Effects of Bubbling and Stirring on Mass Transfer Coefficients in Liquids

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In the hydrogenation of α-methylstyrene by means of a suspended palladium-alumina catalyst in a stirred reactor the mass transfer of hydrogen through the liquid is the rate-controlling step and the resistance to chemical reaction at the catalyst surface is negligible except at extremely rapid rates of stirring. This system therefore provides an excellent means of establishing the effects of operating variables and mechanical construction on mass transfer coefficients in liquids in stirred reactors. It is convenient to consider the total resistance to mass transfer as consisting of two separate resistances: in the liquid adjoining the bubbles and in the liquid adjoining the suspended solid particles; thus $R = R_b + R_s$.

A general equation was evaluated from experimental data based upon unit volume of liquid.

This investigation was undertaken to measure and correlate experimental data on mass transfer coefficients from gas bubbles to suspended catalyst solids in a liquid subject to stirring and bubbling. The results are given in dimensionless terms to make them applicable to other systems. In the system chosen, namely the hydrogenation of α-methylstyrene catlyzed by suspended palladium-alumia in powder form, the transfer of hydrogen from the surface of the bubble to the surface of the catalyst was found to be the rate-controlling step. The chemical reaction at the surface of the catalyst imposed little resistance over the range of experimentation, and the uncatalyzed reaction did not occur. Since the gas phase consisted of pure hydrogen the bubble itself offered no resistance to mass transfer. These results are in remarkable contrast to the behavior of the same reaction in a trickling-bed reactor wherein the resistance to mass transfer was found to be negligible and the reaction at the surface of the catalyst was the rate-controlling step, as reported by Babcock, Mejdell, and Hougen (*1*).

PREVIOUS WORK

Milligan and Reid (*10*) investigated the hydrogenation of cottonseed oil in a stirred reactor in contact with bubbles of hydrogen and a suspended nickel catalyst. They found that reaction rates were nearly proportional to the rate of stirring, an indication that mass transfer was rate controlling. No rate equations were given. Maxted (*9*) gave a summary of rates of hydrogenation of organic liquids with similar observations. No other investigations dealing with the specific problem of mass transfer from gas bubbles to suspended solids in stirred vessels were found; however a few related investigations are summarized here.

Hixson and Gaden (*8*) gave the following equations for over-all mass transfer coefficients of oxygen from air bubbles into sulfite solutions. The reaction took place in the liquid phase with no solid catalyst present.

1. Single bubble sparger with no mechanical agitation

$$K_G \alpha V_s^{0.82} \tag{1}$$

2. Single bubble sparger with mechanical agitation using a vaned-disk impeller rotating at 300 to 430 rev./min.

$$K_G \alpha V_s^{0.68} \tag{2}$$

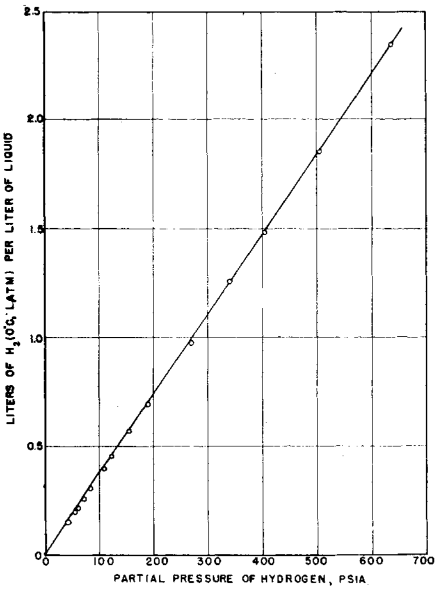

Fig. 1. ↑Solubility of hydrogen in α-methylstyrene at 80°F.

3. Sintered stainless steel sparger with no mechanical agitation with openings of 65μ in the sintered sparger.

$$K_G \alpha V_s^{0.33} \tag{3}$$

Cooper, Fernstrom, and Miller (*2*), measured rates of oxygen transfer from air into aqueous solutions of sodium sulfite in a reactor stirred with a flat-blade impeller using a single open-end sparger. Their data were correlated with the following equation. No solid catalyst was involved.

$$K_G \alpha V_s^{0.67} \tag{4}$$

These experiments covered a tenfold variation in linear gas flow rates ranging from 20 to 360 ft./hr.

Hixson and Baum (*5*, *6*, *7*) reviewed the work of several investigators on reaction rates between solids and liquids in stirred reactors. No gas phase was involved. In general these rates could be expressed in terms of stirring speed N as

$$r \alpha N^{\beta} \tag{5}$$

In systems where the reaction rate is controlled by mass transfer β is nearly unity; where the surface reaction is rate controlling β is zero.

From dimensional analysis Rushton (*11*) developed the following general mass transfer equation for a liquid in a stirred reactor:

$$\left(\frac{kD}{\mathbf{D}}\right) = a\left(\frac{D^2 N \rho}{\mu}\right)^x \left(\frac{\mu}{\rho \mathbf{D}}\right)^y \tag{6}$$

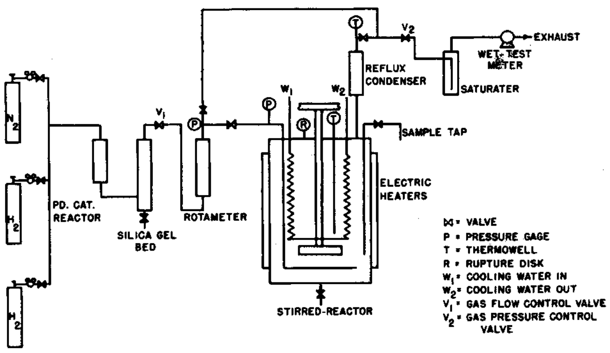

Fig. 2.→Flow diagram.

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No experimental data were supplied to support this equation and no values were given for the constants. This case does not cover reactions with gas bubbles.

THEORY

The theory of reaction rates in gas-liquid reactions catalyzed by suspended solids in stirred reactors is discussed herein with specific reference to the hydrogenation of α-methylstyrene in the presence of a suspended palladium-alumina catalyst with bubbling of the hydrogen through the liquid. Reaction rates and mass transfer rates are based upon unit volume of bubble-free liquid. The volume of bubbles entrained per unit volume of liquid is designated as hydrogen holdup H and is dependent upon the speed of rotation and the rate of hydrogen flow through the liquid.

The rate of reaction is controlled by three resistances in series, namely, the resistances to transfer of hydrogen through the liquid film surrounding the bubble and through the liquid film surrounding the solid particles and the resistance offered to the chemical reaction itself taking place at the surface of the catalyst. In this case the reaction takes place at the surface of a 300-mesh powdered palladium catalyst with no uncatalyzed reaction occurring.

With this particular catalyst the resistance offered by the surface reaction is negligible over the range of experimental conditions used for evaluating mass transfer coefficients.

The rate of mass transfer of dissolved hydrogen through the liquid may be expressed as

$$r = k_0'(c_b' - c_s') \qquad (7)$$

Where mass transfer is controlling and the resistance to the surface reaction is negligible, c_s' is negligible and Equation (7) becomes

$$r = k_0' c_b' \qquad (8)$$

The concentration of hydrogen dissolved in α-methylstyrene was found experimentally to be directly proportional to pressure and over the temperature range of experimentation (77° to 95°F.) inversely proportional to temperature; hence

$$c_b' = \frac{\alpha p}{T} \qquad (9)$$

In this case p is equal to the total pressure since the vapor pressure of the liquid is negligible.

The concentration of hydrogen in the gas phase can be expressed by ideal gas laws at the temperatures and pressures used in this experiment.

$$c_b = \frac{p}{RT} \qquad (10)$$

where p = atmospheres of pressure

R = gas-law constant, 0.08205 (liter)(atm.)(g.-mole)(°K.)

Combining (9) and (10) gives

$$c_b' = \alpha R c_b \qquad (11)$$

Combining (8) and (11) gives

$$r = k_0 c_b \qquad (12)$$

where $k_0 = \alpha R k_0'$

In terms of resistance

$$r = \frac{c_b}{R_o} \qquad (12a)$$

where $R_0 = R_b + R_s$

R_b, R_s, R_0 = resistances of liquid surrounding the bubble and surrounding the catalyst and over-all resistance, all per liter of liquid.

Resistance of Liquid Surrounding the Bubbles

The resistance of the liquid surrounding the bubbles is inversely proportional to the bubble area A_b per unit volume of liquid and to the mass transfer coefficient k_b''; thus

$$R_b = \frac{1}{A_b k_b''} \qquad (13)$$

This resistance may also be expressed in terms of the hydrogen holdup H. For a bubble of diameter D_b

$$\text{Volume} = \pi D_b^3/6 \qquad (14)$$

$$\text{Area} = \pi D_b^2 \qquad (15)$$

Hence, the number of bubbles per liter of liquid is

$$6H/\pi D_b^3 \qquad (16)$$

and the total bubble area per liter of liquid is

$$6H/D_b \qquad (17)$$

Combining Equations (17) and (13) gives

$$R_b = \frac{D_b}{6Hk_b''} \qquad (18)$$

The diameter D_b of a bubble is dependent upon the diameter of hole in the sparger from which the bubble emerges but also upon the rate of stirring, decreasing with increase in stirring rate. These facts were established experimentally by observations in glass vessels.

The holdup H is dependent upon the rates of gas flow and of stirring. The mass transfer coefficient k_b'' is dependent upon the rate of stirring. These combined effects can be expressed by dimensional analysis in terms of the Schmidt number

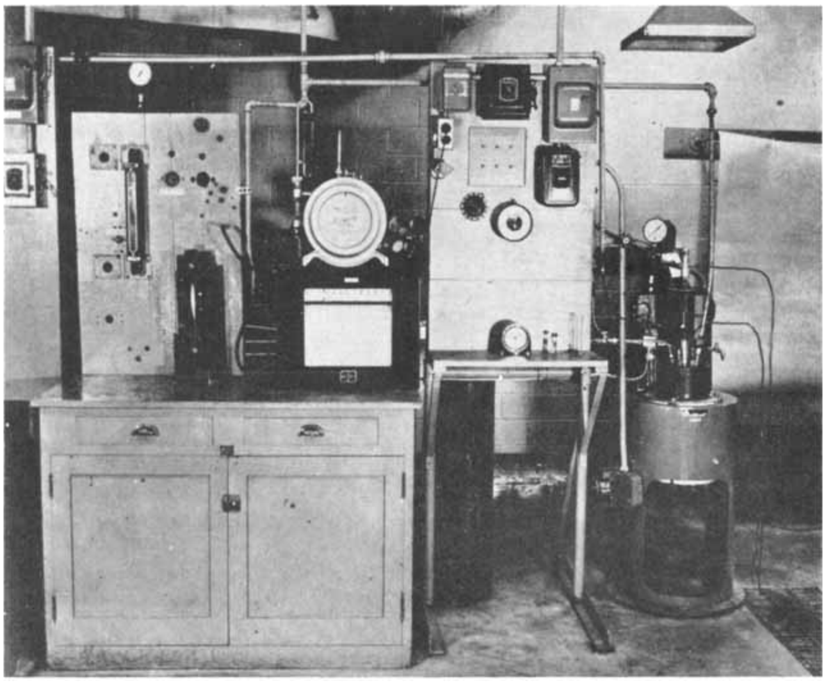


Fig. 3. Experimental assembly.

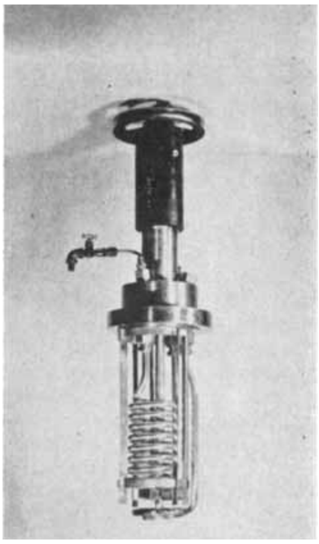


Fig. 4. Stirrer, baffle, and heat exchanger.

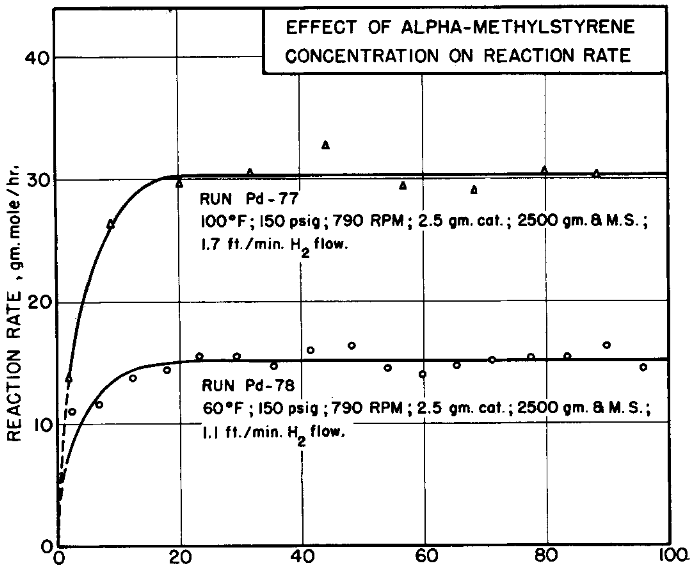


Fig. 5. Mole percentage of α-methylstyrene.

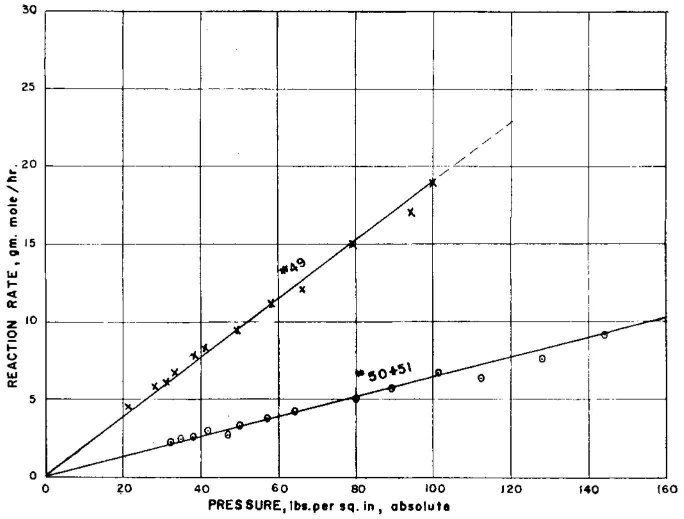


Fig. 6. Effect of hydrogen pressure on reaction rate. Palladium-49: 80°F., 790 rev./min., 14.0 cu. ft./hr., H_2 out, S.C.; palladium-50, 51: 80°F., 203 rev./min., 30.5 cu. ft./hr., H_2 out, S.C.

$\mu/(\rho\mathbf{D})$, a gas flow number $\sigma/(\mu V_S)$, and a Reynolds number $(D^2N\rho)/\mu$, thus

$$R_b = A'\left(\frac{\rho D}{\mu}\right)^{1/3}\left(\frac{\sigma}{\mu V_s}\right)^{\alpha}\left(\frac{D^2N\rho}{\mu}\right)^{\beta} \quad (19)$$

The velocity V_s is calculated by dividing the volume of gas flowing per minute at the temperature and pressure of the system by the total cross-sectional area of the reaction. Values of V_s were taken as the averages of inlet and outlet values. A large excess of hydrogen was used in every case. The physical properties of the liquid solution were evaluated as additive for a given composition.

Resistance of Liquid Surrounding the Solid

The resistance to transfer of hydrogen through the liquid surrounding the solid is inversely proportional to the area A_s of the solid per liter of liquid and upon the mass transfer coefficient k_s''; thus,

$$R_s = \frac{1}{A_s k_a''} \quad (20)$$

The area A_s is proportional to the catalyst loading m and inversely proportional to the density ρ_s and diameter D_s of the catalyst particle.

For a single spherical particle,

$$\text{area} = \pi D_s^2 \quad (21)$$

$$\text{mass} \quad w_p = \pi D_s^3 \rho_s/6 \quad (22)$$

For a catalyst loading of m g./liter of liquid the number of particles n per liter from Equation (22) is

$$n = \frac{m}{w_p} = 6m/\rho_s \pi D_s^3 \quad (23)$$

The area of solid surface A_s per liter of liquid is obtained by combining Equations (21) and (23) to give

$$A_s = \frac{6m}{\rho_s D_s} \quad (24)$$

The total resistance of the liquid surrounding the solid is obtained by combining Equations (20) and (24) to give

$$R_s = \frac{\rho_s D_s}{6mk_s''} \quad (25)$$

For particles other than spherical a constant other than 6 would appear.

The turbulence in the liquid surrounding the solid is dependent upon the velocity of the stirrer and the viscosity and density of the liquid. These combined effects can be expressed by dimensional analysis in terms of a Reynolds number $(D^2N\rho)/\mu$, a catalyst loading term (ρ_s/m) and a Schmidt number $(\mu/\rho\mathbf{D})$ for the liquid; thus

$$R_N = B'\left(\frac{D^2N\rho}{\mu}\right)^{\gamma}\left(\frac{\rho_s}{m}\right)\left(\frac{\rho\mathbf{D}}{\mu}\right)^{1/3} \quad (26)$$

where B' is a constant dependent upon the mechanical dimensions of the stirrer, baffles, and reactor.

The total resistance R_0 offered to the transfer of hydrogen through the liquid from bubble to solid is then the sum of the two resistance, $R_0 = R_b + R_s$.

Combining Equations (19) and (26) gives

$$R_0 = A'\left(\frac{\rho\mathbf{D}}{\mu}\right)^{1/3}\left(\frac{\sigma}{\mu V_s}\right)^{\alpha}\left(\frac{DN\rho}{\mu}\right)^{\beta} + B'\left(\frac{\rho\mathbf{D}}{\mu}\right)^{1/3}\left(\frac{\rho_s}{m}\right)\left(\frac{D^2N\rho}{\mu}\right)^{\gamma} \quad (27)$$

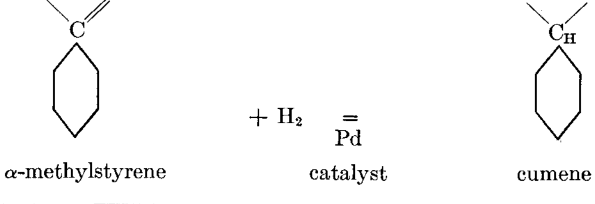
The over-all resistance R_0 is inversely proportional to the over-all mass transfer coefficient k_0. To introduce k_0 into this equation and retain dimensionless form, the dimensionless number $\mathbf{D}/(k_0D^2)$ is used with a corresponding change in constants A' and B' to A and B.

Equation (27) becomes

$$\left(\frac{\mu}{\rho\mathbf{D}}\right)^{1/3}\left(\frac{\mathbf{D}}{k_0D^2}\right) = A\left(\frac{\sigma}{\mu V_s}\right)^{\alpha}\left(\frac{D^2N\rho}{\mu}\right)^{\beta} + B\left(\frac{D^2N\rho}{\mu}\right)^{\gamma}\left(\frac{\rho_s}{m}\right) \quad (28)$$

SELECTION OF SYSTEM

The hydrogenation of α-methylstyrene in a stirred reactor catalyzed by palladium was selected as an appropriate system for study because for this system rate data were already available for the same reaction taking place in a trickling-bed flow reactor. This system is also favorable because the vapor pressures of α-methylstyrene and cumene are low; hydrogenation yields only one product, cumene, and the liquid is easy to analyze accurately by measurements of indexes of refraction. The reaction involved is



Palladium was selected as the catalyst because it directed the hydrogenation to the side chain without causing polymerization or hydrogenation of the benzene ring and permitted the surface reaction to proceed so rapidly as to confine the resistance to mass transfer. The α-methylstyrene was 98.5% pure with 1.0% of β-methylstyrene and traces of impurities.

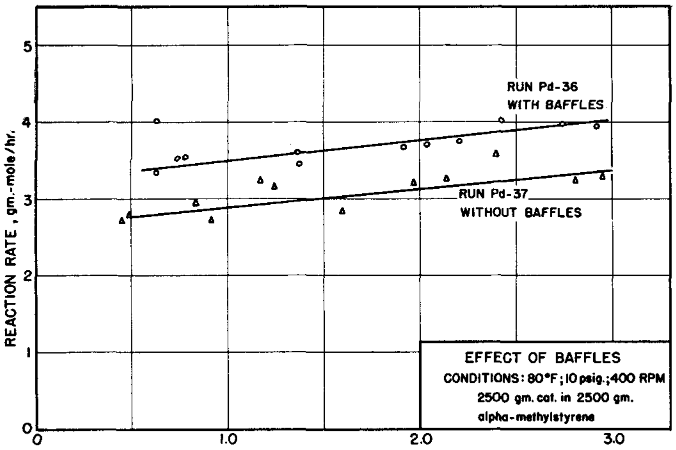


Fig. 7. Effect of baffles; conditions: 80°F., 10 lb./sq. in. gauge, 400 rev./min., 2,500 g. catalyst in 2,500 g. α-methylstyrene.

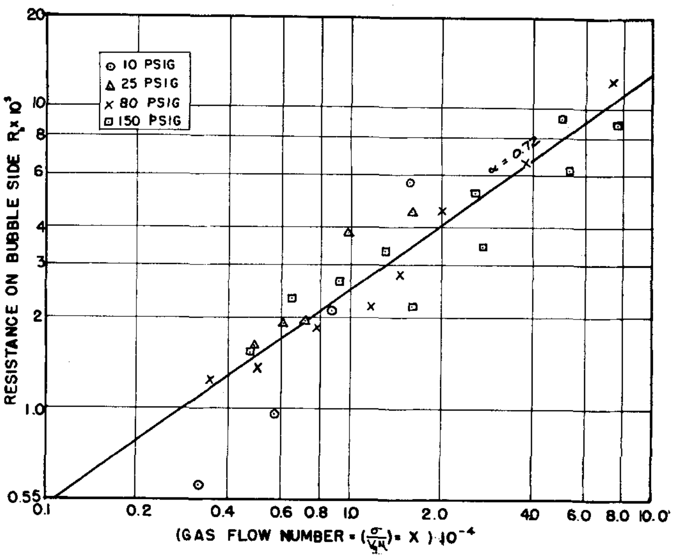


Fig. 8. Evaluation of α at 80°F.

Some physical properties of α-methylstyrene and cumene needed in this investigation are the following:

	α-methylstyrene	cumene
Boiling point at 760 mm. Hg	165.38°C.	152.4°C.
Freezing point, 760 mm. Hg	−23.21°C.	−96°C.
Density at 25°C., g./cc., 20°/4	0.9062	0.862
Index of refraction at 25°C.	1.53586	1.48890
Viscosity at 20°C., centipoise	0.940	0.791
Surface tension at 20°C. dynes/cm.	31.5	28.2

The hydrogen supply was purified to remove traces of oxygen by passing the gas over an auxiliary palladium catalyst. The resultant water vapor was removed by silica gel. The removal of water vapor was important, as its presence caused coagulation of the suspended catalyst.

The catalyst consisted of palladium supported on a 300-mesh alumina powder (2% metal), supplied by Baker and Company with the following properties,

Surface mean diameter = 7.15 μ
Volume mean diameter = 13.46 μ
Density at 20°C. = 4.14 g./cc.
Internal surface area = 75 sq. meters/g.

EXPERIMENTAL EQUIPMENT

A flow chart of the experimental process is shown in Figure 2 and a photograph of the assembly in Figure 3.

The reactor consists of a 316-stainless-steel high-pressure forged vessel of 1-gal. capacity, 5 in. I.D., and 12 in. inside height, designed to operate at a maximum pressure of 1,200 lb./sq. in. gauge and at a maximum temperature of 650°F., as manufactured by Autoclave Engineers. The agitator consisted of impellers with two flat turbine blades.

Diameter of blade rotation, in.	3.50
Length of blades, in.	1.25
Width of blades, in.	0.75

The impellers were driven by a ¾-hp. motor with V-belt speed reducers to permit variations in speed from 130 to 800 rev./min.

To promote agitation and prevent vortex motion four equally spaced baffles ½ in. wide and 11⅛ in. long surrounded the agitator and were held in place 1/16 in. from the cylinder walls. A photograph of the stirrer, sparger, heat exchangers, and baffles is shown in Figure 4. Hydrogen was introduced through a ring sparger placed ½ in. from the bottom of the reactor with holes of 0.0135-in. diam. directed downward.

Diameter of ring, in.	3½
Holes in ring	25
Diameter of holes, in.	0.0135

Temperature was controlled by electrical heaters surrounding the vessel.

A cooling coil of stainless steel with a heat transfer surface of 0.77 sq. ft. was immersed in the charge. Temperatures were measured by an iron-constantan thermocouple mounted in a stainless steel well. Pressure was measured by a Bourdon gauge.

The rate of hydrogen flow to the reactor was controlled by a needle valve in combination with a rotameter. The hydrogen leaving the reactor was passed through a reflux condenser consisting of a ⅜-in. stainless steel coil immersed in ice water. The hydrogen was cooled to 5°C. with return of condensate to the reactor.

A second precision needle valve on the outlet of the condenser permitted control of the reactor pressure by release of hydrogen to the atmosphere. The hydrogen leaving the condenser was saturated with water and its rate of flow measured with a wet-test meter.

The liquid feed and product were analyzed by a dipping refractometer with bath temperature maintained at 25° ± 0.01°C. and with room temperature maintained at 24° to 26°C. This dual control of temperature permitted measurements of index to a precision of ±0.00001, corresponding to ±0.05 mole % α-methylstyrene.

EXPERIMENTAL PROCEDURE AND DATA

Many preliminary runs were made to establish proper techniques, to obtain reproducible operation, and to ensure that cumene was the only product of hydrogenation.

The following variables were studied: rate of stirring, rate of hydrogen flow, temperature, pressure, liquid composition, catalyst loading, number of propeller blades, effect of baffles, and type of sparger. The detailed experimental data are filed.*

With a given reactor fixed in every detail of mechanical design the effects of such operating variables as pressure, temperature, liquid composition, gas velocity, and stirring rate were each studied independently as far as practicable. In each run 2,500 g. of liquid feed were used and 2.5 g. of catalyst powder suspended therein. Later the effect of loading was studied with variation in mass of catalyst per liter of liquid. The percentage conversion of the α-methylstyrene with time was measured from changes of index of refraction. From a plot of such data the reaction rate at any instant of time is obtained from the slope of the conversion-time curve. For concentrations above 20 mole % α-methylstyrene a plot of conversion x vs. time gave straight lines.

Polymerization Negligible

First it was confirmed that the only product in the hydrogenation of α-methylstyrene with a palladium catalyst in a stirred reactor was cumene with no polymerization products and with no hydrogenation in the benzene ring.

Reverse Reaction Negligible

Complete conversion of α-methylstyrene to cumene could be obtained with no reverse reaction over the range of temperatures and pressures used in this investigation.

Uncatalyzed Reaction Negligible

In the absence of the catalyst no appreciable hydrogenation took place over the experimental range of operation.

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*Data have been deposited as document 5308 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for \$2.50 for photoprints or \$1.75 for 35-mm. microfilm.

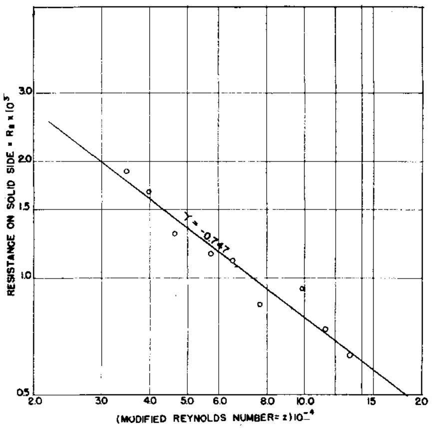

Fig. 9. Evaluation of γ.

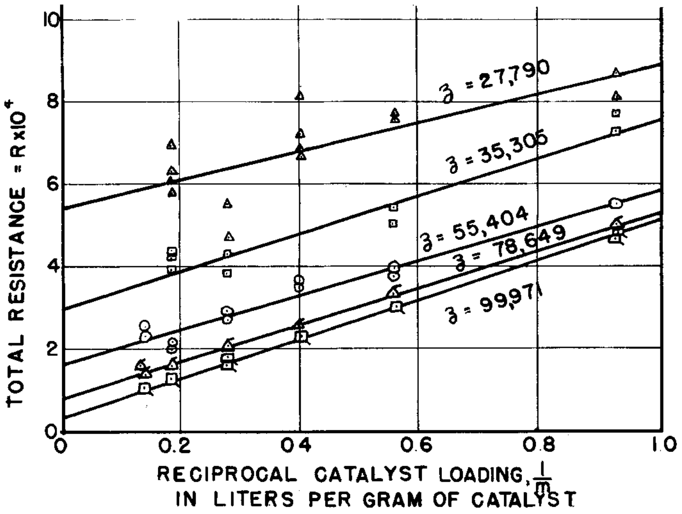

Fig. 10. Evaluation of R_b.

Negligible Effect of Catalyzed Support and Equipment Surface

It was proved experimentally that the catalyst support of alumina powder did not catalyze the hydrogenation reaction nor did the surface of the vessel, stirrers, heat exchanger, or baffles.

Negligible Effect of Liquid Level and Removal of Samples

Removal of samples of liquid during an experimental run resulted in an appreciable lowering of the liquid level. It was found that reduction of the liquid content of the reactor by even one third had no noticeable effect on the reaction rate when such rates were based upon unit volume of liquid. The mass of catalyst per liter of liquid was the same inside the reactor as in the sample withdrawn. The rate of reaction per liter remained independent of liquid level over the experimental range.

Effect of Liquid Composition

The reaction rate was found to be independent of the composition of the liquid solution for concentrations above 20% α-methylstyrene, as shown in Figure 5. This independence is evidence that mass transfer controls the reaction rate except at low concentrations.

The independence of reaction rate on liquid composition in the stirred reactor was established by thirty runs over a temperature range from 60° to 100°F. at a pressure of 150 lb./sq. in. gauge, gas velocity of 1.7 ft./min., and a stirring rate of 790 rev./min. By reducing the rates of bubbling and stirring and by lowering pressure and temperature this independence of reaction rate on concentration could be extended to concentrations of α-methylstyrene below 20%.

Effect of Hydrogen Pressure

Forty runs were made at 80°F. over a pressure range from 20 to 144 lb./sq. in. abs. at stirring rates of 203 and 790 rev./min. and at a hydrogen flow rate of 30.5 ft./hr. and 14.0 ft./hr. respectively. For pressures up to 150 lb./sq. in. gauge the reaction rates were found to increase linearly with pressure, as shown in Figure 6. This straight line relationship supports the theory that mass transfer is the rate-controlling step. At pressures above 150 lb./sq. in. gauge the resistance of the surface reaction became evident as shown by a downward trend.

Effect of Baffles

The presence of baffles increased turbulence and uniformity in mixing and prevented the formation of a vortex in the agitated liquid. The effect of baffles was to increase the reaction rate by 13%, as shown in Figure 7. Baffles were used in all subsequent runs.

Effect of Number of Impeller Blades

Comparisons were made of two- and eight-blade impellers with the same size, shape and dimensions of blades. Five tests were made at 80°F. and 10 lb./sq. in. guage. The eight-blade impeller increased the rate of mass transfer by 65% in the range of low stirring rates from 130 to 300 rev./min. but only 22% in the high range from 600 to 800 rev./min.

Visual Observation of Holdup and Bubble Size

In order to observe and measure the effects of bubbling and stirring rates on hydrogen holdup and bubble size, separate visual experiments were made by bubbling hydrogen through α-methylstyrene with a suspended catalyst in a stirred glass vessel of the same dimensions as the reactor autoclave and using the same stirrer, paddles, heat transfer coils, and baffles. The following observations were made:

1. The diameter of bubbles decreased with the rate of stirring.
2. The diameter of bubbles was not influenced by the rate of gas flow.
3. The gas holdup increased with the 0.5 power of the rate of stirring.
4. The gas holdup increased with the 0.6 power of the rate of gas flow.

These observations are consistent with the theory presented and with the experimental data on mass transfer rates.

Mass Transfer the Rate-controlling Step

That mass transfer imposes the rate-controlling resistance in the hydrogenation of α-methylstyrene in a stirred reactor is based upon the following evidence: In the stirred reactor the mass transfer rate (1). is greatly dependent upon the rate of stirring, (2) is greatly dependent upon the rate of bubbling, (3) varies directly with pressure, (4) is independent of concentration of α-methylstyrene. In contrast to these findings, from independent experiments made on the same reaction in a trickling-bed reactor where mass transfer was negligible and the resistance of the chemical reaction at the surface was rate controlling, opposite effects were found by Babcock, Mejdell, and Hougen (*1*). In the trickling-bed reactor the chemical reaction rate (1) is independent of rate of liquid flow, (2) is independent of rate of gas flow, (3) varies nearly as the square root of pressure, and (4) varies greatly with concentration of α-methylstyrene.

Correlation of Data

Over conditions of operation where resistance offered by the surface reaction is negligible, the total resistance offered to hydrogen transfer is represented by the following equation:

$$R_0 = Ax^{\alpha}z^{\beta} + B\left(\frac{\rho_s}{m}\right)z^{\gamma} \qquad (29)$$

The principal objective of this investigation was to confirm or modify the theory summarized by Equation (29) and, if confirmed, to establish the constants A, B, α, β, and γ.

Effect of Schmidt Number. Several investigators have found that the mass transfer coefficients of dissolved gases through liquids vary with the 1/3 to 1/2 power of the Schmidt number. No detailed correlation of this variable was attempted. Calculation of all the data with both exponents by the method of least squares showed the exponent ⅓ to give better agreement between experimental and calcplated results.

Effect of the Gas Flow Number, x. Under conditions of constant Reynolds number z, Equation (29) may be written as

$$R_0 = A'x^{\alpha} + R_s \qquad (30)$$

Values of R_o at constant temperature and constant rate of stirring N were plotted against values of x and extrapolated to a zero value of x. A value of x equal to 0 corresponds to an infinite rate of gas flow where the resistance of the liquid surrounding the bubble becomes zero ($R_b = 0$) and hence R, becomes equal to R_s. Values of R_b were thus obtained at 135 rev./min. at temperatures of 60°, 80° and 100°F.

Values of R_b were plotted against x on logarithmic scales as shown in Figure 8 to give a slope of α equal to 0.72 at 80°F. The same procedure was repeated at 60° and 100°F. to give values of 0.78 and 0.77. an average value of $\alpha = 0.75$ was accepted.

Effect of the Reynolds Number upon the Resistance of the Liquid on the Solid Side. Where the flow number x equals 0, corresponding to an infinite rate of gas flow, the mass transfer resistance exists entirely in the liquid surrounding the solid and is zero surrounding the bubble. Under these conditions

$$R_0 = R_s = B'z^{\gamma} \qquad (31)$$

These values of R_s were obtained by extrapolating values of R_0 at constant values of z to zero values of x. These values of R_s were plotted against the modified Reynolds number on a logarithmic scale to give a slope γ equal to -0.75, as shown in Figure 9.

Effect of the Reynolds Number upon the Resistance of the Liquid Surrounding the Bubbles. From Equation (29) it will be observed that when the catalyst loading m is increased the mass transfer resistance surrounding the solid disappears as $1/m$ approaches zero. This relationship was shown earlier by Davis (*3*). For constant values of gas flow numbers x and for four values of Reynolds numbers z, values of R_0 were plotted against reciprocal values of loading, $1/m$, as shown in Figure 10. The various plots were established by the method of least squares. These values of R_0 extrapolated to values of $1/m$ equal to zero correspond to the resistance R_b on the bubble side; thus

$$\text{at } 1/m = 0, \quad R_0 = R_b = Ax^{\alpha}z^{\beta} \qquad (32)$$

Values of R_b were plotted against the Reynolds number z at constant values of gas flow numbers both on logarithmic scales, Figure 11. The slope of this plot was evaluated by the method of least squares to give a value of β equal to -1.67; thus

$$R_b = Ax^{0.75}z^{-1.67} \qquad (33)$$

Effect of Catalyst Loading. According to Equation (29) the resistance to mass transfer at constant values of gas flow numbers x and rates of stirring z varies with the reciprocal of catalyst loading m.

$$\frac{R_s}{z^{0.75}} = \frac{B\rho_s}{m} \qquad (34)$$

A plot of $R_s/z^{0.75}$ against m on logarithmic scales, Figure 12, gave a slope of -1, in agreement with the original Equation (29), where the exponent of the term ρ_s/m is unity.

The final equation for mass transfer of a gas through a liquid to a solid surface in a stirred recator with bubbling of the gas through the liquid is given by the relation.

$$\left(\frac{\mathbf{D}}{k_0 D^2}\right)\left(\frac{\mu}{\rho\mathbf{D}}\right)^{1/3} = A\left(\frac{\sigma}{V_s\mu}\right)^{0.75} \qquad (35)$$
$$\cdot\left(\frac{D^2N\rho}{\mu}\right)^{-1.67} + B\left(\frac{\rho_s}{m}\right)\left(\frac{D^2N\rho}{\mu}\right)^{-0.75}$$

where the values of the constants A and B are characteristics of the mechanical construction and position of impellers, baffles, sparger, and vessel.

For the given two-blade flat impeller and construction the $A = 29.4$ and $B = 6.55 \times 10^{-4}$. The average deviation of calculated from experimental values is ±14%. This deviation is due to the intrinsic difficulties involved in the simultaneous control of pressure, temperature, stirring, and loading.

The relative resistances of the liquid surrounding the bubble and surrounding the solid as a function of gas velocity are shown in Figure 13 at 135 and 790 rev./min. It will be observed that the resistance of the liquid film surrounding the bubbles becomes negligible at high gas velocities and suggests that higher rates of bubbling represent a waste of gas and power without increasing the rate of mass transfer. The same effects are shown in Figure 14, where the relative resistance of the two liquid films is shown as a function of gas velocity at four rates of stirring.

DISCUSSION OF RESULTS

The exponent 0.75 on x for the effect of gas velocity on the bubble resistance surrounding the bubbles is comparable with the value of 0.68 obtained by Hixson and Gaden (*8*) and Cooper et al. (*2*) on the rate of absorption of oxygen in bubbling through sodium sulfite solutions where only one resistance is involved.

The exponent -0.75 on the effect of rate of stirring on the film surrounding the solid is comparable with the value of -0.6 obtained by Hixson and Baum (*5*) on the dissolution of a solid in a solvent where any one resistance was involved.

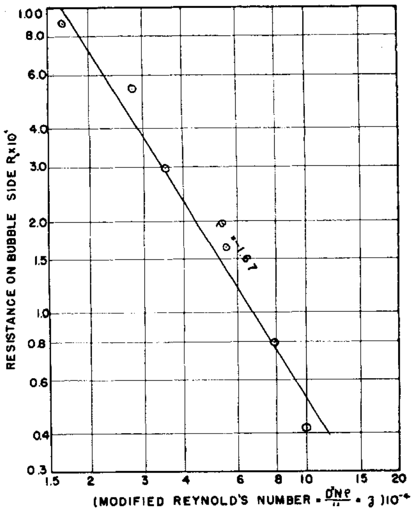

Fig. 11. Effect of Reynolds number z on R_b at constant gas-flow numbers.

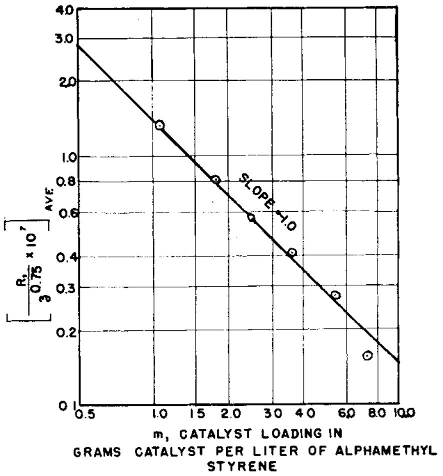

Fig. 12. Effect of catalyst loading on R_s at constant gas-flow and Schmidt numbers.

The exponent -1.67 on z for the effect of stirring rate on the film surrounding the bubble is comparable with the exponent -1.5 obtained by Vermeulen at al. (*12*) on the interfacial area of bubbles in an agitated liquid.

SUMMARY OF RESULTS

1. A theory with experimental confirmation of the effects of bubbling and stirring on mass transfer coefficients from gas bubbles to solid particles in liquids has been presented.
2. The total resistance to mass transfer from bubble to solid per unit volume of liquid is equal to the resistance of liquid surrounding the bubble plus the resistance of the liquid surrounding the solid.
3. The resistance of the liquid surrounding the bubble is given by the relation $R_b = Ax^{0.75}z^{-1.67}$.
4. The resistance of the liquid on the solid side is given by the relation

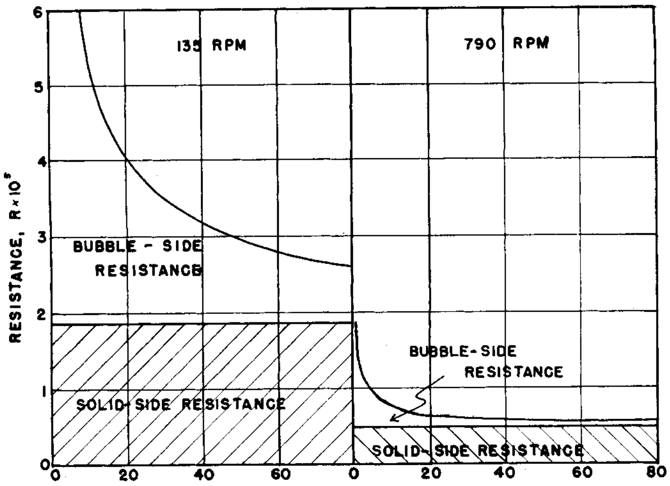

Fig. 13. Change of resistances with gas-flow rate.

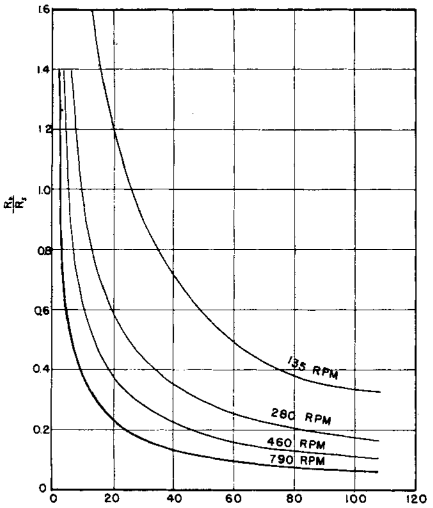

Fig. 14. Ratio of bubble-side to solid-side resistances.

$$R_s = B \frac{\rho_s}{m} z^{-0.75}$$

5. The constants A and B depend upon the mechanical construction of the vessel, agitator, baffles, and sparger and require separate evaluation in terms of these mechanical factors for scale-up purposes.

6. The effects of bubbling rates, stirring rates, and catalyst loading on holdup, bubble size, and particle motion were observed visually in a glass vessel with the same stirring equipment, heating coils, and baffles as used in the steel reactor. These observations were consistent with the theory proposed for mass transfer.

7. At high gas velocities the resistance surrounding the bubble becomes negligible. High gas velocities result in a waste of gas and power with no corresponding increase in rates of mass transfer.

8. The hydrogenation of α-methylstyrene by use of a suspended palladium catalyst provides a simple and convenient means for evaluating the mass transfer performance of stirring equipment and the effects of changes in mechanical construction and baffling thereon.

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NOTATION

A, A' = constants
A_b = area of bubbles, sq. cm./liter of liquid
A_s = area of solid surface; sq. cm./liter of liquid
A_p = surface area per particle, sq. cm.
B = number of blades on impeller
B, B' = constants
c_b', c_s', c' = concentration of hydrogen in liquid phase, g.-moles/liter
c_b, c_s, c = concentration of hydrogen in gas phase, g.-moles/liter
$\mathbf{D}$ = diffusivity of hydrogen through liquid, sq. c./secm.
D = diameter swept by impeller, cm.
D_b = diameter of bubble, cm.
D_s = diameter of solid particle, cm.
H = total holdup, liter/liter of liquid
K_G = over-all mass transfer coefficient
k_b, k_s, k_0 = proportionality constants
k_b', k_s', k_0' = mass transfer coefficients
k_b'' = mass transfer coefficient/unit area of bubble
k_s'' = mass transfer coefficient/unit area of solid surface
m = catalyst loading, g./liter of liquid
N = stirring rate, rev./sec.
n = number of moles
n = catalyst loading, particles/liter
p = partial pressure of hydrogen, atm.
R = gas law constant 0.08206 (liter) (atm.)/(g.-mole)(°K.)
R_b, R_s, R_0 = resistances to mass transfer
r = reaction and transfer rate, g.-moles/(liter)(sec.)
T = absolute temperature, °K.
V = volume, liters
V_s = average superficial gas velocity based on inside diameter of reactor and temperature and pressure of gas, cm./sec.
α = constant
α = exponent of gas flow number
β = constant
β = exponent of Reynolds number (bubble side)
γ = exponent of Reynolds number (solid side)
μ = viscosity of liquid, g./(sec.)(cm.)
σ = surface tension, g./sec.^{2}
π = total pressure, atm.
π = 3.1416
ρ = density of liquid, g./cc.
ρ_s = density of solid, g./liter

Subscripts

b = bubble side
0 = over all
s = solid side

Dimensionless Numbers

$S_s = (\mu/\rho\mathbf{D})$ = Schmidt number
$x = (\sigma/\mu V_s)$ = gas flow number
$z = (D^2N\rho/\mu)$ = modified Reynolds number
$Nu = (k_0D^2/\mathbf{D})$ = modified Nusselt number

LITERATURE CITED

1. Babcock, B. D., G. T. Mejdell, and O. A. Hougen, *A.I.Ch.E. Journal.*
2. Cooper, C. M., G. A. Fernstrom, and S. A. Miller, *Ind. Eng. Chem.*, **36**, 504 (1944).
3. Davis, H. S., C. Thomson, and G. S. Crandall, *Jour. Am. Chem. Soc.*, **54**, 2340 (1932).
4. Dow Chemical Company, "Alpha-methylstyrene Monomer," Bulletin of Coatings Technical Service, Midland, Mich. (1955).
5. Hixson, A. W., and S. J. Baum, *Ind. Eng. Chem.*, **33**, 478 (1941).
6. *Ibid.*, **34**, 194 (1942).
7. *Ibid.*, **36**, 528 (1944).
8. Hixson, A. W., and E. L. Gaden, *Ind. Eng. Chem.*, **42**, 1792 (1950).
9. Maxted, L. B., "Handbuch der Katalyze."
10. Milligan, C. H., and E. E. Reid, *Ind. Eng. Chem.*, **15**, 1048 (1925).
11. Rushton, J. H., *Chem. Eng. Progr.*, **47**, 485 (1951).
12. Vermeulen, Theodore, C. M. Williams, and G. E. Langlois, *Chem. Eng. Progr.*, 51, 85 (1955).