MASS TRANSFER AND HYDROGENATION OF ACETONE

IN A VIBRATING SLURRY REACTOR

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by

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ABSTRACT

When a column of liquid is made to oscillate vertically, gas bubbles are entrained and carried to the bottom of the column, where they aggregate and form a large slug which, in turn, rises to the top. Large volumes of gas are entrained and the fluid becomes highly agitated. A study of the solid-liquid mass transfer and of an heterogeneous catalyzed reaction in this equipment and the kinetic analysis of the hydrogenation of acetone over Raney nickel have been carried out.

A large increase in the mass transfer coefficient for solid-liquid systems in the vibrating liquid column over those reported in a stirred tank has been observed.

Two correlations for the Sherwood number as a function of the Reynolds, Schmidt and Froude numbers and the relative amplitude of oscillation have been found, one corresponding to the case no bubble cycling occurs and the other to the case it does.

In the kinetic study, a Langmuir-Hinshelwood type equation to represent the rate of hydrogenation of acetone in n-octane, isooctane, isopropanol and water and a correlation for the hydrogen solubility in different solvents and their mixtures have been developed. Activation energies and the order of reaction with respect to hydrogen have been determined.

Finally, the behaviour of the vibrating column of liquid as an heterogeneous slurry reactor has been analysed by using two Raney nickel catalysts of different average particle size in the hydrogenation of aqueous acetone. The effect the diffusional resistances play in the overall rate of reaction and the value of the tortuosity factor of the catalyst have been determined.

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To Diana

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CHAPTER 1

INTRODUCTION

Many industrial chemical processes involve heterogeneous gas-liquid catalytic reactions, the catalyst being a solid substance. The rate of reaction is generally affected by one or several mass transport steps. Different types of reactors have been developed in order to improve the contact between the different phases and therefore obtain higher reaction rates.

Fixed beds, where the solid catalyst particles remain in a fixed position to one another and the fluid passes over the particle surface, are widely used in semicontinuous processes. They must be shut down periodically to regenerate the catalyst. When the feed consists of both a gas and a liquid, the latter is allowed to flow down over the bed of catalyst, while the gas flows up or down through the empty spaces between the wetted pellets. These are called trickle bed reactors and have been introduced in the petroleum industry during the last 15 years.

The possibility of operating continuously was made easier with the fluidized bed reactors. The fluid is passed upwards through a bed of solids at a rate high enough to suspend the particles, which can be pumped into and out of the system like a fluid. The high turbulence and heat transfer rates enable a remarkably uniform temperature throughout the reactor to be maintained.

Slurry reactors, in which the solid catalyst is suspended in a liquid in the form of fine particles, are used particularly

in cases where three phases, gas, liquid and solid catalyst, must be brought into intimate contact. At present, they are used in the chemical industry, mainly for hydrogenation.

The slurry reactor has several advantages over the fixed or trickle beds:-

a) the agitation of the liquid, while ensuring the total suspension of the solid particles, keeps a uniform temperature throughout the reactor and increases the selectivity that can be achieved,

b) the large mass of liquid is a safety factor in the cases of exothermic reactions,

c) the small particles reduce diffusional resistances and, at the same time, the cost of pelleting is avoided,

d) heat recovery is possible because of the large heat transfer coefficient of the liquid slurry,

e) the catalyst can be regenerated continuously by withdrawing a side stream from the reactor.

However, the handling of catalyst suspensions and the design of continuous slurry reactors are two fields where information available is inadequate.

Several versions of slurry reactors have been developed up to now, each involving a different contacting method. The simplest is a stirred autoclave used in batch processes. A system resembling a fluidized bed, for the reactant gas enters through the bottom of a column and mixes its contents, is also

found. A more sophisticated one uses a pump to circulate the slurry through an external heat exchanger, and at the same time provides agitation to the reactor.

It has been found that in all these systems the mass transfer rate is generally controlling. This is due to the fact that the reactants and products are gases or liquids, and they are transported to or from the catalyst surface at a relatively slow rate. The path involved may be described in the following general terms:-

(i) diffusion of the gas from the bubbles to the gas-liquid interface,

(ii) diffusion of the gas from the gas-liquid interface to the bulk liquid,

(iii) diffusion of both dissolved gas and reactant from bulk liquid to the catalyst surface, which may involve diffusion into the catalyst pores,

(iv) surface reaction, involving adsorption of reactants and desorption of products,

(v) diffusion of products from the catalyst surface to the bulk liquid or gas phase, including eventually diffusion from the catalyst pores.

Therefore the performance of slurry reactors can be improved if both the gas-liquid and liquid-solid resistances are reduced.

Vibrations, which have been found to satisfy the above conditions in general (Baird - 1966), and the resonant bubble contactor, developed for gas absorption (Buchanan et al - 1963,

Jameson - 1966b), will be considered as solutions to this problem.

The experiments performed with the resonant bubble contactor on gas absorption showed that much higher interfacial areas are produced than in more conventional devices. To improve knowledge of the behaviour of this contactor in mass transfer processes, the liquid-solid diffusional resistance has been studied in Part I. A description of the apparatus and experimental techniques used is given in Chapter 3, and the results and correlations for the solid-liquid mass transfer coefficient are given in Chapter 4, where a discussion is also included.

The reaction chosen to analyse the performance of the resonant bubble contactor as a slurry reactor is the hydrogenation of liquid acetone catalyzed by Raney nickel. Although there are several studies of this reaction in the literature, it has always been assumed that the concentration of hydrogen in the liquid phase is only proportional to the gas pressure. In Part II the effect of the solvent on hydrogen solubility is taken into account, and the parameters in the kinetic equations are estimated. The apparatus and techniques used in these experiments are described in Chapter 5. The results and their discussion are given in Chapter 6.

Finally, data obtained in the operation of the slurry reactor is presented in Part III. Chapter 7 deals with the experimental set up, while the analysis and discussion of the results are given in Chapter 8. The general conclusions are given in Chapter 9.

CHAPTER 2

BACKGROUND

No previous studies on mass transfer to or from suspended solid particles or heterogeneous catalysis in a vibrating column of liquid have been found in the literature. However, a series of experiments on gas-liquid absorption has been carried out in the same equipment. Because of the very large interfacial areas produced, the efficiency of gas absorption is substantially increased.

Many studies have been concerned with the influence of vibrations and pulsations on the performance of chemical engineering processes and were reviewed by Baird (1966). Several experimental and theoretical studies have been carried out in order to analyse the increase in the rate of heat or mass transfer from a solid when it is oscillating with simple harmonic motion, and a few analysed the behaviour when the solid is fixed and the liquid is pulsating. In all these cases a considerable improvement in the performance was reported.

Because this thesis deals with a new type of equipment to be used in mass or heat transfer from suspended particles and in heterogeneous catalysis, a literature survey on the behaviour of stirred tanks in both processes is included. A comparison of the results obtained here with those obtained in more conventional equipment will be carried out.

At the same time, those works in the literature studying the hydrogenation of liquid acetone over Raney nickel are discussed in detail.

2.1 Resonant bubble contactor

Only in the last decade interest was developed to study the effects of vibrations and pulsations on gas absorption.

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 and Davidson - 1966, Jameson - 1966a). It was found experimentally that if

$$\frac{n^4 A^2 \rho h}{2 g P} = 1{\cdot}5 \qquad 2.1.1$$

where P is the total pressure, the bubble will remain seemingly stationary in space.

However, if the frequency of vibration is increased up to a point where equation 2.1.1 is transformed into an inequality, 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, with a period which depends upon the conditions of vibration. The resonant bubble contactor is based on this phenomenon.

In experiments where the rate of absorption of oxygen from air in solutions of Na_2SO_3 (Buchanan et al - 1963) and of pure oxygen in the same solution (Jameson - 1966b) were

measured, unusual high values in comparison with other contacting methods were reported. The production of very high interfacial areas seems to be the main factor.

2.2 Mass transfer to and from an oscillating solid

The earliest experimental work on vibration-assisted heat transfer to liquids was done by Martinelli and Boelter (1938) using an electrically heated tube oscillating in water. An improvement in natural convection of up to 400 per cent was reported, but correlation of the results was impossible.

Lemlich (1961), Fand and Kaye (1961) and Richardson (1967a) have published comprehensive reviews on the subject. An analysis of previous experimental work and new data for mass transfer from an oscillating cylinder was given by Sugano and Ratkowsky (1968). They covered a fairly wide range of parameter values, and found that the results were correlated by

$$Sh = 0{\cdot}178\ Re_v^{\cdot 633}\ Sc^{\frac{1}{3}}\ (A/R)^{\cdot 243} \qquad 2.2.1$$

where $Re_v = nAd/\nu$.

Using redox systems, Noordsij and Rotte (1967) studied the mass transfer to a vibrating sphere, and found the correlation

$$Sh = 2 + 0{\cdot}096\ Re_v^{\frac{1}{2}}\ Sc^{\frac{1}{2}} \qquad 2.2.2$$

but the range of applicability is rather narrow.

Richardson (1967b) studied the heat convection from a circular cylinder oscillating in a fluid. His analysis was based on the convection by acoustic streaming, which is induced by the movement of the cylinder. Neglecting buoyancy effects, he was able to derive expressions for the average Nusselt number for three different cases:

a) Convection by inner streaming, namely for large Prandtl (or Schmidt) numbers

$$Nu = 1{\cdot}36\ Re_{osc}^{\frac{1}{2}}\ Pr^{\frac{1}{3}}\ (A/R)^{\frac{1}{6}}\ H_c^{\frac{1}{3}} \qquad 2.2.3$$

where $Re_{osc} = \sqrt{2}\ U_\infty\ R/\nu$, H_c is a correction factor for large inner boundary layers, and U_∞ is the maximum relative velocity of the cylinder;

b) convection by outer streaming (small Prandtl numbers) at small streaming Reynolds numbers ($Re_s = U_\infty^2/n\nu$)

$$\frac{Nu}{Re_{osc}} = \frac{0{\cdot}718\ Pr^{\frac{1}{2}}\ (3\nu/n)^{\frac{1}{2}}}{R(1 + 1{\cdot}66(A/d)Pr^{\frac{1}{2}})} \qquad 2.2.4$$

with $n(\ = 2\pi f)$ being the oscillation frequency, and

c) convection by outer streaming at large streaming Reynolds numbers

$$Nu\ R\ (1 + 0{\cdot}95\ \frac{A}{d}) = 0{\cdot}484\ Re_{osc} Pr^{\frac{1}{2}} (3\nu/n)^{\frac{1}{2}} \qquad 2.2.5$$

Favourable comparisons with previous experiments, where the influence of natural convection is small, are presented.

Gibert and Angelino (1973) studied the mass transfer between a solid sphere and a liquid when each one is subject to vertical oscillation. The difference between the two series of results was less than 10%. When the sphere was vibrating, the correlations

$$Sh = 0{\cdot}489\ (Re_v\ (A/R)^{\frac{1}{2}})^{{\cdot}538}\ Sc^{\frac{1}{3}} \qquad 2.2.6$$

for $0{\cdot}4 < A/R < 1{\cdot}5$

and

$$Sh = 0{\cdot}557\ Re_v^{\cdot 538}\ Sc^{\frac{1}{3}} \qquad 2.2.7$$

for $1{\cdot}5 < A/R$

proved to be very accurate. They pointed out that by integrating, along half a period of oscillation, the correlation corresponding to a permanent flow around a sphere, namely

$$Sh = 0{\cdot}477\ Re^{\cdot 538}\ Sc^{\frac{1}{3}} \quad \text{for } Re > 1250 \qquad 2.2.8$$

a mass transfer coefficient is obtained which is always 25% smaller than the experimental one. They concluded that no quasi-stationary state can be assumed in the case of a vibrating sphere.

A few authors studied the influence of the pulsating motion of a fluid on the rate of mass transfer from a suspended solid. Bretsznajder et al (1963) reported increases in the value of the mass transfer coefficient of up to 13 times the value in the absence of pulsations. They covered a wide range of conditions by working with solid-gas, solid-liquid and gas-liquid systems.

2.3 Mass transfer in stirred tanks

The importance of stirred tanks in the chemical industry and the fact that many mass or heat transfer processes such as heterogeneous catalysis, gas absorption, solvent extraction, heat exchange and crystallization occur in it, have determined that quite a large number of works are found in the literature.

More than fifty studies of transfer to or from particles in baffled or unbaffled tanks have been reported. There are several good reviews on this subject (Harriott- 1962, Sykes and Gomezplata - 1967, Nienow - 1969, Brian et al - 1969, Levins and Glastonbury - 1972a). In spite of the large number of reports, the large number of variables involved is one of the reasons for a wide divergence in results, opinions and correlations.

One of the theories applied is the slip velocity theory (Harriott- 1962, Nienow - 1969), in which the Reynolds number is calculated on the basis of an average slip velocity. Several methods have been proposed to obtain an appropriate value. Harriott suggested the terminal velocity to be used, assuming for light particles a density difference of 0·3 g/cc. A mass transfer coefficient k_c^* for falling particles is obtained from the Froessling equation

$$Sh = 2 + 0{\cdot}6\ Re^{\frac{1}{2}}\ Sc^{\frac{1}{3}} \qquad 2.3.1$$

An enhancement factor is then calculated, for the agitation conditions and particle size, to correct the above result. This method will accurately predict a minimum value for the mass transfer coefficient.

Lately, special emphasis has been put on trying to correlate experimental results as a function of power input per unit volume. Kolmogoroff's theory of local isotropic turbulence (Brian et al - 1969, Levins and Glastonbury - 1972b) postulates that the kinetic energy is transferred from the large primary eddies generated by the stirrer to slow moving streams producing smaller eddies of higher frequency and so on, until finally the smallest disintegrate and dissipate the energy viscously. As the smaller eddies are isotropic and independent of the bulk motion, the turbulence generated is only a function of the power input per unit volume and the kinematic viscosity of the fluid. Brian et al (1969) did correlate their and other mass and heat transfer results in terms of Kolmogoroff's theory. However, some reports (Levins and Glastonbury - 1972b) suggest that it is not generally applicable.

2.4 Hydrogenation of acetone over Raney nickel

The use of Raney nickel as catalyst in organic reactions, mainly in hydrogenations, began in the 1930's. Although the basic technique to obtain it is simply to dissolve the aluminium of a 50:50 nickel-aluminium alloy with a concentrated solution of sodium hydroxide, variations in the catalyst activity and surface area are observed according to the experimental conditions and the storage solvent (Orito et al - 1965, Kubomatsu and Kishida - 1965); the product is extremely pyrophoric in air.

Early experiments showed (Adkins - 1937) that complete hydrogenation of acetone could be obtained even at room temperature and low pressure after only 11 hours. However, almost all the first studies of this reaction were carried out at high temperature (100-200°C) and/or pressure (10-50 atm) (de Ruiter and Jungers - 1949, Van Mechelen and Jungers - 1950, Heilmann and de Gaudemaris - 1951, Kiperman and Kaplan - 1964).

Over Raney nickel, acetone and other non-cyclic ketones yield the secondary alcohol selectively (Anderson and MacNaughton - 1942, Adkins - 1937). The promotive and poisoning effect of several compounds on the catalyst have been extensively studied (Sokol'skaya et al - 1966). The influence of the pH has been interpreted as a result of the formation of an interfacial electrical double layer on the surface of the catalyst (Watanabe - 1962). This explains the greater stability of adsorbed hydrogen and the increase in the rate of reaction when alkali is added to the system. It has also been shown

that the addition of HCl deactivates the Raney nickel.

The poisoning effect of carbon dioxide (Adkins and Billica - 1948), carbon disulfide (Kishida and Teranishi - 1969), oxygen and halogen compounds (Pattison and Degering - 1951) has also been reported.

The first kinetic study on the hydrogenation of liquid acetone on Raney nickel at room temperature and atmospheric pressure was done by Freund and Hulburt (1957). They measured volumetrically the uptake of hydrogen at constant pressure with isopropanol as a solvent. The apparent order with respect to hydrogen was determined to be ½, while the apparent activation energy of only 8 K-cal/g-mole. In their experimental conditions (particle diameter = 50μ) it was shown that internal diffusion was controlling and therefore the actual reaction order with respect to hydrogen was zero and the activation energy of 13 K-cal/g-mole.

Kishida and Teranishi (1968) put forward a Langmuir-Hinshelwood type kinetics to explain the influence of the solvent on the rate of reaction. The rate of consumption of hydrogen was measured over a wide range of concentrations of acetone in n-hexane, cyclohexane, methyl alcohol and isopropyl alcohol at 10°C, but maintaining the hydrogen pressure constant. The influence of the temperature was studied when n-hexane was used as a solvent. From the maximum apparent activation energy observed (12 K-cal/g-mole), they concluded that no diffusional process was controlling. All their results were correlated by assuming that the surface reaction between hydrogen and acetone is the controlling step, and that the rate of reaction constant

is the same in the different solvents. This is debatable since it is known that the solvent affects the rate of reaction (Amis - 1962).

Iwamoto et al (1970) extended this study by analysing the effect of a series of solvents on the rate of hydrogenation at 10°C and varying the concentration of acetone as above and the hydrogen pressure up to 70 cm Hg. Hexane, methanol, ethanol, 1- and 2-propanol and 1- and 2-butanol were used as solvents. With the first two the rate determining step was found to be the reaction between adsorbed hydrogen and the half hydrogenated acetone. With the remaining alcohols, the desorption of isopropyl alcohol was controlling. The true activation energy was found to be dependent on the solvent and varied between 7·4 and 10·3 K-cal/ g-mole, while the apparent heat of hydrogen adsorption was approximately constant (2·7 K-cal/g-mole). They tried unsuccessfully (Iwamoto et al - 1971) to find a correlation between the reaction rate constant and a characteristic parameter of the solvent.

However, neither of the above studies have taken into account the change in hydrogen solubility with the composition of the solution. It must be pointed out that the solubility in acetone is ½ of that in saturated hydrocarbons and more than 10 times the value in water.

In the present work, a correlation for the solubility of hydrogen in mixtures of solvents is developed, and kinetic expressions of the Langmuir-Hinshelwood type are applied to represent the experimental results.

2.5 Mass transfer effects in slurry reactors

The chemical industry has introduced the slurry reactors in some processes involving heterogeneous catalysis, where one of the reactants is in the gas phase, and the other in the liquid one. Up to now, it has been mainly used in small scale batch reactions, such as hydrogenations and in certain continuous operations of the Fischer-Tropsch reaction (Sherwood and Farkas - 1966).

Although diffusional rate limitations are found both in trickle bed and slurry reactors, very few studies have been carried out on this subject. An early report by Milligan and Reid (1925) on the hydrogenation of cottonseed oil, catalyzed by nickel in a stirred reactor, showed that mass transfer was the controlling rate, since it increased with the rate of stirring.

The hydrogenation of α-methylstyrene in the presence of supported or black palladium was investigated in different slurry reactors. Johnson et al (1957) showed that the mass transfer of hydrogen through the liquid was controlling and analysed the effect the rate of bubbling and stirring had on it. Both the resistances to mass transfer from the bubbles to the bulk liquid and from it to the catalyst surface were considered.

Sherwood and Farkas (1966) used a reactor where the stirring was obtained by the bubbling of hydrogen through a fritted glass disc at the bottom of the column. By analysing the effects of catalyst loading and temperature, they concluded that mass transfer to the solid catalyst was the rate deter-

mining step.

Satterfield et al (1968) carried out a more complete study on this same reaction. The catalyst (0·5% palladium on alumina) was used in three different physical forms:- a) finely crushed pellets (d = 50μ); b) whole pellets (3·17 mm by 3·17 mm) and c) pellets cut in half (3·17 mm by 1·27 mm).

The kinetics of the reaction was first established with the powdered catalyst. Even in the experiments with whole pellets, the mass transfer resistance between liquid and solid was negligible, hence it was possible to determine the effectiveness factor. Values of approximately 0.10 were found for the two types of pellets used. Their experimental results were satisfactorily correlated assuming that α-methyl-styrene was not limiting the process and that the tortuosity factor had a value of 3·9.

Snyder et al (1957) studied two catalyzed reactions, one heterogeneous (hydrogenation of nitrobenzene to aniline with 5% palladium on charcoal as a catalyst), and the other homogeneous (oxidation of an aqueous sodium sulphite solution in the presence of cupric ion). Several types of bench scale reactors were used. They differed mainly in the way they were agitated (shaking, rocking, dashing). The influence of the catalyst concentration and rate of mixing on the rate of reaction was reported.

The hydrogenation of cyclohexene in the presence of 5% platinum on activated alumina was analysed by Price and Schiewetz (1957). They used a semicontinuous slurry reactor where

the gas bubbled through the solution agitated mechanically. Mass transfer effects were studied by varying the hydrogen pressure, flow rate, stirring rate, temperature and reactor shape. With palladium black as a catalyst, Sherwood and Farkas (1966) reported that the rate of hydrogenation was controlled by the diffusion to the catalyst particles.

They also analysed the experimental results obtained by Kolbel and Maennig (1962), who studied the hydrogenation of ethylene over Raney nickel suspended in paraffin oil. Due to the small size of particles (d = 5μ), the chemical reaction was found to be controlling.

Kenney and Sedriks (1972) carried out a similar study to the one reported by Satterfield et al (1968), but with the hydrogenation of crotonaldehyde over commercial palladium on alumina catalysts. The metal was confined to a thin layer at the surface of the pellet. An effectiveness factor of 0·10 and a mean value for the tortuosity factor of 1·6 were estimated.

Recently, Ruether and Puri (1973) studied the mass transfer effects on the hydrogenations of allyl alcohol in water and ethanol, and of fumaric acid over Raney nickel. They worked in such conditions that not hydrogen but the substrate diffusion was controlling. Liquid-solid mass transfer coefficients were determined from the rate of reaction measurements. It is pointed out that for reaction orders less than one, it is possible to work in such conditions that there is external mass transfer control even with an effectiveness factor equal to 1.

From the above review, it is seen that mass transfer processes play an important role in the performance of a slurry reactor. In the present work, a new type of reactor is introduced. The higher mass transfer rates obtained with the resonant bubble contactor form the basis for the development of the vibrating slurry reactor. The effect of the operational conditions on the overall reaction rate will be determined.

PART I : MASS TRANSFER

CHAPTER 3

APPARATUS AND EXPERIMENTAL TECHNIQUES

There have been some experimental studies on the influence of vibrations of liquid columns on solid-liquid mass transfer. However, in all the cases the solid was a single particle maintained fixed. In the present work, mass transfer to suspended solid particles in a vibrating liquid column will be studied. Since considerable increase in gas absorption has already been reported with this contacting device in comparison with a stirred tank, a similar behaviour is expected in solid-liquid mass transfer.

In the following sections of this chapter, a description of the equipment and techniques used to obtain experimental results will be given. For particle diameters less than 1 mm, the mass transfer coefficient was obtained from the diffusion controlled neutralization of NaOH with acid ion exchange resins in water and glycerol solutions. For larger sizes of particles, the dissolution of spheres of pivalic acid in water was studied. In both cases, conductivity measurements were done.

3.1 Description of the apparatus

Mass transfer experiments were performed in a 7·3 cm i.d. aluminium cylinder. A jacket was built around it to maintain the liquid temperature constant throughout the experiments by circulating water from a constant temperature bath. The cylinder 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 whole apparatus was mounted on a 60 cm square double plate 5 cm thick, which in turn rested in rubber cushions. A rubber bung, with several inlets for the adding of solids and liquids, and from which hung a conductivity cell, was inserted in the top of the cylinder.

The frequency of oscillation, measured by a stroboscope, was varied during the experiments from 650 to 1900 rpm. The amplitude of the motion was kept at 0·467 cm, and was measured by a cathetometer.

3.2 Experiments with pivalic acid

After sizing, a weighed quantity of spheres of pivalic acid, average diameter of 0·368 cm (see Appendix I), was dispersed in the cylinder containing distilled water at 7°C, and immediately the motor was switched on and the variable gear adjusted to obtain the desired frequency of oscillation. The particle dissolution was followed by measuring the electrical conductivity with a Philips direct reading conductivity measuring bridge PR9501. Readings were taken every 10 seconds. The conductivity cell was kept immersed in the liquid, and oscillated together with the cylinder. It was verified that the vibration did not interfere with the conductivity readings. Neither did the aluminium of the cylinder.

As soon as the conductivity stopped changing, namely when the solid was completely dissolved, a sample of the solution was taken and titrated with a standard solution of NaOH in order to determine the final concentration of pivalic acid and therefore the cell constant.

It was not possible to obtain stable readings when bubble cycling occurred in the system. In this case, the conductivity cell was placed together with a thermometer in an external recycle of solution, which was pumped by means of a peristaltic pump. Particles were prevented from entering this recycle by filtration of the solution with glass wool. Results obtained with this disposition were corrected for the amount of solution being extracted from the cylinder.

The temperature of the system was measured by a thermocouple connected to a potentiometer, or simply by a thermometer.

It was verified that it did not change more than ± 0·5°C throughout any experimental run.

3.3 Experiments with ion exchange resins

Zeo Carb 225 (4·5% DVB), a strong acidic ion exchange resin was used in these experiments. Several batches of the resin of different diameters were treated to regenerate the hydrogen form as it is described in Appendix I. Volume and diameter of the swollen resin, in water and solutions of glycerol, were determined as a function of its dry weight and its diameter when in equilibrium with saturated air (see Appendix I).

A known volume of 0·1 N NaOH solution was added to the cylinder containing a weighed amount of resin beads dispersed in the solvent. The motor was switched on to produce the oscillations at a predetermined frequency. The neutralization was followed by measuring the electrical conductivity of the solution, as described earlier. The temperature was measured during the neutralization, and no change of over 0·5°C was detected.

Water and two solutions of glycerol, one 30% and the other 67% by weight, were used as solvents. No external circuit was necessary for the glycerol solutions when bubble cycling occurred in the cylinder, because the oscillations in the conductivity readings were short and spaced in time as to allow to obtain a stable value in between. In the case of bubble cycling in water, no filtration of the solution was possible, because the fine particles determined a large pressure drop in the filter and a very low flow rate in the external circuit. Therefore no external circuit was used, but the frequency of oscillation was reduced at intervals of

30 seconds in order to stop the bubble cycling and make the readings possible. As soon as the conductivity was measured, the frequency was restored to its original value. The error introduced was estimated to be less than 5%.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter the results of the experimental work on mass transfer are given and discussed. The experiments were performed to study the influence of the vibration on the liquid-solid mass transfer and to analyse the effects of the bubble cycling on the behaviour of the system.

A summary of the physical properties of the substances used is given in Table 4.1. Densities of the ion exchange resins and glycerol solutions were determined experimentally (see Appendix I). Viscosities were measured with a Ferranti rotating concentric cylinders viscosimeter and the remaining data was taken from the literature (Hales - 1967, Harriott - 1962).

Table 4.1

Physical properties

System	T (°C)	ρ_p (g/cc)	ρ (g/cc)	μ (cp)	$Dx10^5$ (cm^2/s)	Sc (-)	c_s (g/cc)
Pivalic acid in water	7	0·95	1·00	1·45	0·513	2830	0·025
NaOH + resin in water	20	1·12	1·00	1·00	1·93	518	
NaOH + resin in 30% glycerol	20	1·16	1·07	2·35	0·965	2290	
NaOH + resin in 67% glycerol	20	1·22	1·165	17·9	0·142	107500	

4.1 Mass transfer from pivalic acid spheres

For a weak acid the dissociation constant at a certain concentration c can be expressed as

$$K_{AH} = c \frac{\Lambda_c^2}{\Lambda_o^2} \qquad 4.1.1$$

where Λ_o is the equivalent conductivity at infinite dilution. Since the conductivity of a solution is related to its concentration by

$$\kappa = \frac{c \Lambda_c}{1000} \qquad 4.1.2$$

it follows that

$$c = C\kappa^2 \qquad 4.1.3$$

Hence, the rate of dissolution of pivalic acid will be expressed by

$$\frac{dc}{dt} = 2C\kappa \frac{d\kappa}{dt} \qquad 4.1.4$$

The derivative of conductivity with respect to time was determined by fitting a polynomial

$$\kappa = a_1 t^{1/6} + a_2 t^{1/3} + a_3 t^{1/2} + a_4 t^{2/3} + a_5 t^{5/6} \qquad 4.1.5$$

to the experimental results and differentiating it analytically. In the above expression, κ represents the conductivity of the resulting solution corrected for the solvent and t, the corresponding time.

From a mass balance between a dissolving sphere and its surrounding solution, we can establish that

$$k_L(c_s - c) = -\rho_p \frac{dR}{dt} = \frac{V}{\pi d^2 N} \frac{dc}{dt} \qquad 4.1.6$$

where V is the volume of solution, N, the number of spheres, d, the instantaneous diameter, and the subscript p represents properties of the solid.

Expressing equation 4.1.6 as a function of the mass of spheres, the mass transfer coefficient results

$$k_L = \frac{\rho_p \, d_o^3 \, VC}{3 \, m_c} \quad \frac{\kappa \, d\kappa/dt}{d^2 (c_s - C\kappa^2)} \qquad 4.1.7$$

where

$$d = d_o \left(1 - \left(\frac{\kappa}{\kappa_f} \right)^2 \right)^{\frac{1}{3}} , \qquad 4.1.8$$

κ_f being the final conductivity of the solution.

The corresponding Sherwood number for each particle diameter will be given by

$$Sh = \frac{k_L \, d}{D} \qquad 4.1.9$$

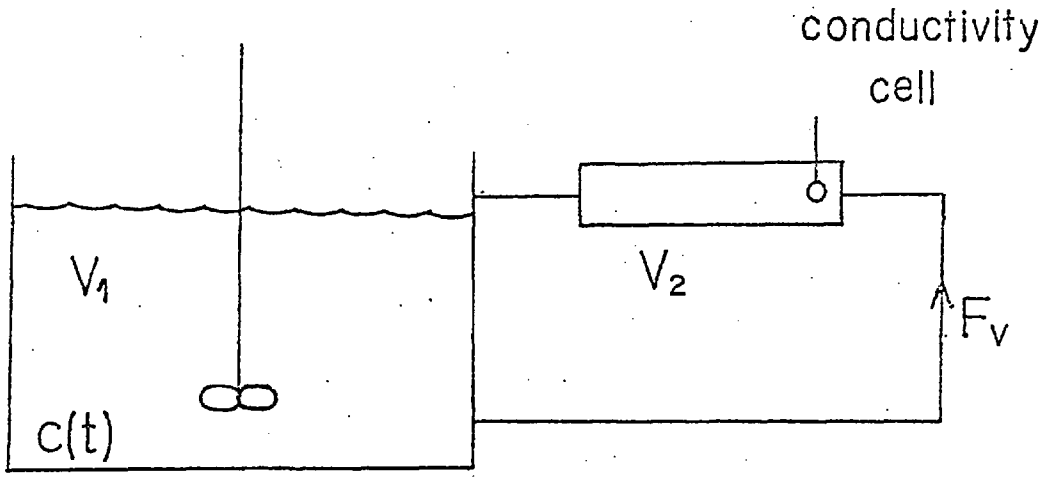
where D is the diffusion coefficient of pivalic acid in water.

In order to estimate the correction term when an external recycle was used, a simple model was assumed where the flow in the recycle was considered to be plug flow (see Figure 4.1).

From a mass balance in the system, it follows that

$$V_1 \frac{dc(t)}{dt} = -k_L \, \pi \, d^2 N \, (c_s - c(t)) + F_v \left(c(t - V_2/F_v) - c(t) \right) \qquad 4.1.10$$

By expanding the last term in Taylor's series, we obtain an expression for the mass transfer coefficient:



4.1 Model of vibrating liquid column with external recycle

$$k_L = \frac{\rho_p \, d_o^3 (V_1+V_2)}{6d^2 m_c (c_s - c(t))} \left[\frac{dc(t)}{dt} - \frac{V_2}{F_v} \frac{V_2}{V_1+V_2} \frac{d^2c(t)}{dt^2} \right] \quad 4.1.11$$

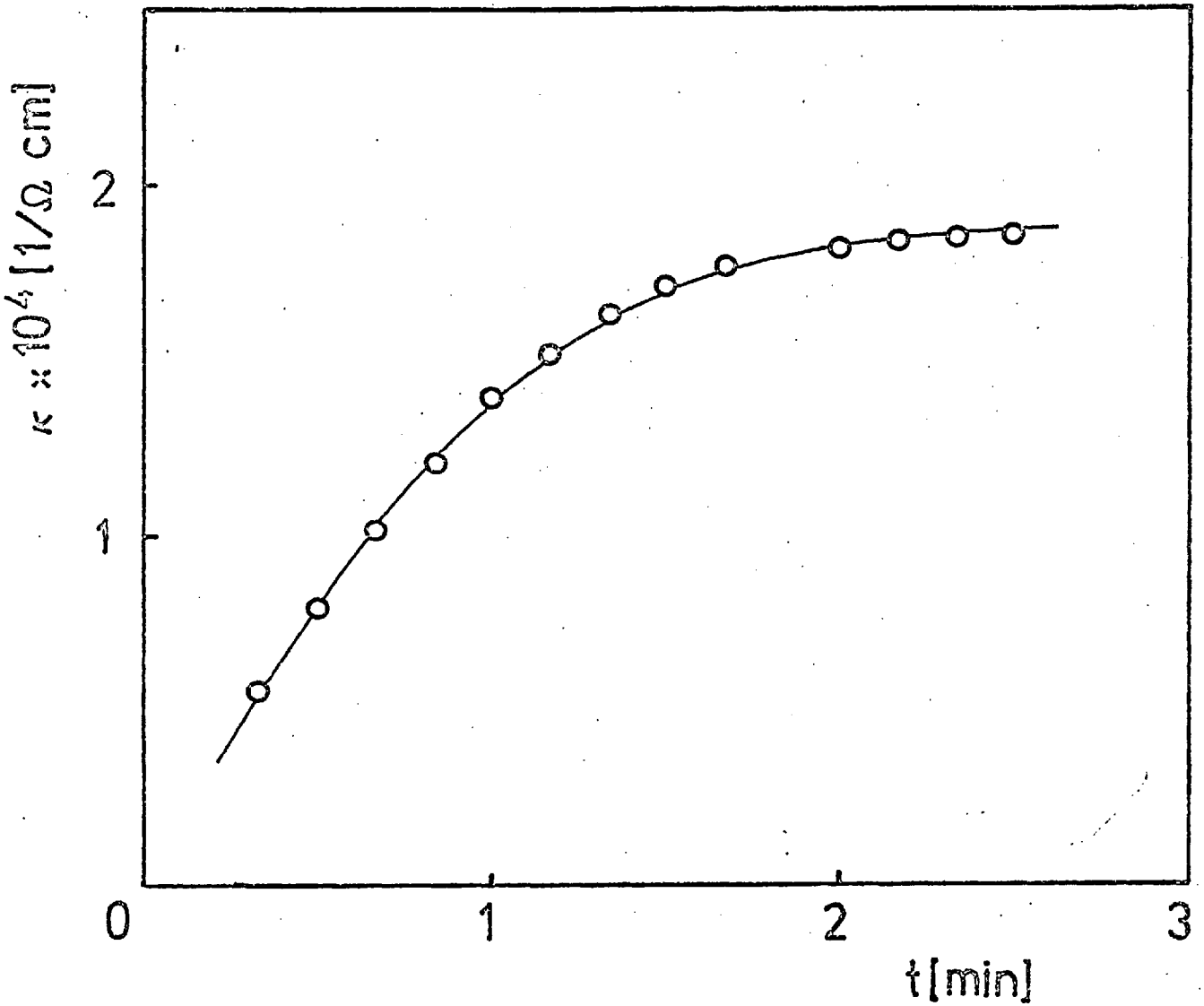
Substituting equation 4.1.4 in the above

$$k_L = \frac{\rho_p \, d_o^3 (V_1+V_2) C}{3 \, m_c} \frac{\kappa \left[\frac{\kappa}{dt} - \frac{V_2}{F_v} \frac{V_2}{V_1+V_2} \left(\frac{d^2\kappa}{dt} + \frac{1}{\kappa} \left\{ \frac{d\kappa}{dt} \right\}^2 \right) \right]}{d^2 (c_s - C\kappa^2)} \quad 4.1.12$$

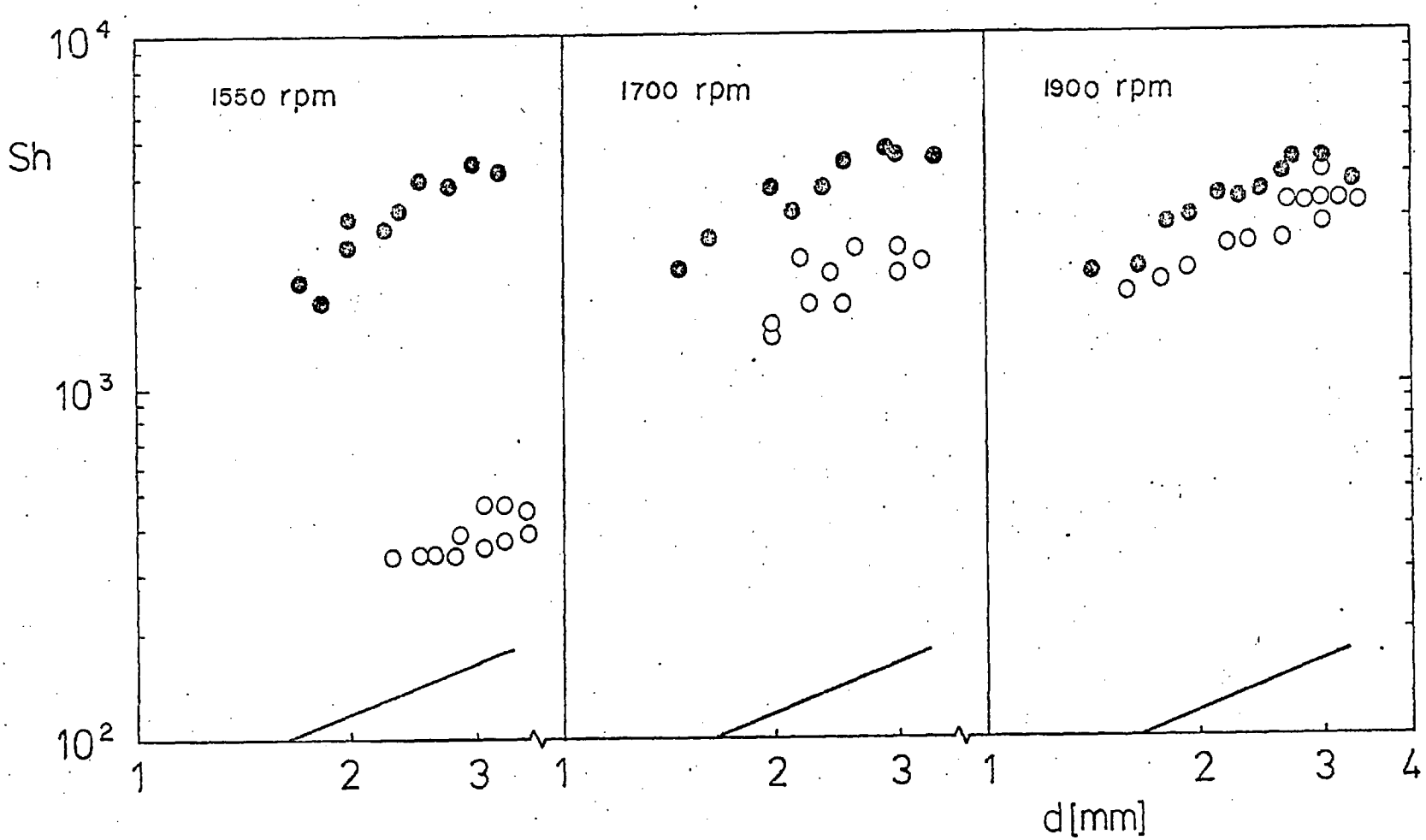
The volume of the external circuit was always less than $1/7$ of the total volume and the mean residence time in it was approximately 5 seconds. As the rate of change of conductivity with time was not very high, the correction term was generally less than 10% of the uncorrected value of the coefficient.

Several values for the mass transfer coefficient and the Sherwood number were obtained at various stages in each experiment on the dissolution of pivalic acid. A typical plot of the conductivity of the pivalic acid solution as a function of time is represented in Figure 4.2. Both the initial and final values in each experiment were neglected, the former because of the inaccuracy in the fitting of the polynomial at the initial times, and the latter due to irreproducibility of the results.

Values of the Sherwood number for different frequencies were plotted in Figure 4.3 as a function of the particle diameter. Series of results were obtained with and without bubble cycling. The results are compared with those obtained by Brian et al (1969) in a conventional stirred tank. An increase of up to 25 times the previous values is observed, showing the importance of vibrations and bubble cycling in improving the performance of mass transfer processes.



4.2 Conductivity measurements during pivalic acid dissolution
(n = 1875 rpm, bubble cycling)



4.3 Sherwood numbers from pivalic acid dissolution

○ no bubble cycling, ⊛ bubble cycling, —— Brian et al (1969)

Figure 4.3 shows that the vibrational frequency has relatively greater effect when no bubble cycling occurs.

4.2 Mass transfer to ion exchange resins

Helfferich (1965) and Blickenstaff et al (1967) studied the kinetics of neutralization of a strong acid ion exchange resin by strong bases. From the analysis of film and particle diffusion a criterion was established to determine which one is controlling. It was shown that when the ratio $6\bar{D}\bar{c}/k_L cR$, where the symbols with over bars denote properties in the interior of the ion exchanger, is very much greater or much smaller than one, the control is by film-diffusion or particle-diffusion, respectively.

For film-diffusion control and for $cV < \bar{c}\bar{V}$, namely when the resin is in excess over the alkali, the fractional approach to equilibrium is given by

$$F(t) = 1 - \exp\left(-\frac{6k_L \bar{V}}{d\ V}t\right) \qquad 4.2.1$$

but in this case it also represents the fractional consumption of alkali, hence

$$F(t) = 1 - \frac{c(t)}{c(t_o)} \qquad 4.2.2$$

Then, the mass transfer coefficient for NaOH is obtained from

$$k_L = -\frac{V\ d}{6\ \bar{V}} \frac{\ln\left(\kappa(t_2)/\kappa(t_1)\right)}{t_2 - t_1} \qquad 4.2.3$$

since for a strong electrolyte the conductivity of very dilute solutions is given by

$$\kappa = \frac{\Lambda_o\ c}{1000} \qquad 4.2.4$$

where κ is corrected for the conductivity of the solvent.

A semi-logarithmic plot of the experimental results of conductivity as a function of time was found to be linear for $c/c_o > 0{\cdot}20$, and the slope was used in equation 4.2.3 to calculate a value for the mass transfer coefficient.

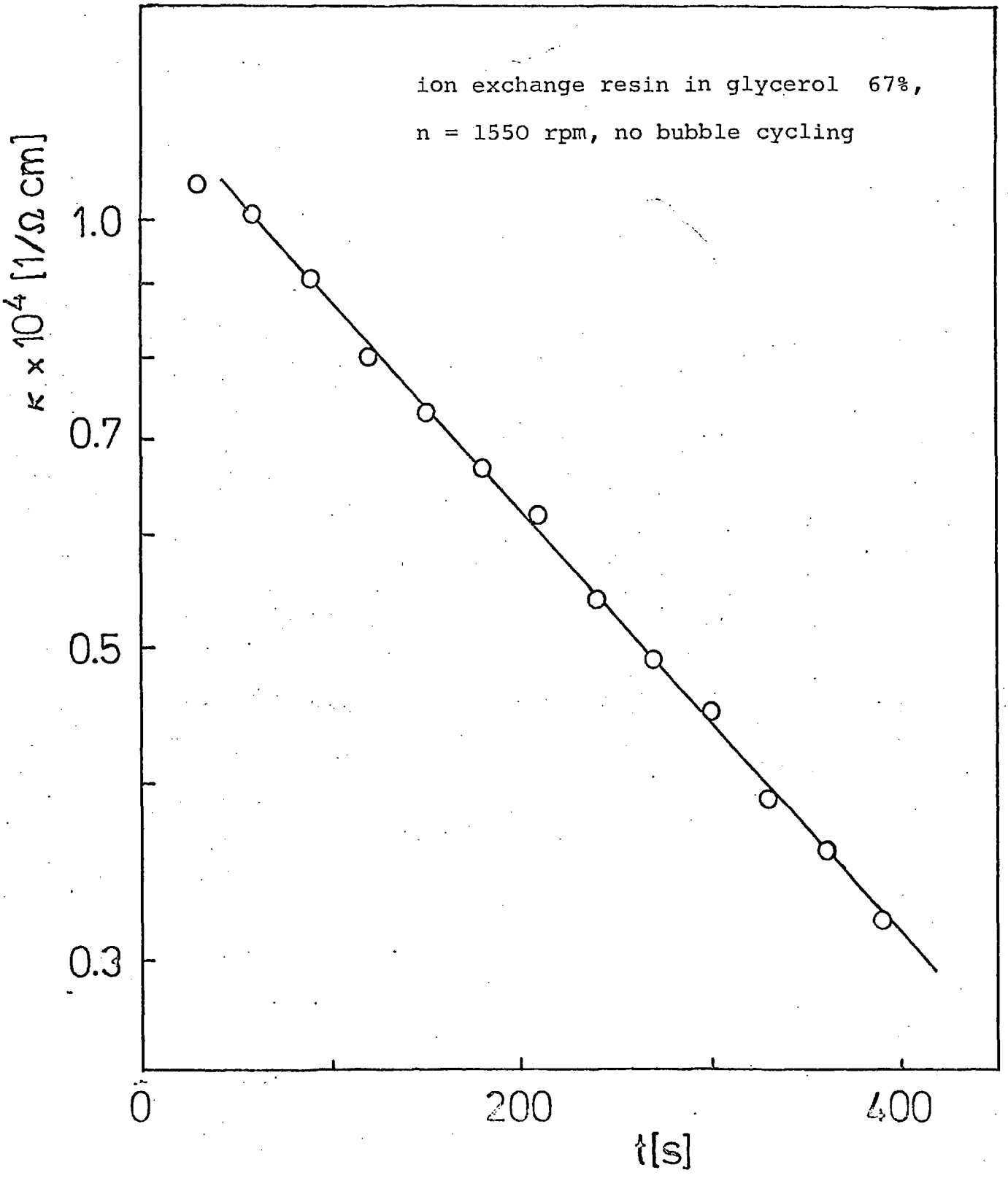
The experimental results obtained for the mass transfer to ion exchange resins are summarized in Appendix III, while a typical semi-logarithmic plot of the measured conductivity as a function of time can be seen in Figure 4.4.

Sherwood numbers were obtained by applying equation 4.1.9 with the diffusion coefficient of NaOH being given by

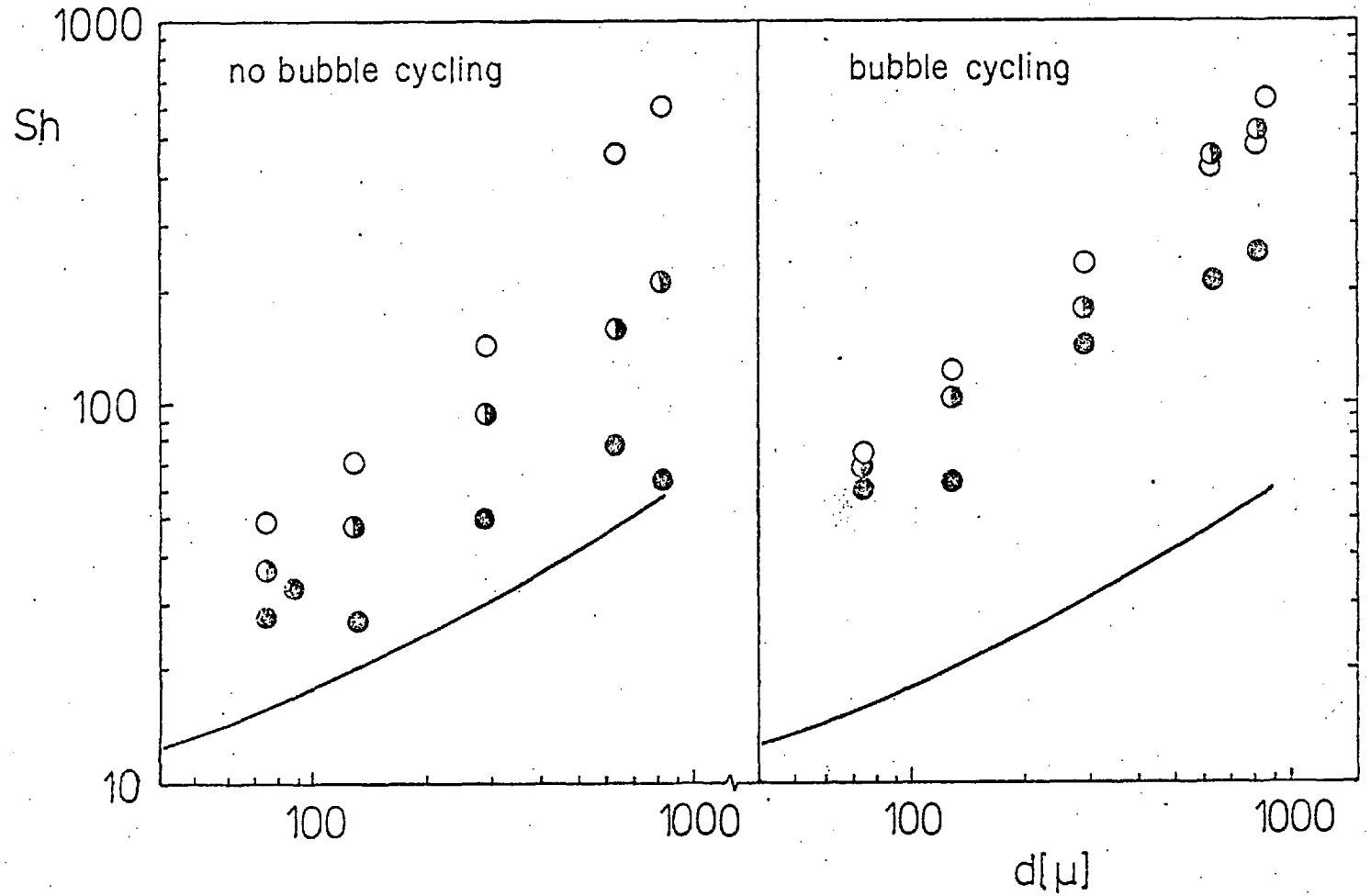
$$D = \frac{2D_{Na^+} D_{OH^-}}{D_{Na^+} + D_{OH^-}} \qquad 4.2.5$$

Values for the Sherwood number for different frequencies were plotted as a function of the particle diameter. The data is presented in Figure 4.5 with and without bubble cycling. Comparing these with the results obtained by Harriott (1962) with similar reactants but in a stirred tank, a considerable increase in the rate of mass transfer is observed, although not as large as with the pivalic acid spheres.

Ionic diffusion coefficients were obtained from the literature (Int. Crit. Tables - 1929).



4.4 Conductivity measurements during neutralization of NaOH



4.5 Sherwood numbers from neutralization of ion exchange resins in glycerol 67%
○ 1900 rpm, ◑ 1700 rpm, ◉ 1550 rpm, — Harriott (1962)

4.3 Correlation of experimental results

In order to correlate the experimental values of Sherwood number obtained with the vibrating cylinder, it is necessary to determine the parameters or group of parameters which may influence the mass transfer.

An analysis of the effects of transpiration and changing diameter on the mass transfer coefficient was carried out by Brian and Hales (1969). They showed that both effects are negligible in the neutralization of ion exchange resins and the dissolution of pivalic acid.

An analysis of the equation of motion of a particle in a vibrating fluid derived by Tchen is given in Appendix II. It follows that the Sherwood number depends on five parameters:

a) Reynolds number, $Re_v = 2nAR/\nu$

b) relative amplitude of oscillation, $H = A/R$

c) Froude number, $G = n^2A/g$

d) density ratio, ρ_p/ρ

e) Schmidt number, $Sc = \nu/D$

In the experiments, the relative density (ratio of particle density to liquid one) did not vary more than 10%, and therefore it is not sensible to include that parameter in a correlation.

In most of the research dealing with mass transfer to or from an oscillating solid, the correlations reported include a dependence with Schmidt number to the power $\frac{1}{3}$ (see Section 2.2). Assuming this same dependence is valid

in the present case, the least squares method will be applied to the logarithmic form of the equation

$$\frac{Sh - 2}{Sc^{\frac{1}{3}}} = \alpha \, Re_v^{\beta} \, H^{\gamma} \, G^{\varepsilon} \qquad 4.3.1$$

in order to estimate the values of the coefficients.

Two series of experimental results were available, one corresponding to the case when no bubble cycling occurred in the cylinder and the other when it did occur.

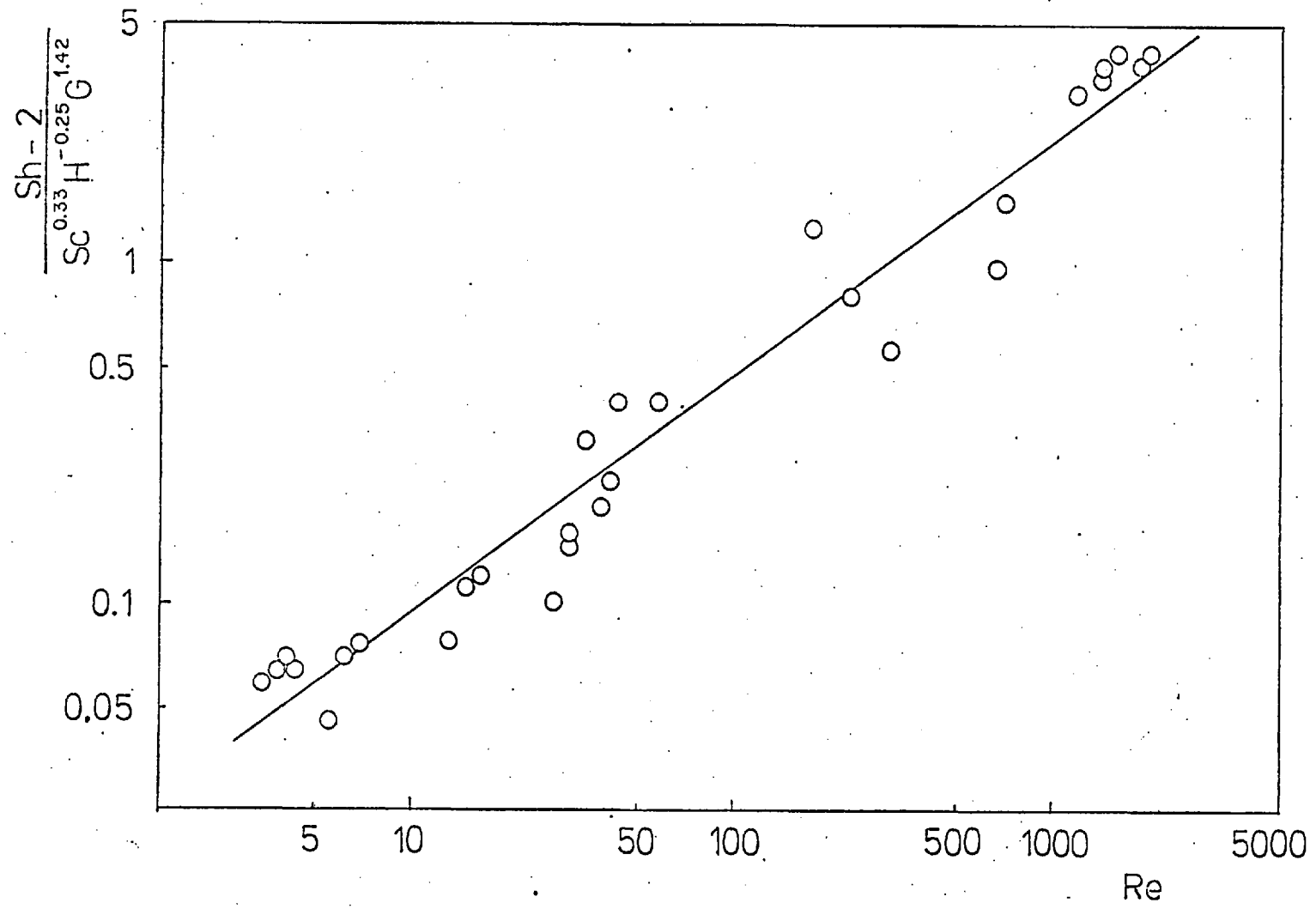
Since in each experiment with pivalic acid a series of values of the Sherwood number is obtained (shrinking particle) while in each experiment with ion exchange resins only one value, a different weight should be given to each one of those in the correlation. Assuming the error affecting each measurement is the same, and since the variance of the estimated Sherwood number decreases when the number of points used to calculate it increases, a unit weight will be given to the results obtained with ion exchange resins and a weight of 1/8 to those from the pivalic acid dissolution.

When no bubble cycling occurs in the system, the estimated values of the parameters are

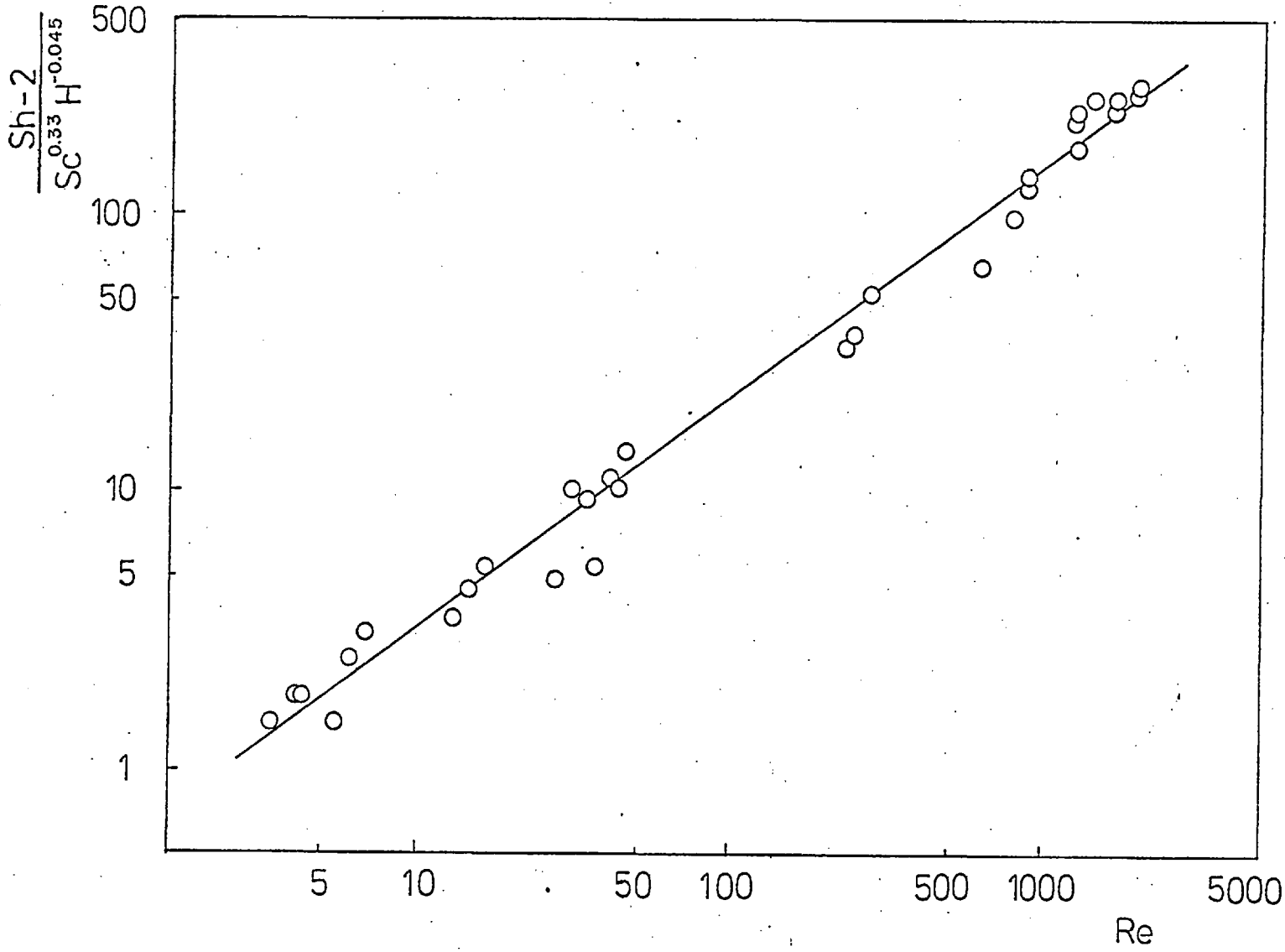
$$\alpha = 0{\cdot}0132; \quad \beta = 0{\cdot}75; \quad \gamma = -0{\cdot}25; \quad \varepsilon = 1{\cdot}42 \qquad 4.3.2$$

the standard error being 0·026 (see Figure 4.6).

When bubble cycling occurs in the system, the Froude number G should not be included because the change in the frequency of oscillation is less than 20%. Therefore we



4.6 Correlation of solid-liquid mass transfer results (no bubble cycling)



4.7 Correlation of solid-liquid mass transfer results (bubble cycling)

will look for a correlation of the Sherwood number with the Reynolds and Schmidt numbers and the relative amplitude of vibration. A linear regression gives the values

$$\alpha = 0{\cdot}434; \qquad \beta = 0{\cdot}85; \qquad \gamma = -0{\cdot}045 \qquad 4.3.3$$

with a standard error of 0·010 (see Figure 4.7).

The dependence of the mass transfer coefficient on the independent variables can be derived from the obtained correlations. It follows that

$$k_L \propto R^{0} \quad \nu^{-0{\cdot}42} \; D^{0{\cdot}67} \qquad 4.3.4$$

when no bubble cycling occurs in the system, and that

$$k_L \propto R^{-0{\cdot}1} \nu^{-0{\cdot}52} \; D^{0{\cdot}67} \qquad 4.3.5$$

when the bubble cycling does occur.

It is interesting to note that the dependence on Reynolds number and relative amplitude is almost the same in equations 4.3.2 and 4.3.3, which represent the cases when the bubble cycling does and does not occur, respectively. If we compare the effect of particle diameter, viscosity and diffusion coefficient (arising from Sherwood and Schmidt numbers) observed in the experiments with those reported for mass transfer in a stirred tank (Levins and Glastonbury - 1972a), we conclude that it is very similar to the average effect calculated there.

In addition, we can point out that the influence of the oscillation frequency when no bubble cycling occurs is reflected in an exponent of 3·59. In a qualitative way, we can say that this variable has much less influence when the bubble cycling occurs in the system.

4.4 Comparison with stirred tanks

Many studies of solid-liquid mass transfer have been carried out in stirred tanks. In Chapter 2 we analysed the corresponding literature.

Harriott (1962) studied the mass transfer to ion exchange resins in water and in several other more viscous solutions. The experiments were carried out in a baffled 10 cm round bottom flask, and the impellers were six-blade turbines, ranging from 4 to 18 cm in diameter. For the larger impeller sizes, 20 and 54 cm baffled flat-bottom tanks were used. The influence of the power input was determined and, in the correlation obtained, an exponent of 0·15 was found to be the most appropriate. We have compared the results obtained in the resonant bubble contactor with ion exchange resins with those reported by Harriott for a power input of 0·024 $m^2 s^{-3}$ (see Figure 4.5). For the system with bubble cycling, an increase in the mass transfer coefficient ranging from 4 to 10 times Harriott's values is observed. A smaller increase results for the system without bubble cycling. In other experiments, at higher power inputs, Harriott obtained mass transfer coefficients up to twice those found at 0·024 $m^2\ s^{-3}$, that is up to half those found here.

For the experiments with larger particles (pivalic acid spheres), the results reported by Brian et al (1969) were taken as a comparison. They used both baffled and unbaffled 12 cm round bottom flasks. Two types of impeller, one a 6·3 cm diameter three-bladed marine type, and the other a four-

bladed open turbine were used, but only the first in the mass transfer experiments. The stirrer speed was varied between 100 and 400 rpm. In Figure 4.3, the results of Brian et al for the mass transfer coefficient from pivalic acid spheres in the baffled stirred tank are plotted. They correspond to a stirrer speed of 300 rpm and a power input of $0{\cdot}053\ m^2s^{-3}$.

In this case the resonant bubble contactor is up to 25 times more effective.

These results are very encouraging for the further development of this kind of contactor, since in many cases the size of the equipment to be used is directly related to the rate of mass transfer. At the same time, an increase in the efficiency of the process will be observed.

PART II : KINETICS OF ACETONE HYDROGENATION

CHAPTER 5

APPARATUS AND EXPERIMENTAL TECHNIQUES

The influence of the solvent on the hydrogenation rate of liquid acetone catalyzed by Raney nickel was studied by Kishida and Teranishi (1968), who explained their experimental results in terms of a rate equation derived from a Langmuir-Hinshelwood type mechanism.

A more complete study was carried out by Iwamoto et al. (1970) in the same and other solvents. Different rate equations to the previously reported were found to represent the results. However, neither work took into account that, for a fixed hydrogen pressure, the hydrogen solubility changes when the solvent composition changes.

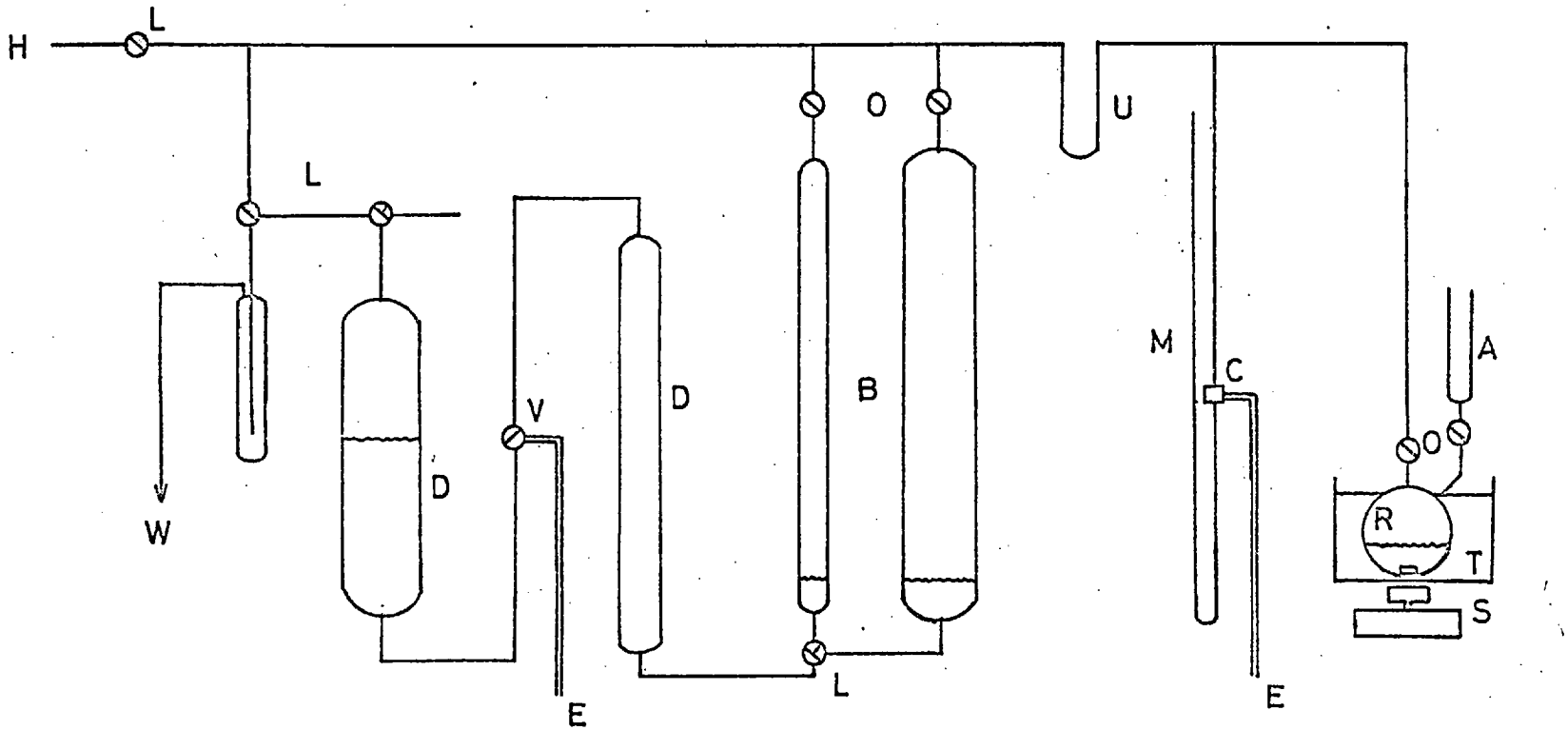
Therefore the adsorption and rate of reaction constants they determined are affected by this error. This fact and the controversial reports on the influence of water on this reaction (Watanabe - 1962, Sokol'skii and Erzhanov - 1953) determined a study of the kinetics of acetone hydrogenation in various solvents to be carried out. Two nonpolar-n-octane and 2,2,4-trimethylpentane (isoctane)-, one polar-isopropyl alcohol- and one highly polar solvent- water- were chosen for the experiments.

A description of the apparatus and the experimental techniques involved in measuring the consumption of hydrogen in a stirred tank reactor is given in this chapter.

5.1 Description of the apparatus

Hydrogenation rates were measured in a stirred glass reactor of half a liter capacity. It was kept immersed in a constant temperature bath and was stirred with a magnetic stirrer (see Figure 5.1). The reactor was connected to the measuring system by means of a glass joint. The measuring system consisted of two gas burettes, one of 50 ml and the other of 500 ml capacity, connected in parallel. By means of a three-way stopcock, one or the other could be used at any time during the experiments. The reaction rate was determined at constant pressure by measuring the dibutyl phthalate level in the gas burette.

The pressure sensing device consisted of an electric cell attached to a mercury manometer. When a small change in the mercury (less than 0·1 mm) was detected by the cell, a relay was activated and opened the solenoid valve, allowing the dibutyl phthalate to flow from its reservoir and adjust its level in the gas burette, so that the pressure in the system remained constant. The pressure in the reservoir was always 0·20 atm greater than the one in the system. Once the pressure was restored to its original value, the relay closed the valve until a new cycle began. The pressure in the reactor could be fixed at any value up to atmospheric pressure, and it was kept constant within an error of $\pm 10^{-4}$ atm. The reactor had a vessel attached to it for the addition of liquids.



A	acetone reservoir	H	hydrogen cylinder	S	magnetic stirrer
B	gas burette	L	three-way stopcock	T	constant temperature bath
C	electric cell	M	mercury manometer	U	U-tube with Na_2CO_3
D	dibutyl phthalate	O	one-way stopcock	V	solenoid valve
E	electric relay	R	reactor	W	vacuum pump

5.1 Schematic diagram of the reaction system

5.2 Materials

The catalyst used was Raney nickel Nicat 102, supplied by Joseph Crosfield & Sons. It is obtained from a minus 200 mesh nickel/aluminium alloy and it is stored under water. A summary of its physical properties can be seen in Table 5.1. The average particle size as supplied by the manufacturers is 21 μ, but for the kinetic measurements, a sample of the smallest particles was separated by sedimentation.

An analysis of the new particle size distribution was done with the Coulter Counter Model A (Table 5.2), and the average size was found to be 10 μ. During the period the experiments were carried out, the catalyst was kept under nitrogen atmosphere and at 5°C. Its activity was checked at the beginning and at the end of the kinetic measurements and no change was detected. All the experiments were carried out over a period of three months.

Oxygen free hydrogen supplied by British Oxygen Co. Ltd. was used for the reaction, while the organic solvents, acetone and isopropyl alcohol were BDH ANALAR and n-octane and 2,2,4-trimethylpentane, BDH pure reagents. The analysis by gas chromatography showed that the percentage of impurities in no case exceeded 0·5%.

The water used was distilled and passed through a column of ion exchange resins.

Table 5.1

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

TABLE 5.2

PARTICLE SIZE DISTRIBUTION

SAMPLE : NICAT 102 ELECTROLYTE : ISOTON 50% MANOMETER VOLUME : 0,5 ml

APERTURE DIAMETER : 140 µ APERTURE RESISTANCE : 244 Ω CALIBRATION FACTOR (K) : 4.67

GAIN INDEX	THRESHOLD t'	APERTURE CURRENT SWITCH	SCALE EXPANSION FACTOR F	AVERAGE CORRECTED COUNTS N	RELATIVE PARTICLE VOLUME V=t' F	PARTICLE DIAMETER $d=K\sqrt[3]{V}$ (µ)	PARTICLE FREQUENCY ΔN	AVERAGE PARTICLE VOLUME $\bar{V}$	TOTAL VOLUME OF PARTICLES ΔN $\bar{V}$	WEIGHT PERCENTAGE
3	300	1	1.00000	2.75	300.000	31.0				
							1.75	255.000	446	2.20
3	210	1	1.00000	4.50	210.000	27.5				
							1.83	180.000	329	1.62
3	150	1	1.00000	6.33	150.000	24.6				
							5.81	120.000	697	3.43
3	90	1	1.00000	12.14	90.000	20.7				
							8.86	75.000	664	3.27
3	60	1	1.00000	21.00	60.000	18.2				
							28.00	45.000	1260	6.21
3	60	2	0.50000	49.00	30.000	14.5				
							85.00	22.500	1912	9.42
3	60	3	0.25000	134.00	15.000	11.4				
							303.00	11.260	3412	16.81
3	60	4	0.12500	437.00	7.530	9.1				
							746.00	5.660	4222	20.80
3	60	5	0.06300	1183.00	3.780	7.2				
							952.00	2.840	2704	13.32
3	60	6	0.03170	2135.00	1.900	5.7				
							1617.00	1.440	2328	11.47
3	60	7	0.01625	3752.00	0.975	4.6				
							1831.00	0.741	1357	6.68
3	60	8	0.00845	5583.00	0.507	3.7				
							1558.00	0.390	608	2.99
3	60	9	0.00454	7141.00	0.272	3.0				
							1690.00	0.214	362	1.78
3	30	9	0.00260	8831.00	0.156	2.50				

WEIGHT AVERAGE PARTICLE DIAMETER = 10.0 µ

5.3 Procedure

A sample of the aqueous slurry of the catalyst containing 0·5-1·0 g of nickel was transferred to the reaction vessel, already weighed, and dried under vacuum for one hour at room temperature. The mass of Raney nickel was determined by weighing the vessel with the dry catalyst. The reactor was then introduced into a glove box with a nitrogen atmosphere, where 20 to 50 ml of degassed solvent were added to the catalyst, and finally, it was connected to the measuring system. The whole apparatus was purged with hydrogen and filled to the required pressure. To ensure that both the solvent and the catalyst were saturated with hydrogen, the liquid was stirred. Once the equilibrium was reached, degassed acetone was added to the reactor from the adjoining vessel and the hydrogen began to be consumed. After the dibutyl phthalate level was adjusted to the bottom of the burette and the electric cell to the appropriate level in the manometer, readings of the volume consumed were made every 15 seconds. When the reaction was slow, the smaller gas burette was connected.

Runs lasted for about 10 minutes and were made at temperatures of 0, 7 and 14°C, except in the case of 2,2,4-trimethylpentane, when only experiments at 7°C were carried out. The hydrogen pressure was varied from 60 to 10 cm Hg, and the pressure in the dibutyl phthalate reservoir was simultaneously reduced in order to keep a small pressure difference. With this arrangement, the level in the gas burette was automatically adjusted every 5-10 seconds.

The catalyst was renewed daily and measurements of the reaction rate at the same conditions at the beginning and at the end of the day were carried out. No definite trend was observed, and the values obtained did not differ in more than 5%.

The stirring of the reacting solution ensured that the temperature was uniform throughout the reactor.

Preliminary experiments showed that no reaction occurred in the absence of catalyst and that, when Raney nickel was present, the only product of reaction was isopropanol. This was checked in all the solvents by gas chromatographic analysis of the liquid. By comparing these results with the consumption of hydrogen, it was found that the number of moles formed and consumed were the same.

CHAPTER 6

RESULTS AND DISCUSSION

The present chapter deals with the determination of a kinetic expression for the hydrogenation of acetone on Raney nickel. The hydrogen concentration is calculated from the correlation of solubility in solvent mixtures developed in this thesis. A Langmuir-Hinshelwood type mechanism is put forward and the corresponding parameters are estimated by means of a non-linear regression. The effect of the solvent on the rate of reaction is discussed.

6.1 Hydrogen solubility in liquid mixtures

The difficulty in developing a theory to understand the solutions of nonreacting gases in liquids and liquid mixtures has been partially overcome by several attempts to correlate the values of solubility of the gas with the properties of the solvents. A general review of this aspect has been done by Battino and Clever (1966). An analysis of all the published data is included.

Shair obtained a good correlation for the solubility of gases in nonpolar systems (Hildebrand et al - 1970). He derived for a gas A dissolving in a solvent 1 at temperature T and total pressure P the equation

$$- \ln x_A = \ln \frac{f_A^L \text{ (at P)}}{\psi_A \, y_A \, P} + \frac{v_A (\delta_1 - \delta_A)^2 \phi_1^2}{Rg \, T} \qquad 6.1.1$$

where f_A^L is the fugacity (in atm) of pure "liquid A", ψ_A the fugacity coefficient of A in the gas phase, y_A its mole fraction, v_A the molar volume of pure "liquid A", ϕ_1 the volume fraction of the solvent, given by $\phi_1 = x_1 v_1 / (x_1 v_1 + x_A v_A)$ and δ_1 and δ_A the solubility parameters of the solvent and the condensed gas, respectively. The solubility parameters are proportional to the cohesive energy densities of the liquids and are calculated from

$$\delta = \left(\frac{\Delta E^V}{v} \right)^{\frac{1}{2}} = \left(\frac{\Delta H^V - Rg \, T}{v} \right)^{\frac{1}{2}} \qquad 6.1.2$$

where ΔE^V is the molar energy and ΔH^V the molar enthalpy of vaporization (Int. Crit. Tables - 1929).

At the normal operating conditions, namely pressures below one atmosphere and temperatures around 20°C, the gas phase fugacity coefficient is equal to one (Reid and Sherwood - 1958) and the solubility is so low that the volume fraction of the solvent approaches unity. Hence

$$- \ln x_A = \frac{\ln f_A^L \text{ (at P)}}{y_A P} + \frac{v_A (\delta_1 - \delta_A)^2}{R_g T} \qquad 6.1.3$$

Since the liquid phase fugacity can be expressed as

$$f_A^L \text{ (at P)} = f_A^L \text{ (1 atm)} \exp\left[\frac{v_A (P - 1)}{R_g T}\right] \qquad 6.1.4$$

the solubility will be given by

$$- \ln x_A = \frac{\ln f_A^L \text{ (1 atm)}}{y_A P} + \frac{v_A (\delta_1 - \delta_A)^2}{R_g T} + \frac{v_A (P - 1)}{R_g T} \qquad 6.1.5$$

In the above equation, three of the parameters - f_A^L, v_A and δ_A - must be obtained from solubility data. When the gas phase contains only hydrogen and its pressure is one atmosphere, equation 6.1.5 is reduced to

$$- \ln x_A = \ln f_A^L \text{ (1 atm)} + \frac{v_A (\delta_1 - \delta_A)^2}{R_g T} \qquad 6.1.6$$

It can be seen that several sets of the above mentioned parameters will be able to represent experimental solubility data. Therefore we accept a priori the value of 2·1 for the solubility parameter of liquid hydrogen (Hildebrand and Scott - 1950). By applying the least squares method to available

data for fluoroheptane, isooctane, n-octane, n-heptane, toluene and benzene (Battino and Clever - 1966) values of the remaining parameters, namely f_A^L and v_A are obtained at different temperatures and summarized in Table 6.1. The standard error of regression is 0·01.

But equation 6.1.6 holds only for solutions of hydrogen in nonpolar solvents and, since we are also interested in estimating the solubility in polar solvents and their mixtures, the solubility parameter will be modified in order to extend the correlation. From solubility data in acetone, isopropyl alcohol, methanol and water, a correction factor arises and the solubility parameter for polar liquids with $\delta > 9{\cdot}0$ is modified to

$$\delta^c = \frac{\delta}{1{\cdot}772 \log(\delta - 2{\cdot}1) - 0{\cdot}509} \qquad 6.1.7$$

If we compare the estimated solubility arising from equations 6.1.6 and 6.1.7 with experimental values (Battino and Clever - 1966), we find they agree reasonably well (see Table 6.2).

Table 6.1

Parameters in the solubility correlation

T (°C)	$\ln f_A^L$ (atm)	v_{H_2} (cm^3/mole)	δ_{H_2} ($cal^{\frac{1}{2}}/cm^{3/2}$)
0	6·246	22·9	2·1
7	6·174	24·1	2·1
14	6·106	25·2	2·1
25	5·982	26·8	2·1

Table 6.2

Comparison between estimated and experimental hydrogen solubilities in various solvents at 25°C and 1 atm

Solvent	ΔH^V (cal/mole)	v (cm^3/mole)	δ ($\frac{cal^{\frac{1}{2}}}{cm^{3/2}}$)	δ^c ($\frac{cal^{\frac{1}{2}}}{cm^{3/2}}$)	x_{H_2} x10^4 est (-)	x_{H_2} x10^4 e (-)
acetone	7604	73·3	9·8	9·2	2·545	2·390
n-octane	9914	162·5	7·6	-	6·373	6·832
i-propanol	9790	76·2	11·0	9·4	2·232	2·173
2,2,4-trimethyl-pentane	8395	165·1	6·9	-	8·846	7·815
water	10481	18·0	23·4	12·7	0·152	0·142

Up to now, we have only dealt with solutions of gases in pure liquids. For solvent mixtures (liquids 1 and 2) Hildebrand et al (1970) suggest that a good estimation of the solubility of the gas is obtained when the expression

$$\ln x_{A,mix} = \phi_1 \ln x_{A,1} + \phi_2 \ln x_{A,2} - v_A \beta_{12} \phi_1 \phi_2 \qquad 6.1.8$$

with

$$\beta_{12} = \frac{(\delta_1 - \delta_2)^2}{R_g T} \qquad 6.1.9$$

is applied. To extend this equation to polar solvents, the solubility parameter to be used is the one corrected according to equation 6.1.7.

When the gas pressure is no longer 1 atm, we can rewrite equation 6.1.5 as

$$- \ln x_A = \ln f_A^L (1 \text{ atm}) + \frac{v_A(\delta_1 - \delta_2)^2}{R_g T} + \frac{v_A(P-1)}{R_g T} - \ln y_A P \qquad 6.1.10$$

The first two terms in the right hand side represent the gas solubility when its pressure is 1 atm, and since the third term is approximately 10^{-3} (the pressure will always be less than 1), it can be neglected. Therefore

$$x_A = x_A(1 \text{ atm})\ y_A\ P = x_A(1 \text{ atm})\ p_A \qquad 6.1.11$$

and the solubility is proportional to the partial pressure of gas.

6.2 Mass transfer and thermal effects

For the reaction to take place, both the reactants, acetone and hydrogen, must be transported to the catalyst surface. Since the acetone concentration in the liquid phase is more than 1000 times that of hydrogen, and their diffusion coefficients are similar, the acetone concentration drop will be so small that the concentration inside the solid will be the same as the one in the bulk fluid. We will therefore restrict our analysis to the transport of hydrogen from the gas phase to the solid surface. This process may be divided into three parts: dissolution of hydrogen gas, transport from bulk fluid to the outer surface of particle and finally, transport to the active centres of the porous catalyst.

In order to ensure that the first steps did not control the overall process, all the experiments were carried out at such a stirring rate that the measured rate of reaction was maximum. In this condition, the catalyst powder was totally in suspension.

The calculation of the concentration drop across the boundary layer surrounding the catalyst particle clearly shows that the external diffusion was not limiting the rate of reaction.

Let us consider the highest rate of hydrogenation in the acetone-water system, namely $1{\cdot}2 \times 10^{-3}$ mole/min g, which corresponds to a temperature of $14^{\circ}C$ and a mole fraction of $0{\cdot}5$. In this condition, the liquid density is $0{\cdot}85$ g/cm^3, its viscosity about $0{\cdot}76$ cp and the diffusion coefficient is

estimated from Wilke and Chang's correlation (Satterfield - 1970) as $9{\cdot}9 \times 10^{-5}$ cm^2/s. The solubility of hydrogen in the mixture is derived from equations 6.1.5 and 6.1.8 to be $2{\cdot}7 \times 10^{-6}$ mole/cm^3.

The settling velocity of the catalyst particles is

$$u = \frac{g\, d^2\, \Delta\rho}{18\, \mu} = \frac{(980)\,(0{\cdot}001)^2\,(4{\cdot}5 - 0{\cdot}85)}{(18)\,(0{\cdot}0076)} = 0{\cdot}0261 \text{ cm/s} \qquad 6.2.1$$

Hence the Peclet number is

$$Pe = \frac{u\, d}{D} = \frac{(0{\cdot}0261)\,(0{\cdot}001)}{9{\cdot}9 \times 10^{-5}} = 0{\cdot}264 \qquad 6.2.2$$

It follows now that the corresponding Sherwood number is 2·0 (Satterfield - 1970). Assuming the actual value is twice the value for a free falling particle, we can calculate the concentration drop around the solid. The rate of mass transfer to the solid surface can be expressed as

$$N_A = \frac{Sh\ 6\ D}{d^2\ \rho_p} (c_{H_2} - c_{H_2 s}) \qquad 6.2.3$$

but it must be equal to the observed rate of reaction, therefore

$$1 - \frac{c_{H_2 s}}{c_{H_2}} = \frac{r\ d^2 \rho_p}{6\ Sh\ D\ c_{H_2}} = \frac{(2{\cdot}0 \times 10^{-5})\ (0{\cdot}001)^2\ (4{\cdot}5)}{(6)\,(4)\,(9{\cdot}9 \times 10^{-5})\,(2{\cdot}7 \times 10^{-6})}$$

$$= 0{\cdot}014 \qquad 6.2.4$$

and the hydrogen concentration on the catalyst surface is, in these extreme conditions, 0·986 of the value in the bulk liquid.

To estimate the influence of the internal diffusion, the effectiveness factor will be calculated for the same conditions as above. The modulus ϕ_L is given by

$$\phi_L = \frac{r\ \rho_p d^2}{36\ D_{eff}\ c_{H_2}} = \frac{(2{\cdot}0\ x10^{-5})(4{\cdot}5)(0{\cdot}001)}{(36)(1{\cdot}25\ \ x10^{-5})(2{\cdot}7\ x10^{-6})}$$

$$= 0{\cdot}074 \qquad 6.2.5$$

where the tortuosity factor is assumed to be equal to 4 and therefore the effective diffusivity is eight times smaller than the molecular one.

Since the order of reaction with respect to hydrogen is ½ (see Section 6.3), the estimated value of the effectiveness factor is greater than 0·99, and no diffusional process is limiting the rate of reaction (Satterfield - 1970). This conclusion is also confirmed by the observed value of the activation energy of about 10 K-cal/mole (see Section 6.4.3), which is very much larger than the one corresponding to diffusional processes.

In order to determine whether the thermal effects are significant inside the catalyst, the maximum temperature difference that could exist between the particle surface and the interior will be estimated from

$$\Delta T_{max} = \frac{c_{H_2 s}(-\Delta H)\ D_{eff}}{\lambda} \qquad 6.2.6$$

where ΔH is the enthalpy change of reaction and λ the thermal conductivity of the catalyst. No data of thermal conductivity of porous solids is available, but it can be estimated in this case to be 10^{-3} cal/cm s ^{o}C (Satterfield - 1970), without

introducing a large error. Since the enthalpy change of reaction at 18°C is 19·2 K-cal/g-mole (Int. Crit. Tables - 1929), it follows that

$$\Delta T_{max} = \frac{(2{\cdot}7 \times 10^{-6})(-19200)(1{\cdot}25 \times 10^{-5})}{(10^{-3})}$$

$$= 6{\cdot}5 \times 10^{-4} \ ^{\circ}C \qquad 6.2.7$$

and the thermal effects in the catalyst are completely negligible. Moreover, since $E_A \ T_{max} / R_g \ T^2 = (1.0 \times 10^4)(6.5 \times 10^{-4})/(1.987)(287)^2 = 4.0 \times 10^{-5}$, it can be shown that no drop in temperature occurs in the film surrounding the catalyst (Hlavacek and Kubicek - Chem. Eng. Sci. 25 1761-1771 (1970)).

6.3 Mechanism of reaction

Anderson and MacNaughton (1942) studied the hydrogenation of acetone on various catalysts using a mixture of hydrogen and deuterium as reducing agent. They were able to determine that at low temperatures and over Raney nickel the addition of hydrogen occurs on to the keto form.

Previous kinetic measurements suggest that the reaction mechanism can be described (Kishida and Teranishi - 1968, Iwamoto et al - 1970) according to the following steps, where the hydrogen dissociates during adsorption and its addition to the acetone takes place in two stages,

$$A + \ell = A\ell$$
$$H_2 + 2\ell = 2H\ell$$
$$A\ell + H\ell = AH\ell + \ell$$
$$AH\ell + H\ell = P\ell$$
$$P\ell = P + \ell$$

where A, AH and P describe the acetone, monohydrogenated acetone and isopropyl alcohol, respectively, and ℓ denotes an active site.

Assuming Langmuir isotherms of adsorption for all the components and that the first step in the reaction is the controlling one, an expression for the rate of reaction is obtained

$$r = \frac{k_1 K_A K_H^{\frac{1}{2}} c_A \, c_{H_2}^{\frac{1}{2}}}{(1 + K_A c_A + K_H^{\frac{1}{2}} c_{H_2}^{\frac{1}{2}} + K_P c_P (1 + 1/K_2 K_H^{\frac{1}{2}} c_{H_2}^{\frac{1}{2}}) + K_S c_S)^2} \qquad 6.3.2$$

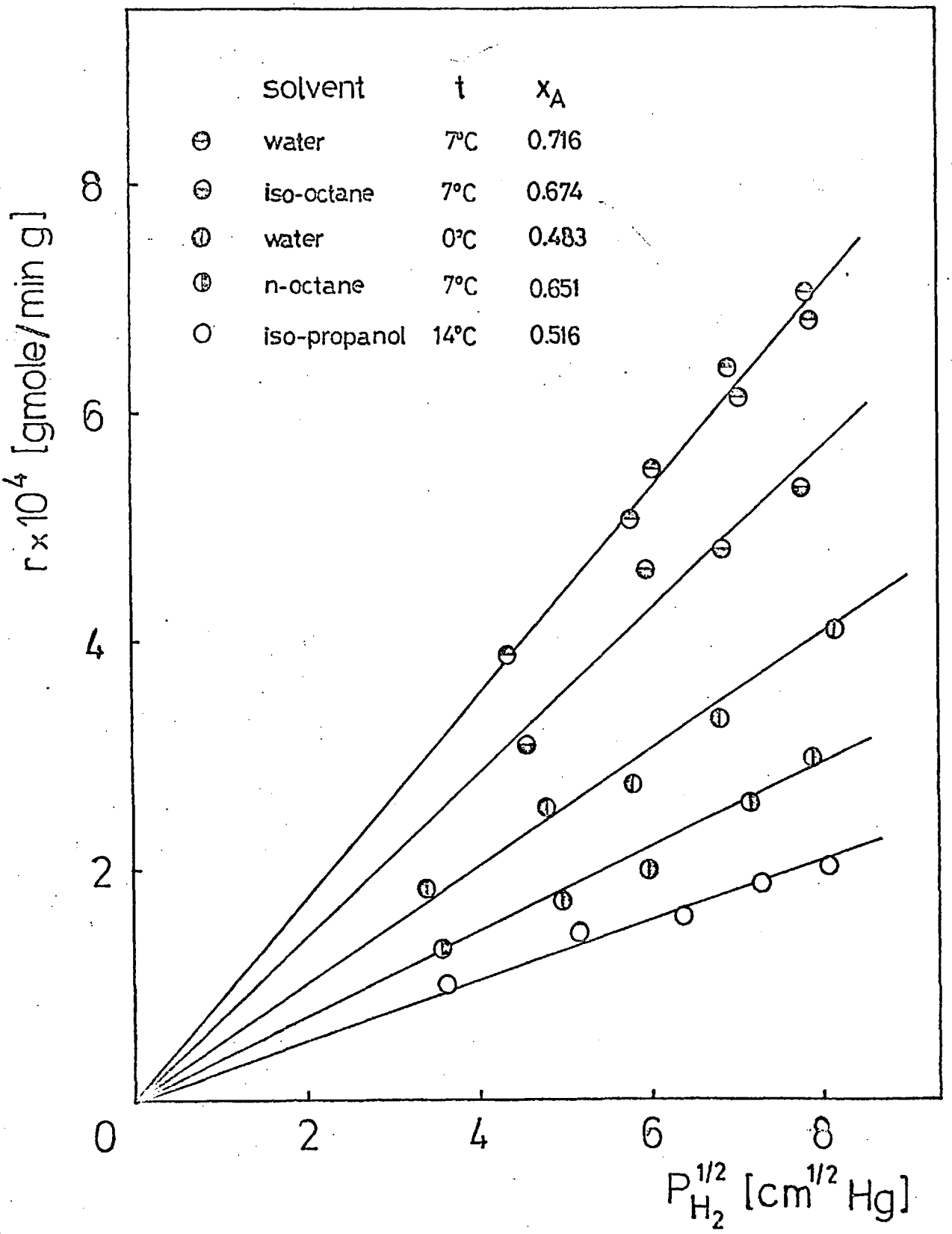
where $K_S c_S$ is due to the adsorption of the solvent on the catalyst.

Simonikova et al (1973) studied the same reaction in the gas phase over different metal catalysts (Cu, Pt, Pd and Rh on kieselguhr), and found that the adsorption constant of hydrogen is between 10 and 100 times lower than that of acetone. In addition, in the liquid phase the concentration of hydrogen is 10^{-3} times lower than the acetone one, and therefore it is reasonable to neglect the amount of adsorbed hydrogen in the denominator. At the same time, since the second reaction rate constant is greater than the first and the monohydrogenated acetone is an intermediate product, its adsorbed concentration will also be negligible. The expression for the rate of reaction is reduced to

$$r = \frac{k_1 K_A K_H^{\frac{1}{2}} c_A c_{H_2}^{\frac{1}{2}}}{(1 + K_A c_A + K_p c_p + K_S c_S)^2} \qquad 6.3.3:$$

The apparent order with respect to hydrogen resulting from this equation is verified by plotting the rate of reaction as a function of the square root of the hydrogen concentration for a fixed concentration of acetone. It has been shown (Section 6.1) that the hydrogen concentration is proportional to its gas pressure, and therefore, the straight line obtained confirms that the first step in the surface reaction is controlling (see Figure 6.1). On the contrary, by deriving the rate of reaction equation with the assumption that the second step is controlling, an apparent order of one with respect to hydrogen is obtained.

A kinetic equation developed on the assumption that the acetone is adsorbed on two sites, as proposed by some authors (Bond - 1962) did not represent the experimental results in a satisfactory way. For any combination of parameters, the ratio between



6.1 Order of reaction with respect to hydrogen

the maximum rate of reaction and the one corresponding to pure acetone did not exceed a value of 2. In Figures 6.2, 6.3 and 6.5, this ratio is very much higher.

6.4 Analysis of experimental results

In order to estimate the values of the parameters in equation 6.3.3, which best represent the experimental results, a non-linear regression will be applied. Since the concentrations of acetone and solvent in the reacting mixtures are related by $x_A = 1 - x_S$, and accepting that the total molar density of the solution changes linearly with the concentration of acetone, it follows

$$c_S = c_S^o - \frac{c_S^o}{c_A^o} c_A \qquad 6.4.1$$

where c_S^o and c_A^o are the molar concentrations for pure solvent and pure acetone, respectively. Equation 6.3.3 becomes

$$r = \frac{k_1 K_A K_H^{\frac{1}{2}} c_A \, c_{H2}^{\frac{1}{2}}}{(1 + K_S c_S^o + (K_A - K_S c_A^o/c_S^o) \, c_A)^2} \qquad 6.4.2$$

and redefining the parameters

$$r = \frac{c_A \, c_{H_2}^{\frac{1}{2}}}{(a + b \, c_A)^2} \qquad 6.4.3$$

where $a = (1 + K_S c_S^o)/(k_1 K_A K_H^{\frac{1}{2}})^{\frac{1}{2}}$ and $b = (K_A - K_S c_A^o/c_S^o)/(k_1 K_A K_H^{\frac{1}{2}})^{\frac{1}{2}}$.

From the expression above, only two parameters can be estimated, while in the original equation we have three, namely $k_1 K_H^{\frac{1}{2}}$, K_A and K_S. In the following section, a procedure to estimate their values will be explained.

6.4.1 Isopropyl alcohol, n-octane and 2,2,4-trimethyl-pentane as solvents

Several studies of metal catalyzed reactions involving aliphatic hydrocarbons and of the adsorption on Raney nickel (Limido and Grawitz - 1954, Bond - 1962, Kishida and Teranishi - 1968) have concluded that their adsorption constants are negligible compared with that of acetone. When the regression is carried out with the results obtained in n-octane, K_S will be taken as zero, and therefore $a = 1/(k_1 K_A K_H^{\frac{1}{2}})^{\frac{1}{2}}$ and $b = K_A/(k_1 K_A K_H^{\frac{1}{2}})^{\frac{1}{2}}$. It follows that

$$k_1 K_H^{\frac{1}{2}} = 1/ab \qquad K_A = b/a \qquad 6.4.4$$

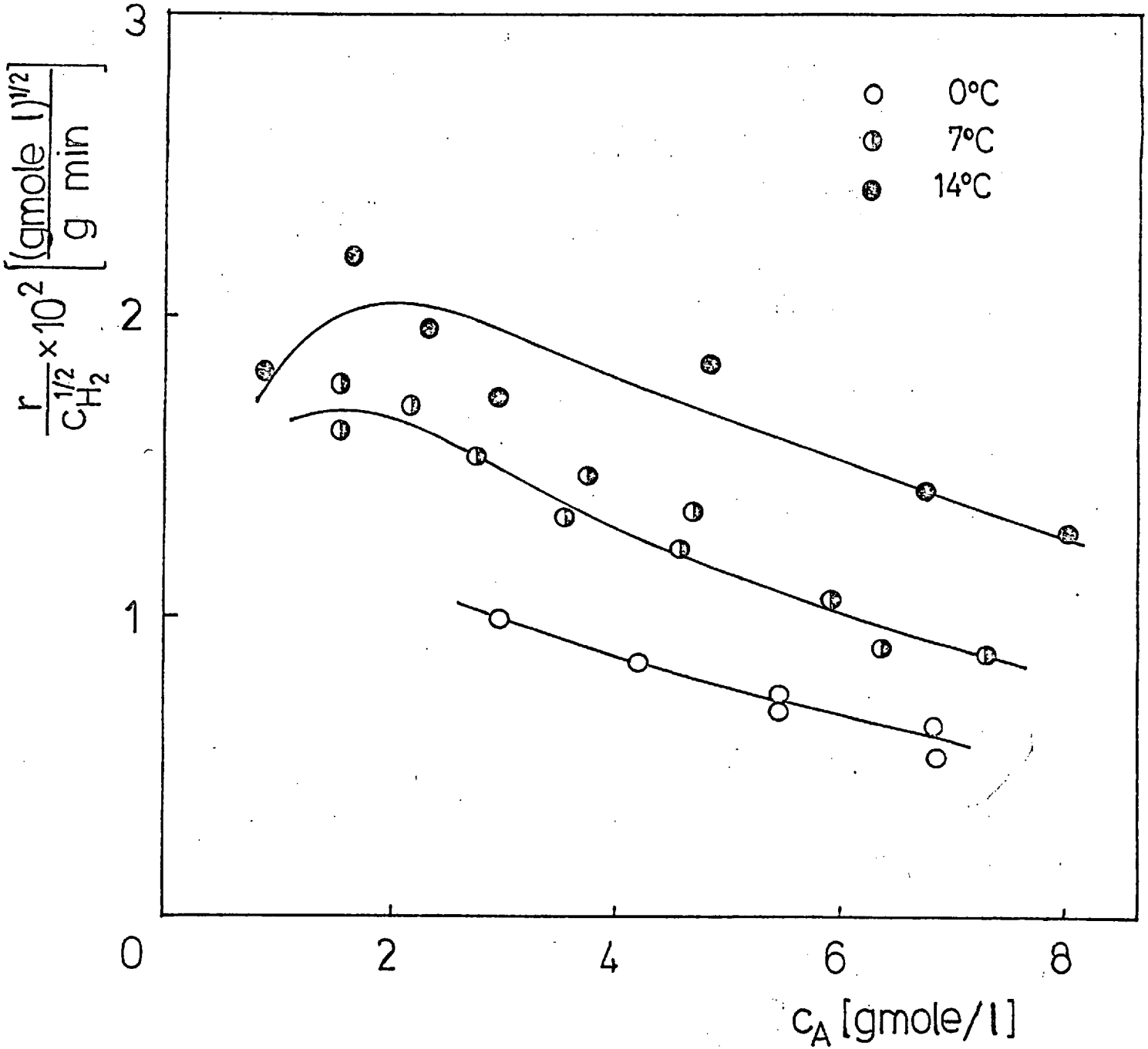
Once the value of K_A at a certain temperature has been obtained, both the rate of reaction constant in isopropyl alcohol and isooctane and their adsorption constants are obtained from

$$K_S = \frac{K_A - b/a}{(b/a)c_S^o + c_S^o/c_A^o} \qquad k_1 K_H^{\frac{1}{2}} = \frac{1}{K_A}\left(\frac{1 + K_S c_S^o}{a}\right)^2 \qquad 6.4.5$$

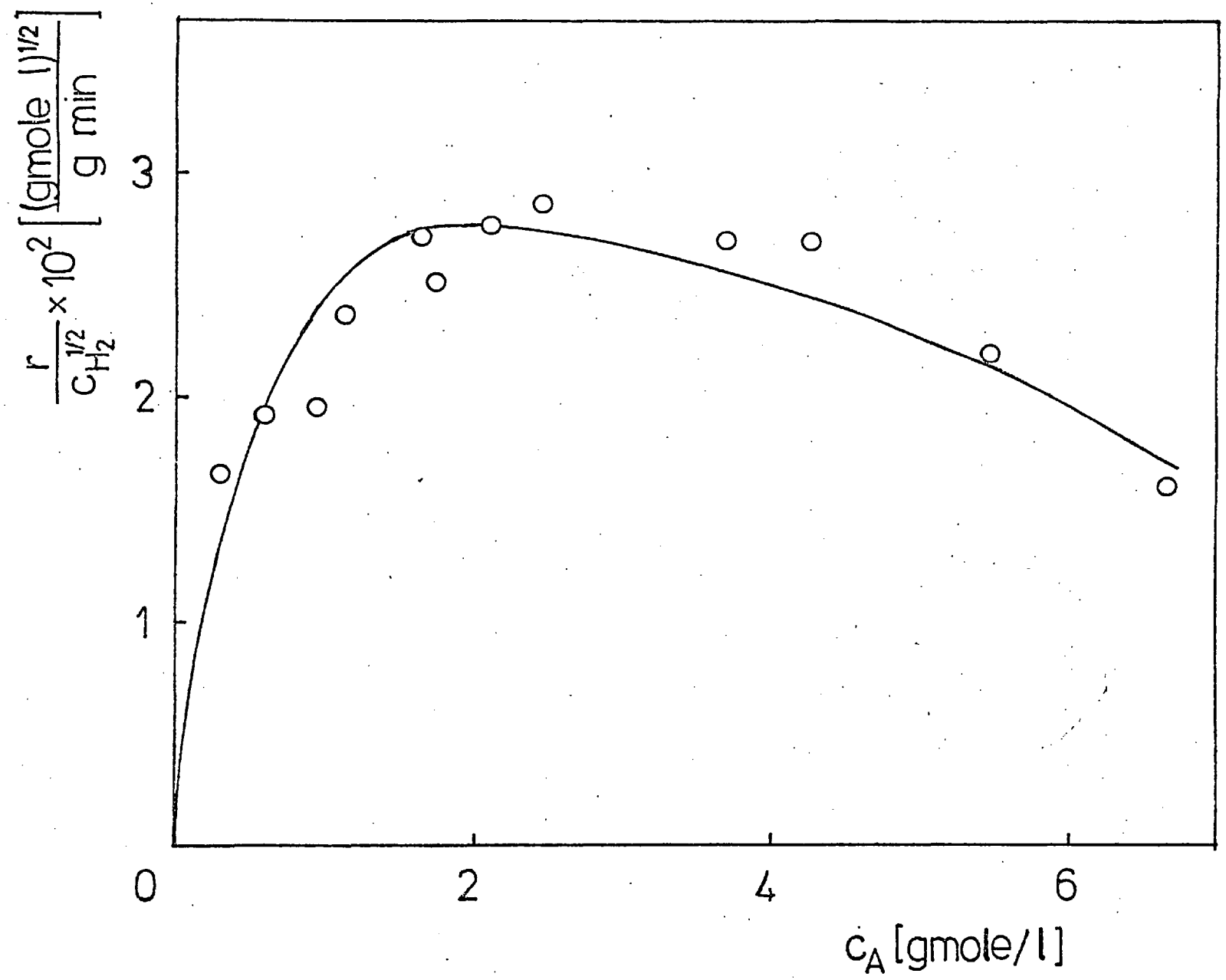
In order to start the non-linear regression, it is necessary to have an initial estimate of the values of the parameters. For this purpose, a linear regression of the experimental results is carried out with the rate of reaction equation in the form

$$\left(\frac{c_A c_{H_2}^{\frac{1}{2}}}{r}\right)^{\frac{1}{2}} = a + b\, c_A \qquad 6.4.6$$

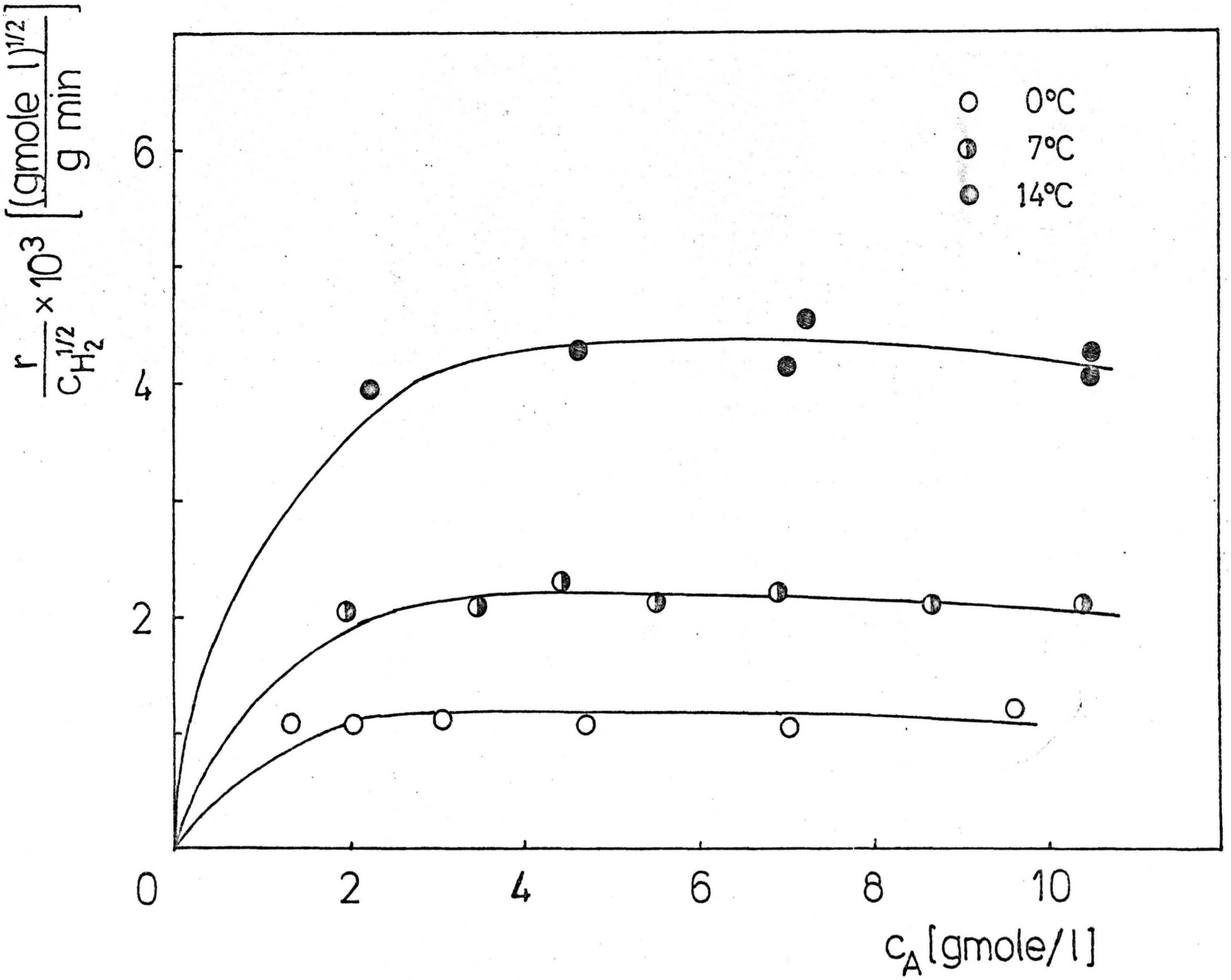
An estimation of a and b is obtained and used as initial



6.2 Rates of reaction (solvent: n-octane)



6.3 Rates of reaction (solvent: isooctane)



6.4 Rates of reaction (solvent: isopropanol)

Table 6.3

Parameters estimated by nonlinear regression

Solvent	T ^{o}C	a	b $\frac{\ell}{gmole}$	S(0) $\left(\frac{gmole}{min\ g}\right)^2$	$k_1 K_H^{\frac{1}{2}}$ $\frac{(\ell\ gmole)^{\frac{1}{2}}}{min\ gr}$	K_A $\frac{\ell}{gmole}$
n-octane	0	5·05	4·19	$7·76 \times 10^{-9}$	0·0472	0·830
n-octane	7	4·37	3·31	$3·92 \times 10^{-8}$	0·0692	0·757
n-octane	14	4·88	2·50	$2·14 \times 10^{-8}$	0·0816	0·515
						K_S
isooctane	7	4·04	2·25	$1·87 \times 10^{-7}$	0·140	0·0523
isopropanol	0	31·10	6·50	$2·70 \times 10^{-10}$	0·0128	0·168
isopropanol	7	23·67	4·65	$2·05 \times 10^{-10}$	0·0225	0·159
isopropanol	14	17·70	3·14	$5·81 \times 10^{-10}$	0·0342	0·103
water	0	21·18	1·41	$3·72 \times 10^{-9}$	0·111	0·098
water	7	21·63	0·383	$1·90 \times 10^{-8}$	0·234	0·146
water	14	10·44	0·909	$2·48 \times 10^{-8}$	0·239	0·048

guess for the non-linear regression.

The concentration of dissolved hydrogen at a fixed gas pressure is a function of the solution composition and temperature of experiment and is calculated with the correlation developed in Section 6.1.

The non-linear regression is carried out for each solvent at the different temperatures and the sum

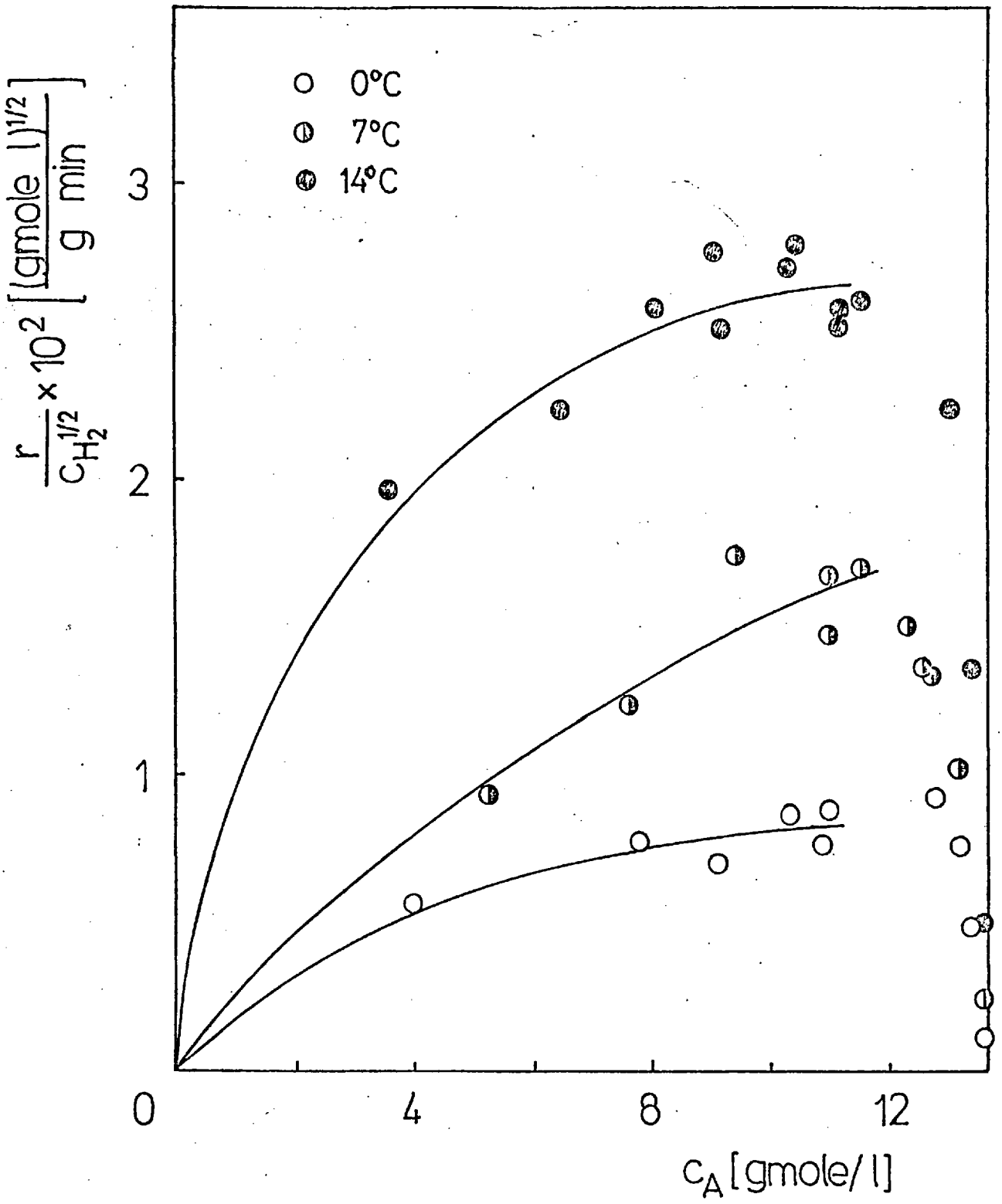
$$S(\theta) = \sum_{j=1}^{N} (r_{ej} - r\ (p_j, \theta))^2 \qquad 6.4.7$$

is minimized, where r_{ej} is the experimental rate of reaction, p_j the independent variable, θ the parameters of the equation, and the subscript j denotes the j-th experiment. A computer programme "Least squares estimation of non-linear parameters", based on an algorithm developed by Marquardt (1963), is used and the results obtained are summarized in Table 6.3.

6.4.2 Water as solvent

When water is added to acetone, a very large increase in the rate of hydrogenation is observed. Further increases in the concentration of water decreases the measured rate (see Figure 6.5). Analysis of the solubility of hydrogen in acetone-water mixtures shows that it decreases from pure acetone to pure water, but this does not explain the effect observed in the consumption of hydrogen.

The occurrence of a maximum in the rate of reaction at high concentrations of acetone was not observed in any other solvent (Kishida and Teranishi - 1968, Iwamoto et al - 1970) and the



6.5 Rates of reaction (solvent: water)

compensating effect of two factors may be its cause. We can affirm that the final decrease in the rate of reaction is due to the depletion of acetone at the catalyst surface at high concentrations of water.

Several authors have reported the promotive effect of water in the hydrogenation of acetone over Raney nickel (Sokol'skii and Erzhanov - 1953, Selyakh and Dolgov - 1965, Tsutsumi et al - 1951). Moreover, Orito and Imai (1961) observed the same effect when Ni-kieselguhr and Co-Cr_2O_3-kieselguhr are used as catalysts, but with Cu-Cr_2O_3-kieselguhr an inhibiting effect is found. No definite explanation has been proposed, but two likely possibilities arise from the experimental evidence.

Selyakh and Dolgov (1965) suggested that the water promotes the enolization of the adsorbed acetone and, since the double bond C=C is more readily hydrogenated than the carbonyl group, an increase in the rate of reaction is to be observed. No enolization of acetone is detected in aqueous solution in the absence of a catalyst (Hine - 1956), but since in the adsorbed state a rearrangement of electrons is occurring, the existence of the enol form as substrate for the hydrogenation is possible.

At the same time, it is widely accepted that hydrogen is adsorbed on to the solid with two different strengths, the strongly bound one being mainly responsible for the carbonyl reduction (Watanabe - 1956, Sokol'skii and Erzhanov - 1953). In a study of the hydrogenation of benzalacetone on Raney nickel, Sokol'skii and Erzhanov (1953) found that both the

hydrogenation of the ethylenic bond and the carbonyl group could be studied independently since the ethylenic bond is reduced first at a high rate, and only after this is completed, the carbonyl group is attacked. The addition of water increases the second rate and an increase in the amount of hydrogen adsorbed is suggested to be its cause. The observed effect can also be attributed to a change in the ratio of the two different forms of adsorbed hydrogen, so that the strongly bound one required for the carbonyl hydrogenation is favoured.

It follows that the addition of water changes the structure of the adsorbed substances and a detailed study on this subject is necessary. However, since it is reasonable to assume that changes in the adsorption and rate of reaction constants occur only at high concentrations of acetone, in order to determine a kinetic equation, we will only consider the data for acetone concentrations below 11 gmoles/l. A similar procedure to the one described in Section 6.4.1 is applied here. The parameters obtained from a nonlinear regression are summarized in Table 6.3.

6.4.3 Heats of adsorption and activation energies

The values of the adsorption constants of acetone, isopropanol and water determined at 14°C from the kinetic measurements are: 0·515, 0·103 and 0·048 ℓ/gmole, respectively (see Table 6.3). If we compare their ratio with the one determined at 20°C by Delmon and Balaceanu (1957) from adsorption measurements, we find a reasonable agreement. For the system acetone-water, the ratios are 10·7 and 21, while for

acetone-isopropanol, 5·1 and 3, respectively.

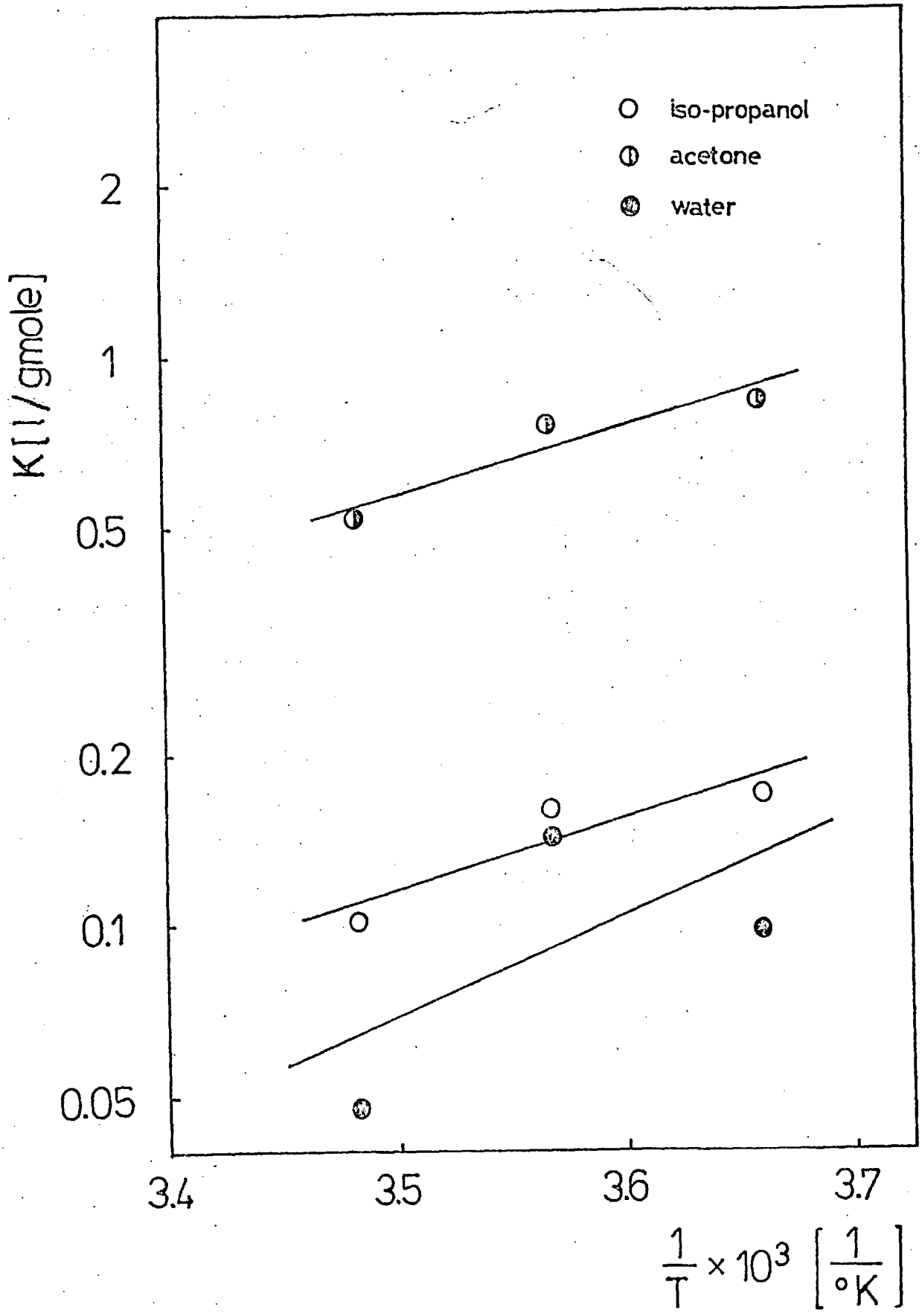
The heats of adsorption can be determined from the slope of the graph when the logarithm of the adsorption constant is plotted as a function of the inverse of the absolute temperature (Figure 6.6). The values for isopropanol, acetone and water are 5·5, 5·3 and 8·0 Kcal/gmole, respectively, and are higher than those expected if the adsorbed species were held by ordinary dispersion forces. Kishida and Teranishi (1968) found a similar value for acetone (4·3 Kcal/gmole) which suggests that chemisorption does not take place and the C = O bond is not broken during the adsorption.

The apparent activation energy is obtained from the slope in Figure 6.7. This value can be related with the true one,

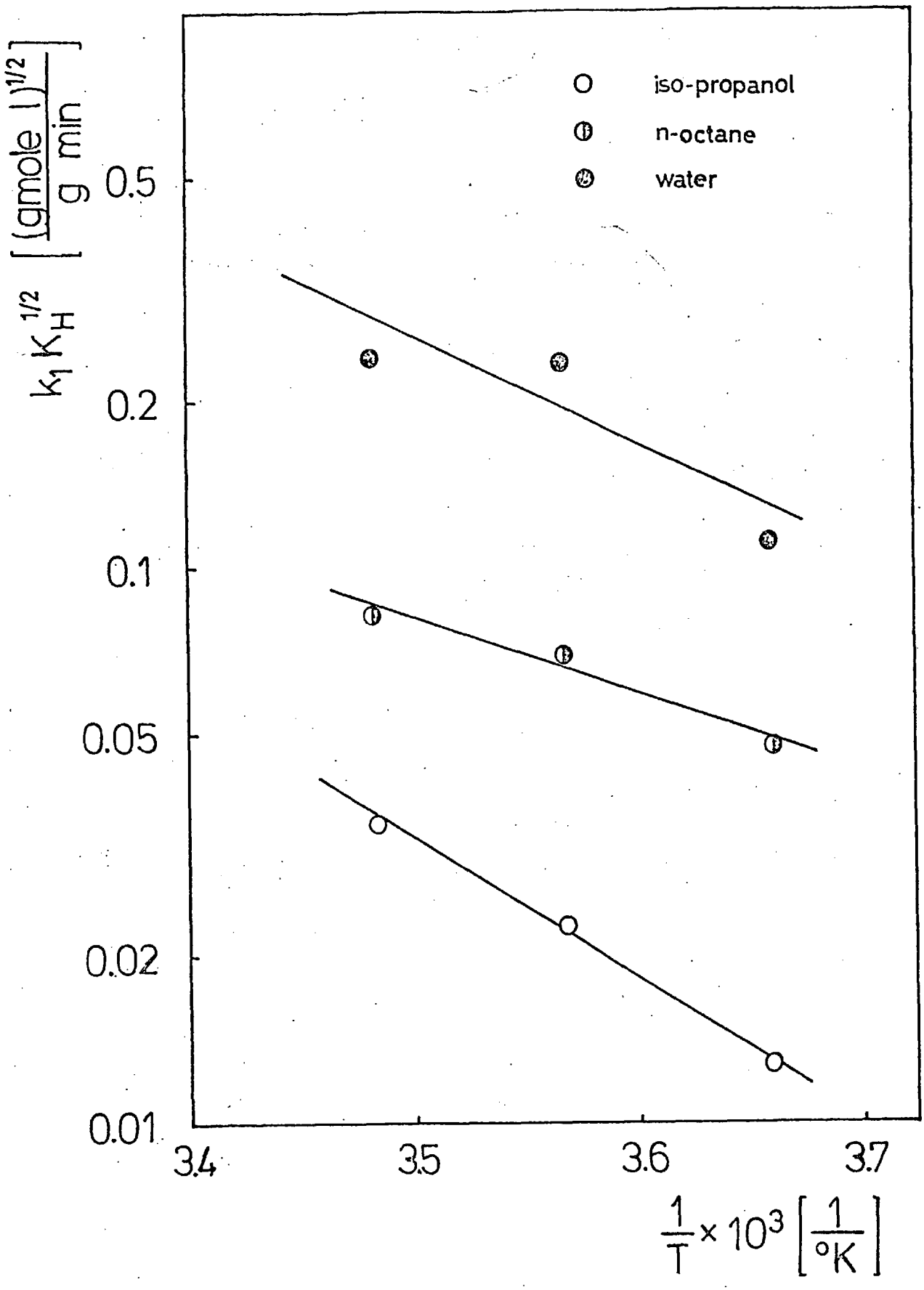
$$E_{Aapp} = -\frac{d \ln k_{app}}{d(1/R_g T)} = -\frac{d \ln k_1}{d(1/R_g T)} - \tfrac{1}{2}\frac{d \ln K_H}{d(1/R_g T)} = E_A - \tfrac{1}{2}\Delta H_H^a \qquad 6.4.8$$

where ΔH_H^a represents the heat of adsorption of hydrogen. The apparent activation energies determined with n-octane, isopropanol and water as solvents are 6·2, 11·0 and 8·6 Kcal/gmole, respectively. It can be seen that the maximum activation energy corresponds to the case isopropanol is the solvent.

In previous research work, similar values have been determined. Freund and Hulburt (1957) obtained an apparent activation energy of 8 Kcal/gmole for a molar fraction of acetone in isopropanol of 0·3. It must be pointed out that this result is low since it is affected by the solubility of hydrogen and its diffusion to and into the catalyst.



6.6 Adsorption constants



6.7 Rate of reaction constants

Iwamoto et al (1970) found a value of 10·3 Kcal/gmole for their results in isopropanol, but they did not take into account the change of solubility with concentration and temperature. The same criticism applies to the value of 10·1, found by Kishida and Teranishi (1968) for their experiments in n-hexane. In addition, they ignored the adsorption of hydrogen on the catalyst.

Several authors (Bond - 1962) have determined the heat of adsorption of hydrogen from the gas phase on nickel. They found initial values ranging from 20 to 30 Kcal/gmole. Watanabe (1956) studied the adsorption on Raney nickel and obtained an enthalpy of adsorption of 15 Kcal/gmole. No data on the heat of adsorption of hydrogen from solution is available, but since dissociation of the molecule takes place during the adsorption, it is expected not to be very much smaller than the values given above. The average value for the heat of adsorption reported by Iwamoto et al (1970) of 2·7 Kcal/gmole is an apparent one, since it includes the enthalpy change of the surface reaction.

This justifies the rather low values obtained for the activation energy, in particular in n-octane. The true values will be about 7 Kcal/gmole higher than the apparent ones.

PART III : SLURRY REACTOR

CHAPTER 7

APPARATUS AND EXPERIMENTAL TECHNIQUES

No studies of the behaviour of the resonant bubble contactor as a reactor have been reported yet. Buchanan et al (1963) and Jameson (1966b) found a very large increase in the rate of gas absorption when using the mentioned equipment instead of other more traditional contacting devices. In Chapter 4, it was shown that the mass transfer to or from solids in suspension is enhanced when the vessel containing them is oscillating at a high frequency, namely about 1500-2000 rpm.

Since in heterogeneous catalysis mass transport generally constitutes a rate determining step, the previous results suggest that the development of a vibrating slurry reactor is of practical interest. Therefore an experimental study of the hydrogenation of liquid acetone catalyzed by Raney nickel will be carried out in the resonant bubble contactor.

A description of the equipment and experimental techniques involved in the analysis of the behaviour of the vibrating slurry reactor is given in this chapter.

7.1 Description of the Apparatus

The rate of hydrogenation of acetone in a slurry reactor was measured in the same cylinder used in the mass transfer experiments. It was connected to the measuring system described in Section 5.1 and had a rubber bung at its top where a small vessel for the addition of acetone was attached.

The frequency of oscillation of the cylinder was varied from 350 to 1600 rpm and the amplitude was the same as in Section 3.1, namely 0·467 cm.

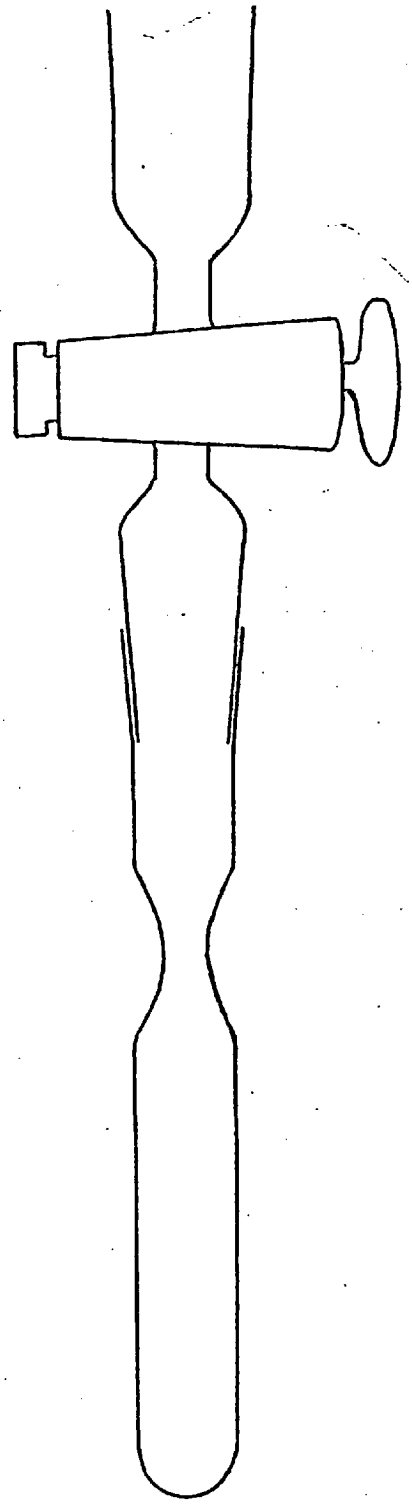
7.2 Materials and procedure

In the slurry reactor experiments, the catalysts used were Raney nickel Nicat 102 and Nicat 820, manufactured by Joseph Crosfield & Sons. The latter was sieved under nitrogen atmosphere and the sample obtained had an average diameter of 65 ± 5μ, determined with a microscope. The catalysts physical properties are summarized in Table 5.1. The main difference between them is their average particle size, but their activity is the same. The rate of hydrogenation was determined in isopropanol with both catalysts in the stirred vessel, and no difference was observed. To ensure that no diffusional control occurred, experiments were carried out at a low temperature.

The same reactants as in Part II were used.

A sample of the wet catalyst was initially transferred to a weighed glass tube (see Figure 7.1) where it was dried under vacuum and at room temperature. Nitrogen was admitted to the tube, and after weighing it to determine the mass of Raney nickel, it was sealed off and the stopcock removed.

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 minutes it was purged with hydrogen, and degassed acetone was added to obtain a solution with a mole fraction of acetone of 0·33. The hydrogen pressure was adjusted as well as the dibutyl phthalate level in the burette and the electric cell in the mercury manometer. The tube containing the Raney nickel was broken by switching



7.1 Diagram of the sampling tube

on the oscillating mechanism at a high frequency (approximately 1800 rpm) and the reaction begins to take place.

Runs were carried out at a fixed concentration of acetone in water, but varying the temperature (7 to 21°C), the hydrogen pressure (10 to 55 cm Hg) and the frequency of oscillation (350 to 1600 rpm). When bubble cycling occurred in the cylinder, fluctuations of the pressure of about 10 mm Hg were observed. In such conditions, the measuring system would not work. This problem was solved by inserting a capillary tubing between the vibrating cylinder and the manometer, so that pressure fluctuations were damped out. By reducing instantaneously the frequency of oscillation, and therefore eliminating the fluctuations, and bypassing the capillary tubing, it was checked that there was no difference between the measured value and the average of the fluctuating pressure.

In preliminary experiments, it was verified that the aluminium of the cylinder did not interfere with the measurements. Several experiments were carried out with the catalyst Nicat 102 and in the same conditions as in the stirred reactor, and no difference in the rate of hydrogenation was observed.

No temperature gradients existed in the reactor throughout the experiments. A thermocouple was placed in different positions in the liquid, and the registered temperature did not vary even at low frequencies of oscillation.

CHAPTER 8

RESULTS AND DISCUSSION

This chapter deals with the analysis of the rates of hydrogenation of acetone over Raney nickel measured in the vibrating slurry reactor. Two grades of catalyst of different average particle size are used, and the influence of the diffusional resistances is studied. The value of the tortuosity factor of the catalyst is determined.

8.1 Diffusional effects

For a solid catalyzed reaction between a gas B and a liquid A, the gas must first dissolve, and both reactants diffuse to the internal surface of the catalyst where they will react. The rate of consumption of B can generally be expressed in terms of the concentrations at the particle surface

$$-\frac{1}{m_c}\frac{dn_B}{dt} = k_m c_{As}^m c_{Bs}^p \eta = \frac{k_v}{\rho_p} c_{As}^m c_{Bs}^p \eta \qquad 8.1.1$$

where k_m and k_v are the reaction rate constants per unit mass and unit volume of catalyst, respectively, m and p are the orders of reaction and η is the effectiveness factor and takes into account the resistance to the diffusion of the reactants from the surface of the catalyst to the active sites. If A and B have similar diffusion coefficients (not very different size of molecules) 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 the concentration inside the solid is the same as the one in the bulk fluid. In such conditions, the rate of diffusion of B will be limiting and the effectiveness factor will be that of B.

For hydrogen reacting with acetone, the assumption made above is correct, since the ratio of diffusion coefficients D_{H_2}/D_A is only of about 4, while the ratio of concentrations c_{H_2}/c_A is about 10^{-3}. This can be verified by applying equation 6.2.5 to the acetone for a molar fraction in water of 0·33 and the grade Nicat 820 of catalyst. It follows that.

$$\phi_L = \frac{r\,\rho_p d^2}{36\,D_{eff}\,c_A} = \frac{(2{\cdot}0 \times 10^{-5})(4{\cdot}5)(0{\cdot}0065)^2}{(36)(3{\cdot}0 \times 10^{-6})(10^{-2})} = 3{\cdot}5 \times 10^{-3} \qquad 8.1.2$$

and the modulus ϕ_L for the acetone is so low that its corresponding effectiveness factor is unity (Satterfield - 1970).

It can also be shown that the acetone concentration drop around the catalyst particle is negligible even if we consider the lowest possible Sherwood number. By applying equation 6.2.4, it follows that

$$1 - \frac{c_{As}}{c_A} = \frac{r\,d^2\rho_p}{6\,Sh\,D\,c_A} = \frac{(2{\cdot}0 \times 10^{-5})(0{\cdot}0065)^2(4.5)}{(6)(2)(2{\cdot}5 \times 10^{-5})(10^{-2})}$$

$$= 1.3 \times 10^{-3} \qquad 8.1.3$$

which confirms the assumption that the acetone concentration is uniform throughout the system.

In Section 6.2 it has already been determined that thermal effects inside the catalyst are negligible.

8.2 Rate of reaction in a slurry reactor

The rate of reaction in the slurry reactor will be affected by the transport rate of hydrogen from the gas phase to the catalyst active sites. This process can be divided into three steps:

a) dissolution of hydrogen in the liquid phase. Since there is no other gas present, this can be reduced to the transport of hydrogen from the interface to the bulk liquid,

b) transport from the bulk liquid to the catalyst surface and

c) diffusion with simultaneous reaction into the catalyst pores.

Since these are processes in series, the rate of consumption of hydrogen per unit mass of catalyst can be expressed by (Satterfield - 1970)

$$\frac{1}{m_c}\frac{dn_{H_2}}{dt} = k_L' a_v \frac{V}{m_c}(c_{H_2 i} - c_{H_2}) = k_L \frac{6}{d\rho_p}(c_{H_2} - c_{H_2 s})$$

$$= k' c_{H_2 s}^{\frac{1}{2}} \eta \qquad 8.2.1$$

where k_L' and a_v are the gas-liquid mass transfer coefficient and interfacial area respectively, k_L is the solid-liquid mass transfer coefficient, k' the apparent rate of reaction constant, η the effectiveness factor and the subscripts i and s denote the gas-liquid interface and the solid surface, respectively.

Two extreme situations can be found:

a) the effectiveness factor is unity

b) the effectiveness factor lies in the asymptotic zone.

Let us consider in the first place the case when the concentration of hydrogen is uniform throughout the catalyst particle, namely the effectiveness factor is unity. We can rewrite equation 8.2.1 in the form

$$r = \frac{c_{H2i} - c_{H2s}}{\frac{m_c}{k_L' a_v V} + \frac{d\rho_p}{6k_L}} = k' c_{H_2s}^{\frac{1}{2}} \qquad 8.2.2$$

and the mass transfer resistances can be evaluated from

$$\frac{1}{K_L} = \frac{m_c}{k_L' a_v V} + \frac{d\rho_p}{6k_L} = \frac{c_{H2i} - c_{H2s}}{r} = \frac{c_{H2i} - (r/k')^2}{r} \qquad 8.2.3$$

where the apparent rate of reaction constant k' is known and c_{H2i} is the solubility of hydrogen in the liquid phase.

On the other hand, when the Thiele modulus is large enough for the catalyst to operate in the so called 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)

$$\eta = \frac{1}{h_p} = \frac{3}{R}\sqrt{\frac{2}{p+1}\frac{D_{eff}\, c_{H_2s}^{\frac{1}{2}}}{k'}} \qquad 8.2.4$$

and equation 8.2.1 is transformed into

$$r = \frac{c_{H2i} - c_{H2s}}{\frac{m_c}{k_L' a_v V} + \frac{d\rho_p}{6k_L}} = \frac{3}{R}\sqrt{\frac{2}{p+1} k' D_{eff}}\; c_{H_2s}^{\frac{3}{4}} \qquad 8.2.5$$

and the apparent order with respect to hydrogen is increased to 0·75, with $p = \frac{1}{2}$.

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

8.3 Analysis of experimental results

8.3.1 Calculation of the gas-liquid mass transfer coefficient

We have already shown (Section 6.2) that the effectiveness factor for the Raney nickel catalyst Nicat 102 is unity under maximum agitation of the liquid. It is possible to show this is true even when there is a drop in hydrogen concentration due to the diffusion controlled mass transfer. From equation 8.2.1 it follows that

$$c_{H2s} = \left(\frac{r}{k'\eta} \right)^2 \qquad 8.3.1$$

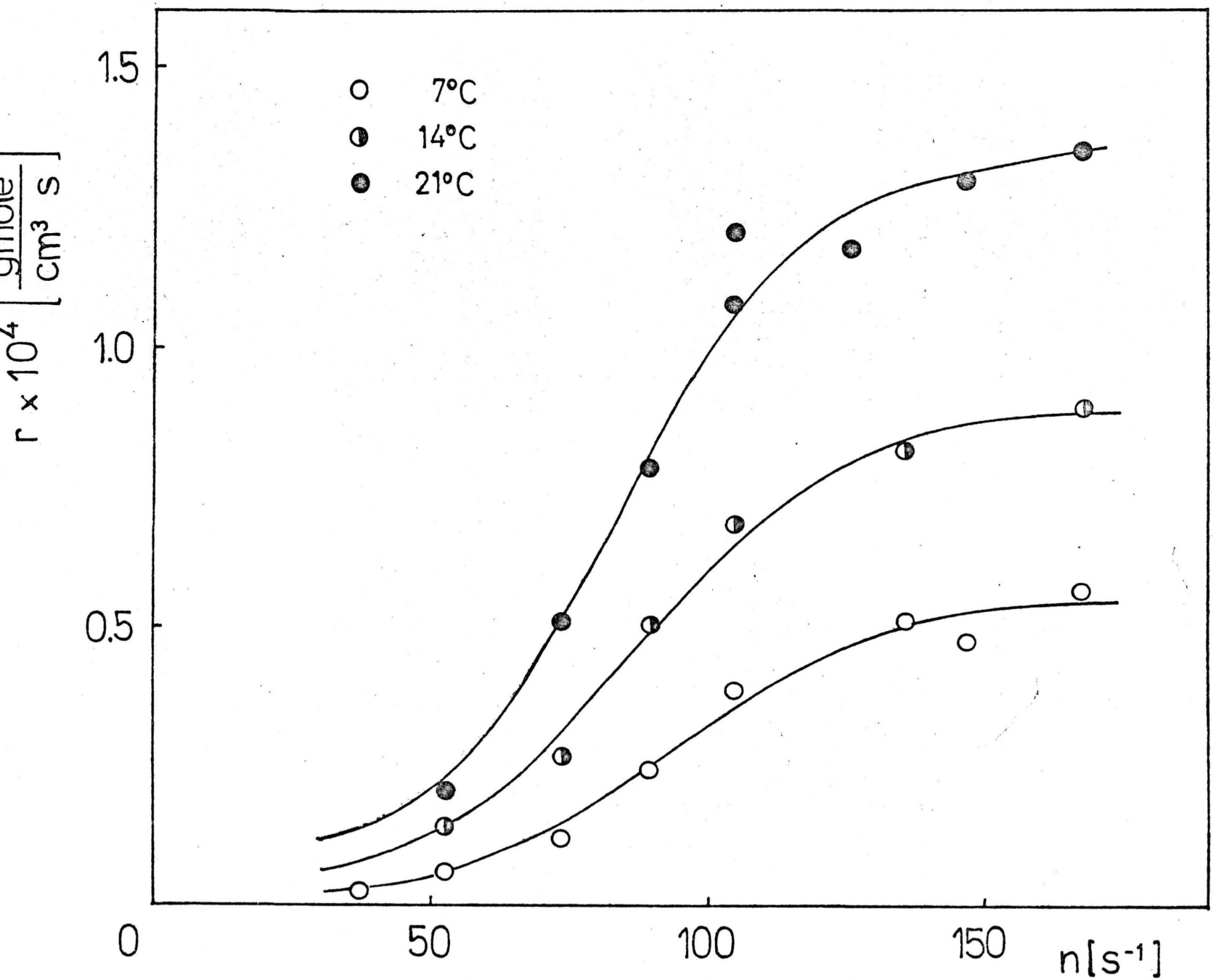
and the Thiele modulus can be evaluated from

$$h_p = \frac{R}{3} \sqrt{\frac{p+1}{2} \frac{k'}{D_{eff}\, c_{H2s}^{\frac{p+1}{2}}}} \qquad 8.3.2$$

Knowing the relationship between the effectiveness factor and the Thiele modulus, the hydrogen concentration at the catalyst surface can be evaluated from the experimental rates of reaction (Figure 8.1) by an iterative method, and the assumption on the effectiveness factor can be checked. Values obtained for Nicat 102 are summarized in Table 8.1 (a tortuosity factor of 4 has been assumed). For frequencies of oscillation above 700 rpm, the internal diffusional control is negligible.

Since the solid-liquid mass transfer coefficient k_L can be calculated with the correlation obtained in Chapter 4, the gas-liquid coefficient $k'_L a_v$ is obtained as a function of the oscillation frequency from

$$k'_L a_v = \frac{m_c}{V} \frac{1}{(c_{H2i} - c_{H2s})/r - d\rho_p/6k_L} \qquad 8.3.3$$



8.1 Rates of reaction with Nicat 102 catalyst (no bubble cycling)

Table 8.1

Gas-liquid mass transfer coefficients in vibrating slurry reactor

T (^{o}C)	n (1/s)	$r_e \times 10^5$ (gmole/cm^{3}s)	η	$c_{H_2i} \times 10^6$ (gmole/cm^3)	$c_{H_2s} \times 10^6$ (gmole/cm^3)	$k'_L a_v \times 10^2$ (1/s)
7	36.7	0.225	0.80	1.67	0.0051	0.0256
7	52.4	0.623	0.93	1.67	0.029	0.0746
7	73.3	1.17	0.99	1.67	0.090	0.146
7	89.0	2.46	1.00	1.67	0.389	0.383
7	104.7	3.88	1.00	1.67	0.967	1.13
7	146.6	4.74	1.00	1.67	1.45	4.69
14	52.4	1.44	0.92	1.66	0.052	0.122
14	73.3	2.72	0.98	1.66	0.162	0.250
14	89.0	5.08	1.00	1.66	0.546	0.643
14	104.7	6.86	1.00	1.66	0.994	1.52
14	136.1	8.14	1.00	1.66	1.40	5.35
21	52.4	2.03	0.86	1.57	0.044	0.140
21	73.3	5.10	0.97	1.57	0.225	0.408
21	89.0	7.83	1.00	1.57	0.495	0.803
21	104.7	10.8	1.00	1.57	0.938	2.01
21	104.7	12.1	1.00	1.57	1.18	4.13
21	125.7	11.8	1.00	1.57	1.12	3.16
21	146.6	13.0	1.00	1.57	1.36	9.19
21	167.6	13.5	1.00	1.57	1.47	26.9

Table 8.1 summarizes the results obtained at different temperatures. In spite of the catalyst Nicat 102 wide particle size distribution, no major error is introduced by using the average particle diameter in the calculations, since the concentration drop due to the solid-liquid mass transfer represents only up to 3% of the hydrogen solubility. At the same time, the sensitivity of the effectiveness factor to variations in the particle diameter is low at low Thiele moduli.

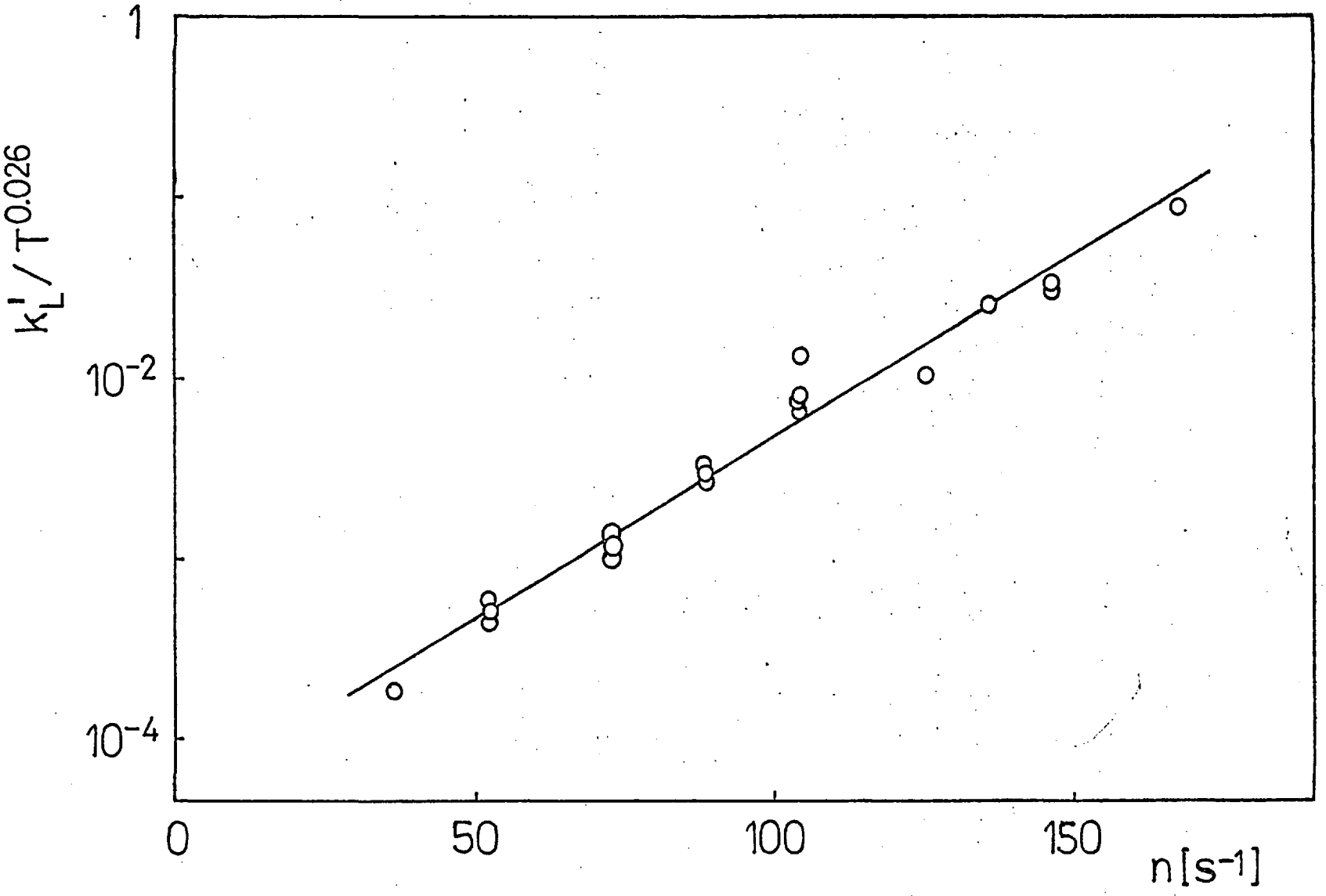
Assuming there is a linear relationship between the logarithm of the mass transfer coefficient and the frequency of oscillation, a linear regression of the experimental results at all temperatures (7, 14 and 21°C) is carried out, and the following equation is obtained

$$\log k_L' a_v = -4{\cdot}36 + 0{\cdot}0260\ T + 0{\cdot}0198\ n \qquad 8.3.4$$

where T is the temperature in degrees centigrade, and n the frequency of oscillation in cycles/sec. These results are plotted in Figure 8.2.

8.3.2 Calculation of the tortuosity factor

Since both the diffusional resistances have been estimated, we can now calculate the rates of reaction which are to be observed in the slurry reactor when acetone is being hydrogenated over the grade 820 of Raney nickel. 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 $D_{eff} = D\varepsilon/\tau$



8.2 Correlation of gas-liquid mass transfer coefficient

and all the parameters but the tortuosity factor are known, the latter will be determined from the experimental results.

The concentration of hydrogen at the solid surface will be given by

$$c_{H2\,s} = c_{H2\,i} - r \left(\frac{d\rho_p}{6\ k_L} + \frac{m_c}{k_L'\ a_v V} \right) \qquad 8.3.5$$

and the Thiele modulus is calculated from equation 8.3.2. The rate of reaction is obtained from

$$r = k'\ c_{H2\,s}^{1/2}\ \eta \qquad 8.3.6$$

where the effectiveness factor η has been estimated from its relationship with the Thiele modulus. Since in equation 8.3.5 the value of the rate of reaction is needed, an iterative method must be applied. The calculation starts by assuming $r_{est} = r_e$, and after one iteration is completed we compare the resulting value r'_{est} with r_{est} . If they differ in more than 1% we repeat the procedure by correcting the initial guess according to

$$r_{est} = r_{est} \left(1 + 0{\cdot}01 \left(\frac{r'_{est}}{r_{est}} - 1 \right) \right) \qquad 8.3.7$$

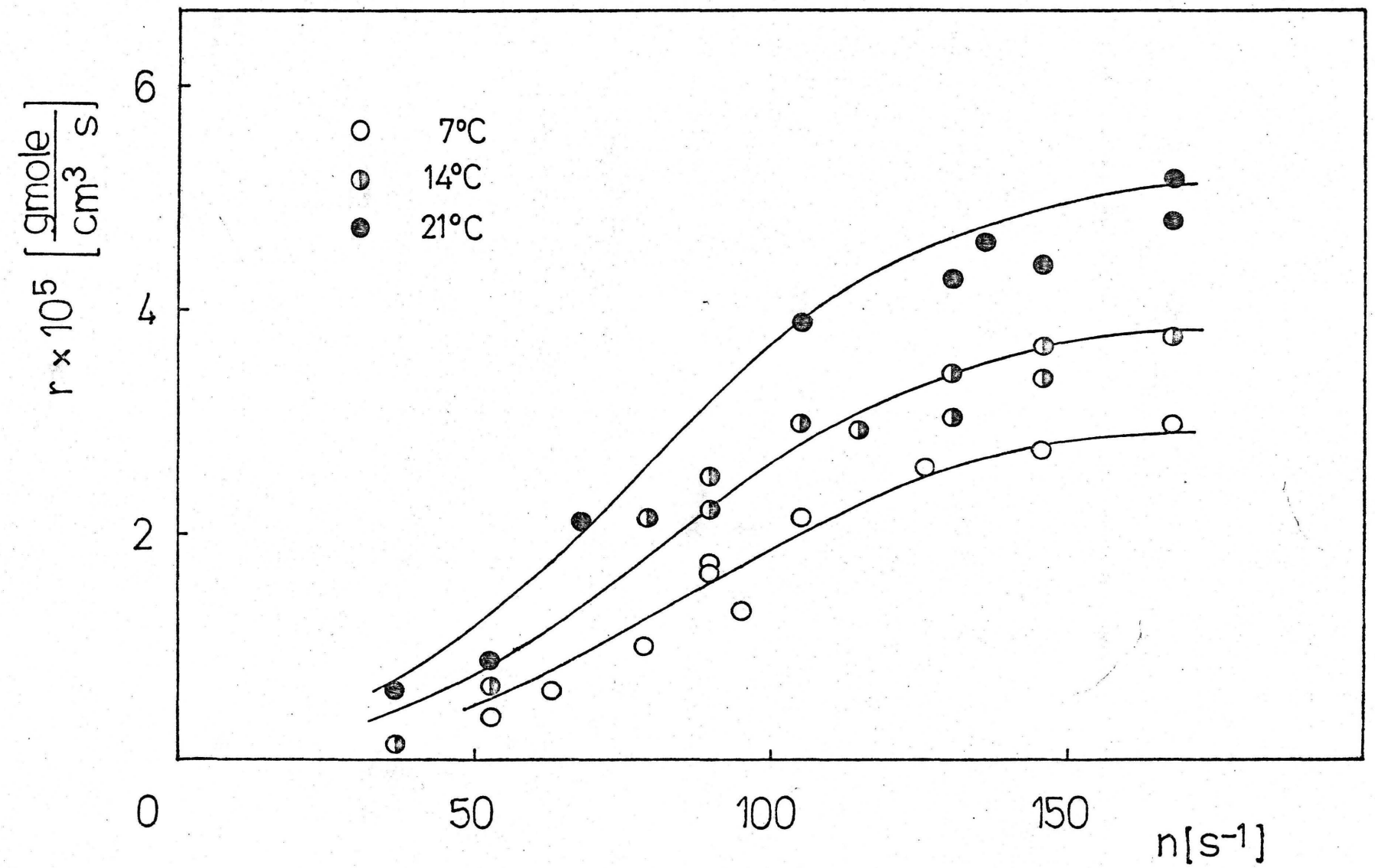
until two successive values are equal within 1% error. A very fast convergence is obtained and the sum

$$S(\tau) = \sum_{j=1}^{N} (r_{ej} - r(\tau))^2 \qquad 8.3.8$$

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

The grid search method is applied in order to find the

minimum of the sum $S(\tau)$. This is carried out by applying the iterative procedure described to all the experimental results obtained with Raney nickel grade 820. The estimated value of the tortuosity factor is 4·0, and is consistent with values quoted in the literature for similar catalysts (Satterfield - 1970). When the grid search method is applied to each of the temperatures 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 8.2 both the experimental and estimated values of rate of reaction are summarized.



8.3 Rates of reaction with Nicat 820 (no bubble cycling)

Table 8.2

Comparison between experimental and estimated rates of reaction with Nicat 820 catalyst

T (°C)	n (1/s)	$r_e \times 10^5$ (gmole/cm^{3}s)	η	$c_{H_2S} \times 10^6$ (gmole/cm^3)	$r_{est} \times 10^5$ (gmole/cm^{3}s)
7	52.4	0.390	0.34	0.187	0.583
7	62.8	0.630	0.40	0.358	0.950
7	78.5	1.02	0.47	0.675	1.53
7	89.0	1.70	0.47	0.660	1.51
7	89.0	1.79	0.47	0.660	1.51
7	94.2	1.33	0.50	0.826	1.78
7	104.7	2.19	0.51	0.914	1.92
7	125.7	2.57	0.55	1.23	2.40
7	125.7	2.57	0.55	1.20	2.35
7	146.6	2.77	0.57	1.40	2.65
7	167.6	3.00	0.58	1.50	2.79
14	36.7	0.105	0.23	0.082	0.458
14	52.4	0.615	0.28	0.174	0.805
14	78.5	2.17	0.36	0.456	1.66
14	89.0	2.51	0.38	0.610	2.06
14	89.0	2.24	0.38	0.590	2.01
14	104.7	3.02	0.42	0.852	2.65
14	115.2	2.90	0.43	0.989	2.96
14	136.1	3.03	0.46	1.25	3.53
14	136.1	3.44	0.46	1.25	3.53
14	146.6	3.32	0.41	0.793	2.51

Table 8.2 (Cont.)

T	n	$r_e \times 10^5$	η	$c_{H_2S} \times 10^6$	$r_{est} \times 10^5$
14	146·6	3·46	0·43	0·981	2·95
14	146·6	3·71	0·46	1·31	3·66
14	167·6	3·79	0·48	1·46	3·96
21	36·7	0·623	0·20	0·093	0·694
21	52·4	0·810	0·24	0·188	1·18
21	68·1	2·15	0·28	0·328	1·79
21	104·7	3·98	0·35	0·801	3·49
21	130·9	4·27	0·39	1·17	4·64
21	136·1	4·59	0·38	1·16	4·61
21	146·6	4·42	0·40	1·30	5·01
21	167·6	4·81	0·40	1·41	5·34
21	167·6	5·17	0·40	1·37	5·21

8.3.3 Energies of activation

When the frequency of oscillation is high, both the gas-liquid and liquid-solid mass transfer resistances are negligible. In the experiments carried out with the catalyst Nicat 102, the effectiveness factor is unity under this condition and therefore, the rate of reaction can simply be expressed as

$$r = k' c_{H2}^{\frac{1}{2}} \qquad 8.3.9$$

Differentiating the logarithm of this expression with respect to the absolute temperature and multiplying by $-R_g T^2$, we obtain

$$-R_g T^2 \frac{d\ln r}{dT} = E_{app1} = -R_g T^2 \left(\frac{d\ln k'}{dT} + \frac{1}{2} \frac{d\ln c_{H2}}{dT} \right) = E_A' \qquad 8.3.10$$

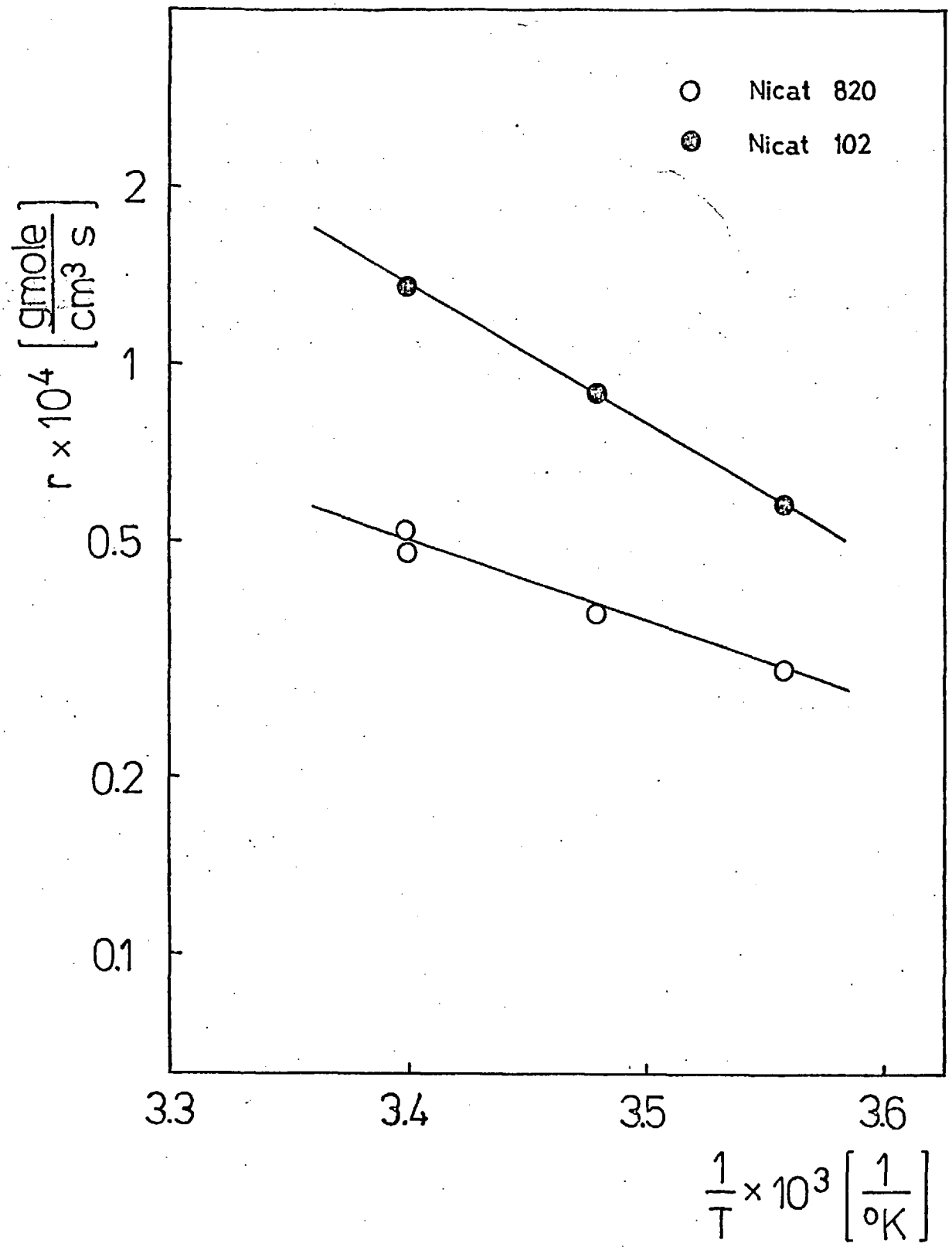
where the heat of solution has been neglected. From the correlation developed in Section 6.1, it is estimated to be less than 0·5 Kcal/gmole.

On the other hand, the grade Nicat 820 operates in the asymptotic zone of the effectiveness factor. Equation 8.2.5 will apply in this case with the hydrogen solubility as its concentration on the catalyst surface. An expression for the apparent energy of activation is obtained by the same procedure applied to equation 8.3.9

$$E_{app2} = \frac{1}{2} E_A' + \frac{1}{2} E_D = \frac{1}{2} E_{app1} + \frac{1}{2} E_D \qquad 8.3.11$$

The activation energy associated with the diffusion of hydrogen is 2·8 Kcal/gmole (Int. Crit. Tables - 1929). In the

experiments with Nicat 102 and 1600 rpm, the activation energy is 10·1 Kcal/gmole (see Figure 8.4). From equation 8.3.11, it follows that the apparent activation energy must be 6·4 Kcal/gmole when the internal diffusion is controlling. This is in good agreement with the experimental value found for Nicat 820 of 5·7 Kcal/gmole (see Figure 8.4).



8.4 Apparent activation energies

8.4 Discussion

In the previous sections, an analysis of the behaviour of a vibrating column of liquid as a slurry reactor has been given. The hydrogenation of liquid acetone over two Raney nickel catalysts of different particle size was carried out.

It has been found that the solid-liquid mass transfer resistance is negligible even at frequencies of oscillation as low as 350 rpm. But the gas-liquid diffusional resistance is important and only above 1300 rpm the hydrogen concentration drop in the liquid phase falls below 10%.

It must be pointed out that the internal diffusion, namely the transport of reactants from the catalyst surface to the active sites, depends fundamentally on the porous structure, and an improvement in the agitation conditions will only help to increase the potential supply of reactants, but will not affect the effectiveness factor considerably. In Table 8.2, the experimental rate of reaction increases its value 10 times from the lowest to the highest oscillation frequency, while the effectiveness factor only twice.

In section 2.5, a survey on the studies of slurry reactors was carried out and in almost all the cases, one of the diffusional resistances was controlling. In Part I of this thesis and in a previous work (Jameson - 1966b), it has already been shown that the resonant bubble contactor will improve the performance of mass transfer processes by reducing those resistances.

If in the hydrogenation over the grade 820 of Raney nickel, we assume there are no external diffusional resistances, and

since the catalyst operates in the asymptotic zone, we can calculate the rate of reaction by applying equation 8.2.5. It follows that at 7°C

$$r = 1{\cdot}48 \times 10^{-6} \, (p_{H_2})^{\frac{3}{4}} \text{ gmole/cm}^3\text{s} \qquad 8.4.1$$

and that the coefficient at 14 and 21°C is $2{\cdot}14 \times 10^{-6}$ and $2{\cdot}93 \times 10^{-6}$, respectively.

We can now compare the experimental results when bubble cycling occurs in the liquid with the rate of reaction calculated from equation 8.4.1, where the hydrogen pressure is the one existing during the experiment. At 7°C and 1800 rpm, a rate of $3{\cdot}14 \times 10^{-5}$ gmole/cm^{3}s was measured, while the estimated one is $3{\cdot}06 \times 10^{-5}$. At 14°C and 1400 rpm, the rates are $2{\cdot}08 \times 10^{-5}$ and $1{\cdot}96 \times 10^{-5}$ gmole/cm^{3}s, respectively.

We hereby confirm that in the resonant bubble contactor, both the gas-liquid and liquid-solid resistances are negligible and the reaction rate obtained is higher than in any other type of slurry reactors.

CHAPTER 9

CONCLUSIONS

The solid-liquid mass transfer and the hydrogenation of acetone over Raney nickel have been studied in a vibrating liquid column. At the same time a kinetic study of the hydrogenation in different solvents has been carried out.

The following conclusions can be made from the work presented in this thesis:

A large increase in the Sherwood number for solid-liquid mass transfer over those reported in a stirred tank is observed in a resonant bubble contactor.

When no bubble cycling occurs in the liquid, the mass transfer coefficient depends on almost the fourth power of the oscillation frequency, but when the bubbles begin to recycle, this dependence is considerably reduced. In both cases, the effect of particle diameter is negligible. The two series of results are successfully correlated as a function of the Reynolds, Schmidt and Froude numbers and the relative amplitude. It follows that

$$\frac{Sh - 2}{Sc^{\frac{1}{3}}} = 0{\cdot}434\ Re_v^{0{\cdot}85}\ H^{-0{\cdot}045}$$

and

$$\frac{Sh - 2}{Sc^{\frac{1}{3}}} = 0{\cdot}0132\ Re_v^{0{\cdot}75}\ H^{-0{\cdot}25}\ G^{1{\cdot}42}$$

when bubble cycling does and does not occur, respectively.

In the kinetic study, rates of hydrogenation of acetone

in n-octane, isooctane and isopropanol are represented with good approximation by a Langmuir-Hinshelwood model, in which it is assumed the surface reaction between adsorbed acetone and hydrogen is controlling. It is shown that both external and internal diffusional resistances were not significant.

The developed model takes into account the dissolution of hydrogen and its further adsorption and dissociation at the catalyst surface. A correlation for the hydrogen solubility in polar and nonpolar solvents and their mixtures is developed.

When water is added to acetone, a very large increase in the rate of reaction is observed and attributed to electronic factors. The enolization of the adsorbed acetone and the increase in the amount of the adsorbed hydrogen responsible for the carbonyl reduction are considered to be the main reasons. In this case, the same kinetic model is applied but only to the experiments with acetone concentrations below 11 gmoles/l.

Apparent activation energies of 6·2, 11·0 and 8·6 Kcal/gmole when n-octane, isopropanol and water, respectively, are used as solvents, are determined. These values differ from the true ones by the hydrogen heat of adsorption. The order of reaction with respect to hydrogen is found to be 1/2.

Finally, the behaviour of the vibrating column of liquid as a heterogeneous slurry reactor is studied. For this purpose the hydrogenation of aqueous acetone is carried out over two Raney nickel catalysts of different average particle size.

For the smaller particle, an effectiveness factor of one is found in all the experiments carried out at frequencies of

oscillation above 700 rpm, while the concentration drop of hydrogen in the liquid phase is very low at frequencies above 1300 rpm. The solid-liquid mass transfer resistance is negligible in all cases.

A tortuosity factor of 4·0 is determined from the measurements with the larger size of particle, which is found to be operating in the asymptotic zone of the effectiveness factor. The value obtained is in agreement with published results for similar catalysts.

When bubble cycling occurs in the reactor, none of the external diffusional resistances play any role in the observed rate of reaction. The apparent activation energy of the reaction when the grades 102 and 820 of Raney nickel are used, are 10·1 and 5·7 Kcal/gmole, respectively.

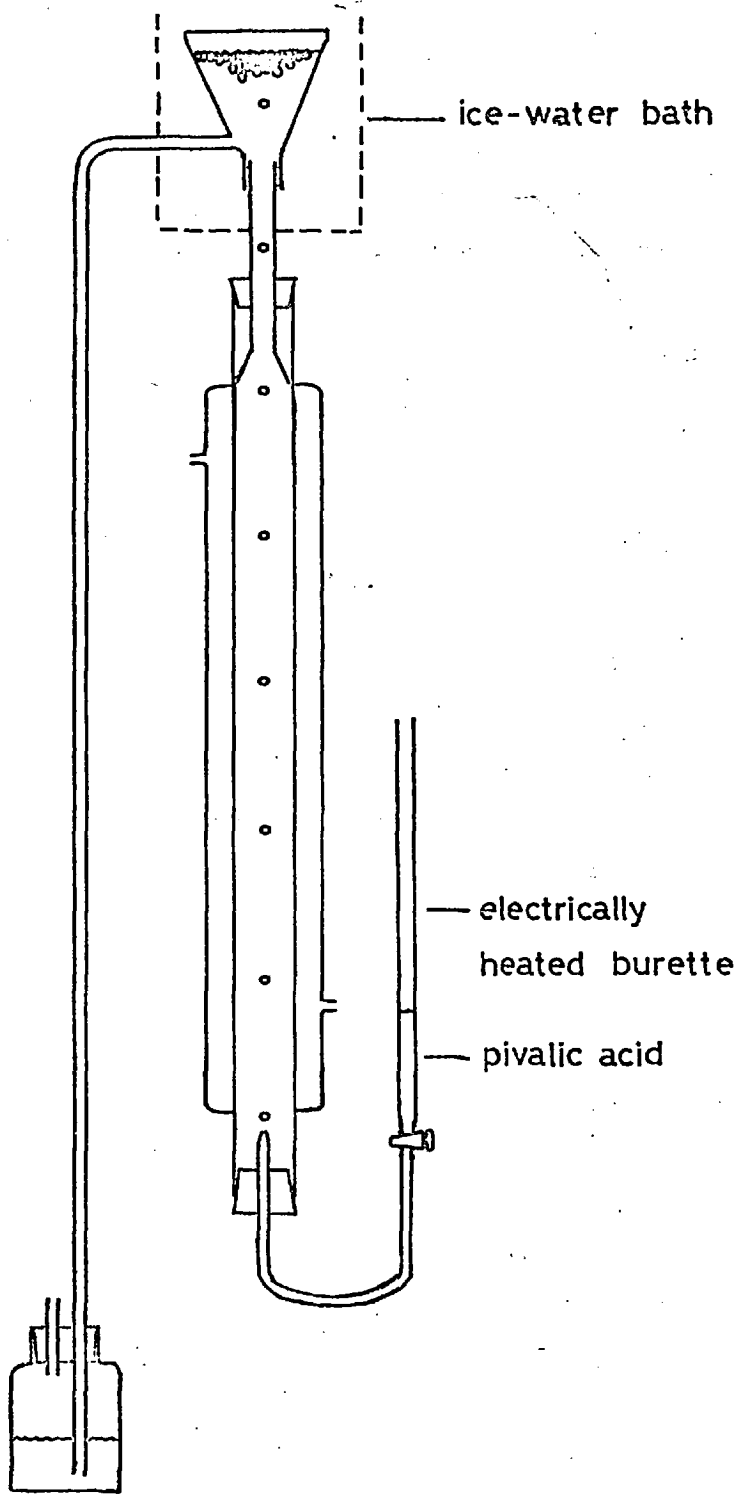
The results of this work show that a very large increase in the rate of mass transfer is obtained when a vibrating column of liquid is used instead of other more conventional contacting devices such as stirred tanks. A marked improvement in the efficiency of processes like liquid-liquid extraction, gas-liquid contacting, heat and mass transfer and heterogeneous catalysis - as it was shown here - is to be obtained with the introduction of the resonant bubble contactor.

APPENDIX I

AI.1 Preparation of pivalic acid spheres

Solid pivalic acid was melted in an electrically heated burette whose exit nozzle was bent to point vertically upwards in the bottom of a large column of water (see Figure AI.1). Cool water circulated through the column jacket, and when the acid was allowed to flow, liquid drops were formed at the tip of the burette which solidified during their rise in the column.

The solid spheres were collected at the top of the column in an inverted flask, immersed in a water-ice bath. The spheres were removed, filtered and dried in a room whose temperature was kept below $5^{\circ}C$. After sizing, they were kept in a refrigerator. Their mean size was determined and found to be $0{\cdot}368 \pm 0{\cdot}014$ cm.



AI.1 Apparatus for the production of pivalic acid spheres

AI.2 Conditioning of acid ion exchange resins

Batches of several sizes of ion exchange resins were placed in different columns and were treated with an excess of 2M HCl solution in such a way that the beads were always covered by liquid and under a constant flow rate, in this case 1 ml/min. An excess of 2M NaCl solution was then passed through the columns for several hours. Finally the resin was regenerated with the same HCl solution used before, until the influent and effluent concentrations were the same. This was checked by titrating both with NaOH solution.

The resin was then rinsed with distilled water until the effluent was free of chloride ion, namely until no precipitate was formed when treated with a standard solution of $AgNO_3$. The wet resin was air dried until it was just free-flowing. Each batch was sieved and different bead sizes were obtained. The moisture content was determined by drying a sample at $110^{\circ}C$ for over 12 hours. During this process there are always some changes in the structure of the resin, as its colour changes to dark brown or black. Hence only undried resins were used during the experiments.

AI.3 Capacity determination

A small sample of regenerated ion exchange resin was placed in a column and an excess of 2M NaCl solution was passed at a low flow rate. The effluent was collected and, when the resin was totally converted to the sodium form, it was titrated with a standard solution of NaOH to obtain the amount of H^+

displaced (Helfferich - 1962).

The capacity of the Zeo Carb 225 resin used in the experiments was determined to be 4·9 meq/g dry resin.

AI.4 Volume and density determinations

The ion exchange resin was treated with a large excess of the solvent and after equilibrium was reached, generally between 30 and 60 min, the beads were transferred into a specific gravity bottle and allowed to settle. After thermal equilibrium was reached, it was weighed in the conventional manner.

The resin was now transferred into a glass tube fitted at one end with a sintered glass disc. The tube was placed in a centrifuge tube containing a few drops of the solvent and was stoppered to avoid losses by evaporation. It was centrifuged at 3000 rpm for 3 min. The glass tube was weighed and the net weight of the resin was determined. The density of the solvent was measured with the same specific gravity bottle.

The volume $\overline{V}$ of the ion exchanger in equilibrium with the solvent results

$$\overline{V} = V_b - \frac{Q_b - \overline{Q}}{\rho} \qquad \text{AI.4.1}$$

and its density

$$\overline{\rho} = \overline{Q}/\overline{V} \qquad \text{AI.4.2}$$

where V_b is the volume of the bottle, Q_b the weight of the bottle content, $\overline{Q}$ the net weight of the ion exchanger and

ρ, the density of the solvent.

In Table AI.1, the measured values of the swollen volume per gram of dry resin are summarized.

The diameter of the swollen resin was determined simultaneously by microscopy and agreed with the results obtained from the volume measurements.

Table AI.1

Swollen volume of ion exchange resin

Solvent	$\bar{V}$ (ml/g dry resin)	
Water	2·932	
30% glycerol solution	2·885	
67% glycerol solution	2·326	for d ⩽ 100μ
	2·928	for d > 100μ

APPENDIX II

Equation of motion of a particle in a vibrating fluid

Dimensional analysis

In order to obtain the relevant parameters to be used for the correlation of the mass transfer results in a vibrating system, the equation derived by Tchen (Hinze - 1959) for the motion of a spherical particle in a fluid moving with variable velocity will be analysed in this Appendix.

Under the following assumptions:

(a) the turbulence of the fluid is homogeneous, steady and extends indefinitely,

(b) the particle is spherical and small compared with the smallest wavelength present in the turbulence, and its motion follows Stokes law of resistance,

(c) during the motion of the particle the neighbourhood will be formed by the same fluid particles,

Tchen derived an expression which represents the motion of the particle

$$\rho_p V_p \frac{du_p}{dt} = 3\Pi\mu d\,(u - u_p) + \rho V_p \frac{du}{dt} + \tfrac{1}{2}\,\rho V_p \left(\frac{du}{dt} - \frac{du_p}{dt} \right)$$

$$+ \frac{3}{2}\, d^2 \sqrt{\Pi\rho\,\mu} \int_o^t \left(\frac{du}{dt'} - \frac{du_p}{dt'} \right) \frac{dt'}{\sqrt{t-t'}} + (\rho_p - \rho) g V_p$$

AII.1

The last of the assumptions is unlikely to be satisfied, because only if the element of fluid containing a small,

discrete particle could be considered an undeformable entity, it could be true (provided that its size was larger than the amplitude of the motion of the discrete particle relative to the fluid).

The first term on the right hand side of equation AII.1 represents the viscous resistance force according to Stokes law. Some authors used the above equation, but considering the drag proportional to the square of the relative velocity, as was first proposed by Newton. This would correspond to separated flow with a laminar boundary layer.

The second term on the right of AII.1 is due to the pressure gradient in the fluid surrounding the particle, caused by the acceleration of the fluid. The third term is the force to accelerate the apparent mass of the particle relative to the fluid (the virtual mass coefficient has been considered equal to $\frac{1}{2}$).

The fourth term is the Basset term, which takes into account the effect of the deviation of the flow pattern around the particle from that at steady state. It is a transient component of the drag. As a result of experimental evidence, it is possible for small particles to neglect the Basset term with respect to the others in equation AII.1.

The last term on the right of AII.1 gives the buoyancy forces on the particle.

Considering that $u = nA \sin nt$ and introducing the dimensionless variables $u_p^* = u_p/nA$ and $t^* = nt$, we get

$$\frac{\rho_p}{\rho}\frac{du_p^*}{dt^*} - \cos t^* = \frac{9H}{Re_v}(\sin t^* - u_p^*) + \tfrac{1}{2}\left(\cos t^* - \frac{du_p^*}{dt^*}\right) + \left(\frac{\rho_p}{\rho} - 1\right)\frac{g}{n^2A} \qquad \text{AII.2}$$

where $Re_v = nAd/\nu$, $H = 2A/d$ is the relative amplitude of oscillation, and the Basset term has been neglected.

Hence the dimensionless velocity of the particle can be expressed as a function

$$u_p^* = u_p^*\,(t^*,\ \rho_p/\rho,\ g/n^2A,\ Re_v,\ H) \qquad \text{AII.3}$$

From mass transfer studies involving translating solid spheres in a fluid, it follows that the Sherwood number, $Sh = k_L d/D$, depends only on the Peclet number, $Pe = u_r d/D$. In the case of an oscillating fluid, we do not have an analytic expression for the relative velocity u_r; moreover, it is not constant in time. But we know that

$$Pe = \frac{du_r}{D} = \frac{dnA}{\nu}\frac{\nu}{D}(u_p^* - u^*) = Re_v\,Sc\,(u_p^* - u^*) \qquad \text{AII.4}$$

Finally, averaging with respect to time, the Sherwood number can be expressed as a function of the following parameters:

$$Sh = Sh\,(Re_v,\ H,\ g/n^2A,\ \rho_p/\rho,\ Sc) \qquad \text{AII.5}$$

being the relative influence of each one determined by the experimental conditions.

APPENDIX III

EXPERIMENTAL RESULTS

PIVALIC ACID DISSOLUTION

EXP. A- 1

n = 1660 RPM m_c = 3.833 g

V = 635 ml V_2 = 150 ml

F_v = 600 ml/min T = 7.5 °C

C = 0.169 E+07 eq Ω^2 cm^2/l K_f = 1.87 $x10^{-4}$ 1/Ωcm

t	K $x10^4$	d	k_L $x10^2$	Sh
min	1/Ωcm	cm	cm/s	
0.333	0.46	0.360	1.51	1727
0.500	0.73	0.348	1.79	2034
0.583	0.78	0.345	1.71	1925
1.000	1.05	0.324	1.75	1849
1.333	1.22	0.306	1.85	1844
1.666	1.38	0.283	2.04	1888
2.000	1.48	0.265	2.09	1816
2.500	1.59	0.240	2.09	1649
3.000	1.70	0.205	2.23	1551
3.500	1.78	0.167	2.54	1424
4.500	1.85	0.102	2.20	801

EXP. A- 2

n = 1880 RPM m_c = 3.833 g

V = 634 ml V_2 = 150 ml

F_v = 600 ml/min T = 7.0 °C

C = 0.164 E+07 eq Ω^2 cm^2/l K_f = 1.90 $x10^{-4}$ 1/Ωcm

t	K $x10^4$	d	k_L $x10^2$	Sh
min	1/Ωcm	cm	cm/s	
0.500	0.63	0.354	2.61	2726
0.667	0.87	0.340	3.10	3346
0.833	1.07	0.324	3.41	3614
1.000	1.31	0.297	4.10	4065
1.167	1.41	0.282	3.92	3746
1.333	1.49	0.268	3.63	3338
1.500	1.59	0.246	3.54	3044
1.667	1.64	0.233	2.97	2478
1.833	1.68	0.222	2.27	1871
2.000	1.72	0.208	1.48	1249

EXP. A- 3

n = 1700 RPM m_c = 5.009 g

V = 843 ml V_2 = 150 ml

F_v = 600 ml/min T = 7.5 °C

C = 0.170 E+07 eq Ω^2 cm^2/l K_f = 1.85 $x10^{-4}$ 1/Ωcm

t	K $x10^4$	d	k_L $x10^2$	Sh
0.500	0.46	0.360	1.28	1434
0.667	0.63	0.353	1.44	1602
0.833	0.82	0.342	1.72	1875
1.000	0.93	0.334	1.82	1944
1.333	1.12	0.316	2.01	2050
1.667	1.29	0.295	2.21	2118
2.000	1.45	0.268	2.49	2172
2.333	1.57	0.242	2.61	2079
2.667	1.63	0.223	2.39	1776
3.000	1.69	0.202	2.08	1426
3.333	1.72	0.189	1.38	919

EXP. A- 4

n = 1550 RPM (BUBBLE CYCLING) m_c = 5.250 g

V = 1132 ml V_2 = 135 ml

F_v = 600 ml/min T = 10.0 °C

C = 0.150 E+07 eq Ω^2 cm^2/l K_f = 1.74 $x10^{-4}$ 1/Ωcm

t	K $x10^4$	d	k_L $x10^2$	Sh
0.667	0.58	0.354	2.32	2491
0.833	0.80	0.340	3.03	3258
1.000	0.99	0.323	3.46	3603
1.167	1.21	0.295	4.18	4026
1.333	1.32	0.277	4.18	3802
1.500	1.43	0.253	4.33	3615
1.667	1.49	0.237	4.05	3167
1.833	1.57	0.210	4.22	2952
2.000	1.60	0.197	3.71	2447
2.250	1.63	0.183	2.84	1741
2.500	1.66	0.165	2.16	1207
2.750	1.67	0.158	1.33	719

EXP. A= 5

n = 1550 RPM m_c = 6.561 g

V = 709 ml V_2 = 0

T = 3.0 °C

C = 0.212 E+07 eq Ω^2 cm^2/l K_f = 2.06 x10^{-4} l/Ωcm

t	K x10^4	d	k_L x10^2	Sh
0.333	0.38	0.364	3.52	410
0.667	0.51	0.360	3.32	383
1.000	0.65	0.356	3.33	386
1.500	0.76	0.350	3.38	380
2.000	0.88	0.344	3.45	381
2.500	0.94	0.340	3.33	364
3.000	1.02	0.335	3.37	361
3.500	1.09	0.330	3.39	359
4.000	1.16	0.324	3.46	359
4.500	1.22	0.318	3.51	358
5.000	1.27	0.314	3.53	354
5.500	1.31	0.309	3.51	348
6.000	1.35	0.305	3.51	343
6.500	1.40	0.300	3.57	343
7.000	1.44	0.294	3.64	343
7.500	1.48	0.289	3.70	343
8.000	1.51	0.284	3.71	338
9.000	1.58	0.274	3.85	338
10.000	1.64	0.263	3.98	336
11.000	1.70	0.251	4.19	338
12.000	1.74	0.242	4.25	331
13.000	1.79	0.230	4.52	333

EXP. A= 6

n = 1700 RPM m_c = 5.690 g

V = 821 ml V_2 = 135 ml

F_v = 600 ml/min T = 8.5 °C

C = 0.187 E+07 eq Ω^2 cm^2/l K_f = 1.91 x10^{-4} l/Ωcm

t	K x10^4	d	k_L x10^2	Sh
0,500	0,52	0.359	1.19	1324
0,667	0,67	0.352	1.35	1501
0,833	0,82	0.344	1.52	1669
1,000	0,94	0.336	1.63	1756
1,167	1,05	0.327	1.73	1824
1,333	1,14	0.318	1.80	1850
1,500	1,22	0.309	1.86	1857
1,667	1,30	0.299	1.93	1873
1,833	1,36	0.291	1.95	1845
2,000	1,44	0.278	2.03	1881
2,167	1,47	0.273	2.01	1781
2,333	1,51	0.266	1.99	1718
2,500	1,58	0.251	2.14	1751
2,667	1,64	0.236	2.30	1771
2,833	1,68	0.224	2.36	1734
3,000	1,71	0.215	2.37	1666
3,250	1,74	0.204	2.26	1511
3,500	1,76	0.196	2.05	1324
3,750	1,79	0.183	1.96	1183
4,000	1,81	0.172	1.75	1003

EXP. A= 7

n = 1900 RPM m_c = 4.974 g

V = 581 ml V_2 = 0

T = 5.0 °C

C = 0.204 E+07 eq Ω^2 cm^2/l K_f = 2.06 x10^{-4} l/Ωcm

t	K x10^4	d	k_L x10^2	Sh
0.500	0,99	0.336	2.18	2345
0.667	1,25	0.314	3.20	3313
0.833	1,56	0.301	3.43	3311
1.000	1,49	0.284	3.58	3257
1.250	1,60	0.265	3.35	2845
1.500	1,69	0.248	3.13	2486
1.750	1,80	0.219	3.61	2532

EXP. A= 8

n = 1700 RPM (BUBBLE CYCLING) m_c = 5.125 g

V = 992 ml V_2 = 135 ml

F_v = 600 ml/min T = 9.0 °C

C = 0.174 E+07 eq Ω^2 cm^2/l K_f = 1.70 x10^{-4} l/Ωcm

t	K x10^4	d	k_L x10^2	Sh
0.500	0,54	0.355	2.69	2741
0.667	0,85	0.336	4.15	4397
0.833	1,07	0.311	4.95	5030
1.000	1,22	0.289	4.92	4719
1.167	1,37	0.259	5.07	4414
1.333	1,45	0.238	4.50	3698
1.500	1,52	0.215	4.25	3094
1.333	1,59	0.184	3.26	2014
2.167	1,64	0.151	3.40	1710

EXP. A- 9

n = 1875 RPM (BUBBLE CYCLING) m_c = 4.820 g

V = 806 ml V_2 = 135 ml

F_v = 600 ml/min T = 9.0 °C

C = 0.161E+07 eq Ω^2 cm^2/l K_f = 1.91 x10^{-4} 1/Ωcm

t	K x10^4	d	k_L x10^2	Sh
0.333	0.56	0.357	1.86	1700
0.500	0.79	0.346	2.99	3159
0.667	1.02	0.329	3.62	3825
0.833	1.21	0.310	3.95	4016
1.000	1.39	0.286	4.32	4099
1.167	1.52	0.264	4.48	3935
1.333	1.63	0.238	4.69	3747
1.500	1.71	0.215	4.70	3461
1.667	1.76	0.196	4.60	3048
2.000	1.82	0.166	3.80	2156
2.167	1.84	0.153	3.29	1736
2.333	1.85	0.146	2.55	1295
2.500	1.86	0.137	1.88	914

EXP. A-10

n = 1700 RPM (BUBBLE CYCLING) m_c = 5.717 g

V = 961 ml V_2 = 135 ml

F_v = 600 ml/min T = 8.0 °C

C = 0.173E+07 eq Ω^2 cm^2/l K_f = 1.83 x10^{-4} 1/Ωcm

t	K x10^4	d	k_L x10^2	Sh
0.333	0.52	0.358	2.37	2382
0.500	0.77	0.345	3.35	3599
0.667	1.04	0.323	4.19	4373
0.833	1.22	0.302	4.43	4438
1.000	1.37	0.280	4.63	4322
1.167	1.52	0.249	5.23	4323
1.333	1.61	0.224	5.38	4021
1.500	1.67	0.203	5.27	3582
1.667	1.73	0.174	5.63	3306
1.833	1.75	0.162	4.85	2665
2.000	1.77	0.147	4.17	2109
2.167	1.78	0.139	3.09	1498

EXP. A-11

n = 1530 RPM (BUBBLE CYCLING) m_o = 5.405 g

V = 1108 ml V_2 = 150 ml

F_v = 600 ml/min T = 7.0 °C

C = 0.188E+07 eq Ω^2 cm^2/l K_f = 1.59x10^{-4} 1/Ωcm

t	K x10^4	d	k_L x10^2	Sh
0.667	0.75	0.338	3.24	3355
0.833	0.92	0.321	3.95	4057
1.000	1.09	0.298	4.50	4387
1.167	1.22	0.273	4.74	4305
1.333	1.31	0.252	4.65	3919
1.500	1.39	0.227	4.59	3516
1.667	1.45	0.203	4.43	3056
1.833	1.48	0.188	3.81	2444
2.000	1.51	0.170	3.35	1955
2.250	1.53	0.154	2.31	1232

EXP. A-12

n = 1900 RPM (BUBBLE CYCLING) m_o = 4.643 g

V = 820 ml V_2 = 150 ml

F_v = 600 ml/min T = 7.5 °C

C = 0.180E+07 eq Ω^2 cm^2/l K_f = 1.75 x10^{-4} 1/Ωcm

t	K x10^4	d	k_L x10^2	Sh
0.500	0.55	0.355	2.03	2066
0.667	0.80	0.340	2.96	3131
0.833	0.95	0.327	3.25	3410
1.000	1.10	0.311	3.51	3565
1.167	1.28	0.285	4.12	3873
1.333	1.37	0.268	4.14	3686
1.500	1.46	0.247	4.28	3542
1.667	1.53	0.227	4.35	3326
1.833	1.62	0.192	5.26	3420
2.000	1.64	0.182	4.66	2904
2.333	1.68	0.157	3.74	2042
2.667	1.72	0.119	3.14	1357

EXP. A-13

n = 1700 RPM m_c = 4.523 g

V = 670 ml V_2 = 150 ml

F_v = 600 ml/min T = 7.5 °C

C = 0.211E+07 eq Ω^2 cm^2/l κ_f = 1.77 x10^{-4} 1/Ωcm

t	κx10^4	d	k_L x10^2	Sh
0.500	0.60	0.353	1.61	1786
0.667	0.76	0.344	1.82	1989
1.000	1.01	0.323	2.18	2268
1.167	1.09	0.314	2.24	2279
1.333	1.21	0.298	2.52	2448
1.500	1.29	0.286	2.66	2484
1.667	1.36	0.273	2.78	2492
1.833	1.42	0.261	2.88	2471
2.000	1.49	0.245	3.07	2487
2.107	1.52	0.236	3.03	2364
2.333	1.58	0.218	3.25	2362
2.500	1.61	0.205	3.30	2252
2.667	1.64	0.192	3.30	2131
2.833	1.67	0.176	3.38	2017
3.000	1.71	0.153	3.73	1984
3.250	1.72	0.141	3.15	1552
3.500	1.74	0.119	2.65	1158

EXP. A-14

n = 1675 RPM m_c = 5.598 g

V = 727 ml V_2 = 150 ml

F_v = 600 ml/min T = 8.0 °C

C = 0.165E+07 eq Ω^2 cm^2/l κ_f = 1.89 x10^{-4} 1/Ωcm

t	κx10^4	d	k_L x10^2	Sh
0.667	0.43	0.361	0.94	912
0.833	0.62	0.354	1.53	1666
1.000	0.79	0.345	2.03	2172
1.167	0.93	0.335	2.30	2443
1.333	1.10	0.320	2.65	2736
1.500	1.23	0.306	2.85	2835
1.667	1.36	0.288	3.10	2924
1.833	1.46	0.272	3.24	2899
2.000	1.55	0.258	3.24	2755
2.167	1.58	0.247	3.11	2539
2.333	1.63	0.234	3.04	2354
2.500	1.68	0.219	3.02	2198
2.750	1.74	0.196	2.93	1956
3.000	1.78	0.178	2.82	1681
3.250	1.81	0.160	2.65	1424
3.500	1.84	0.137	2.72	1256

EXP. A-15

n = 1875 RPM (BUBBLE CYCLING) m_c = 5.141 g

V = 806 ml V_2 = 150 ml

F_v = 600 ml/min T = 8.0 °C

C = 0.183E+07 eq Ω^2 cm^2/l κ_f = 1.84 x10^{-4} 1/Ωcm

t	κx10^4	d	k_L x10^2	Sh
0.500	0.66	0.351	2.45	2466
0.667	0.89	0.337	3.35	3510
0.833	1.10	0.317	4.03	4125
1.000	1.27	0.296	4.49	4371
1.167	1.42	0.272	4.95	4477
1.333	1.55	0.248	5.21	4343
1.500	1.64	0.217	5.83	4332
1.667	1.70	0.194	5.94	3946
1.833	1.76	0.162	6.65	3733
2.100	1.78	0.142	5.71	2980
2.167	1.79	0.139	4.12	2095
2.333	1.81	0.117	2.99	1399

EXP. A-16

n = 1900 RPM m_c = 4.322 g

V = 631 ml V_2 = 120 ml

F_v = 600 ml/min T = 7.0 °C

C = 0.181E+07 eq Ω^2 cm^2/l κ_f = 1.92 x10^{-4} 1/Ωcm

t	κx10^4	d	k_L x10^2	Sh
0.500	0.81	0.345	2.30	2489
0.667	0.99	0.332	2.60	2777
0.833	1.15	0.319	2.72	2823
1.000	1.26	0.305	2.83	2823
1.167	1.39	0.287	3.03	2855
1.333	1.46	0.276	2.96	2682
1.500	1.53	0.263	2.95	2549
1.667	1.60	0.248	3.02	2459
1.833	1.65	0.235	3.00	2323
2.000	1.70	0.221	3.06	2225
2.250	1.77	0.195	3.32	2143
2.500	1.81	0.177	3.38	1973
2.750	1.84	0.159	3.44	1811

EXP. A-17

n = 1550 RPM m_c = 8,983 g

V = 744 ml V_2 = 0

T = 4.0 °C

C = 0.179E+07 eq Ω^2 cm^2/l K_f = 2.57 x10^{-4} l/hcm

t	K x10^4	d	k_L x10^2	Sh
0.667	0.63	0.360	5.19	599
1.000	0.77	0.357	4.27	488
1.500	0.96	0.350	4.06	456
2.000	1.08	0.345	3.98	440
2.500	1.23	0.337	4.27	462
3.000	1.35	0.330	4.49	476
3.500	1.46	0.323	4.71	487
4.000	1.56	0.316	4.88	494
4.500	1.63	0.310	4.85	482
5.000	1.68	0.306	4.67	458
5.500	1.77	0.297	4.76	453
6.000	1.82	0.292	4.52	423
6.500	1.87	0.286	4.25	390
7.000	1.92	0.280	3.93	353

EXP. A-18

n = 1700 RPM m_c = 4.656 g

V = 600 ml V_2 = 0

T = 3.5 °C

C = 0.222E+07 eq Ω^2 cm^2/l K_f = 1.85 x10^{-4} l/hcm

t	K x10^4	d	k_L x10^2	Sh
0.333	0.55	0.357	1.20	1369
0.500	0.68	0.351	1.57	1765
0.667	0.84	0.341	1.86	2034
0.833	0.97	0.331	2.02	2142
1.000	1.08	0.320	2.11	2170
1.167	1.18	0.309	2.19	2173
1.333	1.28	0.296	2.32	2198
1.500	1.35	0.286	2.35	2147
1.667	1.41	0.275	2.37	2088
1.833	1.45	0.268	2.31	1987
2.000	1.51	0.255	2.42	1982
2.250	1.57	0.241	2.49	1917

NEUTRALIZATION OF ION EXCHANGE RESINS

Exp	T	n	bubble cycling	d	m_c	V	solvent	$k_L x 10^2$	Sh
	°C	rpm		μ	g	ml		cm/s	
B 1	17	1700	NO	875	0.581	600	WATER	4.480	217.5
B 2	17	1900	YES	736	0.876	655	GLYCEROL 30%	8.110	665.0
B 3	17	1700	YES	736	0.721	655	GLYCEROL 30%	5.920	486.0
B 4	17	1550	YES	736	0.653	750	GLYCEROL 30%	4.970	408.0
B 5	18	1550	NO	632	0.397	565	GLYCEROL 67%	0.168	78.2
B 6	18	1700	NO	632	0.552	515	GLYCEROL 67%	0.334	155.9
B 7	18	1900	NO	632	0.578	460	GLYCEROL 67%	0.974	455.7
B 8	18	1900	YES	632	0.525	600	GLYCEROL 67%	0.893	419.1
B 9	18	1700	YES	632	0.615	685	GLYCEROL 67%	0.949	443.7
B10	18	1550	YES	632	0.500	685	GLYCEROL 67%	0.454	212.1
B11	18	1900	YES	875	0.714	804	WATER	17.100	812.8
B12	26	1700	YES	875	0.485	845	WATER	19.400	792.1
B13	18	1550	YES	875	0.817	970	WATER	10.600	504.3
B14	18	1900	YES	876	0.381	600	GLYCEROL 67%	0.981	635.5
B15	18	1550	NO	128	0.719	565	GLYCEROL 67%	0.242	23.6
B16	18	1700	NO	128	0.733	515	GLYCEROL 67%	0.495	47.2
B17	18	1900	NO	128	0.813	470	GLYCEROL 67%	0.737	69.8
B18	18	1900	YES	128	0.814	600	GLYCEROL 67%	1.300	123.2
B19	18	1700	YES	128	0.780	625	GLYCEROL 67%	1.100	104.8
B20	18	1550	YES	128	0.866	685	GLYCEROL 67%	0.645	61.2
B21	18	1550	NO	831	0.658	565	GLYCEROL 67%	0.091	55.9
B22	18	1700	NO	831	0.630	515	GLYCEROL 67%	0.338	207.2
B23	18	1900	NO	831	0.599	461	GLYCEROL 67%	0.988	607.9
B24	18	1900	NO	831	0.601	499	WATER	9.810	444.4
B25	18	1900	YES	831	0.688	600	GLYCEROL 67%	0.787	483.5
B26	18	1700	YES	831	0.610	675	GLYCEROL 67%	0.854	527.3
B27	18	1550	YES	831	0.632	684	GLYCEROL 67%	0.405	248.7
B28	19	1550	NO	291	0.601	565	GLYCEROL 67%	0.235	49.3
B29	19	1700	NO	291	0.602	512	GLYCEROL 67%	0.447	93.7
B30	19	1900	NO	291	0.615	461	GLYCEROL 67%	0.668	140.2
B31	19	1550	YES	291	0.617	684	GLYCEROL 67%	0.679	142.8
B32	19	1700	YES	291	0.513	641	GLYCEROL 67%	0.861	180.8
B33	19	1900	YES	291	0.642	600	GLYCEROL 67%	1.120	234.9
B34	19	1550	NO	76	0.895	565	GLYCEROL 67%	0.506	27.7
B35	19	1700	NO	76	0.624	513	GLYCEROL 67%	0.668	36.4
B36	19	1900	NO	76	0.782	461	GLYCEROL 67%	0.891	48.4
B37	19	1550	YES	76	0.715	684	GLYCEROL 67%	1.100	59.9
B38	21	1700	YES	76	0.798	641	GLYCEROL 67%	1.300	66.3
B39	20	1900	YES	76	0.685	600	GLYCEROL 67%	1.400	73.9
B40	19	1550	NO	90	0.675	565	GLYCEROL 67%	0.525	33.8
B41	20	900	NO	548	0.421	508	WATER	0.962	27.3
B42	20	650	NO	548	0.699	522	WATER	0.601	17.0
B43	20	1200	NO	548	0.468	496	WATER	1.330	37.8
B44	20	650	NO	136	0.730	459	WATER	0.505	3.6
B45	20	900	NO	136	1.024	488	WATER	1.420	10.0
B46	20	1050	NO	136	0.926	515	GLYCEROL 30%	0.610	8.9

HYDROGENATION OF ACETONE

SOLVENT WATER

Exp	T	m_c	P	P_{H_2}	T_m	m_A/m_S	x_A	-dV/dt	r x10^4
	^oC	g	cm Hg	cm Hg	^oC			cm^3/min	$\frac{gmole}{min\ g}$
W 1	7	0.222	43.9	35.9	23	3.10	0.490	4.63	4.96
W 2	7	0.222	61.8	53.8	23	3.10	0.490	4.23	6.38
W 3	7	0.222	73.0	65.0	23	3.10	0.490	4.52	8.06
W 4	7	0.222	25.4	17.4	23	3.10	0.490	5.32	3.30
W 5	7	0.222	41.0	33.0	23	3.10	0.490	4.42	4.42
W 6	7	0.222	59.4	51.4	23	3.10	0.490	4.83	7.00
W 7	7	0.140	45.5	36.5	23	8.40	0.716	3.13	5.51
W 8	7	0.140	59.1	50.1	23	8.40	0.716	2.68	6.13
W 9	7	0.140	71.5	62.5	23	8.40	0.716	2.46	6.80
W10	7	0.140	28.1	19.1	23	8.40	0.716	3.57	3.88
W11	7	0.140	42.6	33.6	23	8.40	0.716	3.08	5.07
W12	7	0.140	57.7	48.7	23	8.40	0.716	2.88	6.43
W13	7	0.140	71.1	62.1	23	8.40	0.716	2.58	7.10
W14	7	0.230	59.0	49.5	23	—	1.000	0.96	1.33
W15	7	0.230	69.9	60.4	23	—	1.000	0.85	1.40
W16	7	0.230	26.0	16.5	23	—	1.000	1.36	0.84
W17	7	0.230	40.3	30.8	23	—	1.000	1.08	1.03
W18	7	0.230	55.1	45.6	23	—	1.000	0.92	1.19
W19	7	0.225	66.8	60.8	23	0.50	0.134	2.00	3.22
W20	7	0.225	67.2	61.2	23	0.50	0.134	2.05	3.32
W21	7	0.225	67.9	60.4	23	1.00	0.237	2.79	4.56
W22	7	0.225	68.5	61.0	23	1.00	0.237	2.94	4.85
W23	7	0.225	68.5	60.0	23	1.73	0.350	4.33	7.15
W24	7	0.225	68.7	60.2	23	1.73	0.350	4.52	7.47
W25	7	0.225	69.5	60.5	23	4.00	0.555	4.82	8.06
W26	7	0.225	69.0	60.0	23	4.00	0.555	4.88	8.11
W27	7	0.225	69.1	60.1	23	4.00	0.555	4.88	8.12
W28	7	0.225	69.1	60.1	23	4.00	0.555	4.86	8.08
W29	7	0.225	69.2	59.7	23	6.54	0.670	4.38	7.30
W30	7	0.225	69.2	59.7	23	9.09	0.739	3.92	6.54
W31	7	0.225	69.2	59.7	23	16.30	0.835	3.06	5.10
W32	0	0.231	64.1	61.1	24	0.33	0.092	1.25	1.88
W33	0	0.231	64.3	59.8	24	0.76	0.190	1.31	1.97
W34	0	0.231	65.6	60.1	24	1.51	0.319	1.94	2.98
W35	0	0.231	66.2	60.2	24	2.16	0.401	2.13	3.30
W36	0	0.231	66.6	60.6	24	3.03	0.483	2.63	4.10
W37	0	0.231	17.7	11.7	24	3.03	0.483	4.47	1.85
W38	0	0.231	28.9	22.9	24	3.03	0.483	3.76	2.54
W39	0	0.231	39.4	33.4	24	3.03	0.483	2.96	2.73
W40	0	0.231	52.9	46.9	24	3.03	0.483	2.72	3.36
W41	14	0.159	67.0	61.0	24	0.29	0.081	2.72	6.18
W42	14	0.159	63.7	59.7	24	0.71	0.181	3.48	8.13
W43	14	0.159	69.0	59.0	24	1.14	0.261	4.35	10.20
W44	14	0.159	71.4	60.4	24	1.57	0.327	4.85	11.75
W45	14	0.159	71.6	59.6	24	2.43	0.429	4.99	12.14
W46	14	0.159	72.7	60.2	24	3.57	0.525	4.75	11.72
W47	14	0.159	34.7	22.2	24	3.57	0.525	6.73	7.93

SOLVENT WATER

Exp	T	m_c	P	P_{H_2}	T_m	m_A/m_S	x_A	-dV/dt	r x10^4
W48	14	0.159	45.5	33.0	24	3.57	0.525	5.93	9.16
W49	14	0.159	54.5	42.0	24	3.57	0.525	5.45	10.08
W50	14	0.159	64.0	51.5	24	3.57	0.525	5.11	11.10
W51	14	0.159	72.7	60.2	24	3.57	0.525	4.90	12.10
W52	14	0.159	72.7	60.2	24	3.57	0.525	5.06	12.50
W53	14	0.159	72.7	60.2	24	3.57	0.525	4.67	11.54
W54	14	0.159	72.7	60.2	24	3.57	0.525	4.79	11.82
W55	14	0.159	72.7	60.2	24	3.57	0.525	4.76	11.75
W56	0	0.270	70.2	63.2	24	-	1.000	0.54	0.76
W57	0	0.270	69.0	62.0	24	-	1.000	0.62	0.85
W58	0	0.270	66.6	59.6	24	44.80	0.932	1.86	2.48
W59	0	0.270	67.8	61.3	24	14.94	0.823	2.85	3.86
W60	0	0.270	66.6	60.1	24	8.96	0.735	3.37	4.49
W61	0	0.270	66.7	60.2	24	4.98	0.606	3.57	4.76
W62	0	0.270	68.2	62.2	24	3.11	0.481	2.60	3.54
W63	0	0.270	69.2	63.2	24	2.31	0.417	2.86	3.96
W64	0	0.270	65.6	60.6	24	1.03	0.242	2.34	3.07
W65	14	0.223	74.3	60.3	24	-	1.000	1.39	2.50
W66	14	0.223	73.9	59.9	24	-	1.000	1.36	2.44
W67	14	0.223	73.9	59.9	24	45.60	0.934	3.79	6.79
W68	14	0.223	72.9	59.9	24	15.20	0.824	6.29	11.10
W69	14	0.223	72.1	60.1	24	4.15	0.562	7.33	12.80
W70	14	0.223	72.1	60.1	24	2.53	0.440	7.22	12.60
W71	14	0.223	71.1	60.1	24	1.63	0.335	6.16	10.60

SOLVENT ISOPROPANOL

Exp	T	m_c	P	P_{H_2}	T_m	m_A/m_S	x_A	-dV/dt	r x10^4
P 1	7	0.466	63.0	60.0	25	0.17	0.147	1.32	0.96
P 2	7	0.466	63.6	58.6	25	0.33	0.256	1.35	0.99
P 3	7	0.466	65.0	59.0	25	0.67	0.408	1.35	1.01
P 4	7	0.466	65.0	58.0	25	1.00	0.509	1.37	1.03
P 5	7	0.466	66.8	58.8	25	1.67	0.633	1.30	1.00
P 6	7	0.466	66.8	57.8	25	3.00	0.756	1.32	1.02
P 7	0	0.402	61.6	60.1	23	0.06	0.056	0.71	0.59
P 8	0	0.402	66.0	64.0	23	0.11	0.105	0.59	0.53
P 9	0	0.402	65.5	62.5	23	0.17	0.150	0.58	0.51
P10	0	0.402	64.7	60.7	23	0.29	0.228	0.62	0.54
P11	0	0.402	66.7	62.2	23	0.51	0.347	0.58	0.52
P12	0	0.402	65.5	60.0	23	1.03	0.516	0.58	0.51
P13	0	0.402	24.2	18.7	23	1.03	0.516	0.89	0.29
P14	0	0.402	35.6	30.1	23	1.03	0.516	0.66	0.32
P15	0	0.402	50.0	44.5	23	1.03	0.516	0.65	0.44
P16	14	0.402	22.8	13.1	23	1.03	0.516	3.29	1.01
P17	14	0.402	36.6	26.9	23	1.03	0.516	2.94	1.45
P18	14	0.402	50.7	41.0	23	1.03	0.516	2.33	1.59
P19	14	0.402	63.0	53.3	23	1.03	0.516	2.23	1.89
P20	14	0.402	74.1	65.4	23	1.03	0.516	2.01	2.01
P21	14	0.402	66.6	56.9	23	1.03	0.516	2.11	1.89

SOLVENT ISOPROPANOL

Exp	T	m_c	P	P_{H_2}	T_m	m_A/m_S	x_A	-dV/dt	r x10^4
P22	7	0.218	65.1	60.1	25	0.47	0.326	0.68	1.10
P23	14	0.336	67.4	61.4	26	0.20	0.171	1.77	1.90
P24	14	0.336	69.2	60.7	26	0.50	0.341	1.86	2.06
P25	14	0.336	70.9	59.4	26	1.10	0.532	1.95	2.21
P26	14	0.336	73.1	60.1	26	3.10	0.762	1.72	2.01
P27	14	0.336	73.7	60.7	26	3.10	0.762	1.80	2.12

SOLVENT N-OCTANE

Exp	T	m_c	P	P_{H_2}	T_m	m_A/m_S	x_A	-dV/dt	r x10^4
0 1	7	0.317	61.0	56.5	24	0.14	0.214	6.93	7.20
0 2	7	0.317	61.4	56.4	24	0.21	0.290	6.69	7.00
0 3	7	0.317	62.9	57.4	24	0.28	0.352	5.60	6.00
0 4	7	0.317	64.1	57.1	24	0.41	0.450	4.89	5.34
0 5	7	0.317	65.3	58.3	24	0.55	0.520	3.80	4.23
0 6	7	0.317	65.7	57.7	24	0.83	0.620	3.15	3.53
0 7	7	0.317	68.1	60.1	24	0.83	0.620	3.15	3.65
0 8	7	0.317	66.4	57.9	24	1.24	0.710	2.48	2.80
0 9	0	0.312	63.0	59.0	23	0.30	0.374	3.48	3.81
010	0	0.312	64.0	58.5	23	0.49	0.488	2.70	3.00
011	0	0.312	66.6	60.6	23	0.73	0.588	2.00	2.31
012	0	0.312	66.1	60.1	23	0.73	0.588	2.17	2.49
013	0	0.312	66.3	59.8	23	1.09	0.682	1.74	2.00
014	0	0.312	29.1	22.6	23	1.09	0.682	2.10	1.06
015	0	0.312	39.2	32.7	23	1.09	0.682	2.10	1.43
016	0	0.312	49.3	42.8	23	1.09	0.682	1.87	1.60
017	0	0.312	74.3	67.8	23	1.09	0.682	1.40	1.80
018	14	0.340	60.2	55.2	25	0.08	0.130	9.13	8.70
019	14	0.340	63.2	56.2	25	0.15	0.229	9.76	9.76
020	14	0.340	65.2	57.2	25	0.23	0.308	7.91	8.16
021	14	0.340	68.9	59.9	25	0.30	0.373	6.33	6.90
022	14	0.340	68.8	57.8	25	0.60	0.542	5.86	6.38
023	14	0.340	71.3	58.8	25	1.06	0.675	4.19	4.73
024	14	0.340	71.9	58.9	25	1.51	0.750	3.73	4.25
025	7	0.179	63.2	58.2	26	0.14	0.220	4.21	7.97
026	7	0.160	67.2	60.2	26	0.38	0.429	2.22	5.01
027	7	0.160	69.2	62.2	26	0.57	0.530	2.06	4.79
028	7	0.160	70.6	62.1	26	0.95	0.651	1.26	2.99
029	7	0.160	21.2	12.7	26	0.95	0.651	1.83	1.30
030	7	0.160	32.4	23.9	26	0.95	0.651	1.62	1.76
031	7	0.160	45.5	36.0	26	0.95	0.651	1.31	2.00
032	7	0.160	59.9	51.4	26	0.95	0.651	1.29	2.60

SOLVENT ISOOCTANE

Exp	T	m_c	P	P_{H_2}	T_m	m_A/m_S	x_A	-dV/dt	r x10^4
I 1	7	0.328	69.4	60.9	25	1.06	0.674	4.77	5.43
I 2	7	0.328	29.7	21.2	25	1.06	0.674	6.36	3.10
I 3	7	0.328	44.6	36.1	25	1.06	0.674	6.35	4.65
I 4	7	0.328	56.5	48.0	25	1.06	0.674	5.19	4.81
I 5	7	0.328	69.4	60.4	25	1.06	0.674	4.77	5.43
I 6	7	0.184	61.9	58.9	26	0.03	0.048	5.15	9.30
I 7	7	0.184	63.9	59.9	26	0.05	0.092	5.56	10.36
I 8	7	0.184	65.9	60.9	26	0.10	0.168	6.22	11.95
I 9	7	0.184	66.9	60.9	26	0.15	0.232	6.57	12.82
I10	7	0.184	66.9	60.4	26	0.20	0.288	6.32	12.33
I11	7	0.184	20.4	13.9	26	0.20	0.288	9.37	5.57
I12	7	0.184	20.4	13.9	26	0.20	0.288	10.11	6.01
I13	7	0.184	30.3	23.8	26	0.20	0.288	8.63	7.62
I14	7	0.184	40.1	33.6	26	0.20	0.288	7.06	8.25
I15	7	0.184	55.5	49.0	26	0.20	0.288	6.92	11.20
I16	7	0.184	66.9	60.4	26	0.20	0.288	6.32	12.33
I17	7	0.184	68.9	61.4	26	0.51	0.501	5.08	10.20
I18	7	0.141	64.2	59.2	27	0.08	0.141	4.12	10.04
I19	7	0.141	66.2	59.7	27	0.17	0.247	4.62	11.60
I20	7	0.141	67.1	60.6	27	0.25	0.330	4.85	12.35
I21	7	0.141	69.1	61.6	27	0.42	0.451	4.05	10.60
I22	7	0.141	69.1	61.1	27	0.75	0.596	2.96	7.75

SLURRY REACTOR

RANEY NICKEL NICAT 820

Exp	T	m_c	P	P_{H_2}	T_m	n		-dV/dt	r x10^4
	°C	g	cm Hg	cm Hg	°C	rpm		ml/min	$\frac{\text{gmole}}{\text{min g}}$
SR 1	21	0.483	70.9	55.9	27	1600	A	8.17	6,41
SR 2	21	0.483	70.9	55.9	27	1250	A	7.25	5,69
SR 3	21	0.483	70.9	55.9	27	1400	A	7.51	5,89
SR 4	21	0.617	69.3	54.3	26	1000	A	8.80	5.30
SR 5	21	0.617	69.3	54.3	26	1300	A	10.16	6,12
SR 6	21	0.617	69.3	54.3	26	1600	A	11.44	6,89
SR 7	21	0.617	69.3	54.3	26	350	A	1.38	0,83
SR 8	21	0.617	69.3	54.3	26	500	A	1.79	1.08
SR 9	21	0.617	69.3	54.3	26	650	A	4.76	2.87
SR10	14	0.679	67.3	56.3	24	350	A	0.26	0,14
SR11	14	0.679	67.3	56.3	24	850	A	6.26	3.35
SR12	14	0.679	67.3	56.3	24	1000	A	7.51	4.02
SR13	14	0.679	67.3	56.3	24	1300	A	7.55	4.04
SR14	14	0.679	67.3	56.3	24	500	A	1.53	0.82
SR15	14	0.679	67.3	56.3	24	750	A	5.40	2.89
SR16	14	0.679	67.3	56.3	24	1600	A	9.44	5.05
SR17	14	0.679	67.3	56.3	24	1300	A	8.58	4.59
SR18	14	0.708	21.2	10.2	22	850	A	5.59	0.91
SR19	14	0.708	30.1	19.1	22	850	A	7.61	1.76
SR20	14	0.708	37.6	26.6	22	850	A	7.31	2.11
SR21	14	0.708	53.3	42.3	22	850	A	6.23	2.55
SR22	14	0.708	66.6	55.6	22	850	A	5.85	2.99
SR23	14	0.708	30.1	19.1	22	1100	A	10.99	2.54
SR24	14	0.708	37.6	26.6	22	1100	A	9.01	2.60
SR25	14	0.708	45.6	34.6	22	1100	A	8.17	2.86
SR26	14	0.708	53.3	42.3	22	1100	A	8.01	3.28
SR27	14	0.708	66.6	55.6	22	1100	A	7.57	3.87
SR28	14	0.708	30.1	19.1	22	1400	B	12.81	2.96
SR29	14	0.708	30.1	19.1	22	1400	B	12.03	2,78
SR30	14	0.708	37.6	26.6	22	1400	B	11.12	3.21
SR31	14	0.708	45.6	34.6	22	1400	A	12.65	4.43
SR32	14	0.708	53.3	42.3	22	1400	A	11.26	4.61
SR33	14	0.708	66.6	55.6	22	1400	A	9.66	4.94
SR34	14	0.708	30.1	19.1	22	1100	B	10.56	2.44
SR35	7	0.483	70.9	63.9	27	750	A	1.73	1,36
SR36	7	0.483	63.3	56.3	27	900	A	2.53	1.77
SR37	7	0.483	63.3	56.3	27	1200	A	4.90	3.43
SR38	7	0.483	63.3	56.3	27	1400	A	5.27	3.69
SR39	7	0.483	63.3	56.3	27	600	A	1.20	0.84
SR40	7	0.637	63.4	56.4	24	850	A	4.22	2.27
SR41	7	0.637	63.4	56.4	24	850	A	4.45	2.39
SR42	7	0.637	63.4	56.4	24	1000	A	5.43	2.92
SR43	7	0.637	63.4	56.4	24	1200	A	6.38	3.43
SR44	7	0.637	63.4	56.4	24	1600	A	7.44	4.00
SR45	7	0.637	63.4	56.4	24	500	A	0.97	0.52
SR46	7	0,637	63,4	56.4	24	1800	B	7.80	4,19

RANEY NICKEL NICAT 102

Exp	T	m_c	P	P_{H_2}	T_m	n		-dV/dt	r x10^4
SR47	21	0.424	68.3	53.3	24	500	A	3.10	2.70
SR48	21	0.424	68.3	53.3	24	700	A	7.82	6.80
SR49	21	0.424	68.3	53.3	24	850	A	12.00	10.44
SR50	21	0.424	68.3	53.3	24	1000	A	16.52	14.37
SR51	21	0.424	68.3	53.3	24	1200	A	18.01	15.67
SR52	21	0.424	68.3	53.3	24	1400	A	19.91	17.32
SR53	21	0.424	68.3	53.3	24	1600	A	20.67	17.98
SR54	21	0.424	68.3	53.3	24	1000	A	18.57	16.15
SR55	14	0.548	66.7	55.7	24	500	A	2.92	1.92
SR56	14	0.548	66.7	55.7	24	700	A	5.51	3.62
SR57	14	0.548	66.7	55.7	24	850	A	10.30	6.77
SR58	14	0.548	66.7	55.7	24	1000	A	13.91	9.14
SR59	14	0.548	66.7	55.7	24	1300	A	16.51	10.85
SR60	14	0.548	66.7	55.7	24	1600	A	18.00	11.83
SR61	7	0.795	62.8	55.8	24	350	A	0.70	0.30
SR62	7	0.795	62.8	55.8	24	700	A	3.66	1.56
SR63	7	0.795	62.8	55.8	24	500	A	1.95	0.83
SR64	7	0.795	62.8	55.8	24	850	A	7.69	3.28
SR65	7	0.795	62.8	55.8	24	1000	A	12.12	5.17
SR66	7	0.795	62.8	55.8	24	1300	A	16.06	6.85
SR67	7	0.795	62.8	55.8	24	1600	A	17.65	7.53
SR68	7	0.795	62.8	55.8	24	1600	B	18.15	7.74
SR69	7	0.795	62.8	55.8	24	1400	A	14.82	6.32

NOTE = B INDICATES BUBBLE CYCLING IN THE LIQUID
A INDICATES NO BUBBLE CYCLING

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NOMENCLATURE

A	amplitude of oscillation, cm
a_1, a_2, a_3, a_4, a_5	constants in polynomial defined in eqn. 4.1.5
a_v	gas-liquid interfacial area per unit volume, 1/cm
a	parameter defined in eqn. 6.4.3
b	parameter defined in eqn. 6.4.3
C	constant defined in eqn. 4.1.3
c	concentration, gmole/cm^3
c_s	solubility, gmole/cm^3
D	diffusion coefficient, cm^2/sec
D_{eff}	effective diffusion coefficient, cm^2/sec
d	particle diameter, cm
E_A	activation energy, Kcal/gmole
E_D	activation energy for diffusion, Kcal/gmole
ΔE^v	molar energy of vaporization, cal/gmole
F	fractional approach to equilibrium
F_v	flow rate, ml/sec
f	frequency of oscillation, cycles/sec
f^L	fugacity of liquid, atm
G	Froude number ($=n^2A/g$)
g	acceleration of gravity, cm/sec^2
H	relative amplitude of oscillation (= A/R)
H_c	correction factor in eqn. 2.2.3
ΔH^a	molar enthalpy of adsorption, cal/gmole
ΔH^v	molar enthalpy of vaporization, cal/gmole
h	height of liquid, cm

h_p	Thiele modulus
K	adsorption constant, ℓ/gmole
K_{AH}	acid dissociation constant, gmole/ℓ
K_L	overall mass transfer coefficient, ℓ/g sec
k	rate of reaction constant, $g^{-\frac{1}{2}}$ $sec^{\frac{1}{2}}$/$gmole^{\frac{1}{2}}$
k'	apparent rate of reaction constant, $gmole^{\frac{1}{2}}$ $\ell^{\frac{1}{2}}$/g sec
k_L	solid-liquid mass transfer coefficient, cm/sec
k_L'	gas-liquid mass transfer coefficient, cm/sec
m	order of reaction
m_c	mass of solid
N	number of particles
N_A	rate of mass transfer, gmole/g sec
Nu	Nusselt number
n	frequency of oscillation, 1/sec
n_B	number of moles, gmole
P	pressure, atm
Pe	Peclet number (= ud/D)
Pr	Prandtl number
p	order of reaction
p_j	independent variable
Q	weight, g
R	particle radius, cm
R_g	gas constant (= 1·987 cal/gmole ^oK)
Re	Reynolds number (= ud/ν)
Re_{osc}	oscillating Reynolds number (= $\sqrt{2}\ U_\infty R/\nu$)
Re_s	streaming Reynolds number (= $U_\infty^2/n\nu$)
Re_v	vibrating Reynolds number (= nAd/ν)
r	rate of reaction, gmole/g sec

S	residual sum of squares
Sc	Schmidt number (= ν/D)
Sh	Sherwood number (= $k_L d/D$)
T	temperature, deg C or deg K
t	time, sec
U	maximum relative velocity, cm/sec
u	velocity, cm/sec
u_r	relative velocity, cm/sec
V	volume, cm^3
V_1, V_2	volumes defined in Fig. 4.1, cm^3
v	molar volume, cm^3/gmole
x	liquid phase mole fraction
y	gas phase mole fraction

Greek letters

α, β, γ, ε	parameters in eqn. 4.3.1
β_{12}	parameter defined in eqn. 6.1.9, gmole/cm^3
δ	solubility parameter, $cal^{\frac{1}{2}}/cm^{3/2}$
δ^c	corrected solubility parameter, $cal^{\frac{1}{2}}/cm^{3/2}$
η	effectiveness factor
θ	parameters in rate of reaction equations
κ	conductivity, 1/ohm cm
Λ_c	equivalent conductivity, cm^2/ohm gmole
Λ_o	equivalent conductivity at infinite dilution, cm^2/ohm gmole
μ	viscosity, poise = g/cm sec
ν	kinematic viscosity, cm^2/sec

ρ	liquid density, g/cm^3
ρ_p	particle density, g/cm^3
ψ	fugacity coefficient
ϕ	volume fraction
ϕ_L	modulus defined in eqn. 6.2.5

Subscripts

A	acetone property
app	apparent value
e	experimental value
est	estimated value
f	final value
H	hydrogen property
i	gas-liquid interface
o	initial value
P	isopropanol property
p	particle property
S	solvent property
s	solid-liquid interface

Superscripts

o	pure liquid
*	dimensionless value
-	properties in the interior of ion exchange resin

REFERENCES

ADKINS, H. — Reaction of hydrogen with organic compounds over copper-chromium oxide and nickel catalysts, Chaps. 1, 2, 4; Univ. Winsconsin Press, Winsconsin (1937)

ADKINS, H. and BILLICA, H.R. — Effect of ratio of catalyst and other factors upon the rate of hydrogenation, J. Am. Chem. Soc. 70, 3118-3120 (1948)

AMIS, E.S. — Solvent effects on reaction rates and mechanisms, Chap. 3, Ac. Press, London (1962)

ANDERSON, L.C. and MacNAUGHTON, N.W. — The mechanism of the catalytic reduction of some carbonyl compounds, J. Am. Chem. Soc. 64, 1456-1459 (1942)

BAIRD, M.H.I. — Vibrations and pulsations, bane or blessing? British Chem. Engng. 11(1), 20-25 (1966)

BATTINO, R. and CLEVER, H.L. — The solubility of gases in liquids, Chem. Rev. 66, 395-463 (1966)

BLICKENSTAFF, R.A., WAGNER, J.D. and DRANOFF, J.S. — The kinetics of ion exchange accompanied by irreversible reaction, J. Phys. Chem. 71(6), 1665-1674 (1967)

BOND, G.C. — Catalysis by metals, Chaps. 8, 9, 11, 14, Ac. Press, London (1962)

BRETSZNAJDER, S., JASZCZAK, M. and PASIUK, W. — Increasing the rate of certain industrial chemical processes by the use of vibration Int. Chem. Engng. 3(4), 496-502 (1963)

BRIAN, P.L.T. and HALES, H.B. — Effects of transpiration and changing diameter on heat and mass transfer to spheres, A.I.Ch.E. J. 15(3), 419-425 (1969)

BRIAN, P.L.T., HALES, H.B. and SHERWOOD, T.K. — Transport of heat and mass between liquids and spherical particles in an agitated tank, A.I.Ch.E. J. 15(5), 727-733 (1969)

BUCHANAN, R.H., TEPLITZKY, D.R. and OEDJOE, D. — Oxygen absorption in low-frequency vertically vibrating liquid columns, I&EC Proc. Des. & Devel. 2(3) 173-177 (1963)

DELMON, B. and BALACEANU, J.C. — Adsorption physique sur le nickel de Raney, Compt. Rend. 244(15) 2053-2056 (1957)

DE RUITER, E. and JUNGERS, J.C. — L'hydrogénation en phase liquide sur le nickel, Bull. Soc. Chim. Belg. 58, 210-246 (1949)

FAND, R.M. and KAYE, J. — The influence of sound on free convection from a horizontal cylinder, Trans. Amer. Soc. Mech. Engrs., J. Heat Tr. 83, 133-148 (1961)

FREUND, T. and HULBURT, H.M. — Kinetics of some hydrogenations catalyzed by Raney nickel, J. Phys. Chem. 61, 909-912 (1957)

GIBERT, H. and ANGELINO, H. — Influence de la pulsation sur les transferts de matière entre une sphère et un liquide, Can. J. Chem. Engng. 51, 319-325 (1973)

HALES, H.B. Heat and mass transfer from particles suspended in a stirred tank, Sc.D. thesis, M.I.T., Cambridge (1967)

HARRIOTT, P. Mass transfer to particles, AIChE J. 8(1), 93-102 (1962)

HEILMANN, R. and de GAUDEMARIS, G. Cinétique générale de l'hydrogénation catalytique en phase liquide sur le nickel de Raney, Compt. Rend. 233(2) 166-168 (1951)

HELFFERICH, F. Ion exchange, Chaps. 4, 5, McGraw-Hill, New York (1962)

HELFFERICH, F. Ion exchange kinetics. V. Ion exchange accompanied by reactions, J. Phys. Chem. 69(4), 1178-1187 (1965)

HILDEBRAND, J.H. and SCOTT, R.L. The solubility of nonelectrolytes, Chap. 15, Reinhold Publ. Co., New York (1950)

HILDEBRAND, J.H., PRAUSNITZ, J.M. and SCOTT, R.L. Regular and related solutions, Chap. 8, Van Nostrand Reinhold Co., New York (1970)

HINE, J. Physical Organic Chemistry, Chaps. 8-11, McGraw-Hill, New York (1956)

HINZE, J.O. Turbulence, an introduction to its mechanism and theory, p. 352, McGraw-Hill, New York (1959)

International Critical Tables, Vols. 3, 5 McGraw-Hill, New York (1929)

IWAMOTO, I., YOSHIDA, T., KEII, T. and AONUMA, T. — Solvent effect on the hydrogenation of acetone over Raney nickel, Nippon Kagaku Zasshi 91, 1050-1054 (1970)

IWAMOTO, I., AONUMA, T. and KEII, T. — Solvent effect on heterogeneous hydrogenation reactions, Int. Chem. Engng. 11(3), 573-577 (1971)

JAMESON, G.J. — Motion of a bubble in a vertically oscillating viscous liquid, Chem. Eng. Sci. 21 35-48 (1966a)

JAMESON, G.J. — Some operating characteristics of the resonant bubble contactor, Trans. Instn. Chem. Engrs. 44 T91-T96 (1966b)

JAMESON, G.J. and DAVIDSON, J.F. — Motion of a bubble in a vertically oscillating liquid: theory for an inviscid liquid and experimental results, Chem. Eng. Sci. 21, 29-34 (1966)

JOHNSON, D.L., SAITO, H., POLEJES, J.D. and HOUGEN, O.A. — Effect of bubbling and stirring on mass transfer coefficients in liquids, A.I.Ch.E. J. 3, 411-417 (1957)

KENNEY, C.N. and SEDRIKS, W. — Effectiveness factor in a three phase slurry reactor: the reduction of crotonaldehyde over a palladium catalyst, Chem. Eng. Sci. 27, 2029-2040 (1972)

KIPERMAN, S.L. and KAPLAN, G.I. — Kinetics of hydrogenation in a zero-gradient system, Kinetics and Catalysis 5(5), 778-786 (1964)

KISHIDA, S. and TERANISHI, S. — Kinetics of liquid phase hydrogenation of acetone over Raney nickel catalyst, J. Cat. 12, 90-96 (1968)

KISHIDA, S. and TERANISHI, S. — Poisoning effect of carbon disulfide on the liquid phase hydrogenation of acetone over a Raney nickel catalyst, Bull.Chem.Soc. Japan 42 270-272 (1969)

KOLBEL, H. and MAENNIG, H.G. — Heterogen-katalytishe gasreaktionen in blasen-saulenreaktor, Z.Elektrochem. 66 744-754 (1962)

KUBOMATSU, T. and KISHIDA, S. — Change in activity and structure of Raney nickel catalyst by heating in various organic solvents, Kagaku to Kogyo (Osaka) 39(9), 559-563 (1965)

LEMLICH, R. — Vibration and pulsation boast heat transfer, Chem. Engng. 68, 171-176 (1961)

LEVINS, D.M. and GLASTONBURY, J.R. — Particle-liquid hydrodynamics and mass transfer in a stirred vessel. Part II. Mass transfer, Trans.Instn.Chem.Engrs. 50 132-146 (1972a)

LEVINS, D.M. and GLASTONBURY, J.R. — Application of Kolmogoroff's theory to particle-liquid mass transfer in agitated vessels, Chem. Eng. Sci. 27, 537-543 (1972b)

LIMIDO, G.E. and GRAWITZ, J. — Adsorption coefficients in strongly inhibited heterogeneous catalytic reactions, Bull.Soc. Chim. France 42-44 (1954)

MARQUARDT, D.W. — An algorithm for least-squares estimation of non-linear parameters, J.Soc.Indust.Appl. Math. 11(2), 431-441 (1963)

MILLIGAN, C.H. and REID, E.E. — High speed stirring as an aid to chemical action, Ind. Eng. Chem. 15, 1048-1049 (1923)

NIENOW, A.W. — Dissolution mass transfer in a turbine agitated baffled vessel, Can. J. Chem. Engng. 47, 248-258 (1969)

NOORDSIJ, P. and ROTTE, J.W. — Mass transfer coefficients to a rotating and to a vibrating sphere, Chem. Eng. Sci. 22, 1475-1481 (1967)

ORITO, Y. and IMAI, S. — The role of solvent in the hydrogenation of acetone, Tokyo Kogyo Shikensho Hokoku 56, 496-500 (1961)

ORITO, Y. IMAI, S. and NIWA, S. — On the activity and the surface area of Raney nickel catalyst stored in various liquids, Rep. Gov. Chem. Ind. Res. Inst., Tokyo, 60(7), 242-246 (1965)

PATTISON, J.N. and DEGERING, E.F. — Some factors influencing the activity of Raney nickel catalyst, J. Am. Chem. Soc. 73, 486-487 and 611-613 (1951)

PETERSEN, E.E. — Chemical reaction analysis, Chap. 4, Prentice Hall, New Jersey (1965)

PRICE, R.H. and SCHIEWETZ, D.B. — Catalytic liquid phase hydrogenation, Ind. Eng. Chem. 49, 807-812 (1957)

REID, R.C. and SHERWOOD, T.K. — The properties of gases and liquids, Chap. 9, McGraw-Hill, New York (1958)

RICHARDSON, P.D. — Effects of sound and vibration on heat transfer, Appl. Mech. Rev. 20, 201-217 (1967a)

RICHARDSON, P.D. — Heat transfer from a circular cylinder by acoustic streaming, J. Fluid. Mech. 30(2), 337-355 (1967b)

RUETHER, J.A. and PURI, P.S. — Mass transfer in hydrogenations in slurry reactors, Can. J. Chem. Engng. 51, 345-352 (1973)

SATTERFIELD, C.N. — Mass transfer in heterogeneous catalysis, Chaps. 1-3, MIT Press, Mass. (1970)

SATTERFIELD, C.N., MA, Y.M. and SHERWOOD, T.K. — The effectiveness factor in a liquid-filled porous catalyst, I. Chem. Eng. Symp. Ser. No. 28, 22-29 (1968)

SELYAKH, I.V. and DOLGOV, B.N. — Effect of the medium on the rate of hydrogenation of aliphatic ketones, Zh. Prikl. Khim. 38, 2374-2377 (1965)

SHERWOOD, T.K. and FARKAS, E.J. — Studies of the slurry reactor, Chem. Eng. Sci. 21, 573-582 (1966)

SIMONIKOVA, J. HILLAIRE, L., PANEK, J. and KOCHLOEFL, K. — Kinetic der Hydrierung von Aceton an metallishen Katalysatoren, Z. Phys. Chemie 83, 287-304 (1973)

SNYDER, J.R., HAGERTY, P.F. and MALSTAD, M.C. — Operation and performance of bench scale reactors, Ind. Eng. Chem. 49, 689-695 (1957)

SOKOLSKAYA, A.M., BAKHANOVA, E.N. and SOKOLSKII, D.V. — Hydrogenation of ketones in buffered solutions, Dokl. Akad. Nauk SSSR, 167(3), 600-603 (1966)

SOKOL'SKII, D.V. and ERZHANOV, A.I. — Hydrogenation of the conjugated double bonds in benzalacetone, Doklady Akad. Nauk SSSR, 93, 503-505 (1953)

SUGANO, Y. and RATKOWSKY, D.A. — Effect of transverse vibration upon the rate of mass transfer from horizontal cylinders, Chem. Eng. Sci. 23, 707-716 (1968)

SYKES, P. and GOMEZPLATA, A. — Particle-liquid mass transfer in stirred tanks, Can. J. Chem. Engng. 45, 189-196 (1967)

TSUTSUMI, S., KAYAMORI, H. and KAWAMURA, T. — Catalytic hydrogenation in the presence of water, J. Chem. Soc. Japan, Ind. Chem. Section 54, 27-28 (1951)

VAN MECHELEN, G. and JUNGERS, J.C. — Étude comparative de l'hydrogénation des cetones aliphatiques sur le nickel et le cuivre, Bull.Soc.Chim.Belg. 59, 597-603 (1950)

WATANABE, S. — Adsorption of hydrogen on Raney nickel catalysts, Science and Industry 30, 246-250 (1956)

WATANABE, S. — Studies on the promotive effect of alkalies on hydrogenation over Raney nickel, Kagaku to Kogyo (Osaka) 36 143-150 and 205-212 (1962).