An Experimental Study of Diffusion-controlled Reactions in a Laminar Boundary Layer

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A brief review is presented of the theoretical solution obtained by the authors to the problem of a rapid second-order reaction in the incompressible laminar boundary layer on a flat plate. An experimental system is described for investigating reactions of this type, specifically the dissolution of plates and cylinders of benzoic and cinnamic acids in aqueous solutions of sodium and potassium hydroxide. Experimental data are reported in terms of a reaction factor, that is the ratio of the transfer rate with reaction to that in the absence of reaction. The reaction factor is independent of position. The theory closely predicts the reaction factor for cylinders as well as for flat plates. Data obtained by other investigators for packed beds can also be correlated although less successfully.

In a previous study (*1*) the authors obtained a theoretical solution to the problem of a rapid second-order reaction in the laminar boundary layer on a flat plate. Physically the problem treated was of the following nature: Substance A diffuses across a rigid interface into a fluid flowing over the surface. Substance B diffuses from the mainstream to a point (usually near the surface) where it meets A and the rapid, irreversible reaction

$$aA + bB \rightarrow \text{products} \tag{1}$$

takes place. Components A and B and the products of reaction are convected downstream as the reaction proceeds. The reaction consumes A, steepens the concentration gradient at the interface, and increases the transfer rate. The principal contribution made in reference *1* was the development of a theoretical solution to the problem for an important convective system, namely the laminar boundary layer on a flat plate. This solution also gives a semiquantitative picture of transfer in the laminar boundary layers of other shapes such as spheres and cylinders.

In brief it was shown in the theoretical study that the mean Sherwood number for the entire plate up to any point L along the plate is given by

$$\begin{aligned} N_{ShM} &= \left\{\frac{1}{1 - \theta_{1AR}}\right\} \\ &\quad \cdot (0.664 N_{ScA}{}^{\frac{1}{3}} N_{ReL}{}^{\frac{1}{2}}) \\ &= F_R(0.664 N_{ScA}{}^{\frac{1}{3}} N_{ReL}{}^{\frac{1}{2}}) \end{aligned} \tag{2}$$

The relation between the mainstream concentration of B and the surface (saturation) concentration of A is

$$\frac{aC_{BM}}{bC_{AS}} = \left(\frac{N_{ScB}}{N_{ScA}}\right)^{\frac{2}{3}} \left(\frac{f_R''}{0.332}\right)^{N_{ScA} - N_{ScB}} \cdot \left\{\frac{\theta_{1BR}}{1 - \theta_{1AR}}\right\} \tag{3}$$

where θ_1 is defined by

$$\theta_1(\eta, N_{Sc}) = \frac{\int_\eta^\infty (f'')^{N_{Sc}}\, d\eta}{\int_0^\infty (f'')^{N_{Sc}}\, d\eta} \tag{4}$$

The function θ_1 is plotted by Schlichting (*4*). With these equations the rate of dissolution of any substance A as a function of mainstream concentration of B can be calculated if the Schmidt numbers are known.

The present paper deals with the application of these results to a specific experimental system, namely the dissolution of benzoic and cinnamic acids in dilute solutions of sodium and potassium hydroxide. These substances were chosen since they have been previously investigated and their physical properties are well known (*2*, *3*).

EXPERIMENTAL

Experiments were carried out in the system shown in Figure 1. The solution of base was pumped from the holding tank to the head tank, and it then flowed through the Lucite test section. A well-faired entrance section was used to produce a uniform velocity profile across the duct. Screens inserted in the head tank to break up the large eddies in the water from the return line served also as a disengaging section for any air in the system, since fine bubbles tended to collect and grow on the wire and eventually make their way to the surface. During a run the temperature was constant to the nearest 0.5°C. However the energy imparted to the stream by the pump caused a slow rise in temperature, particularly at high bypass flows. Hence a cooling coil was installed in the holdup tank and the cooling water rate adjusted to keep the temperature constant over a series of runs. Most of the runs were made at a temperature of 25°C.

Figure 2 shows the details of the test section. Velocities up to 60 cm./sec. were attainable in the 9-sq.-cm. duct. The plate was placed in the center of the duct rather than in the wall so that the beginning of the velocity boundary layer would be known exactly. A correction to the theory was necessary because the velocity and concentration boundary layers began at different points, as can be seen from the drawing of the plate holder, Figure 3. The sampling section of the plate holder was approximately 5 cm. wide and 14 cm. long. Seven smaller plates, each 2 cm. long, were carefully fitted together in the

TABLE 1. SLOPES OF THE CURVES IN FIGURE 4

System	Observed $\frac{N_{ShM}}{N_{ReL}{}^{1/2} N_{Sc}{}^{1/3}}$	Standard deviation, ±%	Calculated* $\frac{N_{ShM}}{N_{ReL}{}^{1/2} N_{Sc}{}^{1/3}}$
Benzoic acid plates (A)	0.855	1.6	0.556
Cinnamic acid plates (F)	0.808	1.4	0.556
Benzoic acid cylinders (G)	0.741	1.6	

*By the von Kàrmàn approximate method.

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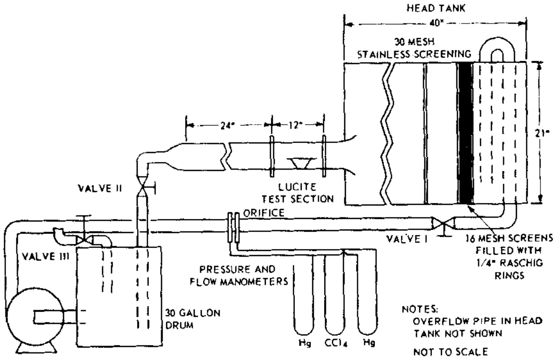

Fig. 1. Experimental apparatus.

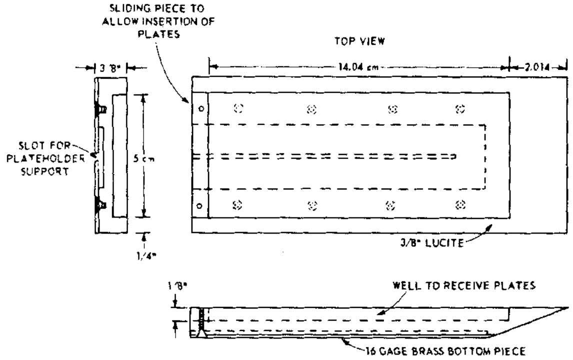

Fig. 3. Detail of plate holder.

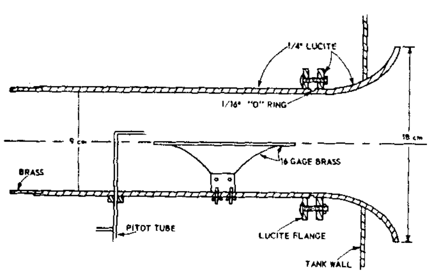

Fig. 2. Detail of test section with plate-holder support.

plate holder. The individual plates allowed determination of local mass transfer rates. Cylinders were used as well as plates to determine how sensitive the theoretical results were to geometry. The cylinders, which were 1 cm. in diameter and about 2 in. long, were held together by stainless steel pins and suspended in a holder.

The test pieces, both cylinders and plates, were pressed from reagent-grade benzoic and cinnanic acids. The powdered acid, as received, was first ground and then sieved to separate the fraction between 40 and 60 mesh. The weight of powder from this fraction necessary to give the desired thickness was poured into the mold and compressed in a laboratory press. No binder was required. The pieces were quite smooth to the touch and did not have the grainy crystal faces which resulted when efforts were made to cast pieces.

Dissolution rates were determined by weighing the test pieces before and after each run. Preliminary tests were run to determine variation of weight with immersion time and water absorption. The benzoic acid specimens were found to absorb a negligible amount of water upon immersion. They could be reweighed as soon as the surface liquid had evaporated, but it was necessary to do this soon after a run had been completed, since they lost weight by sublimation (about 0.5 mg./day). A standard procedure was developed in which the specimens were reweighed an hour after removal from the solution. The specimens were kept in an enclosed box containing Drierite to keep them clean and to promote drying.

The cinnamic acid plates absorbed a considerable amount of water upon immersion, approximately 5% of their original weight, depending upon immersion time. However it was found that after 3 hr. in the dry box the specimens all returned to their original weight. Further checks were made by inserting a complete plate, at zero flow, into the test section for a short time. After 3 hr. in the dry box the specimens had reached their original weight within the precision of the determination. This waiting time was included as part of the standard procedure in the cinnamic acid runs.

Runs were made in the following manner: setting the desired velocity and concentration, checking for constancy of temperature, and inserting the specimen through the entrance section. The time required for insertion and removal of the test pieces was only a small fraction of the total running time.

Because of the large volume of solution recirculated and the relative insolubility of the test materials, the increase of concentration of the dissolved acids was negligible. However to be on the safe side the liquid was changed after each series of runs. The water required aging for several days to remove dissolved air, which otherwise caused bubbles to form in the duct.

RESULTS AND DISCUSSION

Runs were made with water and solutions of sodium and potassium hydroxide. The results obtained with water are shown in Figure 4 and Table 1.* As theory predicted, the mean Sherwood number varied with the square root of the Reynolds number with little deviation from a least-squares line up to a Reynolds number of about 50,000. Above this value the dissolution rates rose sharply, probably owing to the onset of turbulence in the previously laminar boundary layer. The slopes of the lines, given in Table 1, were considerably higher than those predicted by the theory. [The theoretical constant was 0.556 and not 0.664, as in Equation (2), because the velocity and concentration boundary layers began at different points.] The factors contributing to this deviation were as follows.

1. *Mainstream turbulence*—This was

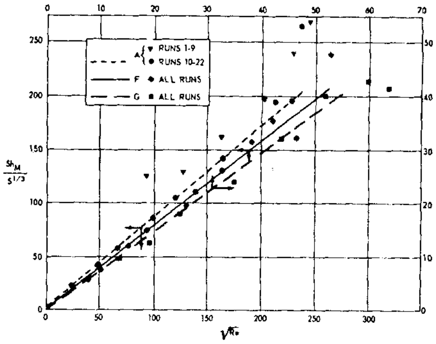

Fig. 4. Dissolution in water as a function of $N_{Re}^{1/2}$.

reduced as much as possible in the design of the apparatus, but at the higher velocities the length of the calming tank was not sufficient to allow the turbulence to die out, as was shown by dye-stream studies.

2. *Surface roughness*—The test pieces were not hydrodynamically smooth as assumed in the theory; moreover, some disturbance was bound to be produced at the point where plates butted up to one another. For the high Schmidt numbers of this study the mass transfer was particularly sensitive to roughness near the surface which would tend to increase the mass transfer rate.

3. *Edge effects*—Since the plate was of finite width, transfer at the edges tended to increase the rate of solution above that predicted by the theory for the semi-infinite plate.

Other factors which may have tended to produce high results were vibration of the pump, stagnation at the front of the plate, and turbulence at the back end of the plate.

While the Sherwood number was higher than that predicted for dissolution in pure water, for the given experimental systems it was reproducible and hence was used to characterize the system in the absence of reaction. The effect of reaction was calculated in comparison to the effect without reaction; that is, the results with reaction are given in the form of a factor which is the ratio of the mean Sherwood number with reaction to that without reaction.

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*The letters in this and the subsequent figures refer to the runs listed in tables of data deposited as document 6093 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C. It may be obtained for $2.50 for photoprints or $1.75 for 35-mm. microfilm.

The results are shown in Figures 5 and 6, where the reaction factors calculted from the mean and local Sherwood numbers, respectively, are plotted. (The values calculated from the local Sherwood numbers were obtained from the data for the first few plates.) The solid line is the reaction factor calculated from Equations (2) and (3), with 900 used as the Schmidt number of the acids and 300 as that of sodium hydroxide. It is seen that agreement between the observed and calculated results is good not only for the plate (which one might have excepted) but also for the cylinders. Also included are several points calculated from the data of Van Krevelen and Krekels (*5*) for sodium hydroxide flowing over a packed bed of benzioc acid pellets. One may conclude that the theory for the flat plate predicts the experimental reaction factor quite closely and is also relatively insensitive to geometry.

The values of the Schmidt numbers used in the calculation of the theoretical curve require some discussion. Schmidt numbers for molecular benzoic and cinnamic acids diffusing through water have been measured by a number of investigators, and some values are tabulated in reference *2*. The proper diffusivity for the sodium hydroxide is more difficult to determine. The reacting species is actually hydroxyl ion, but in the hydroxide boundary layer there are three ionic species: hydroxyl ion, sodium ion, and benzoate ion. The hydroxyl ion cannot diffuse independently of the sodium ion because of the requirements of electrical neutrality; however it is not retarded so much as it would be in pure water because the benzoate ion diffuses from the reaction zone. Data obtained by King and Brodie (*2*) do indeed show a dependence of sodium hydroxide diffusivity on benzoate-ion concentration, the diffusivity increasing with benzoate concentration. It is therefore to be expected that in such a system the actual diffusivity of the sodium hydroxide would lie somewhere between that of the free hydroxyl ion and sodium hydroxide in water. This was found to be the case.

The value of N_{ScB} which best correlated the experimental results was obtained in the following way. At high values of C_{BM}/C_{AS} Equation (3) reduces to

$$\frac{1}{1-\theta_{1AR}} = F_R \approx \left(\frac{N_{ScA}}{N_{ScB}}\right)^{\frac{2}{3}}\left(\frac{aC_{BM}}{bC_{AS}}\right) \qquad (5)$$

and a plot of reaction factor vs. C_{BM}/C_{AS} should be linear with a slope of $(N_{ScA}/N_{ScB})^{2/3}$. Such a plot for the benzoic acid–sodium hydroxide data is shown in Figure 7. A value for $N_{ScB} = 296$ calculated from the slope of the line was used to compute the full curve shown in Figures 5 and 6. It is interesting to note that Equation (5), derived for high values of C_{BM}/C_{AS}, actually holds fairly well for C_{BM}/C_{AS} as low as 1 or 2.

An independent estimate of the proper value of N_{ScB} can be obtained from the relations for ionic diffusion derived by Vinograd and McBain (*6*). From estimates of the concentrations and their gradients the diffusivity was calculated to be about half the value for the free ion, corresponding to a Schmidt number of 330. When one considers the roughness of the calculation, this compares fairly well with the value estimated from the experimental data.

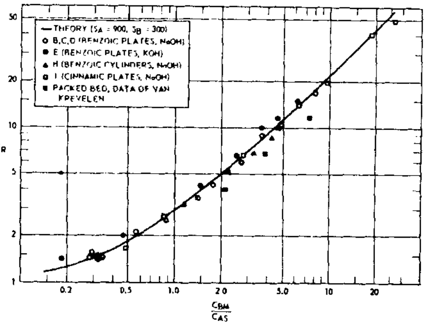

Fig. 5. Reaction factor vs. concentration ratio.

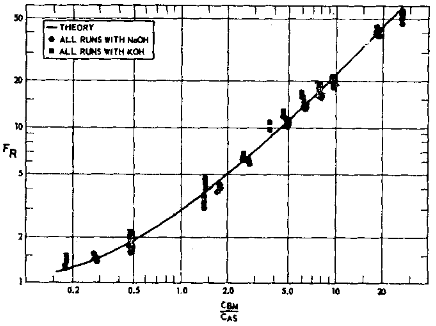

Fig. 6. Reaction factor vs. concentration ratio (calculated from local Sherwood numbers).

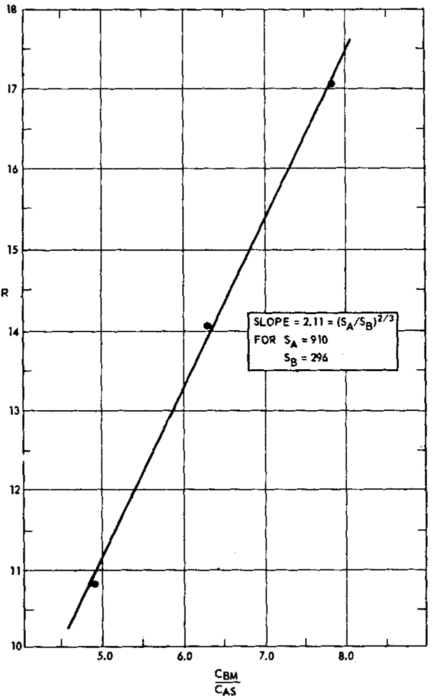

Fig. 7. Reaction factor vs. concentration ratio (series *D* for high C_{BM}/C_{AS}).

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NOTATION

a, b = stoichiometric coefficients of chemical reaction
C_{AS} = surface concentration of A, moles/liter
C_{BM} = mainstream concentration of B, moles/liter
f = dimensionless Blasius stream function
F_R = reaction factor, ratio of Sherwood number with reaction to Sherwood number in the absence of reaction
L = distance from leading edge, cm.
N_{ReL} = Reynolds number with L as the characteristic linear dimension
N_{Sc} = Schmidt number
N_{ScA}, N_{ScB} = Schmidt number for reactant A or reactant B
N_{ShM} = mean Sherwood number
η = dimensionless boundary-layer coordinate
θ_1 = dimensionless boundary-layer temperature
θ_{1AR}, θ_{1BR} = dimensionless boundary-layer temperature based on N_{ScA} or N_{ScB} and evaluated at the reaction zone

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