and, therefore,

$$p = (l - y) - \gamma \frac{4l}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \frac{\cosh\left[\dfrac{(2n-1)\pi x}{l}\right] \sin\left[\dfrac{(2n-1)\pi y}{l}\right]}{\sinh\left[\dfrac{(2n-1)\pi}{l}\right]} \tag{41}$$

The velocity field may be obtained from (41) by Darcy's formula (A.2):

$$\frac{u}{v_0} = \gamma \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{1}{(2n-1)} \frac{\sinh\left[\dfrac{(2n-1)\pi x}{l}\right]}{\sinh\left[\dfrac{(2n-1)\pi}{l}\right]} \sinh\left[\frac{(2n-1)\pi y}{l}\right] \tag{A.12}$$

$$\frac{v}{v_0} = 1 + \gamma \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{1}{(2n-1)} \frac{\cosh\left[\dfrac{(2n-1)\pi x}{l}\right] \cos\left[\dfrac{(2n-1)\pi y}{l}\right]}{\sin\left[\dfrac{(2n-1)\pi}{l}\right]} \tag{A.13}$$

The total incoming and outgoing flow rates at the ends of the bed may be found by integrating v in (A.13) with respect to x from one wall to the other for $y = 0$ and $y = l$, respectively.

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Hydrogenation of Acetone in a Vibrating Slurry Reactor

The behavior of a vibrating column of liquid as a slurry reactor and the dependence of the mass transfer resistances on the frequency of oscillation and liquid temperature were studied. The hydrogenation of liquid acetone over Raney nickel was chosen as the model reaction. The tortuosity factor of the catalyst was determined from measurements with two different particle sizes.

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SCOPE

Slurry reactors are used in the chemical industry in processes involving heterogeneous catalysis where a gas reacts with a liquid on a solid catalyst. They are mainly used in small-scale batch reactions and in hydrogenations.

When stirred tanks are used as slurry reactors, diffusional limitations are found quite often. The hydrogenation of α-methylstyrene on supported and black palladium was investigated in different slurry reactors (Johnson, et al., 1957; Sherwood and Farkas, 1966) and the mass transfer to the solid catalyst was the rate determining step. The same effect was found in the hydrogenation of nitrobenzene over palladium (Snyder et al., 1957) and of cyclohexene over platinum and palladium (Price and Schiewetz, 1957; Sherwood and Farkas, 1966).

Since mass transfer is generally the limiting factor, an improvement in the agitation will increase the yield of the reaction. Several authors have reported that when a column of liquid is made to oscillate vertically, a considerable increase in the gas-liquid (Buchanan et al., 1963; Jameson, 1966) and solid-liquid (Lemcoff and Jameson, 1975) mass transfer rates is obtained. When the oscillation frequency is greater than a certain limit, a cycling of bubbles is produced which generates very high turbulence and interfacial areas (Jameson, 1966), contributing to the above mentioned effect (resonant bubble contactor).

The purpose of this work is to use this vibrating contactor in the hydrogenation of aqueous acetone on Raney nickel and to analyze the effect of the bubble cycling on the diffusional resistances, with a view to using this contactor for solid catalyzed gas-liquid reactions in general. The rate of hydrogenation is determined at constant pressure from volumetric measurements, and the effect the temperature, pressure, oscillation frequency, and bubble cycling have on it is studied. At the same time, the pore diffusion in the catalyst particle is analyzed and its tortuosity factor is determined.

CONCLUSIONS AND SIGNIFICANCE

The tortuosity factor of the Raney nickel catalyst was 4.0, in agreement with published results for similar catalysts (Satterfield, 1970). The apparent activation energies for the hydrogenation of acetone, determined in the absence of external diffusional effects, were 10.1 for Nicat 102 and 5.7 kcal/gmole for Nicat 820. The smallest catalyst particle had an effectiveness factor of one, while the largest operated in the asymptotic zone, and therefore the first value quoted is that associated with the rate of reaction constant.

Solid-liquid and gas-liquid diffusional effects become negligible at frequencies of oscillation above 1500 rev./

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min. When the reactor operates under external diffusional limitations, the effectiveness factor increases with the agitation as far as the catalyst is not in the chemically controlled zone. For the catalyst Nicat 820 only reaches a constant value above 1500 rev./min. On the other hand, the catalyst Nicat 102 operates in the chemically controlled zone above 700 rev./min. and then the effectiveness factor is unity.

Previous studies on the vibrating column of liquid have found that the bubble cycling generates very high turbulence and interfacial areas (Jameson, 1966) and that this contacting device is 20 times more effective than a stirred tank. In the hydrogenation of liquid acetone carried out in the present work, bubble cycling eliminated both the gas-liquid and liquid-solid resistances. Therefore, the same conversion can be obtained in a shorter time compared with a more conventional batch equipment. These results are very encouraging for continuing the development of this kind of contactor not only in gas-liquid reactions but also in processes such as liquid-liquid extraction and heat and mass transfer at solid surfaces.

For a solid catalyzed reaction between a gas B and a liquid A, the gas must first dissolve and both reactants diffuse towards the catalyst and react on its internal surface. If A and B have similar diffusion coefficients and B is very little soluble in the liquid phase, the concentration drop of component A will be so small that it can be assumed it approaches zero and its concentration inside the solid will be the same as the one in the bulk fluid. In such conditions the rate of diffusion of B will be limiting and its rate of consumption can be expressed in terms of the concentrations at the particle surface

$$-\frac{1}{m_c}\frac{dn_B}{dt} = k_m c_{As}{}^m c_{Bs}{}^p \eta = \frac{k_v}{\rho_p} c_{As}{}^m c_{Bs}{}^p \eta \qquad (1)$$

where k_m and k_v are the reaction rate constants per unit mass and unit volume of catalyst, respectively, and η is the effectiveness factor of B. For hydrogen reacting with acetone the above assumptions are correct.

The rate of reaction in a slurry reactor will be affected by the transport rate of hydrogen from the gas phase to the catalyst active sites and its rate of consumption per unit mass of catalyst can be expressed by (Satterfield, 1970)

$$-\frac{1}{m_c}\frac{dn_{H_2}}{dt} = k_L{}' \, a \frac{V}{m_c}(c_{H_{2i}} - c_{H_2})$$

$$= k_L \frac{6}{d\,\rho_p}(c_{H_2} - c_{H_{2s}}) = k' \, c_{H_{2s}}{}^p \, \eta \qquad (2)$$

where $k_L{}'$ and a are the gas-liquid mass transfer coefficient and interfacial area per unit volume respectively, k_L is the solid-liquid mass transfer coefficient, k' the apparent rate of reaction constant, and the subscripts i and s denote the gas-liquid interface and the solid surface, respectively.

Two extreme situations can be found:

1. The effectiveness factor is unity,
2. The effectiveness factor lies in the asymptotic zone.

In the first case we can rewrite Equation (2) in the form

$$r = \frac{c_{H_{2i}} - c_{H_{2s}}}{\dfrac{m_c}{k_L{}'aV} + \dfrac{d\,\rho_p}{6k_L}} = k' \, c_{H_{2s}}{}^p \qquad (3)$$

On the other hand, when the Thiele modulus is large enough for the catalyst to operate in the asymptotic zone, namely when the concentration of the limiting reactant is zero in the centre of the particle, the effectiveness factor will be given by (Petersen, 1965)

$$\eta = 1/h_p; \quad h_p = \frac{R}{3}\sqrt{\frac{p+1}{2}\,\frac{k'\,\rho_p}{D_{\text{eff}}\, c_{H_{2s}}{}^{1-p}}} \qquad (4)$$

and Equation (2) is transformed into

$$r = \frac{c_{H_{2i}} - c_{H_{2s}}}{\dfrac{m_c}{k_L{}'aV} + \dfrac{d\rho_p}{6k_L}} = \frac{3}{R}\sqrt{\frac{2}{p+1}\,\frac{k'\,D_{\text{eff}}}{\rho_p}}\, c_{H_{2s}}{}^{(p+1)/2} \qquad (5)$$

For an intermediate situation the effectiveness factor is obtained from the corresponding graph (Satterfield, 1970).

The objective of this study was to evaluate all the diffusional resistances when aqueous acetone is hydrogenated on Raney nickel in a vibrating slurry reactor. Two different average particle size catalysts were used in order to determine the tortuosity factor. Rates of hydrogenation were measured at various temperatures and oscillation frequencies and the mass transfer coefficients were estimated at the different experimental conditions.

RESONANT BUBBLE CONTACTOR

A small gas bubble in a vibrating column of liquid is under the action of the buoyancy force and a downwards force generated by the vibration (Jameson, 1966). If the frequency of oscillation is high enough, the bubble will be forced to move downwards. Hence, if the surface of the liquid becomes unstable, air bubbles will be formed and caught in the liquid motion. As soon as these bubbles come under the influence of the downward force, they begin to move and tend to aggregate at the bottom of the container. They finally form a large slug, whose volume increases above the resonant volume, and the gas slug rises to the top of the liquid pulsating violently. The cycle repeats itself from the beginning and is the basis of the resonant bubble contactor. Its influence on the diffusional limitations generally present in a slurry reactor will be studied.

APPARATUS AND PROCEDURE

Hydrogenation rates were determined in a vibrating aluminium cylinder by measuring the change in gas volume at constant pressure. The cylinder had a jacket built around it and was bolted to a platform which oscillated in the vertical plane by the action of an eccentrically mounted wheel. A 1-hp motor, coupled through a variable gear and a V-belt, supplied the required power. The reaction rate was determined by measuring the dibutyl-phthalate level in a gas burette connected to the cylinder. The pressure sensing device consisted of an electric cell attached to a mercury manometer. A more detailed description of the reactor and the measuring system can be found elsewhere (Lemcoff, 1974).

The catalysts used were Raney nickel Nicat 102 and Nicat 820, manufactured by Joseph Crosfield and Sons. A sample of the former was separated by sedimentation and its average diameter was determined with a Coulter Counter and found to be 10μ. The catalyst Nicat 820 were sieved under a nitrogen atmosphere and the sample obtained had an average diameter of 65μ. The catalysts' physical properties are summarized in Table 1, and their level of activity was determined from a

TABLE 1. PHYSICAL PROPERTIES OF RANEY NICKEL CATALYSTS

	Nicat 102	Nicat 820
Nickel content	92%	90%
Surface area, m^2/g	50	—
Porosity	0.51	0.51
Apparent density, g/cm^3	4.5	4.5
Average particle diameter, μ	10	65

series of experiments carried out under chemical reaction control. The rate of hydrogenation of acetone in isopropanol at low temperature was measured on both catalysts and the same value was observed, namely they have the same level of activity.

A sample of the wet catalyst was initially transferred to a weighed glass tube where it was dried under vacuum and at room temperature. Nitrogen was admitted to the tube and, after weighing it, was sealed off. The tube was placed in the cylinder, which was partially filled with water and connected to the vacuum pump in order to degas the system. After 15 min. it was purged with hydrogen, and degassed acetone was added to obtain a solution with a molar fraction of acetone of 0.33. The tube containing the catalyst was broken during the initial oscillations.

Runs were carried out at a fixed concentration of acetone in water but varying the temperature (7 to 21°C), the hydrogen pressure (1.33 to 7.33 10^4 N/m^2), and the frequency of oscillation (350 to 1600 rev./min.). The amplitude of the oscillation was 0.467 cm. When bubble cycling occurred in the cylinder, fluctuations in the pressure were observed. In this case a capillary tube was inserted between the vibrating cylinder and the manometer, and the pressure fluctuations were dumped out. It was possible then to continue using the same measuring system.

In preliminary experiments it was verified that the aluminium of the cylinder did not interfere with the measurements. No temperature gradients existed in the reactor throughout the experiments, even at low frequencies of oscillation. It can also be shown that thermal effects inside the catalyst were negligible (Satterfield, 1970).

RESULTS AND DISCUSSION

Calculation of the Gas-Liquid Mass Transfer Coefficient

The gas-liquid mass transfer coefficient can be expressed in terms of the rate of reaction as follows:

$$k_L'\,a = \frac{m_c}{V}\;\frac{1}{(c_{H_{2i}} - c_{H_{2s}})/r - d\rho_p/6k_L} \qquad (6)$$

where k_L can be calculated from the correlations developed by Lemcoff and Jameson (1975) (see Appendix) and the hydrogen solubility in the solvent mixture $c_{H_{2i}}$ from the equation (Lemcoff, 1974)

$$\log c_{H_{2i}} = -\,10.817 + \frac{47.3}{T} + \log p \qquad (7)$$

In order to calculate the gas-liquid mass transfer coefficient, the experimental results on Nicat 102 (Figure 1) will be used and, since the hydrogen concentration at the catalyst surface must be estimated from the experimental rate of reaction, an iterative method will be applied. It has been shown (Lemcoff, 1974) that the rate of hydrogenation of liquid acetone on Raney nickel is given by

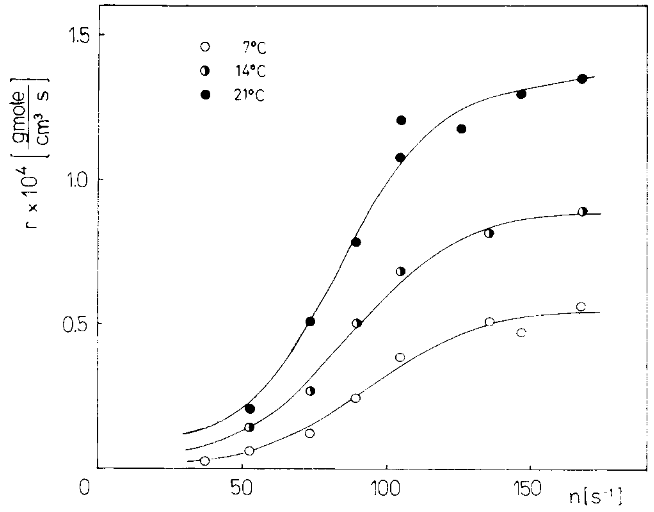

Fig. 1. Rates of hydrogenation over Raney nickel Nicat 102.

$$r = \frac{k_1\,K_A\,K_H{}^{1/2}\,c_A\,c_{H_2}{}^{1/2}}{(1 + K_S c_S{}^0 + (K_A - K_S c_S{}^0/c_A{}^0)c_A)^2} = k'\,c_{H_2}{}^{1/2} \qquad (8)$$

where k' is the apparent rate of reaction constant for a fixed and uniform acetone concentration in the solvent. Therefore

$$c_{H_{2s}} = \left(\frac{r}{k'\,\eta}\right)^2 \qquad (9)$$

The surface concentration can be calculated from the experimental rate of reaction by first assuming that the effectiveness factor is unity. The Thiele modulus is obtained from Equation (4) and the effectiveness factor is corrected. The iterative method is continued until consecutive values of the hydrogen concentration differ in less than 1%. Some of the values obtained are summarized in Table 2 (a tortuosity factor of 4 has been assumed). It is verified that above 700 rev./min., internal diffusional effects are negligible, that is, $\eta = 1$.

The gas-liquid mass transfer coefficient can now be calculated from Equation (6). Some of the results are shown in Table 2.

Calculation of the Tortuosity Factor

The rate of reaction to be observed on Raney nickel Nicat 820 can be estimated from

$$r = k'\,c_{H_{2s}}{}^{1/2}\eta \qquad (10)$$

where the concentration of hydrogen at the solid surface is given by

$$c_{H_{2s}} = c_{H_{2i}} - r\left[\frac{d\rho_p}{6k_L} + \frac{m_c}{k_L'aV}\right] \qquad (11)$$

TABLE 2. GAS-LIQUID MASS TRANSFER COEFFICIENTS IN THE VIBRATING SLURRY REACTOR

T, °C	n, 1/s	$r_e \times 10^5$, g mole/cm^{3}s	η	$c_{H_{2i}} \times 10^6$ g mole/cm^3	$c_{H_{2s}} \times 10^6$, g mole/cm^3	$k_L'\,a \times 10^2$, 1/s
7	73.3	1.17	0.99	1.67	0.0903	0.146
7	89.0	2.46	1.00	1.67	0.389	0.383
7	146.6	4.74	1.00	1.67	1.45	4.69
14	52.4	1.44	0.92	1.66	0.0519	0.122
14	89.0	5.08	1.00	1.66	0.546	0.643
21	89.0	7.83	1.00	1.57	0.495	0.803
21	125.7	11.8	1.00	1.57	1.12	3.16

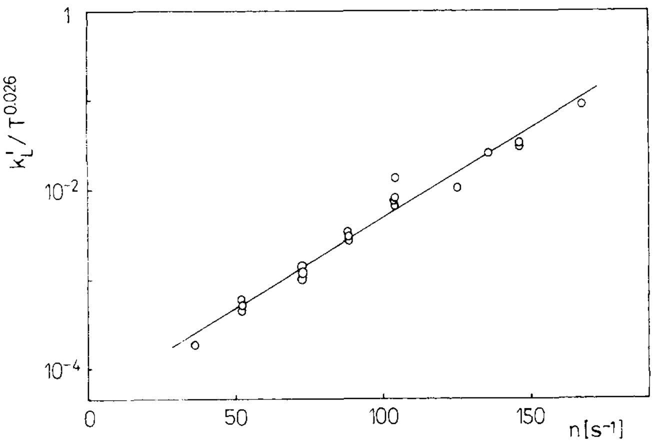

Fig. 2. Gas-liquid mass transfer coefficients.

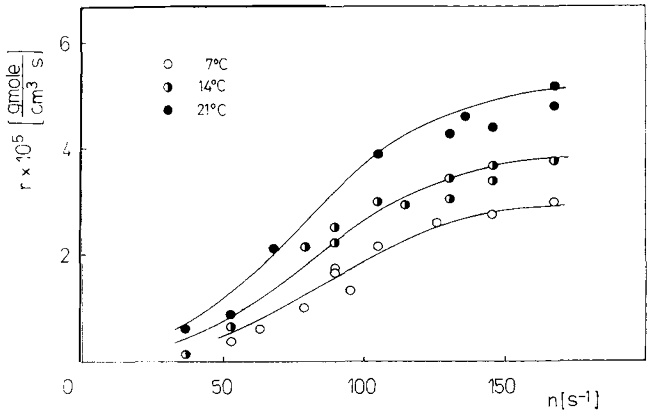

Fig. 3. Rates of hydrogenation over Raney nickel Nicat 820.

and the effectiveness factor can be estimated from its relationship with the Thiele modulus. The gas-liquid mass transfer coefficient is calculated from a correlation arising from the results obtained with Nicat 102, namely

$$\log k_L' a = -4.36 + 0.0260\,T + 0.0198\,n \qquad (12)$$

where T is the temperature in degree centigrade and n the frequency of oscillation in cycles/s (Figure 2).

The estimated rate of reaction will depend on the effective diffusivity, and its value can therefore be determined from the experiments as the one giving the best estimate of the rate of reaction. Since the effective diffusivity is $D_{\text{eff}} = D\epsilon/\tau$ and all the parameters but the tortuosity factor are known, this will be determined from the experimental results (Figure 3).

An iterative method on Equations (10) and (11) is applied, starting by replacing r in Equation (11) by the experimental rate of reaction, and after convergence the sum

$$S(\tau) = \sum_{j=1}^{N} (r_{ej} - r(\tau))^2 \qquad (13)$$

is calculated, where $r(\tau)$ represents the estimated value of the rate of reaction and depends on the value of the tortuosity factor.

In order to find the minimum of $S(\tau)$, a grid search method is applied to all the experimental results obtained with the grade 820 of catalyst. The estimated value of the tortuosity factor is 4.0, which is consistent with values quoted in the literature for similar catalysts (Satterfield, 1970). When the grid search is applied to each temperature separately, the optimum values of the tortuosity factor obtained are 3.5, 3.6, and 4.5 at 7, 14, and 21°C, respectively. In Table 3 some typical experimental and estimated values of reaction rate are summarized. It can be seen that the effectiveness factor values tabulated correspond to the asymptotic zone.

Table 3. Comparison Between Experimental and Estimated Rates of Reaction on Catalyst Nicat 820

T, °C	n, 1/s	$r_e \times 10^5$, g mole/cm³s	η	$c_{H_2s} \times 10^6$, g mole/cm³	$r_{\text{est}} \times 10^5$, g mole/cm³s
7	89.0	1.70	0.47	0.660	1.51
7	104.7	2.19	0.51	0.914	1.92
7	167.6	3.00	0.58	1.50	2.79
14	89.0	2.24	0.38	0.590	2.01
14	115.2	2.90	0.43	0.989	2.96
14	167.6	3.79	0.48	1.46	3.96
21	36.7	0.623	0.20	0.093	0.694
21	104.7	3.98	0.35	0.801	3.49
21	136.1	4.59	0.38	1.16	4.61
21	167.6	5.17	0.40	1.37	5.21

Energies of Activation

When the frequency of oscillation is above 1500 rev./min., the mass transfer resistances are negligible (see Figures 1 and 3). In the experiments with Nicat 102, the effectiveness factor is unity under this condition and, therefore the rate of reaction can simply be expressed as

$$r = k' c_{H_2}^{1/2} \qquad (14)$$

Differentiating the logarithm with respect to the absolute temperature we obtain

$$-R_g T^2 \frac{d \ln r}{dT} = E_1 = -R_g T^2 \frac{d \ln k'}{dT} + \frac{1}{2}\frac{d \ln c_{H_2}}{dT} = E_A \qquad (15)$$

where the heat of solution has been neglected (it is estimated to be less than 0.5 kcal/g mole) and E_A represents the activation energy associated with the rate of reaction constant k'.

On the other hand, the catalyst 820 operates in the asymptotic zone of the effectiveness factor. Equation (5) will apply in this case, with the hydrogen solubility being its concentration on the catalyst surface. An expression for the apparent activation energy is obtained by the same procedure applied to Equation (12)

$$E_2 = \frac{1}{2}(E_A + E_D) = \frac{1}{2}(E_1 + E_D) \qquad (16)$$

The activation energy associated with the diffusion of hydrogen is 2.8 kcal/g mole (*International Critical Tables*, 1929). In the experiments with Nicat 102 at 1600 rev./min. the activation energy is 10.1 kcal/g mole (Figure 4). From Equation (16) it follows that the apparent activation energy must be 6.4 kcal/g mole. This is in good agreement with the experimental value found for Nicat 820 of 5.7 kcal/g mole (Figure 4).

Diffusional Resistances

From Figures 1 and 3 it follows that only above 1500 rev./min. external diffusional resistances become negligible (in the absence of bubble cycling). The increase in rate of reaction with the frequency of oscillation is due to the reduction of the liquid phase diffusional resistances. At the same time, and since the hydrogen concentration at the catalyst surface increases with the mass transfer coefficient, we find from Equation (4) that the effectiveness factor also increases (order of reaction less than 1).

For the catalyst Nicat 820 (see Table 3) the effectiveness factor increases continuously, but at the highest

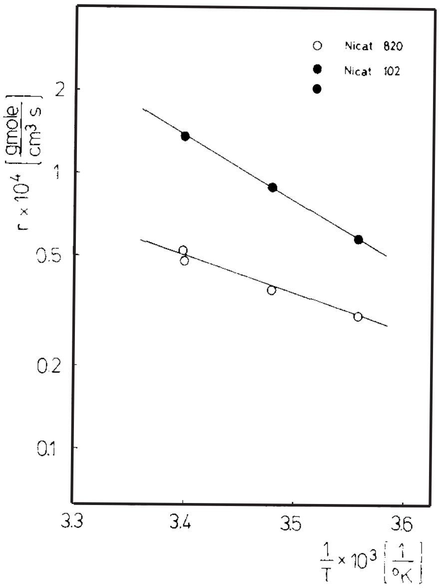

Fig. 4. Activation energies.

vibration frequencies the rate of increase is only 0.5% (from 1300 to 1600 rev./min.). At high frequencies, when the external diffusion is negligible, η has a constant value dependent on the intrinsic rate of reaction, physical properties of the catalyst and solubility of the gas.

Since the catalyst Nicat 102 operates in the chemically controlled zone above 700 rev./min. (see Table 2), that is $\eta = 1$, the increase in the observed rate is only due to the reduction of the external diffusional resistances.

Previous studies have shown (Jameson, 1966; Lemcoff and Jameson, 1975) that the bubble cycling increases the mass transfer coefficient in up to 10 times the values observed at 1600 rev./min. when no bubble cycling occurs and in 20 times those found in a stirred tank. This suggests that bubble cycling will eliminate the diffusional resistances observed in a slurry reactor.

In the hydrogenation on Raney nickel Nicat 820, when the external diffusional resistances are eliminated, and since the catalyst operates in the asymptotic zone, the rate of reaction can be calculated from Equation (5). It follows that

$$r = 6.73 \times 10^{-9}\, p_{\mathrm{H}_2}{}^{3/4} \text{ g mole/cm}^3\text{s} \tag{17}$$

at 7°C and the coefficient is 9.73×10^{-9} at 14°C.

We can now compare the experimental results when bubble cycling occurs in the liquid with the rate estimated from Equation (17), when the hydrogen pressure is replaced by the one at which the experiment was carried out. At 7°C, 7.50×10^4 N/m^2 pressure and 1800 rev./min., a rate of 3.14×10^{-5} g mole/cm^{3}s was measured, while the estimated one is 3.06×10^{-5}. At 14°C, 2.54×10^4 N/m^2 pressure and 1400 rev./min., the rates are 2.08 and 1.96×10^{-5} g mole/cm^{3}s, respectively. The agreement is very good and therefore we verify that the bubble cycling eliminates both the gas-liquid and the liquid-solid diffusional resistances.

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APPENDIX A

The solid-liquid mass transfer coefficient in the vibrating slurry reactor was correlated to various parameters of the system (Lemcoff and Jameson, 1974). Two different expressions were obtained corresponding to the cases when bubble cycling does and does not occur. For the first case

$$\frac{Sh - 2}{(\nu/D)^{1/3}} = 0.434 \left(\frac{nAd}{\nu}\right)^{0.85} \left(\frac{2A}{d}\right)^{-0.045}$$

and for the second case

$$\frac{Sh - 2}{(\nu/D)^{1/3}} = 0.0132 \left(\frac{nAd}{\nu}\right)^{0.75} \left(\frac{2A}{d}\right)^{-0.25} \left(\frac{n^2A}{g}\right)^{1.42}$$

NOTATION

A = amplitude of oscillation, cm
a = gas-liquid interfacial area per unit volume, 1/cm
c = concentration, g mole/cm^3
D = diffusion coefficient, cm^2/s
D_{eff} = effective diffusion coefficient, cm^2/s
d = particle diameter, cm
E_1, E_2 = apparent activation energies, kcal/g mole
E_A = activation energy, kcal/g mole
E_D = activation energy for diffusion, kcal/g mole
g = acceleration of gravity, cm/s^2
h_p = Thiele modulus
K = adsorption constant, 1/g mole
k' = apparent rate of reaction constant, (g mole 1)$^{1/2}$/g s
k_1 = rate of reaction constant, (g s/g mole)$^{1/2}$
k_m = rate of reaction constant per unit mass of catalyst
k_v = rate of reaction constant per unit volume of catalyst
k_L = solid-liquid mass transfer coefficient, cm/s
k_L' = gas-liquid mass transfer coefficient, cm/s
m, p = orders of reaction
m_c = mass of solid, g
N = number of experiments
n = frequency of oscillation, 1/s
p = partial pressure, N/m^2
R = particle radius, cm
R_g = gas constant (= 1.987 cal/g mole °K)
r = rate of reaction, g mole/g s
S = residual sum of squares
Sh = Sherwood number ($= k_L\, d/D$)
T = temperature, °C or °K
t = time, s
V = volume, cm^3

Greek Letters

ϵ = porosity
η = effectiveness factor
ν = kinematic viscosity, cm^2/s
ρ_p = particle density, g/cm^3
τ = tortuosity factor

Subscripts

A = acetone
e = experimental value
H = hydrogen
i = gas-liquid interface
S = solvent
s = solid-liquid interface

Superscripts

0 = pure liquid

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Method of Evaluation and Reduction of Vapor-Liquid Equilibrium Data of Binary Mixtures

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A new method to reduce vapor-liquid equilibrium data of binary mixtures and to evaluate a thermodynamic model is presented. It is based on the principle of maximum likelihood. Deviations between all measured and predicted quantities are calculated and confidence limits in model parameters are evaluated from the given estimates of experimental errors. Many examples illustrate the practical applications of the method.

SCOPE

The purpose of this work is to introduce new concepts in the mathematical treatment of experimental data of vapor-liquid equilibria of binary mixtures. There has been a great emphasis in the literature on consistency tests and comparison of thermodynamic models for the representation of these data. In view of the application of vapor-liquid equilibria to the design of industrial distillations, molecular theories do not provide a predictive method which could be tested only with a few data. One should instead rely on semi-empirical models with adjustable parameters. From classical thermodynamics, we know that such model can be formulated as an expression of the excess Gibbs energy as a function of composition and temperature. Unknown parameters in this function are adjusted upon experimental data. Usual methods of reduction of data yield the optimal values of the parameters only. But much more can be obtained from a careful application to the physical problem of the methods of applied statistics. In this perspective, one should consider as result of experimental measurement not only the value of a variable but also the standard deviation which can be estimated from reproducibility tests. Besides the optimal values of the parameters, the present mathematical treatment gives many other results, from which one can draw conclusions about both the validity of data and suitability of the excess Gibbs energy equation. The results are also useful in planning experiments for a specific utilization.

CONCLUSIONS AND SIGNIFICANCE

In this paper, a new method of treatment of experimental vapor-liquid data of binary mixtures is presented. It is based on the principle of maximum likelihood. A gaussian distribution of random error is assumed for all experimental measurements and an estimate of its variance is used as input to the calculation. The results of the treatment are:

1. Values of the parameters in a given expression for excess Gibbs energy, for instance, those of Van Laar or the NRTL model.
2. Estimate of the error in the values of the parameters.
3. Individual deviation between calculated and experimental value of each measured variables.

It is shown that this method of treatment of data is advantageous to check the validity of experimental measurement, compare models for vapor-liquid equilibria, evaluate their flexibility, verify the independence of parameters, and assess the necessary experimental information for the prediction of vapor-liquid data in an industrial problem of separation.

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