will have to increase significantly in order to prove useful for direct interfacial kinetics measurement.

D. Capillary Method

Guy et al.⁷⁷ recently presented a measurement method for solute-transfer kinetics based on the capillary tube procedure for self-diffusion. A small glass capillary is filled with a solution of radiolabeled solute and immersed in a large, well-stirred volume of the second phase. The concentration of radiolabeled solute in the second phase is monitored as a function of time. The unsteady-state diffusion equation for transfer from the capillary tube can be solved as long as the initial solute concentration in the second phase is zero. An analytical solution is possible for short contact times (typically 5–25 min). The contribution of diffusion to the interface is determined by the equation, so the transfer kinetics can be obtained from the data. The agreement between this method and the rotating-diffusion cell is good.

E. Falling-Film Reactor

Trouvé et al.⁷⁸ developed a falling liquid film apparatus which can be used to measure the overall transfer kinetics from the aqueous phase into an organic film. A film of organic (or emulsion) phase flows up a cylindrical teflon rod and the aqueous phase surrounds the assembly. The interfacial area was determined from the rod diameter, and the concentration in the aqueous phase was monitored as a function of time. The reactor is limited to systems where the organic film adheres to the rod, and ripples in the film during mass transfer must be avoided. The film velocity is a function of the density difference between the aqueous and organic phases. Trouvé et al.⁷⁸ studied the active transport of phosphate ions into an emulsion system. They devel-

oped a simplified model which gave good agreement with experiment for the overall kinetics and the carrier and surfactant concentration dependencies.

V. Interfacial Concentration Measurement

Interfacial-kinetics investigators must generally make some assumptions about the concentration(s) of the reacting species at the interface. Typically, the empirical rate laws for interfacial reactions are expressed as functions of the bulk concentrations. If the transfer process is truly interfacial, then the interfacial concentration determines the rate, and not necessarily the bulk concentration. There is usually a relationship between the bulk and interfacial concentrations, which is probably what allows rate laws to be expressed as functions of bulk concentrations. There is a great need to be able to measure the interfacial concentration directly. This could confirm or deny possible reaction pathways, reveal the extent of adsorption of a reactive species, and produce a rate law based on the interfacial concentrations. Although several good attempts have been made at direct measurement of interfacial concentrations, the available techniques are limited in accuracy and applicability.

A. Analytical Ultracentrifuge

Chandrasekhar and Hoelscher⁷⁹ used an analytical ultracentrifuge equipped with a Schlieren optical system to study interfacial transfer of acetic and propionic acids from water to toluene and water to *n*-butyl alcohol. The optical system measured refractive index gradients within 1 mm of the interfacial region. The concentration of solute varied linearly with refractive index, so the concentration of the diffusing species and the mass flux could be determined near the interface. The centrifuge was operated at about 7000 rpm, which produced enough compression to give a sharp interface but did not affect the diffusion process.

The optical patterns recorded during the experiments revealed a very interesting pattern. In the water-toluene systems, the solute concentration (and correspondingly, the mass flux) peaked at a distance of 0.25–0.4 mm from the interface. In the water-*n*-butyl alcohol system, however, the concentration and mass flux peaked at the interface. Although the data of Chandrasekhar and Hoelscher⁷⁹ suggest that the thickness of the interfacial region is on the order to 100 μm , the photographic resolution is certainly not capable of determining an interfacial thickness on the order of nanometers.

The modeling used by Chandrasekhar and Hoelscher⁷⁹ was called into question by Huang and Winnick,⁸⁰ and Chandrasekhar and Hoelscher⁸¹ rebutted some of the questions raised. Because no additional studies of this type were undertaken by Chandrasekhar and Hoelscher, it is not clear whether or not any of the modeling considerations raised by Huang and Winnick⁸⁰ were necessary for a better interpretation of the data. For these reasons, we have restricted our review and analysis to interpretation of the photographic data.

B. Schlieren Optics

Harada et al.⁸² used a Schlieren-optical device without the aid of an analytical centrifuge to investigate car-

boxylic acid transfer between water and benzene. Because the cell was not contained in a centrifuge, the meniscus produced a blind zone. They measured concentration profiles to within 0.1 mm of the interface for acetic, propionic, *n*-butyric, and valeric acid, and in every case, they observed the maximum concentration at the interface. The blind zone was not large enough to prohibit observation of the 0.25–0.4 mm zone reported by Chandrasekhar and Hoelscher.⁷⁹ Although the results from the two Schlieren-optical studies are in considerable disagreement, it appears that interfacial concentrations can be determined up to approximately 0.1 mm from the interface. We are somewhat surprised that no follow-up work has appeared since these 1975 studies.

C. Interferometry

Traher and Kirwan⁸³ presented a simple microinterferometric technique for interfacial concentration measurement during mass transfer. Drops of immiscible phases were contacted between two partially aluminized microscope slides to form an optical wedge. The interference fringe shifts were related to the solute concentrations through the index of refraction. Traher and Kirwan⁸³ claimed that the blind zone of this method was only 0.005 mm, which is substantially smaller than other methods. They reported data for acetone transfer between water and carbon tetrachloride. The technique is limited by the accuracy of the index of refraction/concentration relationship. Corrections to some of the conclusions were published by Bogue et al.⁸⁴

Thomas et al.⁸⁵ combined interferometry, new refractive-index-concentration correlations and a flowing-junction cell to measure interfacial concentrations in the acetic acid/carbon tetrachloride/water system. They claimed to be able to measure concentrations right up to the interface for both the organic and aqueous phases, but no error margins or physical limits of approach to the interface were reported. Rather than reporting the data as concentration profiles with respect to distance from the interface, interfacial concentration as a function of time was reported. Therefore, direct comparison with other investigations is difficult. The mass transfer predicted by the interferometric method was always in excellent agreement with calculated values. The technique cannot be used on the concave side of the meniscus or when interfacial disturbances are present.

D. ATR Spectroscopy

Trifonov et al.^{86,87} reported a technique for immobilizing a thin liquid film in a teflon membrane and attaching the membrane to an optical prism. The prism allowed them to measure the attenuated total reflection (ATR) spectrum during mass transfer. Through an elaborate mathematical analysis, they were able to determine the mass-transfer coefficient at the liquid-liquid interface. They did not report interfacial concentration, but they propose that the mass-transfer coefficient obtained from the 1–15- μm liquid film is representative of an interfacial-mass-transfer coefficient. Comparison with other work is extremely difficult due to the nature of the technique and the reporting of the results.

E. Scintillation Counting

Greger and Schugerl⁸⁸ reported a novel technique for measuring interfacial concentrations in a cylindrical two-phase flow channel. The measurement techniques discussed to this point have all focused on methods of concentration determination near the interface. All methods suffer from not being able to approach the interface within 10 μm . Because the interfacial thickness may be considerably smaller, and there may be substantial variations in the solute concentrations within the 100- μm region, alternative approaches are necessary. Greger and Schugerl⁸⁸ developed a cylindrical two-phase flow channel and determined the solutions of the Navier-Stokes equations for the system.

In this system, the aqueous phase contained boron or lithium salts which produced alpha particles when exposed to thermal neutrons. The organic phase contained scintillators which quenched the alpha rays after they penetrated only a few micrometers. Because the scintillators emitted light, the interfacial concentration of boron or lithium salts was determined by monitoring the emission from the organic phase. The bulk concentration was determined by other means, and the interfacial concentration was then calculated. Although this technique cannot be applied in many laboratories which are not equipped for nuclear reactions, we believe that this type of novel approach will greatly improve our understanding and ability to measure interfacial concentration.

VI. Modeling

In order to understand the basic physical and chemical processes occurring at the liquid-liquid interface, it is necessary to develop a mathematical description which accurately depicts the interfacial processes. The resulting model needs to be sufficiently detailed and free of empirical parameters so that the physical properties, kinetics, and operating conditions which affect the interface can be correctly identified and quantified.

A critical feature of any model is the ability to properly account for diffusional boundary layers adjacent to the interface. Danesi et al.²³ demonstrated that diffusional resistances in the boundary layers adjacent to the interface can mimic interfacial two-step consecutive reactions. If one cannot accurately separate the different contributions to transport across the interface, the proposed reaction mechanisms and corresponding coefficients will be in doubt.

An accurate and complete model needs to be based on experimentally measurable quantities. Use of quantities which are very difficult or impossible to independently measure would make the usefulness of any model very limited.

A. Models Based on Mass Action

Models based on mass action begin with the balanced stoichiometric equation for the reaction under study. The rate of the chemical reaction is then assumed to be proportional to the concentrations of the reactant raised to the powers equal to their coefficients in the balanced reaction. At equilibrium, the forward and reverse reaction rates are equal.

There are several difficulties with the mass-action approach. Nonidealities in either phase cause deviations which would require accurate activity measurements to correct. In addition, only the rate-limiting step in the reaction can be determined. Consequently, conclusions from mass-action models can be misleading. Despite these shortcomings, models for interfacial kinetics based on mass action are the most prevalent. Some examples of kinetic models based on mass-action principles include Hughes and Rod,⁸⁹ Nitsch and van Schoor,³⁰ and Kondo et al.⁸

B. Modeling

There have been various attempts to model the liquid-liquid interface by modeling the "interfacial resistance" to mass transfer. The interfacial resistance is associated with the interface itself and is separate from any diffusional resistance to mass transfer. Brenner and Leal⁹⁰ proposed a theoretical model based on two considerations.

(1) There exists a potential energy barrier which would require thermal energy of the solute to be removed. The forces associated with overcoming this barrier vary slowly enough that simple Fickian diffusion occurs in all directions.

(2) There is a hydrodynamic wall effect as the solute molecule approaches the interface which causes an increase in the solute diffusion coefficient.

Reconciliation of the micro- and macroscale theories for transport at the interface produces the concept of "interfacial resistance". Microscale theories are based on the size of a solute molecule, while the macroscale theories are based on the length associated with the bulk-concentration gradients. The interfacial resistance is computed from the potential energy functions associated with the interfacial region.

Shaeiwitz and Raterman⁹¹ expanded on the model of Brenner and Leal⁹⁰ by demonstrating that the rate constant formulation (similar in formulation to a first-order reaction) used to explain large interfacial resistances corresponds to two energy maxima at the interface. Shaeiwitz and Raterman⁹¹ also showed that the rate constant formulation corresponds to local equilibrium immediately across the interface in certain limiting cases. Local equilibrium at the interface is a common assumption in many treatments of liquid-liquid mass transfer. They calculated the energy profiles in the vicinity of the interface and determined the interfacial resistance for dilute solutes from the calculated energy profiles. In the absence of a single repulsive potential energy barrier, the calculated profiles for the dilute solute and rate constant formulation show the same shape. Shaeiwitz and Raterman⁹¹ stated that the absence of a single repulsive barrier is the reason why large clean interfaces do not possess large interfacial resistances. They also postulated that large interfacial resistances can occur when a surface-adsorbed film is present.

Shimbashi and Shiba⁹²⁻⁹⁴ considered the case of interfacial absorption of a carboxylic acid during mass transfer. They combined experiments on the butyric acid-benzene-water system with theory to show that the concentrations on opposite sides of the interface were not at equilibrium and that the steady-state adsorption of solute at the interface could be accounted

for mathematically. In a later study, Shimbashi⁹⁵ modified the model to allow the amount of adsorption to change during the mass-transfer process. The boundary conditions for the interface can therefore be modified to account for the adsorption which occurs.

Guy et al.⁵⁹ modeled the transport across the interface based on a rate constant formulation. They assumed that the solute transport can be described as a first-order reaction. The rate constant was then related to the thermodynamics of the interfacial complex (see section III).

Hughes and Rod⁸⁹ proposed a model of the interface in which reactions took place in a zone rather than at a fixed plane. Agreement between experimental and predicted results was good for initial rate experiments and experiments near steady-state.

C. Equilibrium Data Modeling

Forrest and Hughes⁹⁶ discussed the various models for equilibrium data in the liquid-liquid extraction of metals. They indicated that the models fell into three general categories.

(1) Chemically based models which seek to model the data on the basis of known extraction chemistry. Thermodynamic rigor can be employed if activity data is available. (Activity data is not normally available and is difficult to obtain.)

(2) Semiempirical models based on analogies with gas absorption and vapor-liquid equilibrium.

(3) Totally empirical models based on generalized mathematical expressions such as polynomials.

The chemically based models can be used with some confidence to extrapolate data beyond the experimental region. Empirical models can often give better accuracy within the experimentally defined region and do not require as detailed a chemical study, but they cannot be used to extrapolate data and they provide no fundamental insight into the reaction mechanisms occurring at the interface. Forrest and Hughes⁹⁶ discussed a large number of models and the average error associated with each one for the systems studied.

In a separate publication, Forrest and Hughes⁹⁷ discussed models for copper chelation. They determined that a polynomial (empirical fit) gave the best fit, and a semiempirical model was only slightly worse. This result suggests that the proposed reaction mechanisms could be in error (since the data fit was not very good), but the effects of impurities on experimental data could also be responsible for the disagreement.

Based on their previous surveys, Whewell and Hughes⁹⁸ went on to develop an improved chemically based model for copper chelation. The average error between the model and the data was as low as 7%. The revised model incorporated aggregation of the complexing agent, but their experimental data still deviated from theory, particularly at high concentrations of the chelating agent. Again, the effects of impurities may be responsible for some of the disagreement between theory and experiment. Also, the measurement methods used do not produce data which is completely free from error.

D. Models Using Statistical Methods

One method to determine the kinetic rate expression for an interfacial reaction is to use statistical analysis

to accept or reject certain proposed reaction mechanisms or models. Freeman and Tavlarides⁷⁰ used statistical methods to develop an expression for copper chelation kinetics. They proposed various possible models based on different combinations of diffusion, absorption/desorption, and rate-limiting reaction steps at the interface. They collected data and tested the validity of each model with an F ratio between the experimental variance and the regression variance. The F test can determine the statistical-significance level of a model.

The results of Freeman and Tavlarides⁷⁰ indicated that several mechanisms all successfully modeled the copper extraction process. Therefore, postulating a mechanism solely on its ability to fit the data is not necessarily an acceptable approach. They suggested that rate data can be used to reject specific rate models if the model has a low confidence level in the F-ratio test.

E. Empirical Models

The simplest expression for the interfacial reaction rate expression is an empirical fit. By fitting a model to experimental data, one can get an expression which will provide reasonable agreement within the range of the experimental data.

There are two main problems with empirical fits. First, it is impossible to determine their accuracy outside the range of data supplied. Second, they provide little or no information on the basic phenomena underlying the interfacial reaction process. Examples of this approach can be found in Freeman and Tavlarides⁷⁰ and Forrest and Hughes.⁹⁶

VII. Areas of Continuing Research

In order to advance our understanding of interfacial kinetics for liquid-liquid systems, several areas of research will have to be developed. The definition of the liquid-liquid interface (mathematical or physical) is still the subject of some debate. Some researchers believe the thickness of the interfacial region is on the order of 1 nm, which could allow the interface to be defined (mathematically) as a phase boundary. The transition between phases would occur on the order of tens of molecules. Other researchers assert that an interfacial reaction zone exists on the order of 1 μm .⁸⁹ In the reaction zone concept, "interfacial" reactions are really occurring in a bulk region which has properties that are different from either of the individual phases. A resolution of these divergent views is essential in order to move forward with our knowledge of interfacial reaction mechanisms.

A second critical area of research is the role and the accurate determination of boundary layers adjacent to the interface. The experimental methods which are presently in use do not allow for a detailed analysis of the boundary layers. The rotating diffusion cell does allow a comparison between theoretical and observed boundary layer thickness, but the device is not designed to study the role of the boundary layer per se. In order to perform this research, it will be necessary to use a measurement method which has well-characterized hydrodynamics and an interfacial area which remains constant (these requirements are usually satisfied only

in laminar-flow conditions).

Accurate determination of the effect of impurities absorbed at the interface is crucial to measurement of interfacial kinetics. In addition, the role of surfactants needs to be clarified and refined. Most studies on this subject have centered on retardation of kinetics by absorbed layers. More fundamental work on the mechanism of retardation (or enhancement) by surface active agents needs to be performed.

A confusion exists in the literature for systems we have described as "purely diffusive" or "solute-transfer". Chemical engineers have traditionally approached solute-transfer systems empirically using a mass-transfer coefficient k . The flux of solute from phase 1 to phase 2 is typically given by

$$J = k\Delta C \quad (8)$$

where J is the flux, (mass per unit area per time) and ΔC is the concentration driving force. Equation 8 models the transfer process as diffusion across the interface, but the mass transfer coefficient k often includes diffusive boundary layer effects and can be considered a lumped parameter. The flux (or transfer rate) is first order in concentration and also depends on the available area.

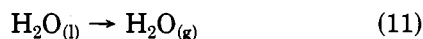
Chemists, on the other hand, have often treated these systems as chemical reactions. Typically, the reaction is written



where the rate of transfer at the interface is given by

$$\text{rate} = k_1[A]_{(aq)} - k_{-1}[A]_{(org)} \quad (10)$$

The total transfer rate must also include contributions from diffusion on each side of the interface. The free energy changes associated with eq 9 are typically small (<10 kJ/mol) and there is no reaction per se; that is, A is still A after the "reaction" has occurred. Equation 9 is really describing a phase change, and although we might write the phase change for water going from liquid to gas as



it would not be appropriate to discuss rate constants for the "reaction" in eq 11. The rate at which eq 11 proceeds is highly dependent on environment, which prompted engineers to use lumped coefficients rather than an approach from first principles. It appears, however, that when all environmental factors (such as diffusion) are stripped away from systems described by eq 9 that an energy barrier exists for solute transfer which can be described by standard chemical kinetics. This energy barrier to transfer has been called "interfacial resistance" or solute-transfer kinetics.

Some systems do not have interfacial resistance, such as acetone transfer from water to carbon tetrachloride,⁸⁴ but carboxylic acids and their esters exhibit interfacial resistance.^{44,52} Although chemical kinetics describes what takes place macroscopically in solute transfer, the chemical reaction which occurs is not yet well defined.

A solute molecule crossing the interfacial region must undergo a transition from an aqueous environment to an organic environment (or vice versa), but is an oversimplification to model this process as a first-order chemical reaction. Many investigators (see section III)

TABLE I. Solute Transfer Data for Organic to Aqueous Systems

acid	solvent	ΔG^\ominus , kJ/mol	k , m/Ms	ΔG^\ddagger , kJ/mol	ref
acetic	IPM	-8.0	7.2	41.0	44
acetic	dodecane	-9.3	3.8	42.4	52
butanoic	dodecane	-2.6	2.6	43.3	52
C ₅	dodecane	0.74	4.0	42.2	52
C ₅	dodecane	2.8	3.8	42.4	52
hexanoic	dodecane	4.3	2.9	41.8	52
hexanoic	dodecane	6.0	4.6	43.0	44
salicylic	IPM	8.0	3.1	43.0	57

have applied activated-state thermodynamics to solute transfer, which assumes that one activated state at the interface is responsible for the limiting rate and the associated energetics of transfer. Again, at a molecular level, it does not seem reasonable to associate one particular activated state with the transfer process. Table I is a collection of solute transfer data at 25 °C for a variety of carboxylic acids and solvents.

In Table I, ΔG^\ominus is the free energy from the partition coefficient, k is the rate constant for the transfer from organic to aqueous, and ΔG^\ddagger is the free energy of activation which corresponds to the rate constant. The unusual feature of the data is the similarity of the free energies of activation. For a large range of acids and solvents, the energies of activation are nearly equal.

Within the interfacial region, the density, the viscosity, and the molecular environment must change rapidly. A species diffusing through this environment will also undergo rapid changes in its sphere of solvation. The diffusion process through the interfacial region will not be adequately described by bulk-phase diffusion theory. The water molecules at the interface will exhibit a structure which is different from the bulk-water structure because of the influence of the nonpolar solvent molecules. A diffusing solute must "puncture" this ordered layer to penetrate into the bulk aqueous phase. The energetics of this disruption may be partially responsible for the observed interfacial resistance. A diffusional model could account for these macroscopic effects and possibly provide more insight as to what properties of each phase affect the interfacial resistance.

Although kinetics describes solute transfer on a macroscopic scale, a better microscopic model could be developed. Diffusion through the interfacial region is an alternative model for the solute-transfer process. Comparing the two models, the energy barriers which have been observed and assigned to "kinetics" arise from the diffusion through the interfacial region, and the temperature dependence of the "rate constants" is the temperature dependence of the diffusional process. Therefore, the discussion of enthalpies, entropies, and free energies of activation does not necessarily represent what is occurring in the interfacial region but is only a mathematical description of the temperature dependence of the diffusion process. This is clearly an area which requires a great deal of additional discussion and research.

VIII. Conclusions

We have summarized the literature on interfacial kinetics measurement for liquid-liquid systems. Although a great deal of research has been performed,

there are still many unanswered questions. Many of the discrepancies between measurements and philosophies have arisen because of the diverse backgrounds of the investigators. Interfacial kinetics has emerged as its own field in recent years, but most of the experienced researchers have approached the problem with their specific application in mind (as opposed to evaluating the general problem of liquid-liquid interfacial kinetics). The 1984 Faraday Society conference on interfacial kinetics (Royal Society of Chemistry, Faraday Discussion No. 77, "Interfacial Kinetics in Solution", University of Hull, Hull, England, April 1984) was a major step forward in approaching the problem of interfacial-kinetics measurement from an objective perspective. We would like to suggest several major needs in interfacial-kinetics research which should be addressed in the next decade.

At present, there are no generally established criteria for proper interfacial-kinetics measurement. The important criteria such as hydrodynamics, surface cleanliness, contribution of diffusion, purity of reagents, accuracy of accompanying physical properties, and surface area need to be defined and detailed so that all investigators can accept them. Once accepted, researchers should make every effort to abide by the criteria so that all research will be on the same basis.

There are many methods presently in use to measure kinetics, but all of the methods have various drawbacks. The modified Lewis cells cannot account for diffusion, the rotating-diffusion cell requires characterization of a membrane, and the liquid-jet recycle reactor is not suitable for strongly surface-active species. A new method is needed which can allow direct liquid-liquid contact and account for the contributions of diffusion. This device would also need to meet the criteria defined in the previous paragraph.

New analytical techniques such as Fourier-transform IR spectroscopy or ellipsometry coupled with absorption spectra need to be creatively applied to interfacial kinetics. We need to understand what takes place at the interface on a more fundamental level, and methods like these may be the next step toward gaining a better molecular picture of the interface. It would also be very beneficial if the vast knowledge gained by studying monomolecular layers on liquids could be extended to the two-phase systems where mass transfer is occurring.

An integrated approach combining experiments with modeling could answer some of the questions raised in section VIII. A general model based on first principles is not currently available. The role of surface active agents, boundary layers, interfacial resistance, and the reaction zone could all be addressed by good models.

Industrially, interfacial-reaction systems have been treated successfully with empirical methods and mass-transfer coefficients for many years. The emergence of biotechnology and economic fine tuning of other processes have increased the need for fundamental information about interfacial transfer. The current methods have been fairly successful at determining reaction orders, but interfacial rate constants have not been measured accurately enough to allow process designers to depend on their magnitudes. Industry can benefit from an increased "data base" which would include rate data and fundamentals of how interfacial transfer works and how to measure it. As

investigators from various fields address the fundamental problems common to all interfacial kinetic systems, our knowledge of these systems will begin to increase rapidly.

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Appendix on Dimensionless Numbers

Engineers have used dimensionless numbers for at least 100 years. These numbers arise in problems of scale where it is advantageous to analyze a small prototype model and project the results to a full scale system. Model airplanes in wind tunnels are an example of scale problems.

Dimensionless numbers are formulated so that their numerical value has physical significance regardless of the system in which it is determined. The numbers (or groups) are often related to ratios of forces or other physical phenomena. A large or small number is therefore indicative of which set of forces is dominant in a particular situation.

There are three dimensionless numbers which arise in the discussions in this review: Reynolds number (Re), Schmidt number (Sc), and Sherwood number (Sh). The Reynolds number is defined as

$$Re = \frac{vL}{\nu} \quad (12)$$

where v is the fluid velocity, L is a characteristic length, and ν is the kinematic viscosity of the fluid. The Reynolds number can be viewed as the ratio of inertial to viscous forces on the fluid. A low value of Re means that viscous forces dominate and the flow is well-ordered (laminar). A large value of Re means that inertial forces dominate and these forces can overcome the viscous drag and lead to turbulence. The onset of turbulence generally occurs at Reynolds numbers between 2000 and 5000 and depends on flow-system geometry.

The Schmidt number is defined as

$$Sc = \frac{\nu}{D_{AB}} \quad (13)$$

where D_{AB} is the diffusion coefficient of the solute in the fluid and ν is the kinematic viscosity. The Schmidt number can be viewed as the ratio of the diffusion of momentum to the diffusion of solute. A large value of the Schmidt number represents a large momentum flux and a large momentum boundary layer (relative to the concentration boundary layer). A small value of Sc implies that the concentration boundary layer is large compared with the momentum boundary layer. The Schmidt number for most liquids is approximately 2000.

The Sherwood number is defined as

$$Sh = \frac{kL}{D_{AB}} \quad (14)$$

where k is the mass-transfer coefficient between the fluid and the interface. The Sherwood number is the ratio of the mass-transfer resistance on the opposite side

of the interface to the mass-transfer resistance in the fluid. A small value of Sh means the dominating mass-transfer resistance is in the fluid and not between the fluid and the interface.

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