

LOUGHBOROUGH  
UNIVERSITY OF TECHNOLOGY  
LIBRARY

AUTHOR

CHAPMAN, J

COPY NO.

065695/01

VOL NO.

CLASS MARK

ARCHIVES  
COPY

FOR REFERENCE ONLY

AROMATIC NITRATION AT HIGH  
SULPHURIC ACID STRENGTHS

by

JOHN WILLIAM CHAPMAN

A Thesis submitted in partial fulfilment of the requirements  
for the award of Doctor of Philosophy of Loughborough  
University of Technology, September 1974.

Supervisor: Dr. A. N. STRACHAN

© by John William Chapman, 1974.

Loughborough University of Technology Library
Date Dec. 74
Class
Acc. No. 065695/01

TO MY PARENTS

The work described in this thesis has  
not been submitted, in full or in part,  
to this or any other institution for a  
higher degree.

### ACKNOWLEDGEMENT

I sincerely thank Dr. A.N. Strachan, my supervisor, for his continual encouragement and inspiration over the last three years. My thanks, also, to my fellow research workers in the Chemistry Department for their help and companionship, to Professor R. F. Phillips for the provision of laboratory facilities and to Hickson and Welch Ltd. (Castleford) for their research grant. Finally, I am indebted to the technical staff of the Department for their help and advice and to Mrs. Christine Sills for typing this thesis.

## CONTENTS

### INTRODUCTION

	<u>PAGE</u>
CHAPTER 1	2
1.1 Homogeneous nitration	3
1.2 Two phase nitration	7
1.3 Danckwerts' Surface Renewal Theory	9
1.4 Kinetic regime	12
1.5 Slow reaction diffusional regime	14
1.6 Fast reaction regime	14

### EXPERIMENTAL

CHAPTER 2	22
2.1 Preparation of aqueous sulphuric acid	22
2.2 Stirred cell runs	22
2.2(a) Determination of the rate of nitration	23
2.2(b) Determination of the physical mass transfer coefficient	23
2.3 Stirred reactor runs	23
2.4 Determination of the solubility of aromatics in aqueous sulphuric acid	24
2.5 Calibration factors	25
2.6 Stopped-flow spectrometry	25
2.7 A typical stopped-flow run	27

RESULTS

CHAPTER 3	Mass Transfer in the absence of chemical reaction in the stirred cell	29
CHAPTER 4	Change in the kinetic order of nitration with respect to toluene in the two phase system	32
4.1	Dependence of initial rate of nitration on the composition of the organic phase in the stirred reactor	32
4.2	Dependence of initial rate of nitration on the nitric acid concentration in the stirred reactor	33
4.3	Dependence of the initial rate of nitration on the sulphuric acid strength in the stirred cell	34
4.4	Distribution coefficient of toluene between acid and organic phases	35
4.5	Zeroth-order kinetics in the homogeneous phase	37
4.6	Half-order kinetics in the two phase system	39
4.7	Danckwerts plot for the stirred reactor	42
4.8	Danckwerts plot for the stirred cell	44
4.9	The kinetic order in the stirred reactor	47
4.10	Estimation of $k_1$ from previous stirred cell data	47



	<u>PAGE</u>
CHAPTER 5	
Change in the kinetic order of nitration with respect to aromatic in the homogeneous system	49
5.1 The nitration of toluene	49
5.1(a) Runs with a low aromatic substrate concentration	50
5.1(b) Runs with a near saturation substrate concentration	51
5.2 The nitration of o-xylene	55
5.3 The limitations of the stopped-flow technique	56
5.4 Comparison of $k_2$ and $k_1$ with previous data	57
CHAPTER 6	
The nitration of chlorobenzene at high sulphuric strengths	65
6.1 Dependence of the initial rate of nitration on temperature in the stirred cell	65
6.2 Dependence of the second-order rate coefficient for nitration on temperature	65
6.3 Dependence of solubility of chlorobenzene in sulphuric acid on temperature	66
6.4 The irreproducibility of rates at very high sulphuric acid strengths	66
6.5 Summation of activation parameters for the nitration of chlorobenzene in the fast reaction regime	68
6.6 The effect of precipitation of nitroproducts from the organic phase on the initial rate of nitration in the stirred cell	71

DISCUSSION

CHAPTER 7	Factors affecting the rate of mass transfer in the stirred cell	76
7.1	Empirical correlations	76
7.2	Interfacial turbulence	83
7.3	Conclusion	86
CHAPTER 8	Zeroth-order kinetics and the mechanism of nitration	87
8.1	The kinetic form of nitration in organic solvents	87
8.2	The existence of the nitronium ion	87
8.3	The effectiveness of the nitronium ion	88
8.4	The mechanism of nitration in the mixed acid system	90
8.5	The industrial nitration of aromatics	91
8.6	Conclusion	92
APPENDIX		96
REFERENCES		97

LIST OF FIGURES

<u>FIGURE</u>	<u>LEGEND</u>	<u>FACING PAGE</u>
1	Dependence of $k_2$ on $-(H_R + \log_{10} a_{H_2O})$ for a number of substrates	4
2	Initial rate of nitration versus percentage sulphuric acid for chlorobenzene and toluene in the stirred reactor	11
3	Concentration profiles for the different regimes	12
4	Danckwerts plots for chlorobenzene and toluene in the stirred reactor	16
5	Initial rate of nitration versus percentage sulphuric acid for chlorobenzene and toluene in the stirred cell	17
6	Danckwerts plots for chlorobenzene and toluene in the stirred cell	17
7	The Stirred Cell	22
8	The Stirred Reactor	23
9	The Stopped-flow Spectrometer	25
10	Plots of $\ln (A_\infty / A_\infty - A)$ versus time for the mass transfer of chlorobenzene and toluene into sulphuric acid in the stirred cell	29
11	$R/[CB]_a^S$ versus sulphuric acid strength for the nitration of chlorobenzene in the stirred reactor and stirred cell.	31
12	Danckwerts plot for the nitration of a dilute solution of toluene in the stirred reactor	42

13	The solubility of toluene in 76.50 per cent sulphuric acid as a function of organic phase composition	47
14	Kinetic order of nitration of a dilute solution of toluene in the stirred reactor	47
15	Stopped-flow oscilloscope traces for the nitration of toluene in sulphuric acid at 25°C	50
16	Typical first-order plots for the homogeneous nitration of toluene in the intermediate-order kinetic region	51
17	Intermediate-order plots for the nitration of toluene	54
18	Intermediate-order plots for the nitration of o-xylene	55
19	Log $k_2$ versus sulphuric acid strength for the nitration of toluene at 25°C	57
20	Log $k_1$ versus sulphuric acid strength at 25°C	57
21	The initial rate of nitration of chlorobenzene at very high sulphuric acid strengths in the stirred cell	67
22	The effect of stirrer position in the stirred cell on the initial rate of nitration of chlorobenzene in 84.50 per cent sulphuric acid	67
23	Dependence of the initial rate of nitration of chlorobenzene in the stirred cell on temperature	69
24	Dependence of the second-order rate coefficient for the nitration of chlorobenzene on temperature	69
25	Dependence of the solubility of chlorobenzene in 79.55 per cent sulphuric acid on temperature	69

26	Dependence of $E_{k_2}$ on the sulphuric acid strength for a number of aromatics	70
27(a)	Diagrammatic representation of the stirred cell system used by Lewis	77
27(b)	Diagrammatic representation of the formation of convection cells	77
28	Plot of absorbance versus $[\text{HNO}_3]$ for the determination of nitric acid in sulphuric acid	96

### NOTATION

$\bar{a}$	interfacial area, $\text{cm}^2$
$a'$	interfacial area per unit volume, $\text{cm}^2 \text{cm}^{-3}$ .
A	absorbance
[ArH]	concentration of aromatic in acid phase, $\text{mol l}^{-1}$
$c^*$	equilibrium concentration of solute in continuous phase, $\text{mol l}^{-1}$
c	concentration of solute in continuous phase, $\text{mol l}^{-1}$
[CB]	concentration of chlorobenzene in the acid phase, $\text{mol l}^{-1}$ .
D	diffusivity, $\text{cm}^2 \text{s}^{-1}$
E	activation energy, $\text{cal mol}^{-1}$ .
[ $\text{H}^+$ ]	concentration of hydrogen ions in the acid phase, $\text{mol l}^{-1}$ (strictly activity, $a_{\text{H}^+}$ )
$\Delta H_{\text{form}}$	enthalpy of formation, $\text{cal mol}^{-1}$ .
$\Delta H_{\text{sol}}$	enthalpy of solution, $\text{cal mol}^{-1}$
$H_{\text{R}}$	acidity function
[ $\text{H}_2\text{O}$ ]	concentration of water in the acid phase, $\text{mol l}^{-1}$ (Strictly $a_{\text{H}_2\text{O}}$ )
$k_0$	zeroth-order rate of nitration, $\text{mol l}^{-1} \text{s}^{-1}$ .
$k_1, k_{-1}$	first-order or pseudo-first order rate coefficients, $\text{s}^{-1}$ .
$k_1', k_{-1}', k_2, k_2'$	second-order rate coefficients, $\text{l mol}^{-1} \text{s}^{-1}$ .
$k_{\text{L}(1)}$	mass transfer coefficient (in phase 1).
L	diameter of stirrer blades (tip-to-tip), cm.
N	stirrer speed, $\text{rev s}^{-1}$ .
R	rate of reaction per unit volume of acid phase, $\text{mol l}^{-1} \text{s}^{-1}$ .
Re	Reynolds number
s	rate of surface renewal, $\text{s}^{-1}$
Sch.	Schmidt number.
t	time, s, min or hour.
T	temperature, $^{\circ}\text{C}$ or K.
[T]	concentration of toluene in the acid phase, $\text{mol l}^{-1}$ .

$V$	instantaneous mass transfer rate, $\text{mol cm}^{-2}\text{s}^{-1}$
$\bar{V}$	average mass transfer rate, $\text{mol cm}^{-2}\text{s}^{-1}$ .
$\Delta x$	thickness of liquid film, cm.
$\gamma$	distribution coefficient.
$\eta$	viscosity, Poise or cP.
$\rho$	density, $\text{g ml}^{-1}$
$\nu$	kinematic viscosity, $\text{cm}^2\text{s}^{-1}$
$\phi(t)$	age distribution function

#### subscripts

a acid phase

b bulk

o zero time

t time t

$\infty$  infinite time

#### superscript

s saturation value

## INTRODUCTION



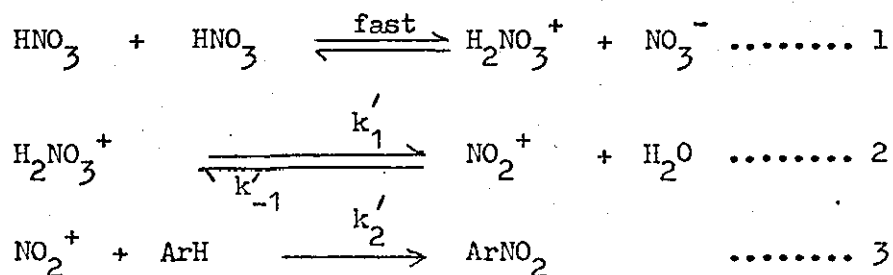
## CHAPTER I.

The nitration of aromatic compounds has been performed on an industrial scale since the turn of the century. The rapid development of nitroaromatics as explosives and their use today in the dye industry and as intermediates in organic syntheses makes nitration an important, large scale process. The importance of nitration as a model electrophilic aromatic substitution reaction for the investigation of electronic effects in organic molecules led to it being studied in great depth in the homogeneous phase. Until recently, however, there was a sparse amount of information on the industrially significant two phase reaction with mixed sulphuric and nitric acids and little attempt had been made to apply the results of kinetic experiments in a single phase to the phenomena observed in two phase batch and continuous nitration plants.

In the last few years, however, much progress has been made and a better understanding of the processes involved in these systems is now possible. The rates of nitration in a miniature stirred batch reactor and stirred cell containing pure toluene and chlorobenzene have been successfully interpreted on the basis of Danckwerts' Surface Renewal Theory of mass transfer<sup>1</sup>. Many of the factors which affect the rate in these systems have been investigated and suitable rate equations tested experimentally. Despite the progress, however, the results obtained are not totally conclusive and several anomalous features have become apparent. The object of this work is to account for these features and hence try to substantiate the Theory of Danckwerts as applied by Cox and Strachan to the nitration of aromatics in two phase systems.

### 1.1. HOMOGENEOUS NITRATION

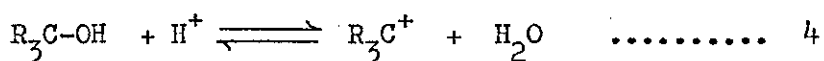
The nitration of aromatic compounds has played a significant role in the development of the electronic theory of organic chemistry. A vast amount of literature is now available on the reactions of benzenoid compounds with nitric acid under a wide variety of conditions. Ingold and his collaborators<sup>2</sup> first established the existence of the nitronium ion as the effective electrophile in organic solvents such as nitromethane and acetic acid. They accounted for the characteristic features of the reactions in terms of a mechanism involving the production of the nitronium ion from nitric acid followed by its attack on the aromatic ring:



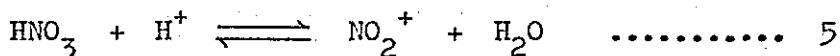
Here, the comparatively slow heterolytic fission of the nitric acidium ion,  $\text{H}_2\text{NO}_3^+$ , is preceded by the fast proton exchange between two molecules of nitric acid. Under most conditions the rate determining step is the electrophilic attack of nitronium ions on the aromatic substrate and the overall rate is dependent on both the concentration of nitric acid and the aromatic substrate.

In aqueous sulphuric acid, the so called mixed acid system, the first step is replaced by the reaction of a nitric acid molecule with a sulphuric acid molecule. The equilibrium concentration of nitronium ions increases rapidly with sulphuric acid strength such

that in ca. 90 per cent acid the nitric acid is fully ionized to nitronium ions<sup>3</sup>. Nitronium ions are observed in such solutions by the appearance of a band at 1400 cm<sup>-1</sup> in the Raman spectra. The band, however, is not detectable in solutions below 85 per cent sulphuric acid. The continual effectiveness of the nitronium ion mechanism in acid strengths lower than 85 per cent has been inferred from correlations of the rate of reaction with the acidity of the medium. Schofield and coworkers<sup>4</sup> correlated the observed second-order rate coefficient for the nitration of a series of activated substrates with the modified acidity function  $-(H_R + \log_{10} a_{H_2O})$  where  $a_{H_2O}$  is the activity of water and  $H_R$ , the acidity function, is based on the ionization of model tri-aryl carbinol compounds.

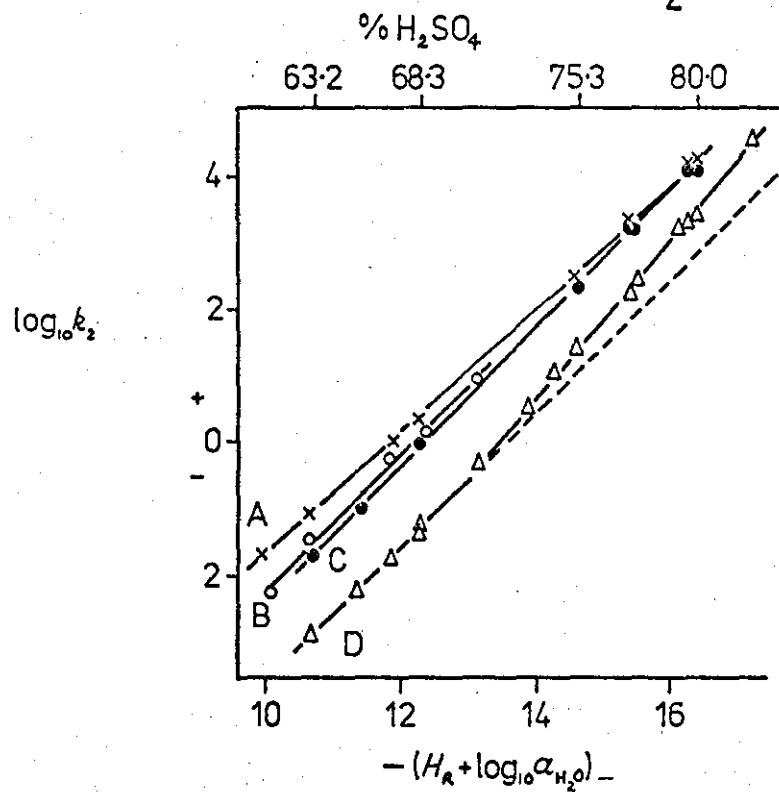


This equilibrium closely resembles the combination of Equations 1 and 2 which may be written:



If it be assumed that the ionizing characteristics of nitric acid are similar to those of the organic indicators used to define the scales of acidity, then close correspondence between the acidity dependence of nitration and  $H_R$  would suggest that Equation 5 is applicable. Schofield and co-workers<sup>5</sup> obtained excellent straight line correlations over the range 60-84 per cent sulphuric acid between the logarithm of the second-order rate coefficient,  $k_2$ , and  $-(H_R + \log_{10} a_{H_2O})$  for a wide range of substrates (Figure 1). Deno

Fig. 1 Dependence of  $k_2$  on  $-(H_R + \log_{10} a_{H_2O})$  for a number of substrates.



Nitration at 25°C in aqueous sulphuric acid.  
 A, Mesitylene x; B, naphthalene (O); C, toluene (⊙); D, benzene (Δ).

and co-workers<sup>6</sup> found that between 58 and 93 per cent sulphuric acid  $H_R$  and percentage sulphuric acid are linearly related. The dependence of  $k_2$  on the activity of water was explained<sup>5</sup> by the assertion that in this particular acid range nitric acid exists predominantly as the monohydrate.

The effect of molecular diffusion upon the rate of nitration of reactive substrates was first discussed by Schofield<sup>4</sup>. The observed second-order rate coefficient,  $k_2$ , was found to approach the theoretical limit due to encounter between two molecules in a concentrated sulphuric acid solution. A large number of reactive substrates, having a wide range of reactivity, were found to nitrate at about the same rate at 25°C in 68.3 per cent sulphuric acid (Table 1).

TABLE 1.

SUBSTRATE	$k_2$ observed /l <sup>2</sup> mol <sup>-1</sup> s <sup>-1</sup>	$k_2$ predicted /l mol <sup>-1</sup> s <sup>-1</sup>
Benzene	0.058	1
Toluene	1.0	23
Diphenyl	0.92	35
p-xylene	2.2	50
o-xylene	2.2	60
m-xylene	2.2	400
Mesitylene	2.1	16,000
Naphthalene	1.6	300
Phenol	1.4	10 <sup>4</sup>

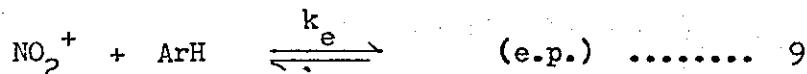
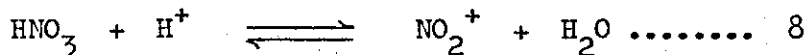
The value of the bimolecular rate coefficient for encounter,  $k_e$ , may be estimated from the equation<sup>7</sup>:

$$k_e = \frac{8RT}{3\eta} \dots\dots\dots 6$$

where R is the Ideal Gas Constant, T is the temperature (K) and  $\eta$  is the viscosity (Poise). This is related to the observed second-order rate coefficient for nitration by the ratio of the equilibrium concentration of nitronium ions to the stoichiometric concentration of nitric acid in 68.3 per cent sulphuric acid:

$$k_2 = k_e \frac{[\text{NO}_2^+]}{[\text{HNO}_3]_{st}} \dots\dots\dots 7$$

In 68.3 per cent acid the concentration ratio can be estimated<sup>4</sup> to be ca.  $10^{-8}$  and  $k_e$  ca.  $6 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ , so that the limiting rate coefficient should be ca.  $6 \text{ l mol}^{-1} \text{ s}^{-1}$ . This is in good agreement with the observed value of ca.  $2 \text{ l mol}^{-1} \text{ s}^{-1}$ . Schofield introduced the concept of an encounter pair (e.p.) and visualized a modified reaction scheme as follows:



Under encounter controlled conditions step 10 is much faster than step 9 and the rate coefficient for nitration is given by Equation 7.

Whether or not nitration is governed by encounter control,  $k_2$  increases rapidly with increasing sulphuric acid strength (Figure 1) since the concentration ratio  $\frac{[\text{NO}_2^+]}{[\text{HNO}_3]_{st}}$  rapidly increases from ca.  $10^{-8}$  in 68.3 per cent to 1 in 90 per cent sulphuric acid. The ease of ionization of nitric acid in sulphuric acid strengths between this range accounts for the use of this mixed acid system in the two phase industrial process.

## 1.2. TWO PHASE NITRATION

In contrast to the more traditional homogeneous kinetic work, nitrations performed in batch or continuous reactors, with the two virtually immiscible phases agitated into a fine dispersion of droplets, are relatively rare. Furthermore, many of the early studies were based on assumptions that have proved to be false and have not stood rigorous criticism. Also, much interest was centred on the isomer proportions of the nitro-products since this is of some economic importance.

Two early papers on the subject came to similar conclusions. Lewis and Suen<sup>8</sup> studied the reaction of benzene in both a batch and continuous reactor whereas McKinley and White<sup>9</sup> concentrated on toluene nitration in a continuous reactor. Both groups recorded a high temperature coefficient of about 2 for a change of  $10^\circ\text{C}$  which pointed to the kinetic control of the overall rate and the elimination of mass transfer resistances. Lewis and Suen assumed that reaction took place in both phases whereas McKinley and White considered that only reaction in the acid phase was significant. Brennecke and Kobe<sup>10</sup> nitrated toluene in a continuous stirred tank reactor and also found a temperature coefficient of about 2. Barduhn and Kobe<sup>11</sup> found that

the nitric acid solubility in the organic phase had the effect of reducing the quantity of nitric acid available for nitration in the acid phase but they considered nitration in the organic phase unlikely. This has since been confirmed by Cox and Strachan for the nitration of chlorobenzene<sup>12</sup>.

Hanson, Marsland and Wilson,<sup>13</sup> in a critical review of the subject, re-examined much of this early work and concluded that the evidence for pure kinetic control of the rate was doubtful. The effect of temperature, they argued, was very complicated and cannot be used as conclusive proof. Wilson,<sup>14</sup> working on the nitration of toluene in a miniature continuous stirred reactor, found temperature coefficients between 1.92 and 1.45 for 12°C intervals. These were of a similar magnitude to those obtained by previous workers who claimed to have eliminated mass transfer resistances. Hanson and co-workers,<sup>13</sup> also properly drew attention to the fact that whilst there was an enormous amount of evidence to show that the nitronium ion mechanism applied in homogenous phase systems, no comparable evidence existed for the two phase industrial process.

The contribution of Hanson and coworkers, with their acceptance of some mass transfer resistances being present whatever the conditions, led the way for the work of Cox and Strachan<sup>1,12,15,16</sup>. They determined the rate of nitration of chlorobenzene and toluene in a miniature stirred batch reactor and a stirred cell and successfully applied the Surface Renewal Theory of Danckwerts<sup>17,18</sup> to the data. This work will now be discussed in some detail.



### 1.3. DANCKWERTS' SURFACE RENEWAL THEORY.

Danckwerts' Surface Renewal Theory is not the only model for the treatment of results from systems where mass transfer is accompanied by chemical reaction. The Film Theory, developed by Lewis and Whitman<sup>19</sup>, and the Penetration Theory, proposed by Higbie<sup>20</sup>, as well as other treatments have all been used. However, the Surface Renewal Theory is the most widely used and was by adopted by Cox and Strachan for their systems.

The Surface Renewal Theory is an extension of the Penetration Theory and was initially developed and used with gas-liquid absorption systems. The mathematical details have been dealt with in great detail by Astarita<sup>21</sup>. Danckwerts pictured turbulent eddies of liquid, located at the interface between both phases, that continually mix the liquid at the interface into the bulk of the continuous phase and expose fresh surfaces to the gas for varying lengths of time. The rate of mass transfer is governed by the lifetime of these elements and not the motion of the liquid beneath the surface. Danckwerts assumed that the diffusion process in each element was governed by Fick's 2nd Law:

$$D \frac{d^2c}{dx^2} = \frac{dc}{dt} \quad \dots\dots\dots 11$$

where  $D$  is the diffusivity of the gas in the continuous phase. The solution to this differential equation is well known and leads to an expression for the concentration gradient at the interface, which determines the rate of mass transfer into the liquid phase. The instantaneous rate of mass transfer is then expressed by the equation, involving the lifetime ( $t$ ) of an element:

$$V = (c^* - c_b) \sqrt{\frac{D}{\pi t}} \dots\dots\dots 12$$

where  $c^*$  and  $c_b$  are the equilibrium and bulk concentrations of solute in the continuous phase. Danckwerts proposed that the lifetimes of the elements varied between  $t$  and  $t+dt$  and that, under constant conditions of turbulence, the rate of surface renewal should be constant and equal to  $s$ . The average rate of absorption is given by:

$$\bar{V} = \int \sqrt{\frac{D}{\pi t}} (c^* - c_b) \phi(t) dt \dots\dots\dots 13$$

where  $\phi(t)$  is an age distribution function. If the rate of disappearance of an element of a certain age is simply proportional to the number of elements of that age, then:

$$\frac{-d\phi}{dt} = s \phi \dots\dots\dots 14$$

Integration of this equation and substitution into Equation 13 followed by further integration from time equal to zero to time equal to infinity gives:

$$\bar{V} = (c^* - c_b) \sqrt{Ds} = k_L (c^* - c_b) \dots\dots\dots 15$$

where  $k_L$  is the mass transfer coefficient in the absence of chemical reaction. This equation applies only when the reaction rate is fast enough to keep the concentration of the solute down to zero in the bulk but not fast enough to prevent accumulation at the interface.

If, however, the concentration profile is maintained throughout the greater part of the elements' life, because chemical reaction is so fast as to prevent further accumulation, the concentration gradient at the interface is dependent upon the chemical rate constant. The diffusion process for a first-order or pseudo-first-order reaction

is now governed by the following:

$$D \frac{d^2c}{dx^2} = kc \quad \dots\dots\dots 16$$

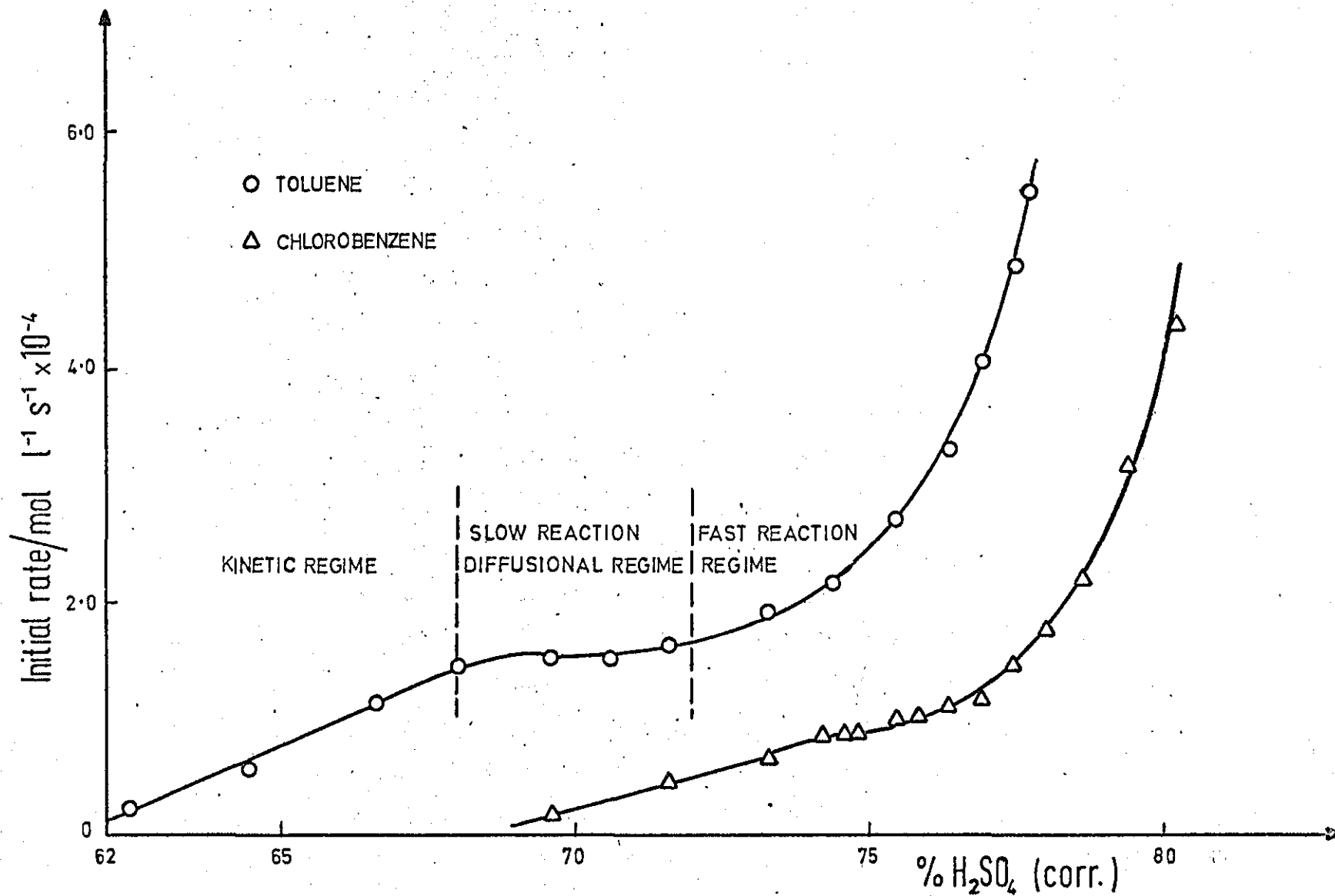
The solution to the above equation gives us an expression for the gradient at the interface, again, and hence the average mass transfer rate:

$$\bar{V} = C^* \sqrt{Dk} \quad \dots\dots\dots 17$$

The overall rate of mass transfer is then seen to depend on two competing factors; the physical diffusion rate (measured by  $k_L$ ) and the chemical reaction rate (measured by  $k$ ). The competition gives rise to the slow reaction diffusional regime and the fast reaction regime. In a system where the reaction rate may be varied over a wide range without an appreciable variation in the physical conditions (i.e. viscosity) these regimes may be sharply defined. This was found to be true for the two liquid phase system in the nitration of aromatics with mixed sulphuric and nitric acids; where a 10 per cent increase in sulphuric acid strength leads to an increase of ca.  $10^4$  in the second-order rate coefficient,  $k_2$ , while at the same time the viscosity varies by only a factor of ca. 2.

Cox determined the initial rate of nitration of toluene and chlorobenzene at 25°C in a 500 ml batch reactor agitated at 2,500 - 2,800 rev.min<sup>-1</sup> by a spectrophotometric method between 60 and 80 per cent sulphuric acid. A plot of initial rate versus per cent acid is shown in Figure 2. For both aromatics a gradual incline was observed at the low acid strengths (Kinetic regime) followed by a plateau region, where acid strength had little effect on the rate of reaction (Slow reaction diffusional regime) which in turn gave way

Fig.2 Initial rate of nitration versus percentage sulphuric acid for chlorobenzene and toluene in the stirred reactor



to a region where the rate was observed to increase dramatically over a small range of acid strengths (Fast reaction regime). Each regime will now be considered separately.

#### 1.4 KINETIC REGIME

In this regime the rate of reaction is so slow compared with the diffusional rate that the aromatic substrate concentration in the continuous acid phase is maintained at its equilibrium value, i.e. it takes the saturation value. The concentration profile near the interface under these conditions is shown in Figure 3(a). Assuming that the customary second-order reaction kinetics applies the overall rate is given by:

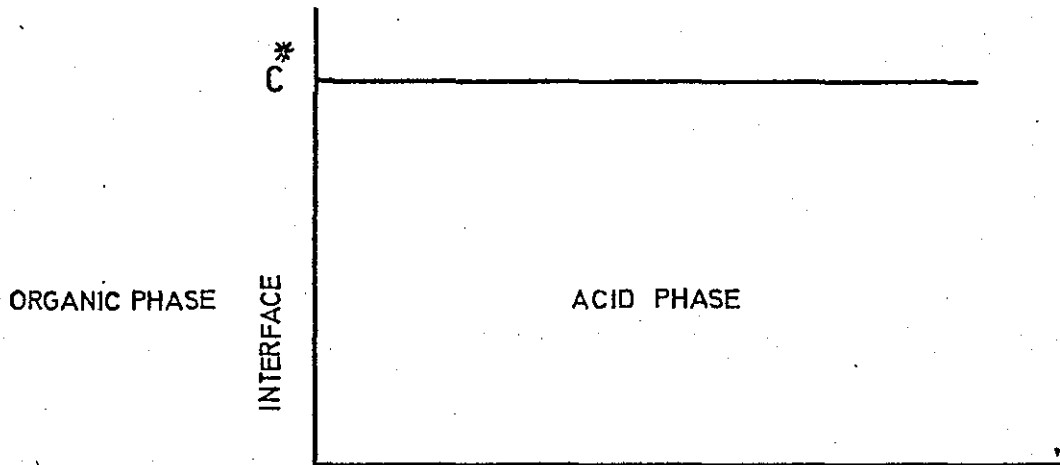
$$R = k_2 [\text{HNO}_3] [\text{ArH}]_a^s \quad \dots\dots\dots 18$$

where  $[\text{ArH}]_a^s$  is the saturation concentration of aromatic substrate in mixed acid media at a particular temperature. This equation is identical to that which applies in the homogeneous system and is independent of any of the physical conditions of the system.

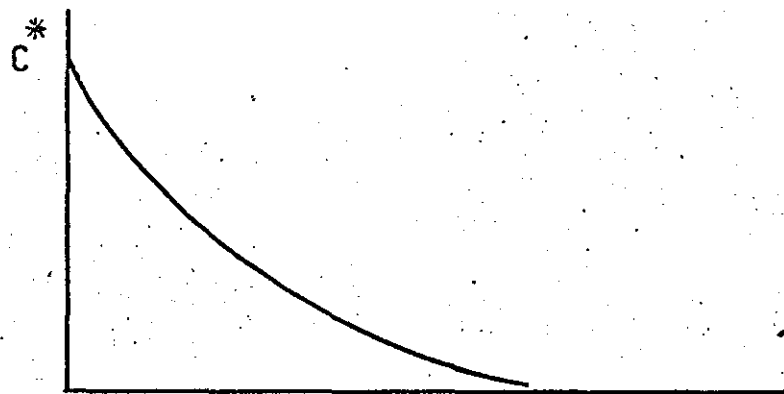
Cox and Strachan<sup>12</sup> performed a series of stirred reactor runs with chlorobenzene in 70.2 per cent sulphuric acid using low concentrations of nitric acid (0.032 mol l<sup>-1</sup>). Good pseudo-first-order behaviour was observed. The effect of temperature on the pseudo-first-order rate coefficient was measured and gave an overall activation energy of 20.9 ± 0.1 kcal mol<sup>-1</sup>. This was in excellent agreement with the value of  $E_{k_2} + \Delta H_{sol}$  which was equal to 20.93 ± 0.3 kcal mol<sup>-1</sup>. This agrees with the prediction that under these conditions kinetic, and not mass transfer, control is in force according to Equation 18.

Fig 3 Concentration profiles for the different regimes

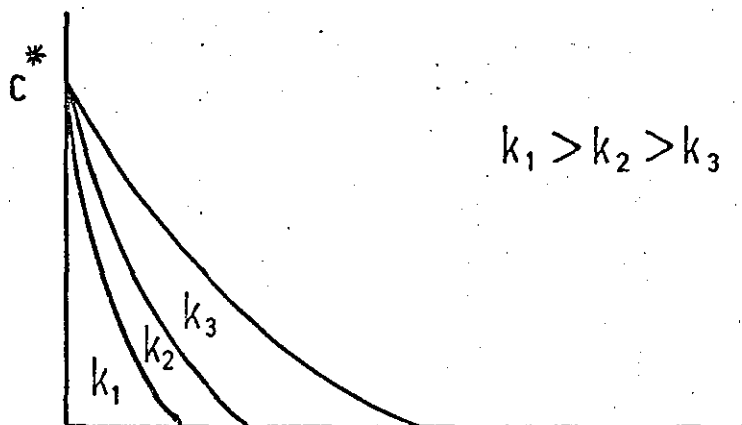
(a) The kinetic regime



(b) The slow reaction diffusional regime



(c) The fast reaction regime



A similar series of runs was performed with toluene. Due to the vastly different reactivities of the two aromatics it was necessary to dilute the organic phase with an inert solvent. Also due to the vastly different reactivities chlorobenzene itself provided the most convenient solvent for this purpose. The dilution resulted in a corresponding decrease in the acid phase concentration of toluene and hence the rate of reaction. This could then be followed by conventional kinetic means. The subsequent logarithmic pseudo-first-order plots were not, however, perfectly linear. During the early stages of reaction a curvature was present which suggested that mass transfer control was beginning to compete with the previous domination of kinetic control. Assuming a steady state is quickly reached and maintained, such that the rate of mass transfer of toluene to the acid phase and its rate of reaction are exactly balanced, the following is true:

$$a' k_L (\chi_T [T]_a^s - [T]_a) = k_2 [\text{HNO}_3] [T]_a \quad \dots\dots 19$$

where  $\chi_T$  is the mole fraction of toluene in the organic phase.

Assuming that both  $a'$  and  $\chi_T$  are constant, then the rate of nitration in the transition region between kinetic and slow reaction diffusional regimes is given by:

$$R = k_2 [\text{HNO}_3] [T]_a = \frac{k_L k_2 a' \chi_T [T]_a^s [\text{HNO}_3]}{k_2 [\text{HNO}_3] + a' k_L} \quad \dots\dots 20$$

The relative magnitudes of  $k_2 [\text{HNO}_3]$  and  $a' k_L$  determine the extent to which the reaction is kinetically or mass transfer controlled. From the results of Cox and Strachan it was evident that  $k_2 [\text{HNO}_3]$  was no longer negligible in comparison with  $a' k_L$  and in the early stages of reaction the rates were reduced below that expected if pure kinetic control was in progress.

### 1.5. SLOW REACTION DIFFUSIONAL REGIME

Figure 3(b) shows the concentration profile for the slow reaction diffusional regime. Under conditions where the rate of reaction is fast enough to keep the concentration of aromatic in the bulk of the acid down to zero but not fast enough to prevent accumulation of toluene at the interface the mass transfer rate is independent of the kinetic rate coefficient (and hence nitric and sulphuric acid concentrations) and is governed by Equation 11. This leads to the rate equation for reaction in the slow reaction diffusional regime:

$$R \cong a' \sqrt{D_s} \cdot [T]_a^s \quad \dots\dots\dots 21$$

### 1.6. FAST REACTION REGIME

In this regime the reaction is fast enough to prevent accumulation and the concentration profile is maintained throughout the greater part of an element's life (Figure 3 (c)). The steepness of the profile, the concentration gradient at the interface, does, however, depend on the kinetic rate coefficient. The greater the rate coefficient the steeper the gradient. The mass transfer rate is governed by Equation 16 and for pseudo-first-order nitration the rate equation is:

$$R = a' \sqrt{D k_2 [\text{HNO}_3]} \cdot [T]_a^s \quad \dots\dots\dots 22$$

The dependence of the rate on the root of the pseudo-first-order rate coefficient,  $k' = k_2 [\text{HNO}_3]$ , results in a steep rise in the rate with sulphuric acid strength.

### 1.7. INTERMEDIATE REGION BETWEEN SLOW DIFFUSIONAL AND FAST REACTION REGIMES.

In this intermediate region the diffusion process is governed by both the rate of accumulation of solute and its rate of reaction:



$$D \frac{d^2c}{dx^2} = \frac{dc}{dt} + kc \quad \dots\dots\dots 23$$

molecular transport = accumulation + reaction.

Solution of this equation is complicated<sup>18</sup> but it leads to a simple expression. The rate is simply given by the sum of the physical mass transfer and kinetic terms inside the root signs in Equations 21 and 22:

$$R = a' \sqrt{D k_2 [\text{HNO}_3] + k_L^2} \cdot [T]_a^s \quad \dots\dots\dots 24$$

Equation 24, known as the Danckwerts equation, can, under suitable conditions, be used to obtain values of the parameters  $a'$  and  $k_L$  in two phase systems. Use of the equation in gas-liquid systems was made by Danckwerts, Kennedy and Roberts<sup>22</sup> who studied the absorption of carbon dioxide by alkaline solutions in a packed column and obtained good correlations for the square of the rate versus the kinetic rate constant. Sharma and coworkers applied the equation to mechanically agitated liquid-liquid contactors with the fast pseudo-first-order alkaline hydrolysis of formate esters<sup>23</sup>. They used it to determine the interfacial area produced in a continuous flow stirred reactor under a wide variety of conditions. Much of the pioneering work has been reviewed by the two principal exponents of the technique, Sharma and Danckwerts<sup>24</sup>, and they continue to publish work in this field<sup>25,26,27,28,29</sup>.

If the interfacial area per unit volume is known, as is the case with two immisible liquids stirred slowly in a stirred cell, the equation may be used to accurately determine the diffusivity and mass transfer coefficient in the absence of chemical reaction. The importance of the Danckwerts equation in the design of batch reactors

and contactors is easily appreciated. Cox and Strachan<sup>1</sup> applied the equation to the two phase nitration of toluene and chlorobenzene in both a stirred reactor and a stirred cell. In the former system there was little trouble in determining the appropriate acid strengths over which the Danckwerts equation applied. Figure 2 shows clearly the transition region between fast reaction and slow reaction diffusional regimes for both aromatics. Danckwerts plots were drawn using the rate data in this region together with values for the saturation concentration<sup>30,31</sup> of aromatic and second-order rate coefficient<sup>4,32</sup> for nitration at each acid strength extrapolated from the data of previous workers. The Danckwerts plots, shown in Figure 4, were constructed assuming the following;

$$\left( \frac{R}{[\text{ArH}]_a^s} \right)^2 = a'^2 ( Dk_2 [\text{HNO}_3] + k_L^2 ) \quad \dots\dots\dots 25$$

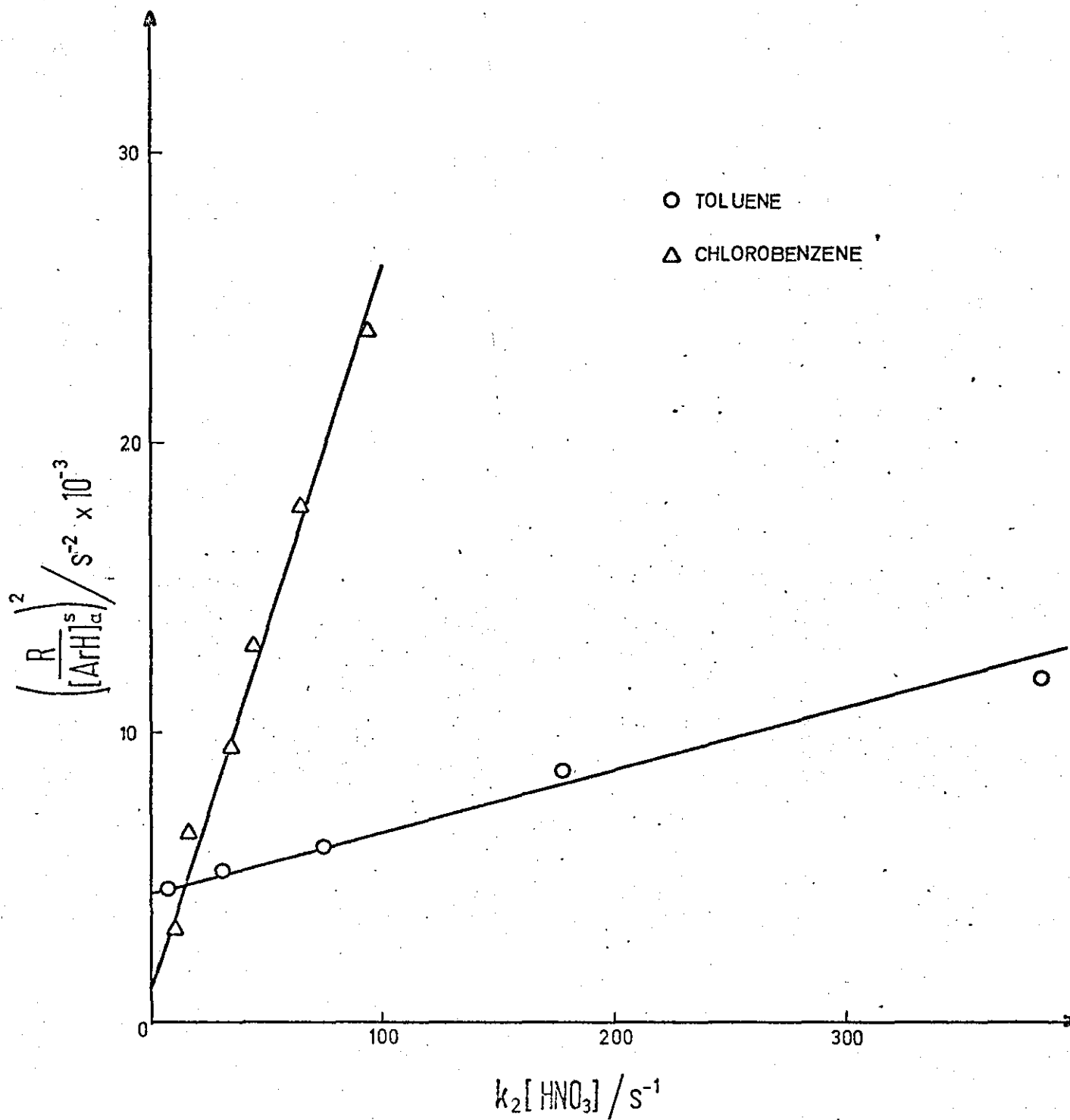
where the nitric acid concentration remained fixed for each run at 0.56 mol l<sup>-1</sup> of acid phase. Good straight line correlations were obtained in each case with the intercept and slope given by (a'k<sub>L</sub>)<sup>2</sup> and a'<sup>2</sup>D, respectively (Table 2).

TABLE 2

SUBSTRATE	SLOPE/s <sup>-1</sup>	INTERCEPT/s <sup>-2</sup>
Toluene	1.9 x 10 <sup>-5</sup>	4.75 x 10 <sup>-3</sup>
Chlorobenzene	2.275 x 10 <sup>-4</sup>	25.0 x 10 <sup>-4</sup>

Since none of the three parameters, a', k<sub>L</sub> and D, involved in Equation 25 was known with any accuracy a series of nitrations was performed at various strengths in a stirred cell. Essentially, this consisted of a small reactor in which only the acid phase was gently stirred at 65 rev.min<sup>-1</sup> to give a virtually flat interface with organic phase above it. The rate of reaction was determined by the same

Fig.4 Danckwerts plots of toluene and chlorobenzene in the stirred reactor



spectrophotometric method used with the stirred reactor. The interfacial area per unit volume of acid phase was constant and calculated from the internal diameter of the vessel to be  $0.2024 \text{ cm}^2 \text{ cm}^{-3}$ . Figure 5 shows the effect of sulphuric acid strength on the initial rate of nitration of toluene and chlorobenzene in the stirred cell at  $25^\circ\text{C}$ . Figure 6 shows the subsequent Danckwerts plots assuming that Equation 25 applies over the same acid range as for the stirred reactor. Table 3 gives the values of the slope and intercept of the least-squares lines through the points together with estimates of  $D$  and  $k_L$  assuming the above measured interfacial area per unit volume of acid phase.

TABLE 3.

SUBSTRATE	SLOPE/ $\text{s}^{-1}$	INTERCEPT/ $\text{s}^{-2}$	$D/\text{cm}^2 \text{ s}^{-1}$	$k_L/\text{cm. s}^{-1}$
Toluene	$1.31 \times 10^{-9}$	$16.3 \times 10^{-7}$	$0.32 \times 10^{-7}$	$6.3 \times 10^{-3}$
Chlorobenzene	$34.25 \times 10^{-9}$	$3.25 \times 10^{-7}$	$0.84 \times 10^{-6}$	$2.8 \times 10^{-3}$

Two major questions arise from this work. First, as shown by the plots of initial rate versus percentage sulphuric acid (Figure 5) in the stirred cell, a plateau region, corresponding to the slow reaction diffusional regime was not observed with either aromatic. A decrease in the acid strength leads to a continuous lowering of the initial rate well below that which might be expected. This was matched by a tailing off from the least-squares lines drawn in the Danckwerts plots, at low values of  $k_2[\text{HNO}_3]$ .

Secondly, the diffusivity of toluene was many times lower than that of chlorobenzene (Table 3) which itself was a further ten times lower than often quoted typical values of  $\text{ca. } 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ .<sup>21,33</sup> This ten fold decrease in the diffusivity of chlorobenzene was explained satisfactorily by Cox and Strachan in terms of increased viscosity

Fig 5 Initial rate of nitration versus percentage sulphuric acid for chlorobenzene and toluene in the stirred cell

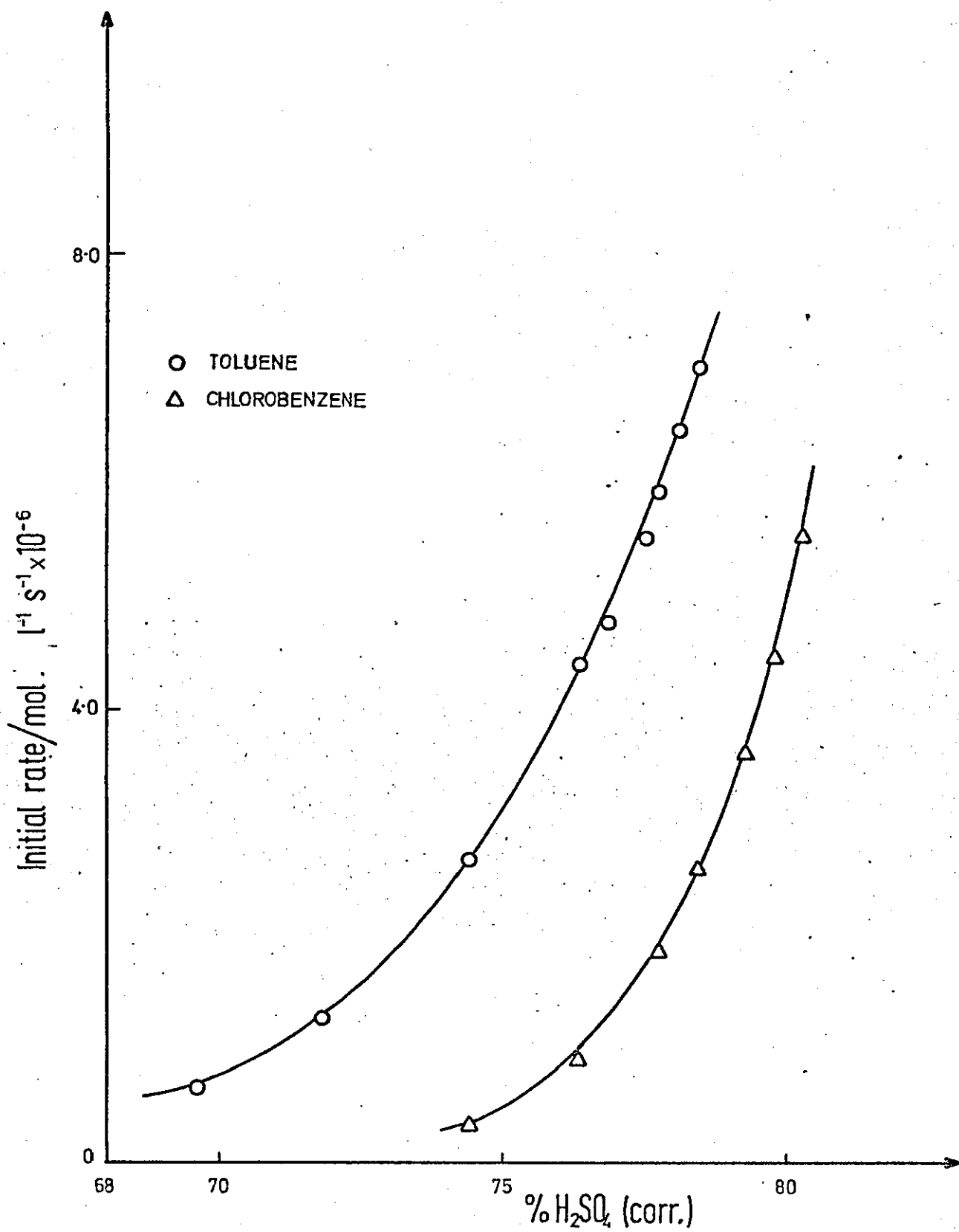
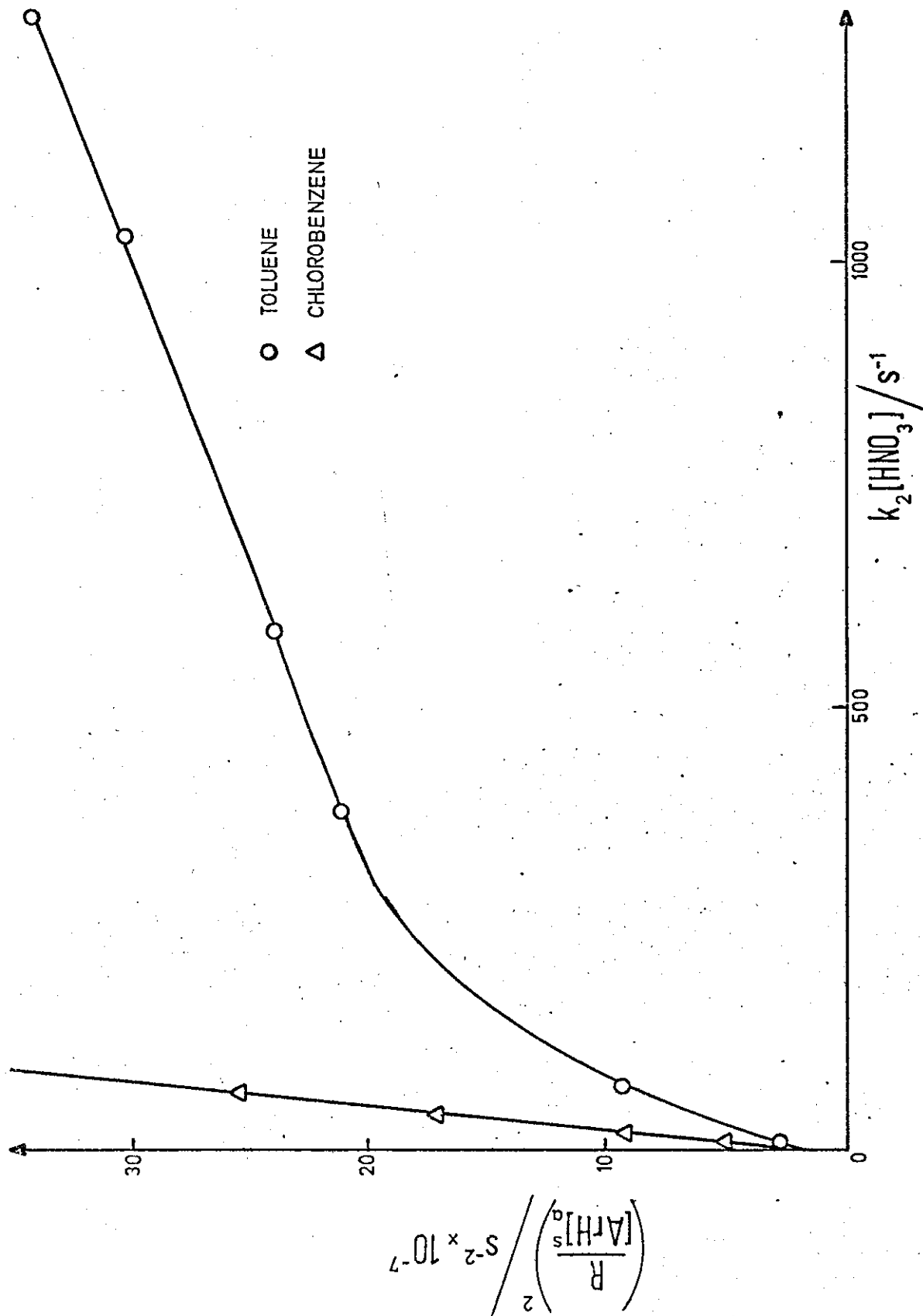


Fig. 6 Danckwerts plots for chlorobenzene and toluene in the stirred cell



of the medium. There is an inverse dependence of diffusivity on the viscosity of the continuous phase, in this case, concentrated sulphuric-nitric acid-water mixtures. They estimated the diffusivity of toluene and chlorobenzene as a function of sulphuric acid strength using the modified Wilke-Chang Equation proposed by Perkins and Geankoplis<sup>34</sup> for a mixed solvent system:

$$D = \frac{7.4 \times 10^{-8} (\bar{X}\bar{M})^{\frac{1}{2}} T}{\eta v^{0.6}} \dots\dots\dots 26$$

where D = diffusivity of solute in the mixed solvent.

- $\bar{M}$  = mean associated molecular weight for a mixed solvent<sup>1</sup>
- $\eta$  = viscosity of the solvent (cP)
- T = temperature (K)
- V = molar volume of solvent.

The values obtained are listed in Table 4. They are very similar for both aromatics and correspond closely to the experimentally determined value for chlorobenzene in the stirred cell over this acid range. Furthermore, they fit closely with values based on direct experimental determination of diffusivities by workers at Bradford University<sup>35</sup>. They determined the diffusivity of toluene at low sulphuric acid strengths, at 30°C, by a laminar-jet method and derived an empirical expression for the dependence of it on viscosity:

$$D = (0.92 + 0.04 N_n) \eta^{-0.8} \dots\dots\dots 27$$

where  $N_n$  is the normality of nitric acid. It is worth noting the change in the exponent of the viscosity from -1.0 to -0.8 compared with that in the Wilke-Chang expression and the small influence of the nitric acid term. Some of the Bradford workers' results, with  $N_n$  equal to zero, are included in Table 4 for comparison.

TABLE 4.

% H <sub>2</sub> SO <sub>4</sub>	D/cm <sup>2</sup> s <sup>-1</sup>	D/cm <sup>2</sup> s <sup>-1</sup>
	TOLUENE	CHLOROBENZENE
5.0	10.12 x 10 <sup>-6</sup>	
14.0	9.82 x 10 <sup>-6</sup>	
21.5 ref. 35	9.34 x 10 <sup>-6</sup>	
38.0	7.07 x 10 <sup>-6</sup>	
63.5	2.56 x 10 <sup>-6</sup>	
69.6	1.36 x 10 <sup>-6</sup>	
71.8	1.22 x 10 <sup>-6</sup>	
74.4	1.04 x 10 <sup>-6</sup>	1.05 x 10 <sup>-6</sup>
76.35	0.92 x 10 <sup>-6</sup>	0.94 x 10 <sup>-6</sup>
76.85	0.90 x 10 <sup>-6</sup>	
77.5	0.87 x 10 <sup>-6</sup>	
77.75	0.85 x 10 <sup>-6</sup>	0.87 x 10 <sup>-6</sup>
78.1	0.83 x 10 <sup>-6</sup>	
78.45	0.81 x 10 <sup>-6</sup>	0.83 x 10 <sup>-6</sup>
79.3		0.80 x 10 <sup>-6</sup>
79.8		0.77 x 10 <sup>-6</sup>
80.3		0.75 x 10 <sup>-6</sup>

The very low diffusivity of toluene compared to chlorobenzene in the stirred cell remained unexplained, however. So also the somewhat higher value for its mass transfer coefficient in the absence of chemical reaction. The two anomalous results were considered to stem from the one effect; a low value for the slope of the Danckwerts plot for toluene compared to chlorobenzene. A factor of ten in the slope results in a factor of ten in the diffusivity since the former is given by  $a'^2 D$ .



An identical effect was observed with the stirred reactor. In the case of chlorobenzene the value of the diffusivity obtained from the stirred cell was inserted into the stirred reactor Danckwerts slope. The value of  $3.0 \times 10^{-3} \text{ cm s}^{-1}$  for  $k_L$  obtained is in excellent agreement with that found in the stirred cell and associated with such systems generally<sup>36</sup>. The interfacial area per unit volume of acid phase was considerably larger than that used in the stirred cell, as one would expect, and had the value of  $16.5 \text{ cm}^2 \text{ cm}^{-3}$ . Toluene, however, gave a slope some ten times lower than that of chlorobenzene in the stirred reactor.

Cox<sup>1</sup> suggested that the difference between the two aromatics was the result of solute-solvent interaction which affects toluene but not chlorobenzene. He considered that in a highly solvating medium such as sulphuric acid the solvation of the  $\sigma$ -complex (Wheland Intermediate) of toluene, with an inherent increase in the effective volume, can account for the low experimentally observed diffusivity in the two phase systems. The exact quantitative effect of such solute-solvent interactions is difficult to estimate. Clearly, though, this explanation is difficult to reconcile with both observed and calculated diffusivities for toluene of  $\text{ca. } 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , at this acid strength. Another explanation must be sought.

To summarize; there are two problems that require further investigation. Firstly, the absence of a plateau due to the slow reaction diffusional regime in the stirred cell. Secondly, the suppressed rates of nitration of toluene compared to chlorobenzene in both two phase systems over the range 70-80 per cent sulphuric acid. It was with these two problems in mind that the following work was undertaken.

EXPERIMENTAL

## CHAPTER 2.

This chapter consists of a description of the apparatus and chemicals used in the experimental work together with a general description of the procedures. Precise details of conditions employed at each stage are to be found in the appropriate chapters of results.

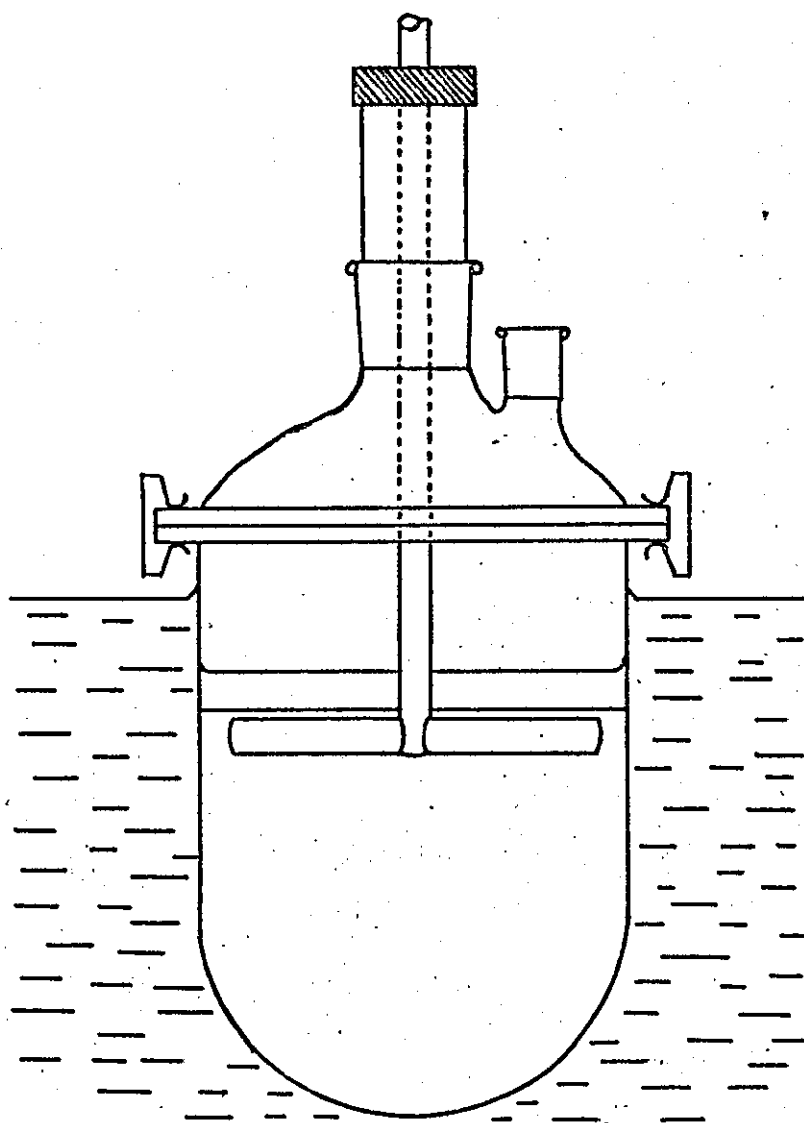
### 2.1. PREPARATION OF AQUEOUS SULPHURIC ACID.

Aqueous solutions of sulphuric acid were made up by the addition of a known volume of concentrated sulphuric acid (Analar grade, s.g. ca. 1.84) to chilled distilled water. The composition was determined by titration with standard sodium hydroxide using methyl orange as indicator and also occasionally by density measurement with a Gallenkamp model hydrometer (1.60 - 1.65 density range).

### 2.2. STIRRED CELL RUNS.

The stirred cell (Figure 7) was that used by Cox<sup>1</sup> and consisted of a cylindrical, parallel-walled flask of 250 ml capacity and internal diameter 6.61 cm. A two-necked lid gave access for a stirrer, driven by an electric motor (Fisons S.A. 4lbs per square ins., 1/30 H.P.) and for sample removal. The cell was mounted in a water bath held at a constant temperature  $\pm 0.2^{\circ}\text{C}$ . Various shapes and sizes of stirrer were used. For most of the runs involving nitration a 6 cm diameter turbine stirrer was used. For the mass transfer runs, however, an almost square flat-bladed propeller was preferred. This gave a more effective agitation of the bulk of the acid phase. The speed of the stirrer was estimated visually and its position held constant in the acid phase (the lower phase) ca. 1mm beneath the interface. Prior to a run the acid phase, contained in the stirred cell, and a quantity of the organic phase, held in a flask, were equilibrated at the desired temperature in the water bath. The stirrer motor was started

Fig.7 The Stirred Cell



and the organic phase pipetted slowly onto the acid phase to start the run. A stop-watch was started half-way through the addition. Two types of run were performed and for each a different sampling technique was necessary.

(a) DETERMINATION OF THE RATE OF NITRATION

In this case the accumulation of nitroproduct in the organic phase was followed by sampling the organic phase at regular intervals of time with a syringe (Summit, 1 ml or Hamilton, 50 $\mu$ l). A known volume of organic phase was then immediately diluted with hexane (Fisons, Spectroscopic grade) and its absorbance measured in a 1 cm. silica cell at a suitable wavelength on a Hilger and Watts H.700 spectrophotometer against a hexane blank.

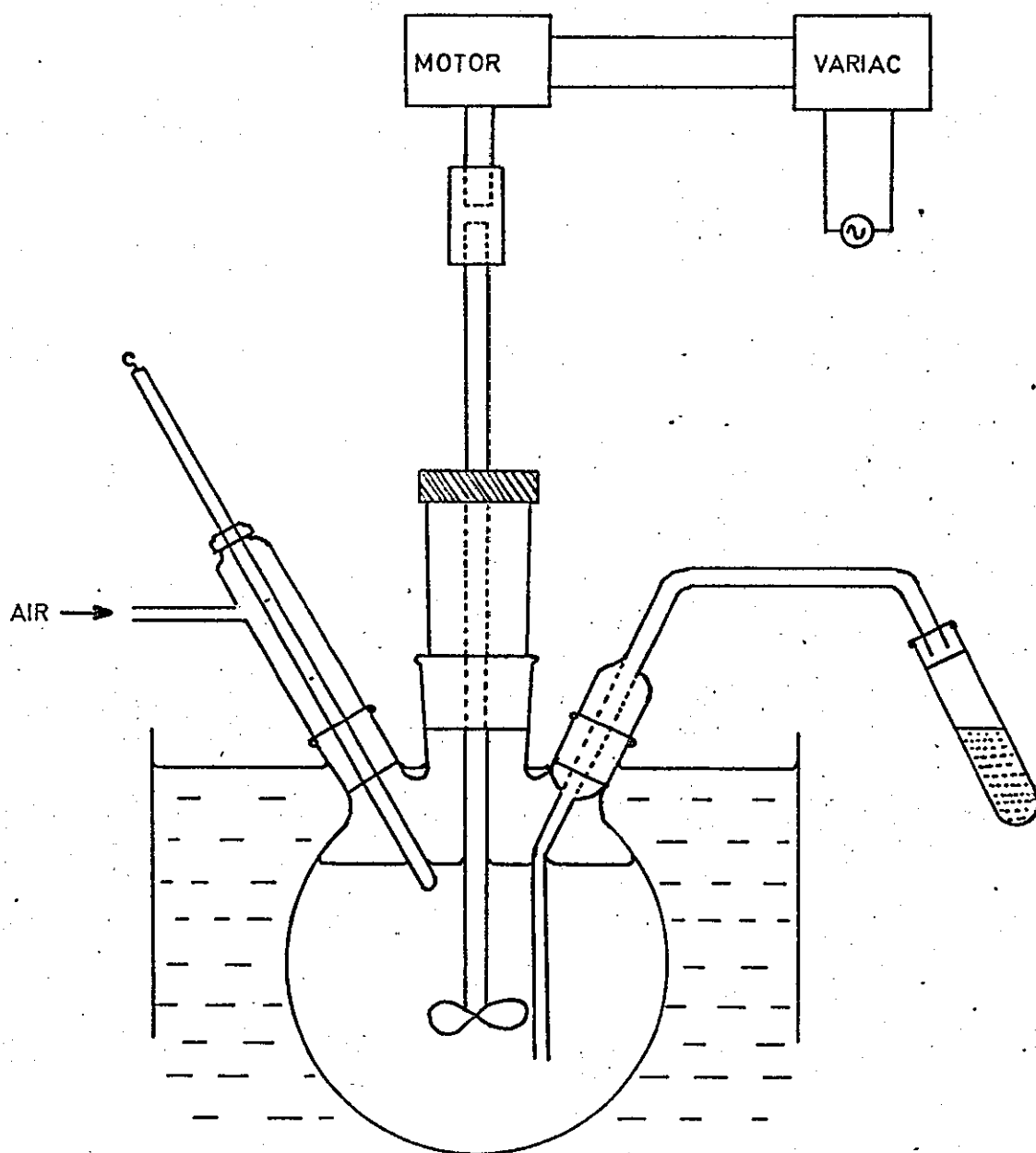
(b) DETERMINATION OF THE PHYSICAL MASS TRANSFER COEFFICIENT.

Here, the accumulation of the un-nitrated organic phase i.e. pure toluene (B.D.H. Analar grade) or chlorobenzene (B.D.H. Reagent grade) in the bulk of the acid phase (Aqueous sulphuric acid only) was observed by withdrawing samples of the acid phase through the organic phase at regular intervals of time. For this purpose, after the stirrer had been momentarily stopped, a 5ml pipette fitted with a pumpette was used to withdraw sufficient acid phase each time to fill a 1cm silica cell directly. The absorbance was measured as before, at a maximum in the benzenoid band for the aromatic, versus a distilled water blank. Great care was taken in this procedure to ensure as little disruption of the flat interface between the two phases whilst sampling and the acid was replaced immediately after its absorbance had been measured.

2.3. STIRRED REACTOR RUNS.

The stirred reactor was the unbaffled 500 ml, three-necked, round-bottomed flask that Cox used<sup>1</sup> (Figure 8). It was stirred by

Fig. 8. The Stirred Reactor



means of a two-bladed glass propeller (2 cm diameter) driven at high speed by a variable speed electric motor (Voss, 1/30 H.P). The reactor was mounted in a similar water bath to that used with the stirred cell. The speed of the stirrer was measured with a stroboscopic tachometer (Dawe Instruments stroboflash, type 1200 E). Prior to a run the two phases were equilibrated at the required temperature, the acid phase in the reactor and an excess quantity of the organic phase in a separate flask. The stirrer was then started and the run initiated by the addition of the required amount of organic phase to the acid phase with a pipette and the simultaneous starting of the stop-watch. Samples of the dispersion were blown over at regular intervals of time through sampling probes, by the gentle application of air pressure, into iced distilled water where the two phases were allowed to settle out. A fresh probe was used for each sample. A quantity of the organic phase was then withdrawn by syringe, diluted with hexane and its absorbance measured at a suitable wavelength as before.

#### 2.4. DETERMINATION OF THE SOLUBILITY OF AROMATICS IN AQUEOUS SULPHURIC ACID.

The method of Cox<sup>1</sup> was followed. The stirred reactor was used to mix equal quantities of aromatic and aqueous sulphuric acid at the required temperature. After about 2 hours agitation the stirrer motor was stopped and a glass tube, having a closed end of thin glass, was inserted into the flask through into the acid phase. The two phases were allowed to settle out overnight. A glass rod was then inserted into the tube and the end gently broken. Gentle application of air pressure allowed samples of the acid layer to be blown over into a flask, held in the water bath, without contamination by the organic layer above it. A sample of this was then withdrawn by pipette and delivered into a weighed graduated flask. The flask was reweighed

and the dissolved organic phase extracted once with hexane. The absorbance of the extract was measured, at a maximum in the benzenoid band for the aromatic, versus a hexane blank.

## 2.5. CALIBRATION FACTORS

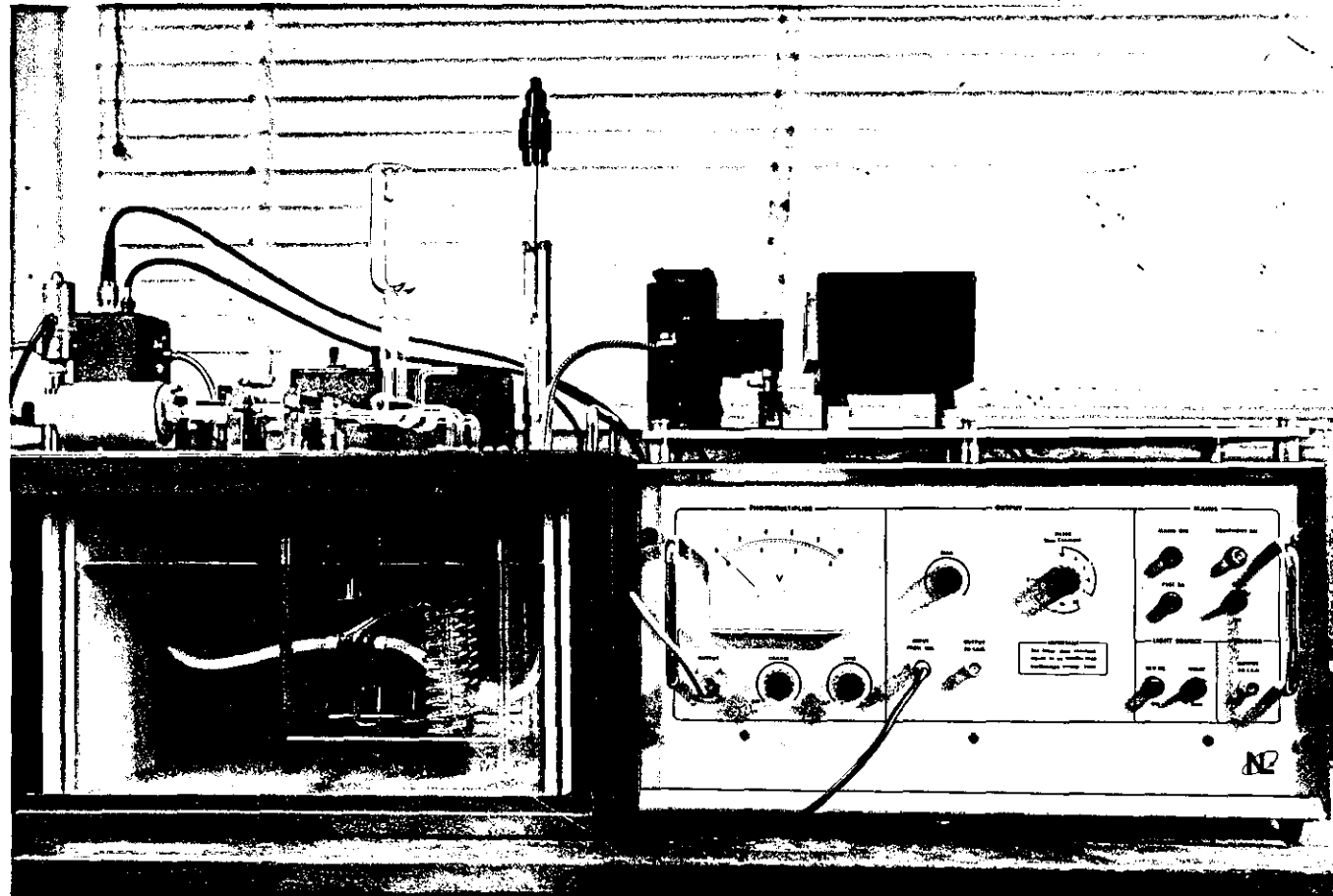
To convert the above absorbance changes per minute for the stirred cell and reactor runs into initial rates, in  $\text{mol l}^{-1}\text{s}^{-1}$ , it was necessary to multiply by a conversion factor. To establish this value Cox<sup>1</sup> made up a mixture of mononitrotoluenes (or mononitrochlorobenzenes) having the same composition as the reaction products i.e. 59 per cent ortho, 4 per cent meta and 37 per cent para in the case of toluene (33 per cent ortho, 1 per cent meta and 66 per cent para for chlorobenzene). A series of toluene (or chlorobenzene) solutions of this mixture was accurately prepared and each solution was analysed in exactly the same way as a reaction sample. In each case a plot of absorbance versus percentage conversion was linear up to at least 30 per cent conversion.

## 2.6. STOPPED-FLOW SPECTROMETRY.

The instrument used was a Nortech SF-3A "Canterbury" stopped-flow spectrometer. It consisted of a corrosion resistant silica and glass flow system with "Teflon" taps (a large part of which was suspended in a thermostatically controlled ( $\pm 0.001^\circ\text{C}$ ) water bath), a light source and photomultiplier unit (Figure 9). The substrate solutions were stored in reservoirs above two glass syringes which were connected to glass thermostat coils beneath the level of the water bath. The two syringes could be closed simultaneously by opening a large piston which had its flat face in contact with both syringe plungers. This forced liquid through the flow system and mixed the two solutions rapidly in the silica optical cell. Spent solution flowed out through the other side of the cell into another syringe



Fig. 9 The Stopped-flow Spectrometer.



which was forced open. The flow was suddenly interrupted when the plunger of the outlet syringe hit a back-stop fitted with a microswitch.

The formation of nitroproducts in the optical cell was followed by conventional spectrophotometric means. A quartz-iodine light source (Nortech, LS-1), operating over the visible region and into the ultra violet region of the spectrum, was employed. Light was channelled from the source through a focussing and filter unit and then to the optical cell, situated beneath the level of water in the thermostatically controlled water bath, by means of a silica fibre light guide. The output from the cell was channelled back up to a fast response photomultiplier (Nortech, PM-1) and its output displayed on an oscilloscope. The oscilloscope was externally triggered by the depression of the microswitch on the back-stop. Two oscilloscopes were employed. For much of the work a storage model was used (Advance, OS2200) whereas for photographed runs a conventional oscilloscope (Hewlett-Packard, 130C) fitted with a polaroid camera (Hewlett-Packard, 196 B) and fast film (Polaroid, type 107) was necessary.

The light from the source was filtered by two methods. For some of the early runs a wide spectrum glass filter (Chance-Pilkington OX<sub>1</sub>) and infra-red water cell were placed between the focussing unit and the converging lens leading to the light guide. For the majority of runs, however, these were replaced by a grating monochromator with variable slit width (Nortech, MG-1). In many cases, especially with high amplification of the input signal to the oscilloscope, some degree of electronic filtering of noise was required. This was made possible by use of a filter unit supplied with the photomultiplier unit. Some discretion was necessary in its use to avoid damping or distortion of the oscilloscope trace. At all times the filter time constant was kept equal to or below the time-base setting on the oscilloscope. For

example, if a time-base of 10ms was used a typical filter setting would be 3ms. Where possible the use of the filter was avoided altogether.

#### 2.7. A TYPICAL STOPPED-FLOW RUN.

1. Two graduated flasks containing aqueous sulphuric acid were equilibrated at the desired temperature in a water bath.
2. The nitric acid solution was made up by the addition of nitric acid (Analar grade, ca.69.5 per cent, s.g. 1.42) to one of the above flasks from a pipette and shaking. The aromatic substrate solution was made up last by the dropwise addition of aromatic from a syringe (Hamilton,  $50\mu\text{l}$ ) onto the surface of the sulphuric acid contained in the other flask and vigorously shaking for 5 minutes. The solution was allowed to settle for a further 30 minutes.
3. The flow system was blown dry with a stream of nitrogen for two hours.
4. Both reactant reservoirs were filled with a different solution which was pushed around the flow system to the outlet by the repeated opening and shutting of the inlet syringes. The solutions were then allowed to equilibrate inside the flow system at the desired temperature.
5. To prepare for a run both inlet syringes were filled up and their piston heads allowed to rest against the flat face of the driving piston. Their taps were opened to the flow system only. The outlet syringe was emptied and its tap opened to the flow system.
6. A run was initiated by a rapid opening of the driving piston with the hand until the outlet piston rammed up against the back-stop and the microswitch was depressed. An accumulation trace was observed on the oscilloscope screen.
7. After each run the outlet syringe was quickly emptied and the microswitch released.

8. A linear trace, representing the absorbance at infinite time, was obtained by manual depression of the microswitch some appreciable time after the run. (The time was dependent upon the half-life of the reaction but was always greater than ten half-lives).

## RESULTS

CHAPTER 3.

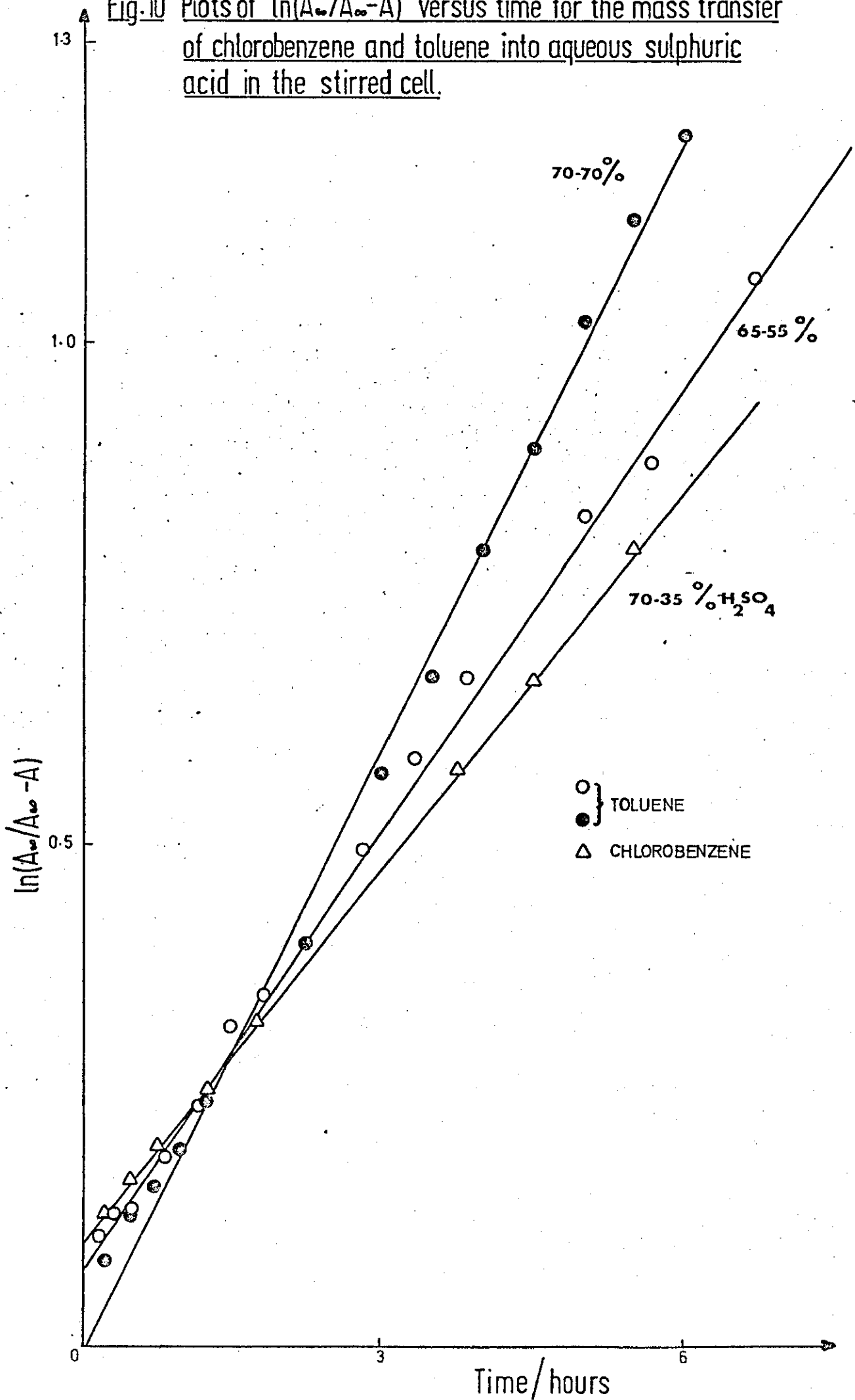
MASS TRANSFER IN THE ABSENCE OF CHEMICAL REACTION IN THE STIRRED CELL.

The mass transfer coefficient in the absence of chemical reaction,  $k_L$ , was determined as described in Section 2.2(b). A 20 ml quantity of chlorobenzene or toluene was stirred at 50 rev min<sup>-1</sup> with 170 ml of aqueous sulphuric acid at 25°C in the stirred cell. The ultraviolet absorption of the aromatic in the acid phase was determined at 262nm in the case of toluene and 265nm for chlorobenzene. Three runs were performed at the highest acid strengths possible, although low enough to avoid any appreciable sulphonation during the course of the run. This was checked by comparing the ultraviolet absorption spectrum of the acid phase at the end of a run with that of pure aromatic in aqueous sulphuric acid. Each run showed a typical exponential increase in absorbance,  $A$ , with time from which linear plots of  $\ln(A_\infty / A_\infty - A)$  versus time were constructed (Figure 10). The slope of each plot, when set equal to  $a'k_L$ , allowed  $k_L$  to be determined since the interfacial area per unit volume of acid phase,  $a'$ , was equal to 0.2024 cm<sup>2</sup> cm<sup>-3</sup>. Table 5 lists these values of  $k_L$  together with the saturation solubility,  $[\text{ArH}]_a^s$ , of aromatic in aqueous sulphuric acid. The latter values were obtained from the absorbance at infinite time,  $A_\infty$ , by calibration of the absorbance with standard solutions of aromatic in aqueous sulphuric acid.

TABLE 5

AROMATIC	%H <sub>2</sub> SO <sub>4</sub>	$k_L/\text{cm s}^{-1}$	$[\text{ArH}]_a^s \text{ mol l}^{-1}$	$[\text{ArH}]_a^s/\text{mol l}^{-1}(\text{ref.1})$
Toluene	65.55	$1.95 \times 10^{-4}$	$1.99 \times 10^{-3}$	$2.07 \times 10^{-3}$
Toluene	70.70	$2.71 \times 10^{-4}$	$2.23 \times 10^{-3}$	$2.28 \times 10^{-3}$
Chloro- benzene	70.35	$1.73 \times 10^{-4}$	$1.73 \times 10^{-3}$	$2.11 \times 10^{-3}$

Fig.10 Plots of  $\ln(A_\infty/A_\infty - A)$  versus time for the mass transfer of chlorobenzene and toluene into aqueous sulphuric acid in the stirred cell.



## COMMENT

The mass transfer coefficients in the absence of chemical reaction were observed to fall in the range  $1-3 \times 10^{-4} \text{ cm s}^{-1}$ . This is some ten times lower than that obtained from the Danckwerts plots for the stirred cell when appreciable chemical reaction is taking place (Table 3). The saturation solubilities are, however, in good agreement with those previously reported by Cox<sup>1</sup> (Table 5), and interpolated from data obtained by the more precise, orthodox procedure involving extraction of the aromatic from the aqueous sulphuric acid followed by spectrophotometric analysis. In the light of these results the difference observed by Cox between stirred cell and stirred reactor mixtures; the absence of a plateau region due to the slow reaction diffusional regime and the tailing off of the Danckwerts plots at low acid strengths, may be explained.

Transition from fast to slow reaction occurs when  $k_2 [\text{HNO}_3]$  becomes less than  $k_L^2/D$ . The Danckwerts plots for the stirred reactor and stirred cell indicate that  $k_L$  appears fairly constant over the fast reaction regime with much the same value in the stirred cell system as in the stirred reactor. Since the same concentration of nitric acid was used in both systems and  $k_2$  depends solely on the sulphuric acid strength, the transition to the slow reaction diffusional regime would be expected to occur in the stirred cell at about the same strength of sulphuric acid as it does with the stirred reactor. The transition should lead to  $R/[\text{ArH}]_a$  becoming constant and equal to  $k_L$ . Figure 11 shows the stirred cell behaviour which might be expected for chlorobenzene on the basis of data obtained from the Danckwerts plot (dashed line). The plateau regime would be expected to extend to much lower sulphuric acid strengths than observed with the stirred reactor since transition to the kinetic regime will not

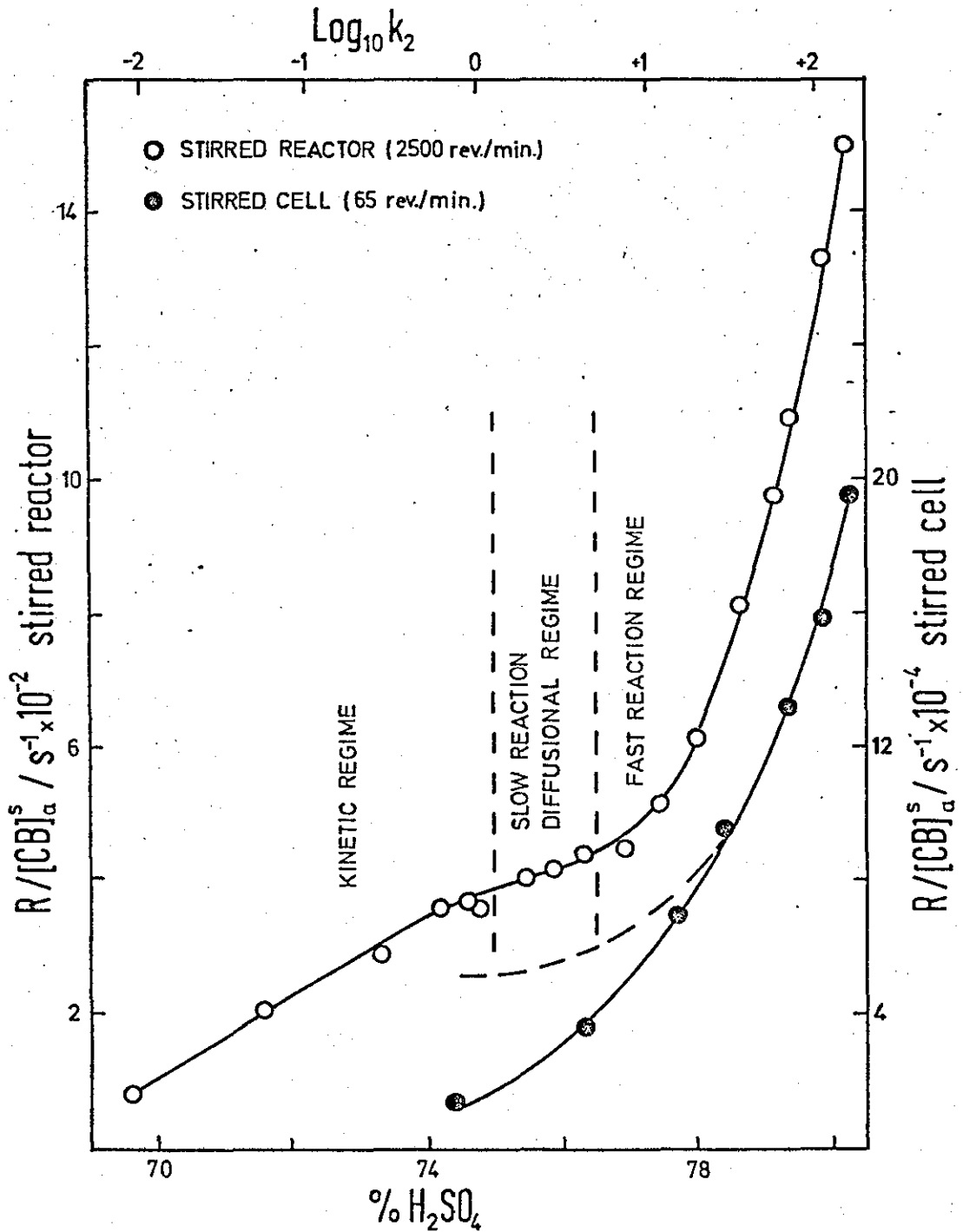


occur until  $k_2[\text{HNO}_3]$  becomes less than  $a'k_L$ . Since  $a'$  for the stirred cell is some 80 times smaller than for the stirred reactor, transition to the kinetic regime is not expected until sulphuric acid strengths below the 70 per cent mark are reached.

Figure 11 clearly shows that this behaviour is not followed. Instead  $R/[\text{CB}]_a$  falls continuously as the sulphuric acid strength is lowered and no plateau is ever reached (full line). Since  $a'$  is fixed,  $k_L$  must fall with the rate of chemical reaction in the stirred cell from its value of  $2.8 \times 10^{-3} \text{ cm s}^{-1}$ , in the fast reaction regime, to ca.  $1.73 \times 10^{-4} \text{ cm s}^{-1}$ , when little or no chemical reaction is taking place. An exactly similar behaviour is observed with toluene. In the stirred reactor system  $k_L$  does not fall with the rate of chemical reaction but is maintained throughout the fast and slow reaction regimes giving rise to the observed plateau of the slow reaction diffusional regime (Figure 11).

It is clear that in the stirred cell chemical reaction promotes good surface renewal which mechanical agitation alone cannot sustain. Stirred cell systems containing water as the continuous phase have observed mass transfer coefficients in the region of  $10^{-3} \text{ cm s}^{-1}$  <sup>36</sup>. The concentrated sulphuric acid medium encountered here has an inherently lower mass transfer coefficient and this is thought to be largely due to the high viscosity of this medium compared to that of water. However, the factors affecting the value of the mass transfer coefficient in stirred cell systems are numerous and the topic will receive a more detailed discussion later in the thesis.

Fig. 11  $R/[CB]_a^S$  versus percentage sulphuric acid for the nitration of chlorobenzene in the stirred cell and the stirred reactor.



## CHAPTER 4

### CHANGE IN THE KINETIC ORDER OF NITRATION WITH RESPECT TO TOLUENE IN THE TWO PHASE SYSTEM.

#### 4.1. DEPENDENCE OF INITIAL RATE OF NITRATION ON THE COMPOSITION OF THE ORGANIC PHASE IN THE STIRRED REACTOR.

The initial rate of nitration of toluene in the stirred reactor was determined with various solutions of toluene in 2,2,4-trimethylpentane as the organic phase as outlined in Section 2.3. Pure 2,2,4-trimethylpentane (Fisons Spectrograde reagent) was used as a diluent because of its high boiling point of  $99^{\circ}\text{C}$ , its unreactivity towards concentrated acids and its transparency to ultraviolet light at the wavelengths to which measurements were confined. The acid phase consisted of 300 ml of 76.50 per cent sulphuric acid to which was added 0.90ml of nitric acid (Analar grade, S.g. 1.42) to give a solution  $4.70 \times 10^{-2} \text{ mol l}^{-1}$  in nitric acid. The sulphuric acid was kept below  $10^{\circ}\text{C}$  during the addition to avoid the production of nitrosyl-sulphuric acid. The amount of nitric acid added was so small that no correction was applied to the sulphuric acid strength for the water added with the nitric acid. The organic phase comprised 50ml of a solution of toluene in 2,2,4-trimethylpentane. Organic phase compositions in the range 0.25-2.00 volume per cent were employed. All runs were performed at  $25^{\circ}\text{C}$  and with a stirring speed of 2,500 rev  $\text{min}^{-1}$ . About 12 ml samples of dispersion were blown over into equal volumes of iced water. Samples of the organic phase (0.5ml) were diluted to 10 ml with hexane and their absorbance measured at 350nm. Linear plots of absorbance versus time were observed in the initial stages of reaction. The slopes of the least-squares lines through the points, in absorbance  $\text{min}^{-1}$ , were converted into initial rates of nitration, in  $\text{mol l}^{-1} \text{ s}^{-1}$ , by multiplying by the conversion factor

of  $2.34 \times 10^{-4}$ . This was obtained in a similar manner to that described in Section 2.5 with the synthetic mixture of nitrotoluenes diluted as above. The value may be compared with that obtained by adapting Cox's<sup>1</sup> value of  $5.86 \times 10^{-3}$  for the change in dilution and volume of organic and acid phases which was necessary in this work. The adapted value according to Cox is  $2.80 \times 10^{-4}$  which is in reasonable agreement with our new measured value. Table 6 shows the variation of initial rate, R, with the volume per cent of toluene in the organic phase.

TABLE 6.

ORGANIC PHASE COMPOSITION (VOLUME PER CENT TOLUENE)	INITIAL RATE/mol l <sup>-1</sup> s <sup>-1</sup>
2.00	$3.66 \times 10^{-5}$
1.50	$2.93 \times 10^{-5}$
1.00	$1.81 \times 10^{-5}$
0.50	$1.07 \times 10^{-5}$
0.25	$5.92 \times 10^{-6}$

4.2. DEPENDENCE OF INITIAL RATE OF NITRATION ON THE NITRIC ACID CONCENTRATION IN THE STIRRED REACTOR.

The initial rate of nitration of a dilute solution of toluene in 2,2,4-trimethylpentane was determined with various nitric acid concentrations in the acid phase between  $1.57 \times 10^{-3}$  and  $6.26 \times 10^{-2}$  mol l<sup>-1</sup> as described in Sections 4.1 and 2.3. The acid phase was made up by the addition of the appropriate volume of nitric acid to 300 ml of 76.45 per cent sulphuric acid. The organic phase comprised 50 ml of a 1 per cent solution (by volume) of toluene in 2,2,4-trimethylpentane. All the runs were performed at 25°C and 2,500 rev min<sup>-1</sup>. The linear initial portions of the absorbance

versus time plots obtained were converted into initial rates of reaction by multiplying by the calibration factor  $2.34 \times 10^{-4}$ , the determination of which has already been described in Section 4.1. The initial rates of reaction for each nitric acid concentration are shown in Table 7.

TABLE 7.

$[\text{HNO}_3]/\text{mol l}^{-1}$	$R/\text{mol l}^{-1} \text{ s}^{-1}$
$1.57 \times 10^{-3}$	5.62, $5.85 \times 10^{-6}$
$3.13 \times 10^{-3}$	$5.59 \times 10^{-6}$
$6.26 \times 10^{-3}$	$7.00 \times 10^{-6}$
$1.57 \times 10^{-2}$	$1.03 \times 10^{-5}$
$3.13 \times 10^{-2}$	$1.48 \times 10^{-5}$
$4.70 \times 10^{-2}$	$1.80 \times 10^{-5}$
$6.26 \times 10^{-2}$	2.11, $2.14 \times 10^{-5}$

4.3. DEPENDENCE OF THE INITIAL RATE OF NITRATION ON THE SULPHURIC ACID STRENGTH IN THE STIRRED CELL.

The initial rate of nitration of a 1 per cent solution of toluene in 2,2,4-trimethyl pentane was determined over a range of acid strengths between 75.60 and 81.50 per cent sulphuric acid as outlined in Section 2.2(a). The nitric acid concentration was kept constant for all the runs at  $6.26 \times 10^{-2} \text{ mol l}^{-1}$ . The temperature was maintained at  $25^\circ\text{C}$  and the stirring speed was  $50 \text{ rev min}^{-1}$ . The acid and organic phase volumes were 150 and 25 ml, respectively, giving rise to a modified interfacial area per unit volume of acid phase of  $0.229 \text{ cm}^2 \text{ cm}^{-3}$ . Samples of the organic phase (0.2ml) were diluted to 10 ml with hexane and analysed as before at 350nm. The least-squares slopes of the linear initial portions of the absorbance

versus time plots were converted into initial rates of reaction as before by multiplying by the calibration factor  $5.85 \times 10^{-4}$ . This value was obtained from the estimate previously made for the stirred reactor of  $2.34 \times 10^{-4}$  by allowing for the different organic and acid phase volumes and dilutions employed here. Table 8 shows the initial rate of nitration at each sulphuric acid strength.

#### 4.4. DISTRIBUTION COEFFICIENT OF TOLUENE BETWEEN ACID AND ORGANIC PHASES.

In order to know the concentration of toluene in the acid phase corresponding to a particular organic phase composition it is necessary to determine the distribution coefficient between the two phases. Thus the solubility of toluene in 69.90 per cent sulphuric acid was determined with various solutions of toluene in 2,2,4-trimethylpentane as the organic phase (Section 2.4). Due to the possibility of sulphonation at higher acid strengths 69.90 per cent sulphuric acid was used rather than 76.50 per cent. All the runs were performed at 25°C and the spectrophotometric determination of toluene in the hexane extract was made at 262 nm ( $\epsilon = 235$ ). Table 9 shows the solubility of toluene in 69.90 per cent sulphuric acid for each organic phase composition together with the distribution coefficient  $\delta$  (69.90%) given by Equation 28.

The solubility of toluene in 76.50 per cent sulphuric acid may be estimated by assuming that the concentration of toluene in the acid phase increases between 69.90 and 76.50 per cent acid by the same constant factor for each organic phase composition. This factor is given by the ratio of the saturation concentration<sup>1</sup> of toluene in 76.50 per cent sulphuric acid ( $[T]_a^s = 3.02 \times 10^{-3} \text{ mol l}^{-1}$ ) to that in 69.90 per cent acid ( $[T]_a^s = 2.19 \times 10^{-3} \text{ mol l}^{-1}$ ) which is equal

TABLE 8

% H <sub>2</sub> SO <sub>4</sub>	R/mol l <sup>-1</sup> s <sup>-1</sup>
75.60	8.42 x 10 <sup>-8</sup>
76.25	1.43 x 10 <sup>-7</sup>
77.85	2.77 x 10 <sup>-7</sup>
77.90	3.25 x 10 <sup>-7</sup>
78.05	2.88 x 10 <sup>-7</sup>
78.45	2.85, 3.06 x 10 <sup>-7</sup>
78.50	3.35 x 10 <sup>-7</sup>
78.65	4.29 x 10 <sup>-7</sup>
78.85	4.97 x 10 <sup>-7</sup>
79.10	4.00 x 10 <sup>-7</sup>
79.45	5.29 x 10 <sup>-7</sup>
79.50	7.08 x 10 <sup>-7</sup>
80.00	6.84 x 10 <sup>-7</sup>
80.50	8.54 x 10 <sup>-7</sup>
80.75	8.54 x 10 <sup>-7</sup>
81.05	1.15 x 10 <sup>-6</sup>
81.10	9.07 x 10 <sup>-7</sup>
81.50	1.19 x 10 <sup>-6</sup>

to 1.38. This leads to the values of the solubility in 76.50 per cent acid shown in Table 9 and the distribution coefficient at this acid strength,  $\gamma$  (76.50%).

$$\gamma = \frac{[T]_{\text{org}} \text{ (organic phase)}}{[T]_{\text{a}} \text{ (acid phase)}} \quad \dots\dots\dots 28$$

TABLE 9.

ORGANIC PHASE COMPOSITION (VOLUME PER CENT TOLUENE)	$[T]_{org-1}$ /mol l <sup>-1</sup>	$[T]_a$ (69.90%) /mol l <sup>-1</sup>	$\delta$ (69.90%)	$[T]_a$ (76.50%) /mol l <sup>-1</sup>	$\delta$ (76.50%)
100	9.380	$2.23 \times 10^{-3}$	4206	$3.08 \times 10^{-3}$	3048
60	5.630	$1.93 \times 10^{-3}$	2917	$2.66 \times 10^{-3}$	2114
30	2.810	$1.12 \times 10^{-3}$	2509	$1.55 \times 10^{-3}$	1818
10	0.938	$5.70 \times 10^{-4}$	1646	$7.87 \times 10^{-4}$	1193
8.5	0.797	$4.24 \times 10^{-4}$	1880	$5.85 \times 10^{-4}$	1362
7.0	0.657	$3.15 \times 10^{-4}$	2086	$4.35 \times 10^{-4}$	1512
5.0	0.469	$2.56 \times 10^{-4}$	1832	$3.53 \times 10^{-4}$	1328
4.0	0.375	$2.04, 2.20 \times 10^{-4}$	1838, 1705	$2.82, 3.04 \times 10^{-4}$	1332, 1236
3.0	0.281	$1.54 \times 10^{-4}$	1825	$2.13 \times 10^{-4}$	1322
2.0	0.188	$1.03 \times 10^{-4}$	1825	$1.42 \times 10^{-4}$	1322
1.0	0.094	$0.94, 0.82 \times 10^{-4}$	1000, 1146	$1.30, 1.13 \times 10^{-4}$	725, 830

COMMENT4.5. ZERO-TH-ORDER KINETICS IN THE HOMOGENEOUS PHASE

The nitration of aromatics in the mixed acid system has hitherto been assumed to follow typical second-order kinetic behaviour such that the rate of reaction is dependent upon the concentration of aromatic substrate and nitric acid in the aqueous sulphuric acid.

In the homogeneous system therefore:

$$R = k_2 [HNO_3] [ArH] \dots\dots\dots 29$$

For the two phase nitration of aromatics in the fast reaction regime it follows that rate is governed by:

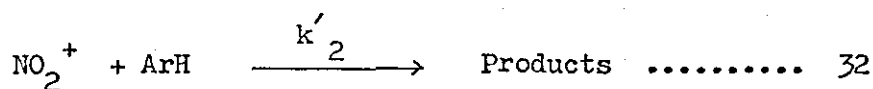
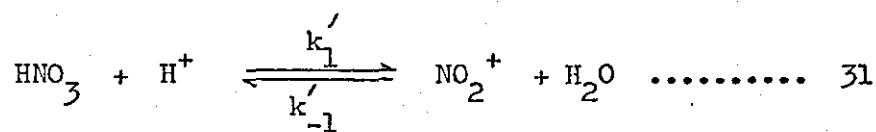
$$R_1 = a' \sqrt{k_2 D [HNO_3]} \cdot [ArH]_a^s \dots\dots\dots 30$$

where the rate of reaction is still dependent upon the first power of



the aromatic substrate concentration. Under suitable conditions, however, nitration in the homogeneous phase may become independent of the aromatic substrate concentration i.e. zeroth-order with respect to aromatic. Ingold and coworkers<sup>2</sup> were the first to report zeroth-order kinetics in the nitration of reactive substrates in organic solvents. Under these conditions, they argued, the rate determining step ceases to be the electrophilic attack by nitronium ion on the aromatic substrate but the ionization of the nitric acid.

The nitration of aromatics in mixed acid may be simply written as:



In theory either Reaction 31 or Reaction 32 may be the rate controlling step. For the general case, where either possibility can obtain, the rate equation is arrived at via the steady-state assumption:

Rate of formation of nitronium ions = rate of removal of nitronium ions

i.e.  $k'_1 [\text{HNO}_3] [\text{H}^+] = (k'_{-1} [\text{H}_2\text{O}] + k'_2 [\text{ArH}]) [\text{NO}_2^+] \dots\dots 33$

Thus,  $[\text{NO}_2^+] = \frac{k'_1 [\text{HNO}_3] [\text{H}^+]}{k'_{-1} [\text{H}_2\text{O}] + k'_2 [\text{ArH}]} \dots\dots\dots 34$

The rate of reaction is now given by:

$$R = k'_2 [\text{NO}_2^+] [\text{ArH}] = \frac{k'_2 k'_1 [\text{HNO}_3] [\text{H}^+] [\text{ArH}]}{k'_{-1} [\text{H}_2\text{O}] + k'_2 [\text{ArH}]} \dots\dots\dots 35$$

Under normal first-order conditions  $k'_{-1} [\text{H}_2\text{O}] \gg k'_2 [\text{ArH}]$  and:

$$R = \frac{k'_2 k'_1 [\text{HNO}_3] [\text{H}^+]}{k'_{-1} [\text{H}_2\text{O}]} \cdot [\text{ArH}] \dots\dots\dots 29$$

$$= k_2 [\text{HNO}_3] [\text{ArH}] \dots\dots\dots 29$$

where  $k_2 = \frac{k'_2 k'_1 [\text{H}^+]}{k'_{-1} [\text{H}_2\text{O}]} = \frac{k'_2 [\text{NO}_2^+]}{[\text{HNO}_3]} \dots\dots\dots 36$

Under zeroth-order conditions, however,  $k'_{-1} [\text{H}_2\text{O}] \ll k'_2 [\text{ArH}]$  and:

$$R = k'_1 [\text{HNO}_3] [\text{H}^+] \dots\dots\dots 37$$

Thus the rate of reaction is independent of the aromatic substrate concentration and governed only by the rate of formation of nitronium ions from nitric acid at a particular sulphuric acid strength.

#### 4.6. HALF-ORDER KINETICS IN THE TWO PHASE SYSTEM

The change in rate determining step in the homogeneous phase has a significant effect on the rate of nitration in the two phase system. Consider a system where the rate of nitration in the fast reaction regime is solely governed by the ionization of the nitric acid i.e. pure zeroth-order kinetics applies. The diffusion process is now governed by:

$$D \frac{d^2c}{dx^2} = k'_1 [\text{H}^+] [\text{HNO}_3] \dots\dots\dots 38$$

This differential equation may be solved by putting  $\frac{d^2c}{dx^2} = 2A$  and

integrating to give:

$$c = A(1-x)^2 \quad \dots\dots\dots 39$$

The concentration gradient is given by:

$$\frac{dc}{dx} = -2A(1-x) \quad \dots\dots\dots 40$$

Both equations satisfy the boundary conditions  $x = 0, c = c_a$  and  $x = 1, c = 0$ ,

$$\frac{dc}{dx} = 0$$

Now, from Equation 38:  $A = \frac{k'_1 [\text{HNO}_3][\text{H}^+]}{2D}$

If  $x = 0, c = [\text{ArH}]_a^s$  and from Equation 39:

$$1 = \sqrt{\frac{[\text{ArH}]_a^s}{A}} = \sqrt{\frac{2D [\text{ArH}]_a^s}{k'_1 [\text{HNO}_3][\text{H}^+]}}$$

and the concentration gradient at the interface is given by:

$$\left(\frac{dc}{dx}\right)_{x=0} = -2A1$$

Assuming that the rate of mass transfer is given by:

$$\bar{V} = -D \left(\frac{dc}{dx}\right)_{x=0} = 2AD1$$

the overall rate of reaction is given by:

$$R_o = \bar{V}a' = a' \sqrt{2Dk'_1 [\text{HNO}_3][\text{H}^+][\text{ArH}]_a^s} \quad \dots\dots\dots 41$$

The above equation predicts a half-order dependence of the rate on the aromatic substrate concentration in the acid phase.

The onset of zeroth-order kinetics in the two phase system would result in a suppression of the rate of reaction compared to

the rate expected assuming first-order kinetics given by:

$$\frac{R_o}{R_1} = \sqrt{\frac{2k'_1 [H^+]}{k'_2 [ArH]_a^s}} \dots\dots\dots 42$$

Substitution of Equation 36 into the above results in:

$$\frac{R_o}{R_1} = \sqrt{\frac{2k'_{-1} [H_2O]}{k'_2 [ArH]_a^s}} \dots\dots\dots 43$$

The fall-off of the rate of reaction in the fast reaction regime under these conditions is dependent upon the ratio  $\frac{k'_{-1} [H_2O]}{k'_2 [ArH]_a^s}$ .

In the case of toluene  $k'_2 [ArH]_a^s$  remains virtually constant as the sulphuric acid strength increases,  $k'_2$  taking the encounter control value at each acid strength, whereas  $k'_{-1} [H_2O]$  decreases with increasing acid strength. The ratio  $\frac{R_o}{R_1}$  would thus decrease with increasing sulphuric acid strength.

The postulation of a changeover in the kinetics of nitration as described above provides an explanation for the results of Cox's work on toluene in the range 70-80 per cent sulphuric acid, where the initial rates of nitration both in the stirred reactor and stirred cell were well below that predicted by Danckwerts' Surface Renewal Theory. If, in this acid range, the nitration of toluene in these systems was changing from one of first-order with respect to toluene to one of zeroth-order in the acid phase Schofield's<sup>4</sup> values of  $k_2$  would no longer apply and the slopes of the Danckwerts plots would be low. To test this hypothesis the rate of nitration of toluene in the stirred reactor and stirred cell was redetermined using an acid phase

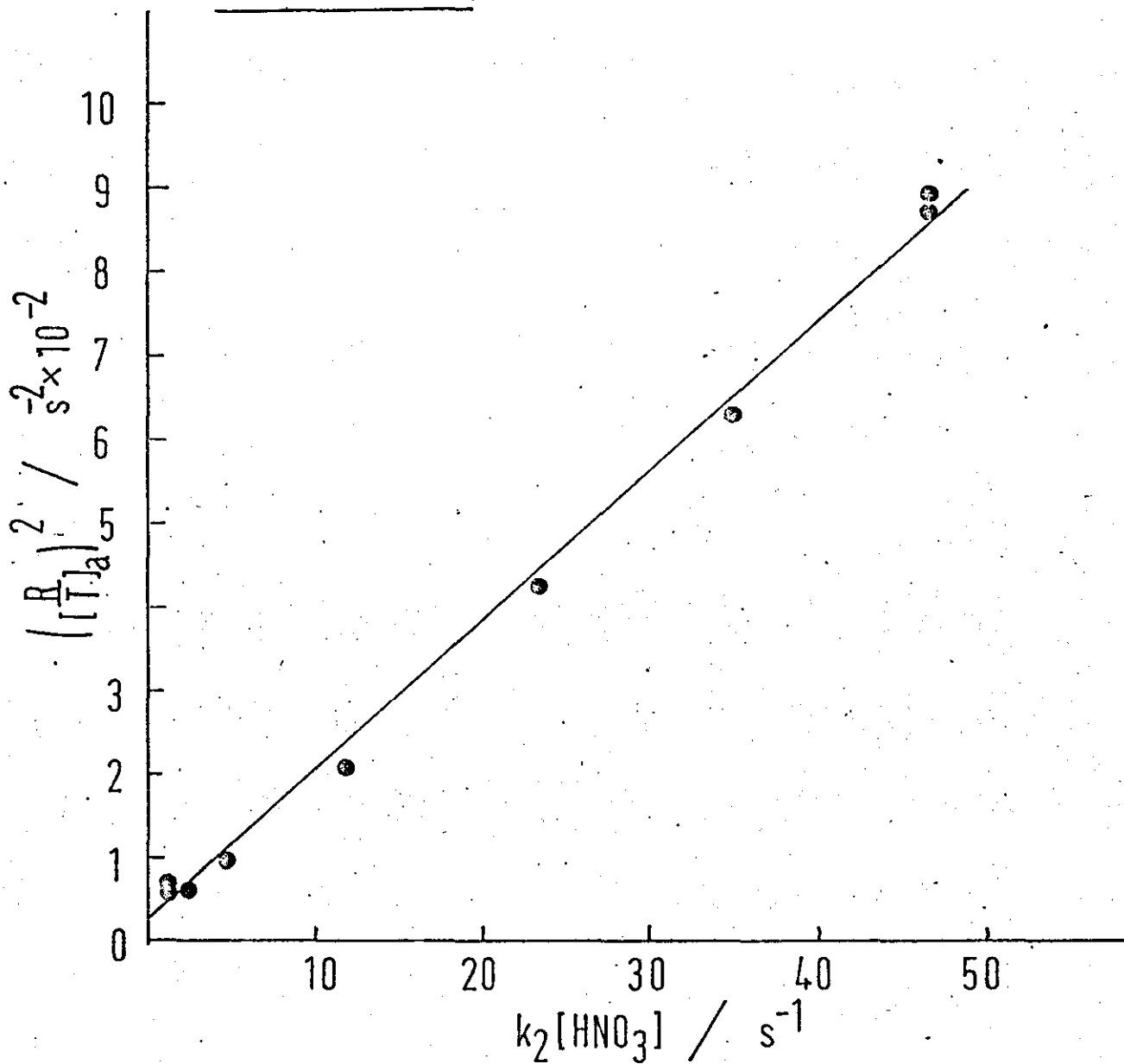
concentration of toluene appreciably lower than that used by Cox. Since the exact order of reaction with respect to toluene is governed by the relative magnitudes of  $k'_2 [\text{ArH}]$  and  $k'_{-1} [\text{H}_2\text{O}]$  and the low concentration of toluene would expect to favour first-order kinetics, the subsequent Danckwerts plots should yield reasonable values of  $a'$  and  $k_L$ .

#### 4.7. DANCKWERTS PLOT FOR THE STIRRED REACTOR.

The results of the stirred reactor nitrations described in Section 4.2. are consistent with reaction occurring in the transition region between fast reaction and slow reaction diffusional regimes. The nitric acid concentrations employed are, of course, appreciably smaller than those used by Cox. This has the effect of shifting the plateau region due to the slow reaction diffusional regime to the right in Figure 2. The transition to the fast reaction regime will then occur at a higher sulphuric acid strength. Figure 12 shows a Danckwerts plot based on the rate data in Table 7 with a sulphuric acid strength of 76.45 per cent. It shows a good correlation to a straight line.

The solubility of toluene in the acid phase,  $[\text{T}]_a$ , corresponding to an organic phase composition of 1 per cent toluene in 2,2,4-trimethylpentane, and necessary for the construction of the Danckwerts plot, was estimated by assuming a mean value for the distribution coefficient in 76.50 per cent sulphuric acid. For the lowest concentrations of toluene in the organic phase this was 1310 (Table 9). Given that a 1 per cent solution contains  $9.38 \times 10^{-2} \text{ mol l}^{-1}$  of toluene,  $[\text{T}]_a$  is estimated at  $7.16 \times 10^{-5} \text{ mol l}^{-1}$ . The second-order rate coefficient,  $k_2$ , and diffusivity,  $D$ , in this sulphuric acid strength were estimated from the data of Cox<sup>1</sup> at  $741 \text{ l mol}^{-1} \text{ s}^{-1}$  and  $0.92 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  respectively.

Fig.12 Danckwerts plot for the nitration  
of a dilute solution of toluene in the  
stirred reactor.



The least-squares line through the points in Figure 12 yields a slope and intercept of  $1.82 \times 10^{-3} \text{ s}^{-1}$  and  $2.09 \times 10^{-3} \text{ s}^{-2}$ , respectively. The slope may be compared with that obtained by Cox with an organic phase of pure toluene in the stirred reactor (Table 2). In the previously reported<sup>16</sup> stirred reactor runs in the transition region between slow reaction diffusional and kinetic regimes  $a'k_L$  had the value of  $0.069 \text{ s}^{-1}$ . Under these conditions i.e. in acid strengths between 62.40 and 71.60 per cent sulphuric acid, first-order kinetics are considered to prevail and thus the value of  $a'k_L$  should be a reasonable estimate for the system. If  $k_L$  is assumed to have a normal value of ca.  $10^{-3} \text{ cm s}^{-1}$ ,  $a'$  must be ca.  $69 \text{ cm}^2 \text{ cm}^{-3}$ . This may be combined with a mean calculated diffusivity for toluene in the acid range 70-80 per cent sulphuric acid to give a predicted value of ca.  $5 \times 10^{-3} \text{ s}^{-1}$  for the slope of the Danckwerts plot. Cox's experimental value is  $1.9 \times 10^{-5} \text{ s}^{-1}$  with a pure toluene organic phase, more than 250 times smaller.

The slope of the least-squares line through the points in Figure 12, if equated with  $a'^2 D$ , gives a value for  $a'$  of  $44.5 \text{ cm}^2 \text{ cm}^{-3}$ . Likewise, the intercept, if set equal to  $(a'k_L)^2$ , leads to a value for  $k_L$  of  $1.03 \times 10^{-3} \text{ cm s}^{-1}$ . Thus the Danckwerts plot with diluted toluene gives reasonable values of  $a'$  and  $k_L$  in marked contrast to the behaviour of pure toluene. The conclusion is drawn that with the nitration of pure toluene in the stirred reactor in the transition region between slow diffusional and fast reaction regimes (71.60-77.75 per cent sulphuric acid) first-order kinetics with respect to the concentration of toluene in the acid phase is rapidly being displaced by zeroth-order kinetics in the acid phase. If, however, the organic phase is sufficiently diluted, such that the concentration of toluene in the acid phase is ca. 40 times lower, first-order kinetics may be restored and the initial rate of nitration is once more governed by Equation 25.

#### 4.8. DANCKWERTS PLOT FOR THE STIRRED CELL

The results of the stirred cell nitrations at different sulphuric acid strengths in the transition region between slow reaction diffusional and fast reaction regimes, shown in Table 8, permit us to confirm the observations made with the stirred reactor. However, the data obtained showed considerably poorer reproducibility than that from the stirred reactor and a Danckwerts plot was not constructed. There are two probable reasons for the irreproducibility between runs. First is the error involved in estimating the sulphuric acid strength by titration ( $\pm 0.1$  per cent). Second, and probably most important, is the small absorbance differences observed which were at the limit of measurement by this procedure. The principal limitation was the volume of organic phase that could be withdrawn and diluted without significantly affecting the volume of the organic phase during the course of the run. The data obtained may be more conveniently treated by means of a statistical average.

The corresponding values of  $[T]_a$  and  $k_2$  at each sulphuric acid strength were obtained. The values of  $k_2$  were interpolated from a plot of  $\log k_2$  versus percentage sulphuric acid based on the data of Cox<sup>1</sup> and which was linear over this acid range. The solubility of toluene in each acid strength corresponding to an organic phase composition of 1 per cent toluene in 2,2,4-trimethylpentane was estimated by the procedure described in Section 4.4, by assuming the concentration of toluene in the acid phase increased with increasing acid strength by the same factor by which the saturation concentration changed from that at 69.90 per cent sulphuric acid. The value of  $[T]_a$  in 69.90 per cent acid corresponding to a 1 per cent organic phase was estimated from the mean distribution coefficient of 1810 at this acid strength. Table 10 includes all the data necessary for the



construction of a Danckwerts plot, including values of  $[T]_a^s$  at each acid strength interpolated from the data of Cox<sup>1</sup>. Also included is the value of the quotient

$$\frac{\left(\frac{R}{[T]_a}\right)^2}{k_2[\text{HNO}_3]}$$

The theoretical intercept of a Danckwerts plot based on the above data may be estimated by assuming a normal value of  $k_L$  of ca.  $10^{-3} \text{ cm s}^{-1}$  and the interfacial area per unit volume of acid phase of  $0.229 \text{ cm}^2 \text{ cm}^{-3}$ . The maximum value of the intercept is given by  $(a' k_L)^2$  at  $5.6 \times 10^{-8} \text{ s}^{-2}$ . Since at low reaction rates in the stirred cell poor surface renewal leads to a lowering of the  $k_L$  value (Chapter 3) the intercept is probably lower than this. Comparison of the intercept value with the values of  $\left(\frac{R}{[T]_a}\right)^2$  in Table 10 indicates that with all the data the intercept is negligible and the value of the quotient accurately gives the slope of the Danckwerts plot at each acid strength. The average of the quotients shown in Table 10 gives an observed Danckwerts slope of  $7.4 \times 10^{-8} \text{ s}^{-1}$  with a standard deviation of  $2.2 \times 10^{-8} \text{ s}^{-1}$ ,

The observed value of the slope shows reasonable agreement with the predicted value of ca.  $4 \times 10^{-8} \text{ s}^{-1}$  given by  $a'^2 D$  and calculated assuming a mean diffusivity in 75.60-81.50 per cent sulphuric acid of  $0.81 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ .<sup>1</sup> It contrasts with the behaviour in the stirred cell containing pure toluene as observed by Cox<sup>1</sup> where the slope was  $1.31 \times 10^{-9} \text{ s}^{-1}$ , some 30 times lower than the predicted assuming first-order kinetics. The results of the stirred cell study therefore confirm, within experimental error, the observations made with the stirred reactor. With a pure toluene organic phase first-order kinetics are being replaced by zeroth-order behaviour in the sulphuric acid range 75.60-81.50 per cent but virtually pure first-order kinetics may be restored by use of a sufficiently dilute organic phase.

TABLE 10

$\%H_2SO_4$	$k_2/1 \text{ mol}^{-1} \text{ s}^{-1}$	$[T]_a^s/\text{mol l}^{-1}$	$k_2[HNO_3]/\text{s}^{-1}$	$[T]_a/\text{mol l}^{-1}$	$(\frac{R}{[T]_a})^2/\text{s}^{-2}$	$\frac{(R/[T]_a)^2}{k_2[HNO_3]}/\text{s}^{-1}$
75.60	355	$2.93 \times 10^{-3}$	22.2	$6.93 \times 10^{-5}$	$1.48 \times 10^{-6}$	$6.67 \times 10^{-8}$
76.25	631	$3.01 \times 10^{-3}$	39.5	$7.12 \times 10^{-5}$	$4.05 \times 10^{-6}$	$10.3 \times 10^{-8}$
77.85	2512	$3.20 \times 10^{-3}$	157	$7.58 \times 10^{-5}$	$1.33 \times 10^{-5}$	$8.47 \times 10^{-8}$
77.90	2630	$3.21 \times 10^{-3}$	165	$7.60 \times 10^{-5}$	$1.83 \times 10^{-5}$	$11.1 \times 10^{-8}$
78.05	2985	$3.23 \times 10^{-3}$	187	$7.64 \times 10^{-5}$	$1.43 \times 10^{-5}$	$7.65 \times 10^{-8}$
78.45	4220	$3.27 \times 10^{-3}$	264	$7.75 \times 10^{-5}$	$1.35, 1.56 \times 10^{-5}$	$5.11, 5.91 \times 10^{-8}$
78.50	4416	$3.28 \times 10^{-3}$	277	$7.77 \times 10^{-5}$	$1.86 \times 10^{-5}$	$6.71 \times 10^{-8}$
78.65	4955	$3.30 \times 10^{-3}$	310	$7.81 \times 10^{-5}$	$3.01 \times 10^{-5}$	$9.71 \times 10^{-8}$
78.85	5957	$3.32 \times 10^{-3}$	373	$7.87 \times 10^{-5}$	$3.99 \times 10^{-5}$	$10.7 \times 10^{-8}$
79.10	7586	$3.36 \times 10^{-3}$	475	$7.95 \times 10^{-5}$	$2.53 \times 10^{-5}$	$5.33 \times 10^{-8}$
79.45	10000	$3.40 \times 10^{-3}$	627	$8.05 \times 10^{-5}$	$4.33 \times 10^{-5}$	$6.91 \times 10^{-8}$
79.50	10720	$3.41 \times 10^{-3}$	671	$8.07 \times 10^{-5}$	$7.69 \times 10^{-5}$	$11.5 \times 10^{-8}$
80.0	15850	$3.46 \times 10^{-3}$	993	$8.20 \times 10^{-5}$	$6.97 \times 10^{-5}$	$7.02 \times 10^{-8}$
80.50	25120	$3.53 \times 10^{-3}$	1570	$8.35 \times 10^{-5}$	$1.05 \times 10^{-4}$	$6.69 \times 10^{-8}$
80.75	31990	$4.56 \times 10^{-3}$	2000	$8.43 \times 10^{-5}$	$1.03 \times 10^{-4}$	$5.15 \times 10^{-8}$
81.05	40740	$3.59 \times 10^{-3}$	2550	$8.51 \times 10^{-5}$	$1.82 \times 10^{-4}$	$7.14 \times 10^{-8}$
81.10	41690	$3.60 \times 10^{-3}$	2610	$8.52 \times 10^{-5}$	$1.13 \times 10^{-4}$	$4.33 \times 10^{-8}$
81.50	61660	$3.65 \times 10^{-3}$	3860	$8.65 \times 10^{-5}$	$1.90 \times 10^{-4}$	$4.92 \times 10^{-8}$

#### 4.9. THE KINETIC ORDER IN THE STIRRED REACTOR.

Further confirmation of the restored first-order kinetics with a diluted organic phase comes from the results shown in Table 6. They may be combined with the values of the distribution coefficient shown in Table 9 to give an estimate of the kinetic order with respect to toluene in 76.50 per cent sulphuric acid. Figure 13 shows the concentration of toluene in the acid phase as a function of organic phase composition. A positive deviation from ideal behaviour is observed with organic phase compositions varying between pure 2,2,4-trimethylpentane and pure toluene and all the points fall above the line drawn through the saturation value. Over the small range of organic phase compositions for which the runs in Table 6 were made, however,  $\gamma$  (76.50%) may be considered to remain constant and take the mean value of 1310. This allows values of  $[T]_a$  for each organic phase composition to be calculated.

Figure 14 shows a plot of  $\log R$  versus  $\log [T]_a$  for the nitration of a dilute solution of toluene in 76.50 per cent acid. A good correlation to a straight line is obtained with a least-squares slope of 0.88. This is reasonably close to the predicted first-order dependence indicated by the Danckwerts plot for the stirred reactor. While the deviation from unity may be due to the order being intermediate between 1.0 and 0.5, it is more likely that it is just due to experimental error.

#### 4.10 ESTIMATION OF $k_1$ FROM PREVIOUS STIRRED CELL DATA

Equation 41 allows us to estimate an important parameter,  $k_1 = k'_1 [H^+]$ , the rate coefficient for the formation of nitronium ions from nitric acid in aqueous sulphuric acid. If, at the highest acid strength for which the initial rate of nitration was determined for

Fig.13 The solubility of toluene in 76.50 % sulphuric acid as a function of organic phase composition.

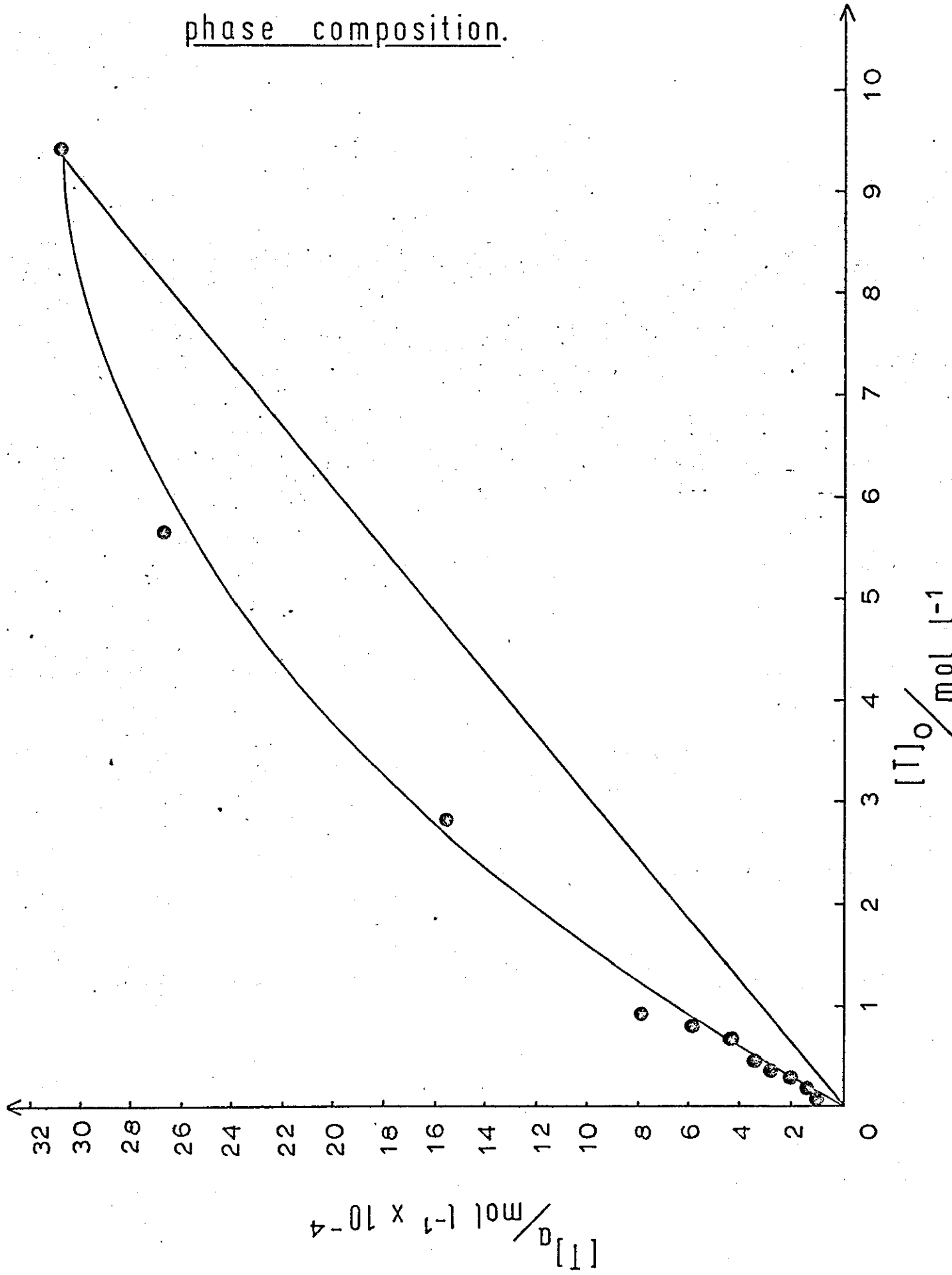
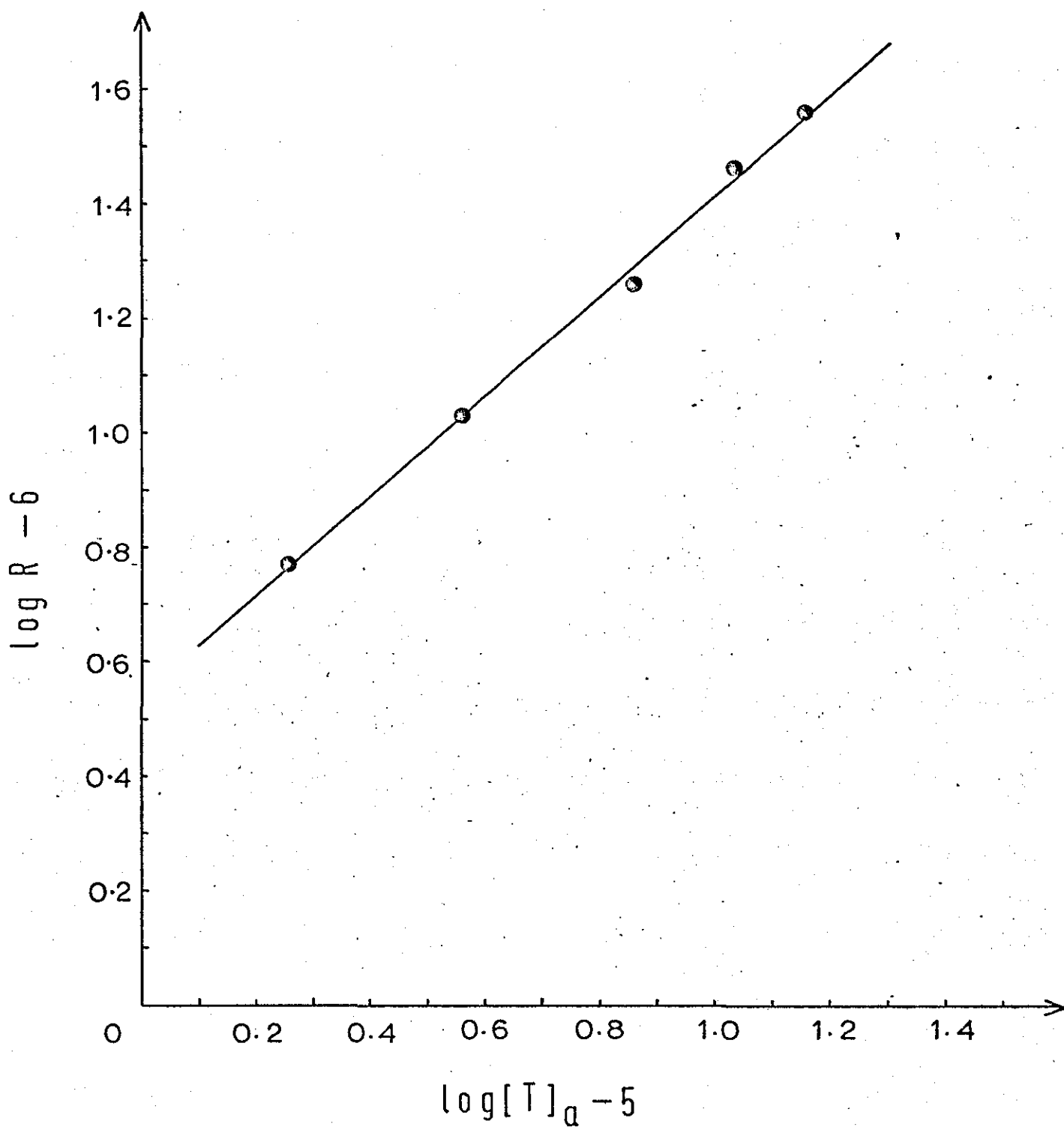


Fig.14 Kinetic order of nitration of a dilute solution of toluene in the stirred reactor.



pure toluene in the stirred cell<sup>1</sup> (78.45 per cent sulphuric acid,  $R = 7.00 \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$ ), pure zeroth-order kinetics prevail with reaction in the fast reaction regime, insertion of the data of Cox<sup>1</sup> into Equation 41 leads to a value of  $k_1 = 0.40 \text{ s}^{-1}$  at this acid strength and at 25°C.

## CHAPTER 5.

### CHANGE IN THE KINETIC ORDER OF NITRATION WITH RESPECT TO AROMATIC IN THE HOMOGENEOUS SYSTEM

The successful interpretation of the results of the two phase nitration of toluene in the high sulphuric acid range, based on a change of kinetic order from first to zero with respect to toluene in the acid phase, immediately gave rise to speculation that the changeover in rate controlling step might be more directly observed in the homogeneous system itself. The homogeneous nitration of reactive substrates such as toluene and xylene in mixed acid media has been extensively studied by Schofield et al<sup>4</sup> and Deno and Stein<sup>37</sup>. They determined the value of the second-order rate coefficient,  $k_2$ , in sulphuric and perchloric acids for a number of aromatics. For half lives greater than 2 minutes they<sup>4</sup> used a conventional spectrophotometric technique whereas for half-lives greater than 50ms a stopped-flow apparatus was necessary. This, for example, allowed values of  $k_2$  to be obtained up to the limit of measurement for toluene in sulphuric acid strengths of ca.80 per cent at 25°C. Schofield utilized aromatic substrate concentrations between  $10^{-4}$  and  $10^{-5}$  mol l<sup>-1</sup> and the nitric acid concentration, which was always at least 10 fold in excess, varied between  $1.2 \times 10^{-4}$  and  $5.5 \times 10^{-2}$  mol l<sup>-1</sup>. Pseudo-first-order kinetics with respect to the aromatic were apparently observed throughout the acid range and with all the aromatic substrates studied including toluene. Our first intention was to try and repeat some of the results with toluene using our own stopped-flow apparatus.

#### 5.1. THE NITRATION OF TOLUENE

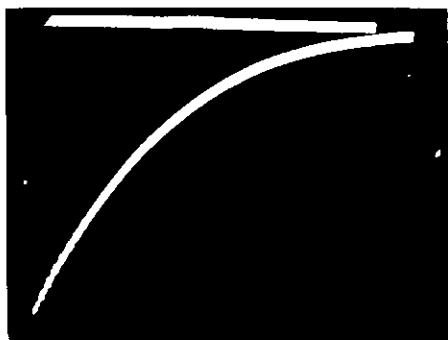
Two series of runs were performed in which the effect of sulphuric acid strength was observed on the nitration of toluene at 25°C. In each case at least a ten fold excess of nitric acid was.

employed by adding aqueous nitric acid (Analar grade, s.g. 1.42, 0.24 ml) to 100 ml of aqueous sulphuric acid giving a solution of  $1.88 \times 10^{-2} \text{ mol l}^{-1}$  in nitric acid. The two series differed essentially in the aromatic substrate concentration used. In the first series a toluene concentration of ca.  $4 \times 10^{-4} \text{ mol l}^{-1}$  after mixing was used whereas in the second a concentration of  $1.4 \times 10^{-3} \text{ mol l}^{-1}$  after mixing. Since the saturation concentration of toluene in aqueous sulphuric acid in the range 70-80 per cent lies between  $2 - 4 \times 10^{-3} \text{ mol l}^{-1}$  this means that a virtually saturated solution of toluene resulted for the second series of runs before mixing in the stopped-flow apparatus. In the first series the Chance-Pilkington glass filter and infra-red water cell were used and the traces were recorded on the storage oscilloscope. With the second series of runs the grating monochromator was used at a wavelength setting of 350nm and slit width of 5mm. This gave a bandwidth of 50nm. At this wavelength the extinction coefficients of toluene and nitrotoluenes are so different that the absorption due to the toluene becomes negligible and only the accumulation of nitroproducts is observed. The traces were displayed on the conventional oscilloscope and photographed so that accurate measurements could be taken. Three typical photographs are shown in Figure 15.

(a) RUNS WITH A LOW AROMATIC SUBSTRATE CONCENTRATION

In the first series of runs the oscilloscope traces showed typical exponential curvature at low sulphuric acid strengths suggesting pseudo-first-order kinetics with respect to toluene. Conventional first-order plots of  $\ln (A_{\infty} - A)$  versus time, where A was the voltage corresponding to a particular absorbance, proved linear up to an acid strength of 78.20 per cent sulphuric acid. They allowed estimates of the pseudo-first-order rate coefficient, and hence the second-order

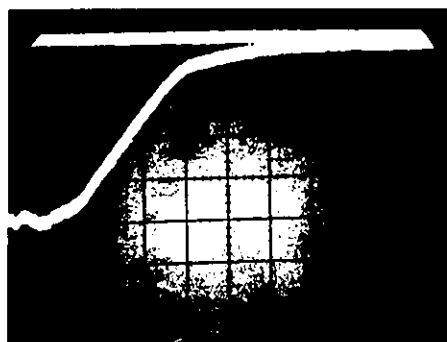




74.7%  $H_2SO_4$



Fig.15 Stopped flow  
oscilloscope traces  
for the nitration  
of toluene in  
sulphuric acid  
at 25° C.



81.45%

rate coefficient, to be determined. These are shown for the various acid strengths in Table 11.

TABLE 11.

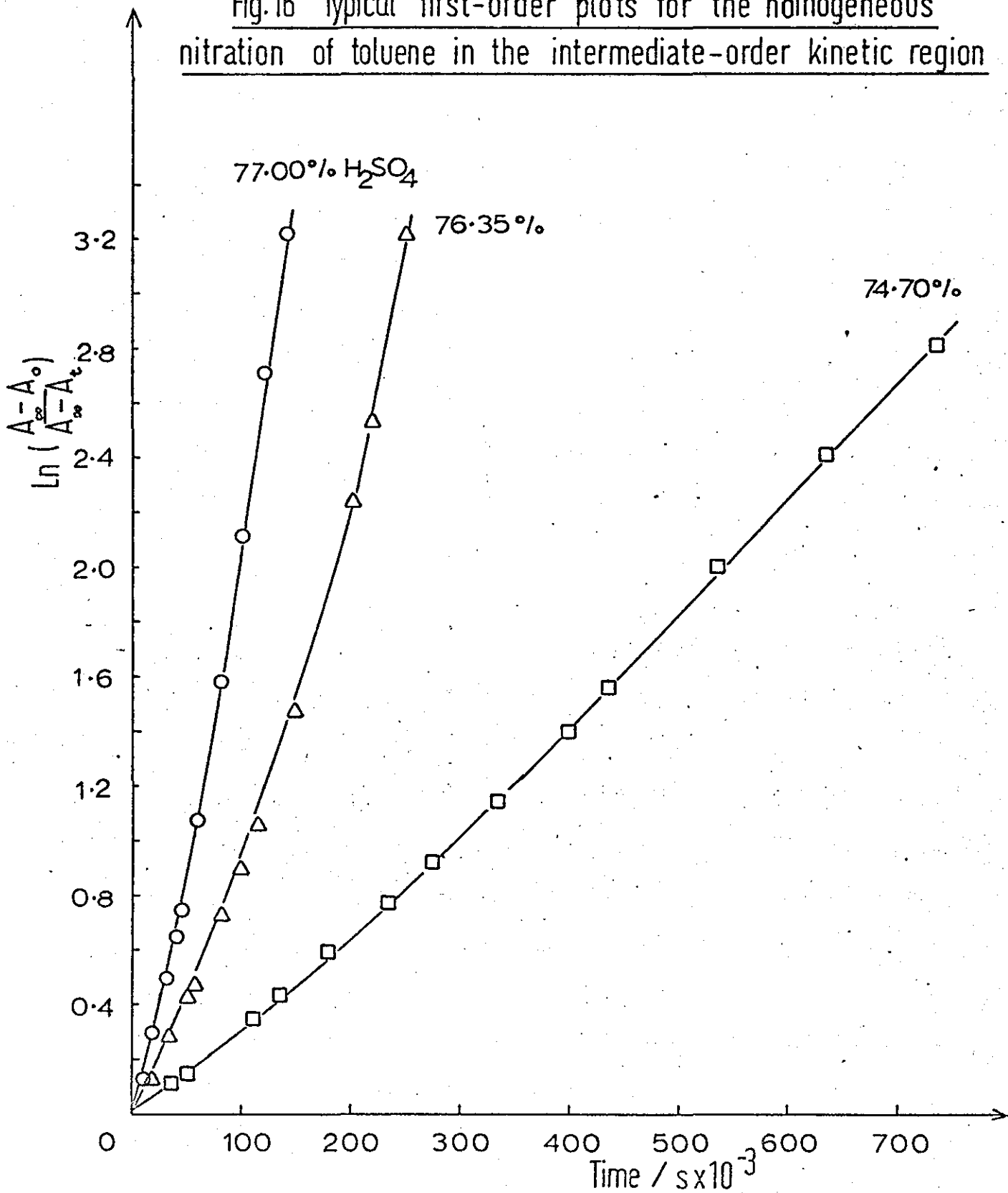
% H <sub>2</sub> SO <sub>4</sub>	k <sub>2</sub> /l mol <sup>-1</sup> s <sup>-1</sup>
73.70	146
74.35	200
76.05	731
77.15	1761
77.95	3218
78.20	3595

At acid strengths greater than 78.20 per cent, however, first-order logarithmic plots ceased to remain linear. Furthermore, the oscilloscope traces began to show a linearity during the initial stages of the run before reverting to the usual exponential curvature at the end of the run. As the sulphuric acid strength was increased so the linear portion extended further into the exponential part of the trace. Both observations are indicative of the onset of zeroth-order kinetics in the system. Thus, during the early part of the reaction, when the toluene concentration is at its highest, the rate of reaction is independent of the aromatic substrate concentration and governed only by the rate of ionization of nitric acid to nitronium ions. The results of the runs performed with substrate concentrations near to the saturation limit allow the effect to be put onto a more quantitative basis.

(b) RUNS WITH A NEAR SATURATION SUBSTRATE CONCENTRATION

In the second series of runs, with aromatic substrate concentrations much closer to the saturation limit, none of the runs showed completely pseudo-first-order kinetic behaviour, even at sulphuric acid strengths as low as 74.70 per cent. Figure 16 shows

Fig.16 Typical first-order plots for the homogeneous nitration of toluene in the intermediate-order kinetic region



some typical first-order logarithmic plots for these runs. They show considerable curvature during the early part of the reaction. The oscilloscope traces themselves showed considerable deviation from the normal exponential curvature; the linearity at the start of the run becoming more pronounced as the sulphuric acid strength was increased such that, at the highest acid strength attainable (81.45 per cent), the rate was observed to increase linearly with time virtually to completion (Figure 15). Under these conditions zeroth-order kinetics are dominant over first-order kinetics and the rate of nitration is constant until virtually all of the toluene has reacted whereupon the reaction suddenly stops.

Analysis of the oscilloscope traces obtained in the transition region between first and zeroth-order kinetics is possible by assuming the general, steady-state, equation for the consumption of nitronium ions by either reversal of Equation.31 or by reaction with aromatic substrate i.e.

$$-\frac{d[\text{ArH}]}{dt} = \frac{k'_2 k'_1 [\text{HNO}_3] [\text{H}^+] [\text{ArH}]}{k'_{-1} [\text{H}_2\text{O}] + k'_2 [\text{ArH}]} \dots\dots\dots 44$$

Inversion and separation of the variables gives:

$$-\left( \frac{k'_{-1} [\text{H}_2\text{O}]}{[\text{ArH}]} + k'_2 \right) \cdot d[\text{ArH}] = k'_2 k'_1 [\text{H}^+] [\text{HNO}_3] dt \dots\dots\dots 45$$

Integration of both sides gives:

$$k'_{-1} [\text{H}_2\text{O}] \ln [\text{ArH}] + k'_2 [\text{ArH}] = -k'_2 k'_1 [\text{H}^+] [\text{HNO}_3] t + \text{constant}$$

Now, when  $t = 0$ ,  $[\text{ArH}] = [\text{ArH}]_0$ , the initial concentration of aromatic substrate.

Therefore,

$$k'_{-1} [\text{H}_2\text{O}] \ln \frac{[\text{ArH}]}{[\text{ArH}]_0} + k'_2 ([\text{ArH}]_0 - [\text{ArH}]) = k'_2 k'_1 [\text{H}^+] [\text{HNO}_3] \cdot t \dots\dots 46$$

The concentration of aromatic may be converted into absorbance (or more correctly, the voltage measured by the oscilloscope, A) since:

$$\frac{[\text{ArH}]_0}{[\text{ArH}]} = \frac{A_\infty - A_0}{A_\infty - A_t}$$

and

$$[\text{ArH}]_0 - [\text{ArH}] = [\text{ArH}]_0 \left( \frac{A_t - A_0}{A_\infty - A_0} \right)$$

where the subscripts t and  $\infty$  refer to the voltage after time t and infinite time respectively.

Substitution into Equation 46 gives:

$$\left( \frac{A_\infty - A_0}{A_t - A_0} \right) \ln \left( \frac{A_\infty - A_0}{A_\infty - A_t} \right) + \frac{k'_2 [\text{ArH}]_0}{k'_{-1} [\text{H}_2\text{O}]} = \frac{k'_2 k_1 [\text{H}^+] [\text{HNO}_3]}{k'_{-1} [\text{H}_2\text{O}]} \left( \frac{A_\infty - A_0}{A_t - A_0} \right)_t \dots 47$$

Plots of  $\left( \frac{A_\infty - A_0}{A_t - A_0} \right) \ln \left( \frac{A_\infty - A_0}{A_\infty - A_t} \right)$  versus  $\left( \frac{A_\infty - A_0}{A_t - A_0} \right)_t$  should be linear

with a slope of  $k_2 [\text{HNO}_3]$  and intercept  $\frac{[\text{ArH}]_0}{k'_1 [\text{HNO}_3] [\text{H}^+]}$  when

$\left( \frac{A_\infty - A_0}{A_t - A_0} \right) \ln \left( \frac{A_\infty - A_0}{A_\infty - A_t} \right)$  is equal to zero.

Alternatively, if the initial portion of the oscilloscope trace is sufficiently linear to permit an accurate measurement of its slope i.e. virtually pure zeroth-order kinetics prevail, then

$\frac{k'_2 [\text{ArH}]_0}{k'_{-1} [\text{H}_2\text{O}]}$  is large compared to  $\left( \frac{A_\infty - A_0}{A_t - A_0} \right) \ln \left( \frac{A_\infty - A_0}{A_\infty - A_t} \right)$

and the latter in Equation 47 may be ignored and:

$$(A_t - A_0) = \frac{k'_1 [H^+] [HNO_3]}{[ArH]_0} \cdot (A_\infty - A_0) \cdot t \quad \dots\dots\dots 48$$

The slope of the initial portion of the trace is then given by

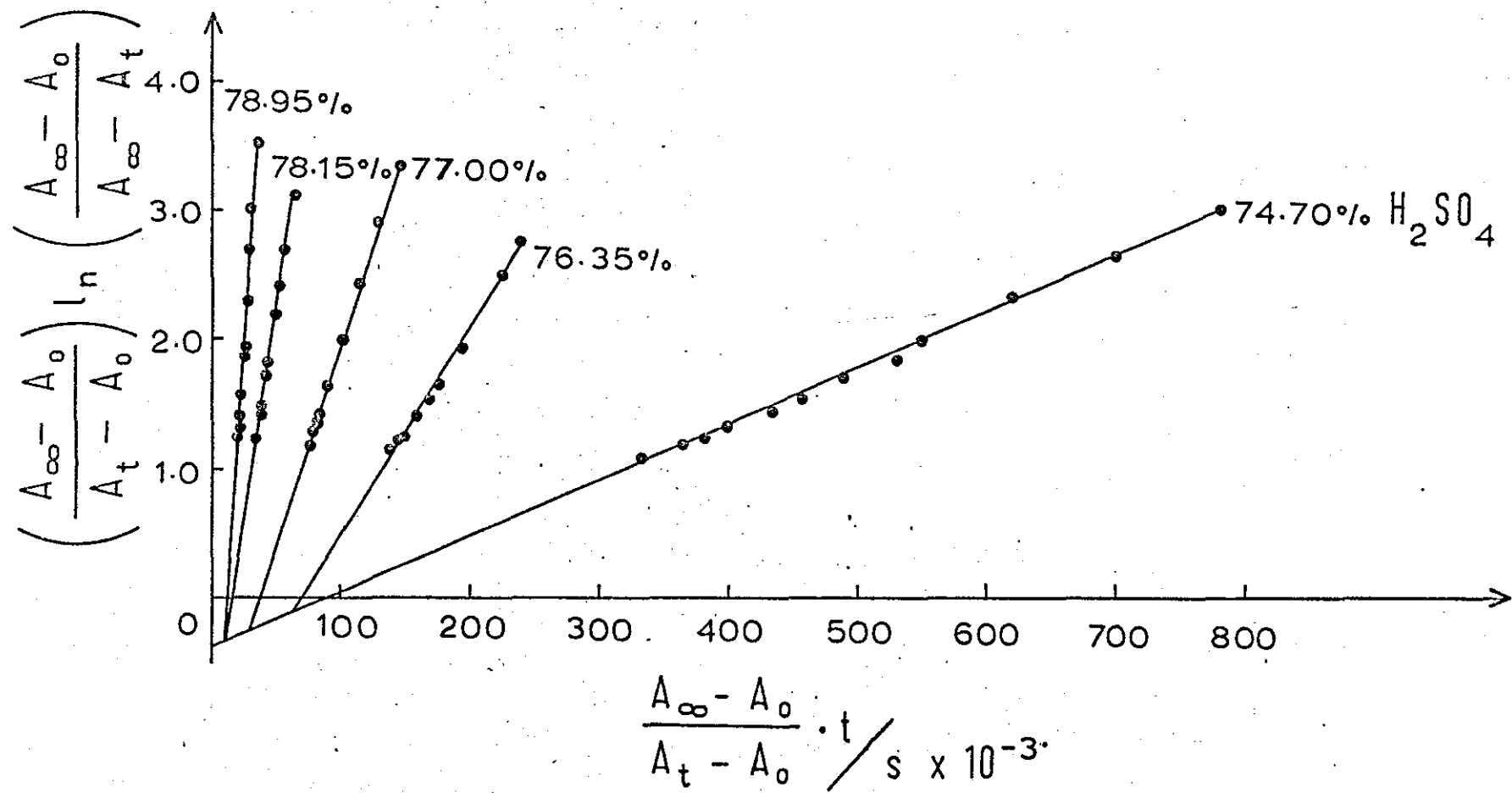
$$k'_1 [H^+] [HNO_3] \frac{(A_\infty - A_0)}{[ArH]_0} .$$

Figure 17 shows the intermediate-order plots for the runs utilizing a near saturation toluene concentration. They show a good correlation to a straight line and lead, via the slope and intercept, to values of  $k_2$  and  $k_1 = k'_1 [H^+]$  at each acid strength (Table 12). The runs at 80.10 and 81.45 per cent sulphuric acid were amenable to treatment by the initial slope method for the determination of  $k_1$  but the values of  $k_2$  were not measurable. The voltage jump, corresponding to the initial concentration of toluene, was estimated from a calibration jump made between a solution containing pure unreacted toluene in aqueous sulphuric acid and a solution after complete reaction had taken place.

TABLE 12.

% H <sub>2</sub> SO <sub>4</sub>	$k_2 / l \text{ mol}^{-1} \text{ s}^{-1}$	$k_1 / \text{s}^{-1}$
74.70	232	0.79
76.35	854	1.07
77.00	1711	1.76
78.15	3398	3.96
78.95	8262	4.98
80.10		6.42
81.45		8.30

Fig.17 Intermediate-order plots for the nitration of toluene



## 5.2. THE NITRATION OF O-XYLENE.

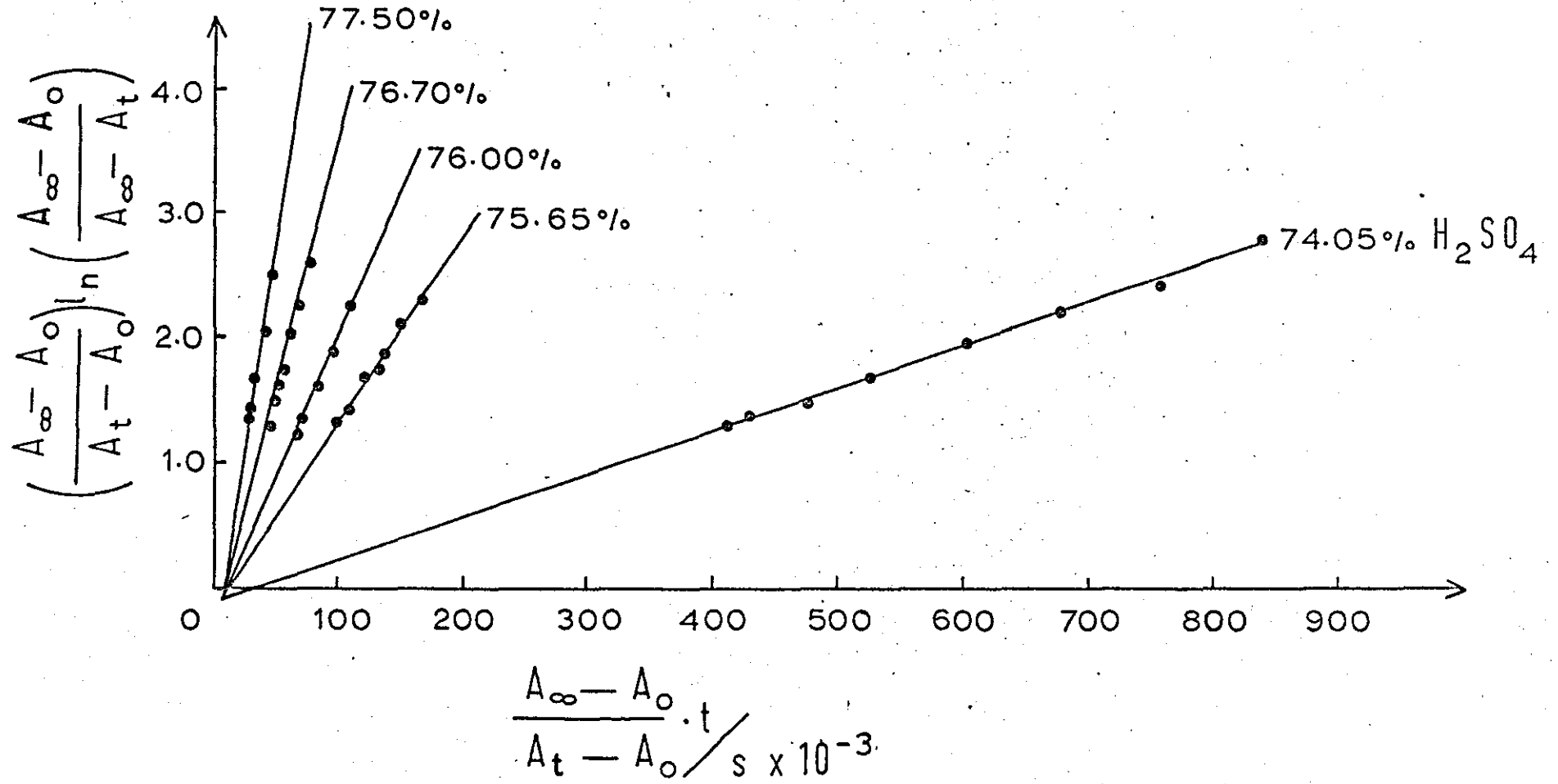
A similar series of runs to that performed on toluene and described in Section 5.1(b) was carried out with o-xylene. Since o-xylene is about 3 times more reactive<sup>4</sup> than toluene and about half as soluble<sup>38</sup> in aqueous sulphuric acid, this was the most likely choice of aromatic that would be expected to show a similar changeover in kinetics as observed for toluene. Stopped-flow runs were performed at various sulphuric acid strengths with a nitric acid concentration of  $1.88 \times 10^{-2} \text{ mol l}^{-1}$  after mixing. The nitric acid concentration was at least ten times in excess of the aromatic substrate concentration ( $4.1 \times 10^{-4} \text{ mol l}^{-1}$  after mixing). All runs were performed at  $25^\circ\text{C}$  with a monochromator setting of 350 nm and a slit width of 5mm as before. Sufficiently good traces were obtained to permit them to be displayed on the storage oscilloscope screen and readings taken directly from this. An exactly similar changeover in kinetics was observed as with toluene. At the highest acid strength the oscilloscope trace was virtually linear to completion. Figure 18 shows the intermediate-order plots for these runs and Table 13 lists values of  $k_1$  and  $k_2$  obtained from them.

TABLE 13.

% $\text{H}_2\text{SO}_4$	$k_2/\text{l mol}^{-1} \text{s}^{-1}$	$k_1/\text{s}^{-1}$
74.05	181	0.69
75.65	758	1.17
76.00	1251	1.10
76.70	2116	1.48
77.50	3036	3.54



Fig.18 Intermediate-order plots for the nitration of o-xylene



### 5.3. THE LIMITATIONS OF THE STOPPED-FLOW TECHNIQUE.

At very fast reaction rates, with half-lives approaching 10ms, the limit of the stopped-flow technique was reached and three intrinsic features of the apparatus began to show up. The first was the effect of dead time, or the time that it takes the mixed reactants to flow from the point of mixing to the point of observation in the optical cell. At normal reaction rates this is not significant compared with the reaction time but at high rates an appreciable amount of reaction may take place during this time. The result was a reduced voltage jump at the higher sulphuric acid strengths where the early stages of the reaction run were not observed (Figure 15).

Second was the effect of the backstop being slightly displaced from the microswitch, such that a small amount of liquid flow occurred after the oscilloscope had been triggered. The result was a tail to the oscilloscope trace prior to the start of the reaction and the rapid increase in voltage with time. This was particularly noticeable at high sweep rates.

The third limitation to the use of the stopped-flow technique, and the most important, was the problem of mixing. The Nortech instrument is quoted to have a mixing time of 2ms. This is an excellent figure and probably represents the best attainable by a commercial instrument. It, however, relates to the mixing of aqueous solutions of reactants. A somewhat higher figure might be expected under the conditions prevalent in our work. The mixing time increases with increasing viscosity of the reactants and in concentrated sulphuric acid solutions (70-80 per cent) the viscosity ranges from  $8-16\text{cP}^{16}$  compared to a value of ca. 1.0 cP for water at normal temperatures. The trace obtained with 81.45 per cent sulphuric acid

(Figure 15) shows the observed effect in our system; a slight curvature at the beginning of the run prior to the rapid increase in voltage with time. The approximate duration of this process has been estimated at 2ms. The increased viscosity of the system apparently had little effect on the mixing time.

#### COMMENT

#### 5.4. COMPARISON OF $k_2$ and $k_1$ with PREVIOUS DATA

Figure 19 shows a plot of  $\log k_2$  versus percentage sulphuric acid for the nitration of toluene in the stopped-flow apparatus. Also included are the values originally obtained by Schofield<sup>4</sup> et al. A reasonable agreement is observed over the extended acid range although a small displacement is evident due to our values being generally somewhat larger at a particular acid strength. This systematic error is probably due to the error in the determination of the sulphuric acid strength since the second-order rate coefficient at least doubles over only one per cent acid increase. A similar comparison of the o-xylene results is not possible since there is very little previous data available. However, Schofield<sup>4</sup> reports a value in 68.3 per cent sulphuric acid of  $2.21 \text{ mol}^{-1} \text{ s}^{-1}$ , very similar to many other reactive substrates at this acid strength, due to the onset of encounter control (Table 1). This value may be compared with that for toluene of  $1.0 \text{ l mol}^{-1} \text{ s}^{-1}$ . At higher sulphuric acid strengths  $k_2$  for o-xylene and toluene should become very similar and this is in fact observed.

The rate of formation of nitronium ions at a particular sulphuric acid strength is independent of the aromatic substrate being nitrated. The values of  $k_1$  for toluene and o-xylene may therefore be directly compared. Figure 20 shows the variation of  $\log k_1$  with

Fig. 19 Log  $k_2$  versus sulphuric acid strength for the nitration of toluene at 25° C.

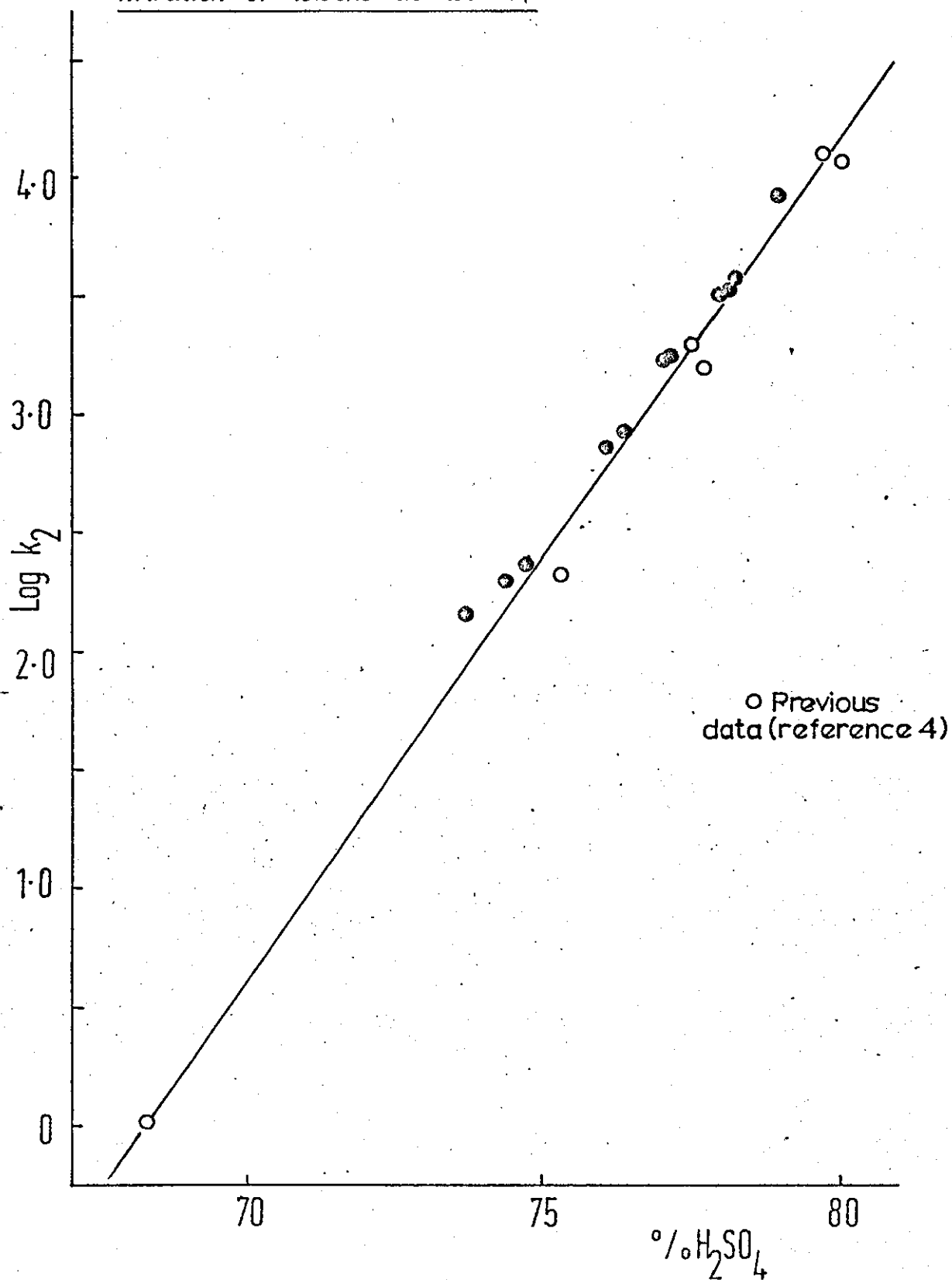
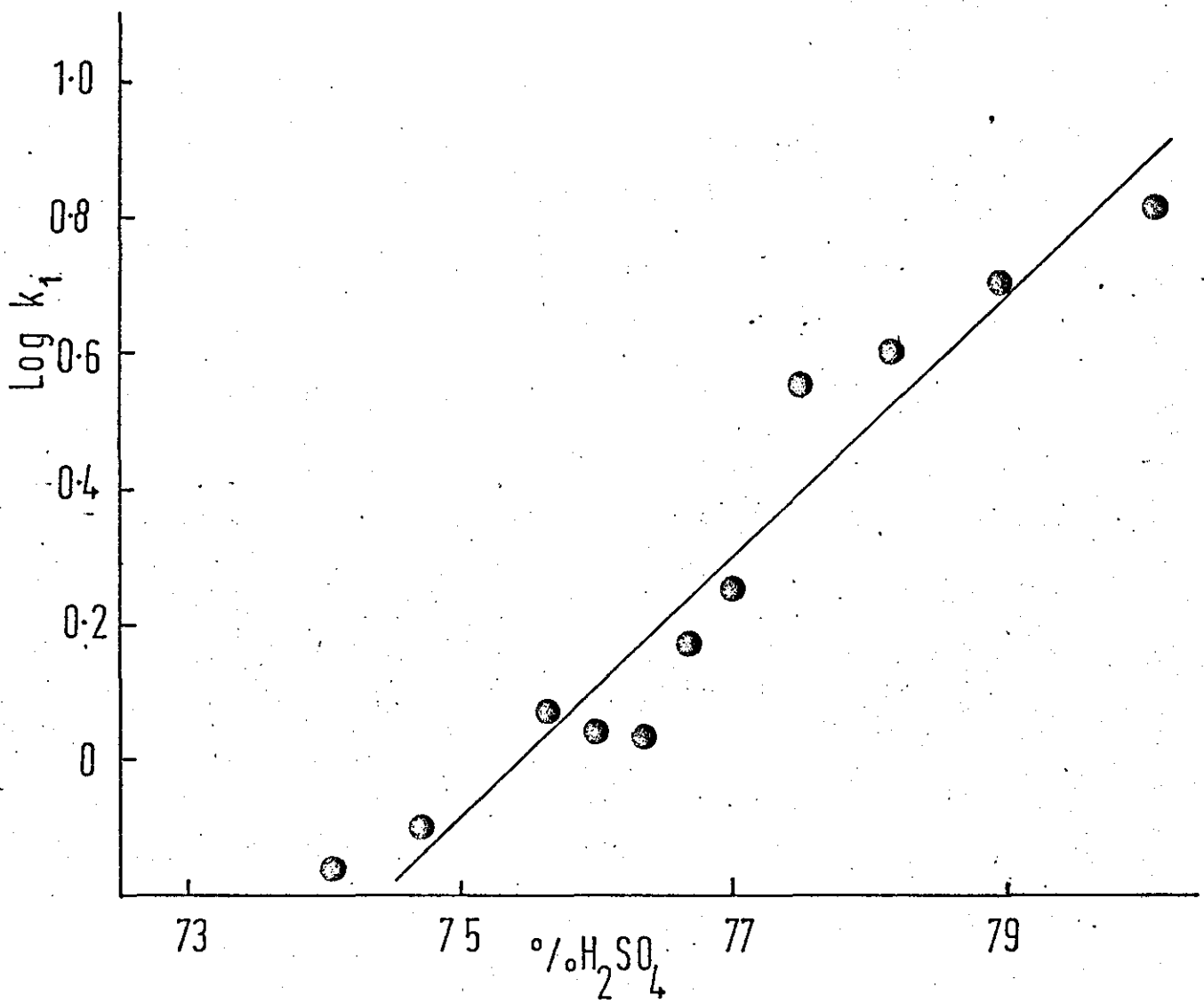


Fig. 20 Log  $k_1$  versus sulphuric acid strength at 25° C.



percentage sulphuric acid for both aromatics studied. Since the dependence of  $\log k_2$  on acid strength is virtually linear over this range a similar behaviour might be predicted for  $\log k_1$ . The results, however, do not allow this claim to be made with any conviction. Figure 20 does nevertheless show the expected increase of  $k_1$  with the acidity, and hence ionizing power, of the medium.

The value of  $k_1$  at 78.45 per cent sulphuric acid of ca.  $4.5\text{s}^{-1}$  (Table 12) may be compared with the estimate made at this acid strength with Cox's stirred cell data, of ca.  $0.40\text{ s}^{-1}$  (Section 4.10). A large discrepancy exists which requires an explanation. A number of theories have been put forward to account for the difference and they will now be discussed.

(a) The estimation of  $k_1$  from the stirred cell data is, of course, dependent upon the validity of two assumptions. That at 78.45 per cent sulphuric acid pure zeroth-order kinetics are in existence and reaction takes place in the fast reaction regime. If either one of these assumptions was untrue and either reaction was taking place well into the transition region between fast reaction and slow reaction diffusional regimes, or with an intermediate kinetic order between 1 and 0 in the homogeneous phase, the value of  $k_1$  could only be lower than already observed. Clearly, this argument cannot be used to account for the low value of  $k_1$  obtained from the stirred cell compared with the stopped-flow estimate.

(b) There was speculation that the disagreement may be due to a change of dependence of the zeroth-order rate of nitration on the nitric acid concentration; from its usual first-order, with the nitric acid concentration employed in the stopped-flow work ( $1.88 \times 10^{-2}\text{ mol l}^{-1}$ ), to nearer zeroth-order with the concentration employed in

the stirred cell ( $0.56 \text{ mol l}^{-1}$ ). The result would be a higher value of  $k_1$  than calculated assuming a first-order dependence. To test this, the value of  $k_1$  was determined by the usual method in the intermediate-order region with toluene in ca.75 per cent sulphuric acid, using as wide a range of nitric acid concentrations as possible. The intercept of the intermediate-order plot may be equated with the zeroth-order rate of nitration,  $k_0$ :

$$\text{Intercept} = \frac{[T]_0}{k_1 [\text{HNO}_3]^n} = \frac{[T]_0}{k_0}$$

An increase in the nitric acid concentration from  $1.88 \times 10^{-2}$  to  $7.52 \times 10^{-2} \text{ mol l}^{-1}$  resulted in a decrease in  $k_1$  from 0.67 to  $0.57 \text{ s}^{-1}$ . This indicates that the value of  $n$  may be decreasing as the nitric acid strength is increasing. This may be misleading, however, since the value of  $k_2$  similarly decreased from 270 to  $255 \text{ l mol}^{-1} \text{ s}^{-1}$  with increased nitric acid concentration. This was due to the effective lowering of the sulphuric acid concentration with the addition of a small amount of water with the aqueous nitric acid. A similar effect, although less marked, would be expected in the case of the  $k_1$  values.

(c) ACCURACY OF DETERMINATION OF  $k_1$  FROM HOMOGENEOUS DATA.

There is somewhat greater error associated with the determination of values of  $k_1$  from intermediate-order plots than with the determination of  $k_2$ . The intercept of the plot is obtained by extrapolation of points some way off the axis. The error in the determination of the intercept may then be considerable whereas the error in the slope remains small. Furthermore, the estimation of  $k_1$  from the intercept, given by  $\frac{[ArH]_0}{k_1 [\text{HNO}_3]}$ , or the slope of the initial

portion of the oscilloscope trace, given by  $k_1 \frac{[\text{HNO}_3]}{[\text{ArH}]_0} (A_\infty - A_0)$ ,

requires the accurate knowledge of  $[\text{ArH}]_0$  whereas the estimation of  $k_2$  does not. Several problems were encountered in the making up of near saturated solutions of aromatic in concentrated sulphuric acid. It was therefore decided to determine accurately, by the spectrophotometric method described in Section 2.4, the effective initial concentration of toluene in ca.76 per cent sulphuric acid. Several solutions were made up at 25°C, in precisely the same manner as for the stopped-flow runs, by adding 30  $\mu$ l of toluene to 100ml of aqueous sulphuric acid in a 100 ml graduated flask. This gave a theoretically predicted concentration of  $2.82 \times 10^{-3}$  mol l<sup>-1</sup>. In each case the solution was allowed to settle and a sample of the acid withdrawn, extracted with hexane and analysed at 262nm. The results are shown in Table 14.

TABLE 14.

$[\text{T}]_a / \text{mol l}^{-1}$
$1.86 \times 10^{-3}$
$1.78 \times 10^{-3}$
$1.98 \times 10^{-3}$
$1.56 \times 10^{-3}$
$1.40 \times 10^{-3}$
$1.30 \times 10^{-3}$
$1.92 \times 10^{-3}$

A considerable variation in the effective toluene concentration is evident. It falls in the range  $1.30 - 1.98 \times 10^{-3}$  mol l<sup>-1</sup> with an average of  $1.69 \times 10^{-3}$  mol l<sup>-1</sup>. This is 40 per cent below the predicted value and suggests that up to about half of the toluene is



lost from the acid by the time extraction takes place. Three possible explanations for the loss of toluene were proposed. The first was that appreciable sulphonation had taken place prior to the extraction or a stopped-flow run. Since the toluene sulphonic acids are virtually insoluble in hexane this would lead to a low value for the absorbance in the hexane extract. The second was that toluene is sufficiently volatile that an equilibrium is set up between the acid and the air space above it giving a low residual concentration in the acid. The final explanation was that not all of the toluene had dissolved in the acid due to the poor mixing of the substrate with the highly viscous sulphuric acid.

The possibility that sulphonation plays a significant role in the reduction of the toluene concentration may be eliminated. The data of Cerfontain et al<sup>39</sup> show that at this strength of sulphuric acid sulphonation is so slow, the half-life in 76 per cent acid being ca.100 hours, that it may be ignored. This was verified by the result of a run in which the concentration of toluene in the acid was estimated as a function of time from when the solution was made up. No appreciable change had occurred after three hours duration.

To investigate whether toluene is vaporizing into the air space above the solution two solutions were made up, as described previously, to give a predicted toluene concentration of  $2.82 \times 10^{-3} \text{ mol l}^{-1}$ . Two different sized flasks were used giving free volumes above the liquid of 7ml and 490ml. The residual toluene concentration in the acid phase was estimated to be 1.92 and  $0.68 \times 10^{-3} \text{ mol l}^{-1}$ , respectively. This suggests that toluene does vapourize into the air space since the larger the air space the lower the residual toluene concentration in the acid. If one mole of gas at S.T.P. occupies

22.4 litres and the vapour pressure of toluene at 25°C is 28mm of mercury, 490ml of air might be expected to hold  $\frac{490 \times 28 \times 273}{22400 \times 760 \times 298} = 7.4 \times 10^{-4}$  mol of toluene. Since  $2.82 \times 10^{-4}$  mol of toluene was originally put into the flask it can be seen that up to ca.3 times this quantity may be accommodated in this air space. With a 7ml air space, however, only ca.3-4 per cent of the original toluene may be accounted for in this way. Furthermore, all attempts at achieving the predicted concentration of  $2.82 \times 10^{-3} \text{ mol l}^{-1}$  with flasks having negligible air space above the liquid, failed, although the concentration obtained was slightly improved. This may, however, be the result of poor mixing due to the absence of air bubbles to act as agitators.

The effect of poor mixing may well be the most significant factor in the low concentrations of toluene observed although it is difficult to estimate the extent to which it affected results. It may be assumed that for solutions near the saturation limit the attainment of an equilibrium concentration, even with effective agitation, is longer than with more dilute solutions. The process is greatly affected by the viscous nature of the solvent. An attempt was made to ascertain whether any toluene was left remaining on the top of the acid after mixing, but this proved negative.

A full explanation for the low substrate concentrations observed in the stopped-flow experiments when solutions are made up in this manner is difficult to find. It is considered that a combination of factors may be present. The present data does, however, allow a correction to be made to the values of  $k_1$  obtained with toluene. If an aromatic substrate concentration is assumed consistently 40 per cent below that predicted for the intermediate-

order runs, the corrected values of  $k_1$  at 25°C, shown in Table 15, are obtained.

TABLE 15.

% H <sub>2</sub> SO <sub>4</sub>	$k_1/s^{-1}$
74.70	0.47
76.35	0.64
77.00	1.06
78.15	2.38
78.95	2.99
80.10	3.85
81.45	4.98

The above values are now considered to be accurate to  $\pm 15$  per cent as indicated by the scatter in Table 14. The overall variation of  $[T]_a$  observed in the making up of solutions by the procedure described agrees well with the calibration jump values obtained in the stopped-flow runs which showed a similar variation. A recommendation for future work suggests itself here, in that many of the problems described above may well be overcome if the solutions of aromatic are made up by a modified procedure. This would involve making a saturated solution up initially, by mixing aqueous sulphuric acid with an excess of toluene, separating the two phases and then diluting the acid phase with, say, an equal volume of aqueous sulphuric acid. Some care would be necessary, however, in the maintenance of temperature since aromatics rapidly come out of solution with only a few degrees drop in temperature at near saturation levels. The correction for low toluene concentrations brings the  $k_1$  values for toluene closer in line with the value obtained from the stirred cell data but still leaves them considerably apart. The discrepancy

is thought unlikely to be the result of experimental error and requires further work so that the gap between the homogeneous and two phase systems may be bridged.

Despite the above arguments the work on the homogeneous nitration of toluene at high sulphuric acid strength has confirmed the suggestion that the lower than predicated initial rates of nitration in the two phase systems was caused by a changeover in the kinetic order of nitration from one to zero in the homogeneous phase. The further implications of the phenomenon will be discussed a little later.

## CHAPTER 6.

### THE NITRATION OF CHLOROBENZENE AT HIGH SULPHURIC ACID STRENGTHS

#### 6.1. DEPENDENCE OF THE INITIAL RATE OF NITRATION ON TEMPERATURE IN THE STIRRED CELL

The initial rate of nitration of chlorobenzene in the stirred cell was determined at various temperatures between 10 and 55°C in 79.80 per cent sulphuric acid according to the procedure described in Section 2.2(a). The acid phase was made up by the addition of aqueous nitric acid (Analar grade, s.g. 1.42, 6.25ml) to 175ml of aqueous sulphuric acid giving a solution  $0.56 \text{ mol l}^{-1}$  in nitric acid. A quantity of this (170ml) was taken and stirred at  $50 \text{ rev min}^{-1}$  with 20ml of chlorobenzene. Samples of the organic phase ( $25 \mu\text{l}$ ) were withdrawn at regular intervals of time and diluted to 10ml with hexane and the absorbance measured at 340nm. The slopes of the initial portions of the absorbance versus time plots obtained were converted into initial rates of nitration by multiplying by the factor<sup>1</sup>  $3.75 \times 10^{-3}$ . The results are shown in Table 16.

#### 6.2. DEPENDENCE OF THE SECOND-ORDER RATE COEFFICIENT FOR NITRATION ON TEMPERATURE.

The second-order rate coefficient for the nitration of chlorobenzene in 79.45 per cent sulphuric acid was measured at various temperatures between 15 and 55°C by means of the stopped-flow technique described in Section 2.6. Runs were performed with an organic substrate concentration of  $0.98 \times 10^{-3} \text{ mol l}^{-1}$  after mixing and a nitric acid concentration, at least ten fold in excess, of  $1.88 \times 10^{-2} \text{ mol l}^{-1}$  after mixing. The monochromator setting was 350nm with a slit width of 5mm. In all cases good pseudo-first-order behaviour was observed and the oscilloscope traces, recorded on the storage instrument, allowed the values of  $k_2$  to be determined by the usual method. They

are shown in Table 16.

### 6.3. DEPENDENCE OF SOLUBILITY OF CHLOROBENZENE IN SULPHURIC ACID ON TEMPERATURE

The solubility of chlorobenzene in 79.55 per cent sulphuric acid was determined in the temperature range 10 - 45°C by the procedure described in Section 2.4. The spectrophotometric determination was made at 265nm ( $\epsilon = 159$ ). Generally, three separate extractions were performed for each run and the average solubility taken. This is shown in Table 16. The accuracy of determination was estimated at ca.  $\pm 3$  per cent.

TABLE 16.

TEMPERATURE/°C	$R/\text{mol l}^{-1}\text{s}^{-1}$	$k_2/\text{l mol}^{-1}\text{s}^{-1}$	$[\text{CB}]_a^s/\text{mol l}^{-1}$
10	$1.82 \times 10^{-6}$		$2.20 \times 10^{-3}$
15		129	$2.29 \times 10^{-3}$
20			$2.98 \times 10^{-3}$
25	$4.43 \times 10^{-6}$	256	$3.18 \times 10^{-3}$
30			$3.15 \times 10^{-3}$
35	$8.14 \times 10^{-6}$	454	$3.73 \times 10^{-3}$
45	$13.7 \times 10^{-6}$	936	$3.91 \times 10^{-3}$
54.5	$21.7 \times 10^{-6}$		
55		1220	

### 6.4. THE IRREPRODUCIBILITY OF RATES AT VERY HIGH SULPHURIC ACID STRENGTHS

Numerous determinations were made of the initial rate of nitration of chlorobenzene in sulphuric acid strengths between 80 and 90 per cent in the stirred cell. Two methods were employed. The first involved the determination of the rate of accumulation of

mononitro -chlorobenzenes in the organic phase as described in Section 2.2(a), and Section 6.1. The second involved the estimation of the loss of nitric acid in the acid phase by a colorimetric determination based on the method devised by F.L. English<sup>40</sup>. This involved the formation of a wine red complex of ferrous nitrosyl sulphate which was estimated spectrophotometrically. The modified procedure is fully described in the Appendix. Stirred cell nitrations were performed at 25°C and 50 rev min<sup>-1</sup> in all cases. Identical phase volumes of 20ml of organic and 170ml of acid were used in both methods with a nitric acid concentration of 0.56 mol l<sup>-1</sup>. In the case of the nitric acid determination, however, 0.1 ml samples of the acid phase were withdrawn, after momentarily stopping the stirrer, by means of a graduated pipette fitted with an all glass "Agla" syringe. They were dispensed into conical flasks containing 1.0ml of distilled water, which satisfactorily quenched any reaction still taking place in the acid as well as suitably diluting the nitric acid for the determination.

Figure 21 shows the results of some 30 runs performed with the stirred cell in the range 80-90 per cent sulphuric acid. Both methods of determination gave initial rates that showed increasing irreproducibility as the sulphuric acid strength was increased. Furthermore, at acid strengths greater than ca.81 per cent the organic phase was observed to go cloudy almost immediately after the start of the run with the precipitation of a white solid at or near the interface. The effect of stirrer position was also observed to become critical at this acid strength. Figure 22 shows the absorbance versus time plots for typical stirred cell runs in ca.84.50 per cent sulphuric acid where the depth of the stirrer beneath the interface was changed during the course of the run from 1mm to 1cm and vice-versa. The

Fig.21 The initial rate of nitration of chlorobenzene at very high sulphuric acid strengths in the stirred cell.

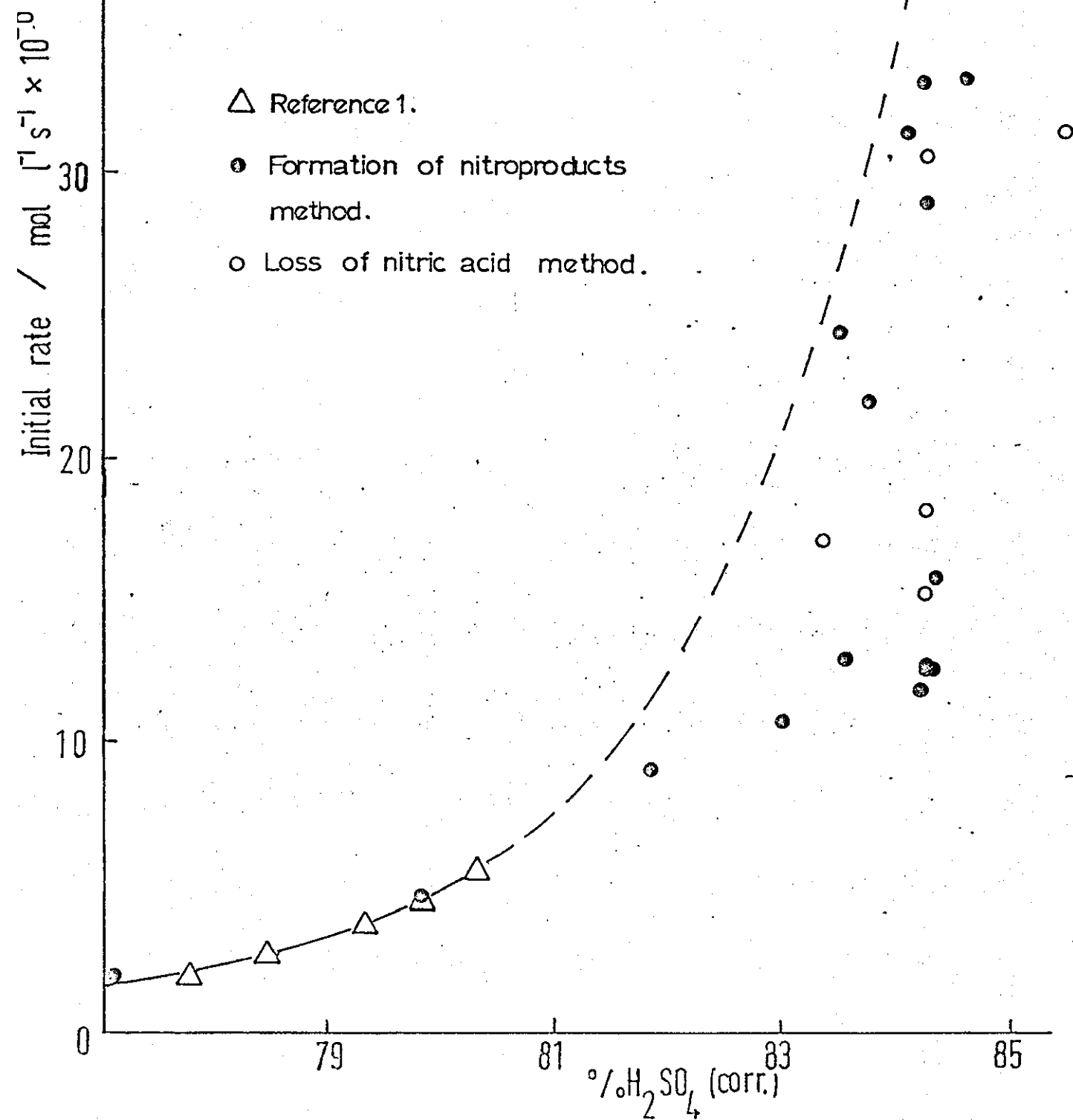
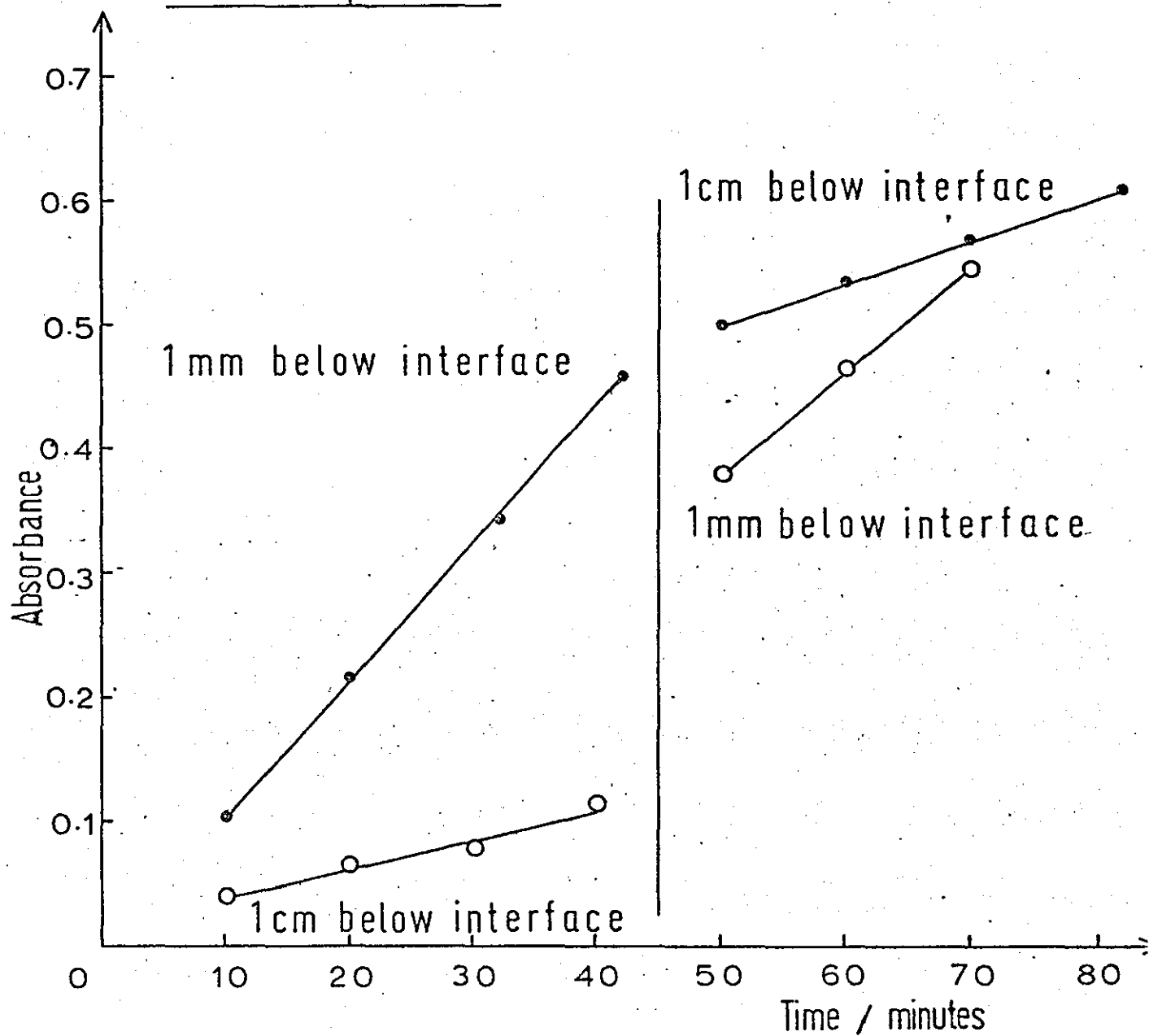




Fig. 22 The effect of stirrer position in the stirred cell on the initial rate of nitration of chlorobenzene in 84.50% sulphuric acid.



absorbance was in each case due to the mononitrochlorobenzene accumulation in the organic phase. It can be seen that as the stirrer was moved further below the interface so the rate decreased. As the stirrer was moved up towards the interface so the rate increased. A similar run performed with 77.10 per cent sulphuric acid showed no significant change in rate of nitration. Furthermore, all initial rates determined up to an acid strength of ca.81 per cent showed good agreement with previous data.

COMMENT

6.5. SUMMATION OF ACTIVATION PARAMETERS FOR THE NITRATION OF CHLOROBENZENE IN THE FAST REACTION REGIME

The nitration of chlorobenzene in the stirred cell and stirred reactor in ca.80 per cent sulphuric acid is considered to take place in the fast reaction regime. The rate of reaction should therefore be given by:

$$R = a' \sqrt{D k_2 [\text{HNO}_3]} \cdot [\text{CB}]_a^s \dots\dots\dots 49$$

Two means by which the equation may be tested experimentally are found in the comparison of the observed initial rate of nitration with the sum of the components on the right-hand-side of the equation and in the comparison of the overall activation energy with the sum of the individual activation parameters. The results shown in Table 16 allow us to determine the validity of Equation 49 by both means.

The initial rate of nitration observed at 25°C is  $4.43 \times 10^{-6}$  mol l<sup>-1</sup> s<sup>-1</sup> in excellent agreement with the value of  $4.44 \times 10^{-6}$  mol l<sup>-1</sup> s<sup>-1</sup> obtained by Cox<sup>1</sup> in the same cell with a slightly higher stirring speed of 65 rev min<sup>-1</sup>. The solubility of chlorobenzene at 25°C, obtained by interpolation from a best line drawn through all the

points in Table 16, is  $3.0 \times 10^{-3} \text{ mol l}^{-1}$ . If the diffusivity of chlorobenzene in 79.80 per cent acid<sup>1</sup> is taken as  $0.77 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  and the interfacial area per unit volume of acid is  $0.2024 \text{ cm}^2 \text{ cm}^{-3}$ , these may be combined with the data at 25°C in Table 16 to give a predicted initial rate of  $6.4 \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$ , in reasonable agreement with that observed.

Arrhenius activation plots were constructed for the dependence of the initial rate of reaction in the stirred cell (Figure 23), the second-order rate coefficient (Figure 24) and the solubility (Figure 25) on temperature. The first two plots showed good correlations to a straight line from which  $E_{\text{overall}}$  and  $E_{k_2}$  were estimated at 10.3 and 11.0 kcal mol<sup>-1</sup>, respectively. The dependence of the solubility on temperature showed a much poorer correlation. This was due to the very small changes in solubility of  $2\text{-}3 \times 10^{-4} \text{ mol l}^{-1}$  (ca.10 per cent) that resulted from a 5°C change in temperature. The accuracy of the determination was estimated at  $\pm 3$  per cent i.e. comparable to the change being measured. The value of  $\Delta H_{\text{sol}}$  obtained from the slope of the least-squares line through the points in Figure 25 is  $3.1 \pm 1 \text{ kcal mol}^{-1}$ . This is of the same magnitude as obtained by Cox<sup>1</sup> and Cerfontain et al.<sup>30</sup> for similar aromatics at this acid strength. Furthermore, Cerfontain observed similar deviations in the value of the solubility and  $\Delta H_{\text{sol}}$  obtained by a similar extraction procedure.

The value of  $E_{k_2}$  is determined by the sum of two activation terms:

$$E_{k_2} = E_{k_2'} + \Delta H_{\text{form}} \quad \dots\dots\dots 50$$

where  $\Delta H_{\text{form}}$  is the heat of formation of nitronium ions from nitric acid at a particular sulphuric acid strength. The value of  $E_{k_2'}$

Fig.23 Dependence of the initial rate of nitration of chlorobenzene in the stirred cell on temperature.

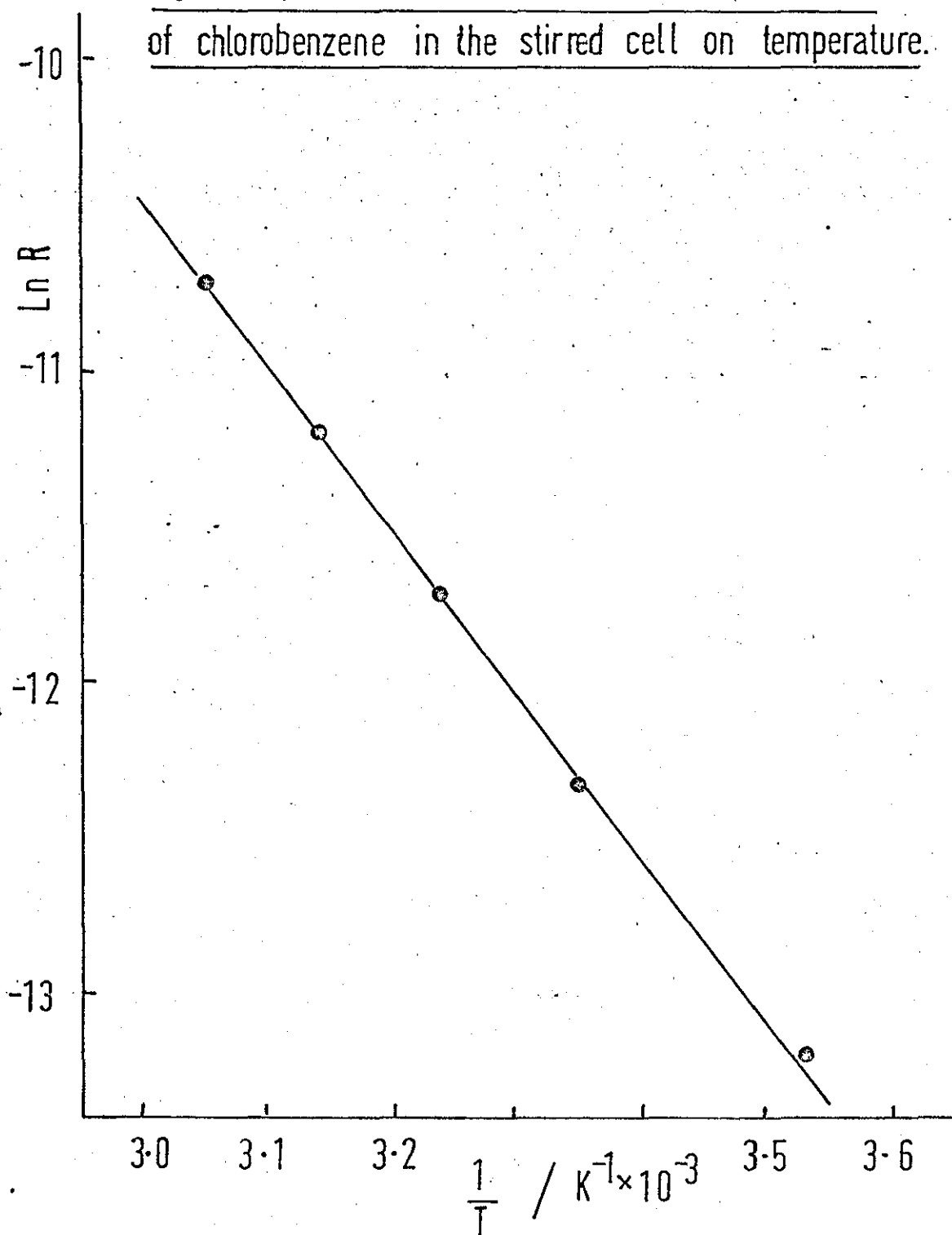


Fig. 24 Dependence of the second-order rate coefficient for the nitration of chlorobenzene on temperature.

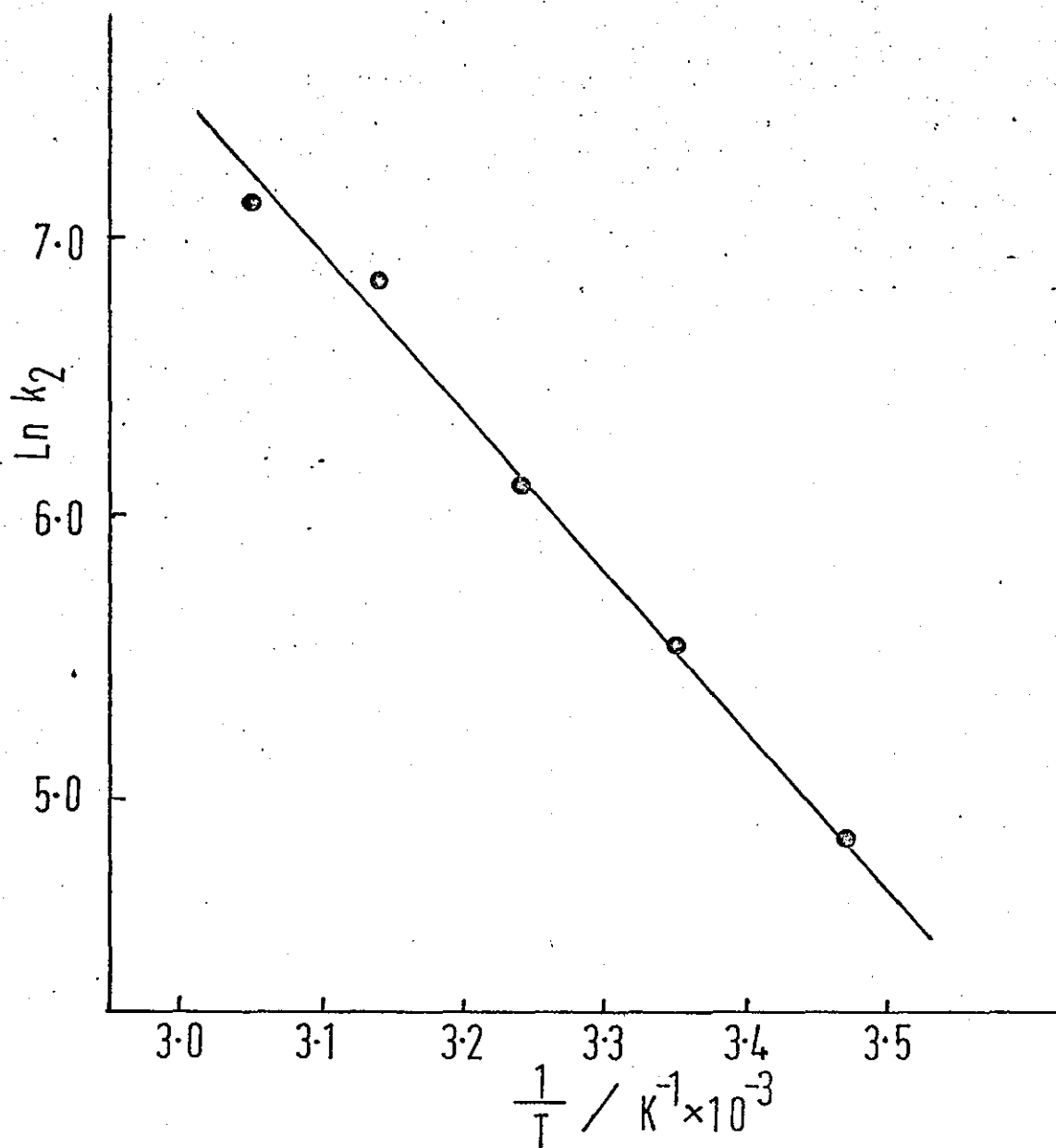
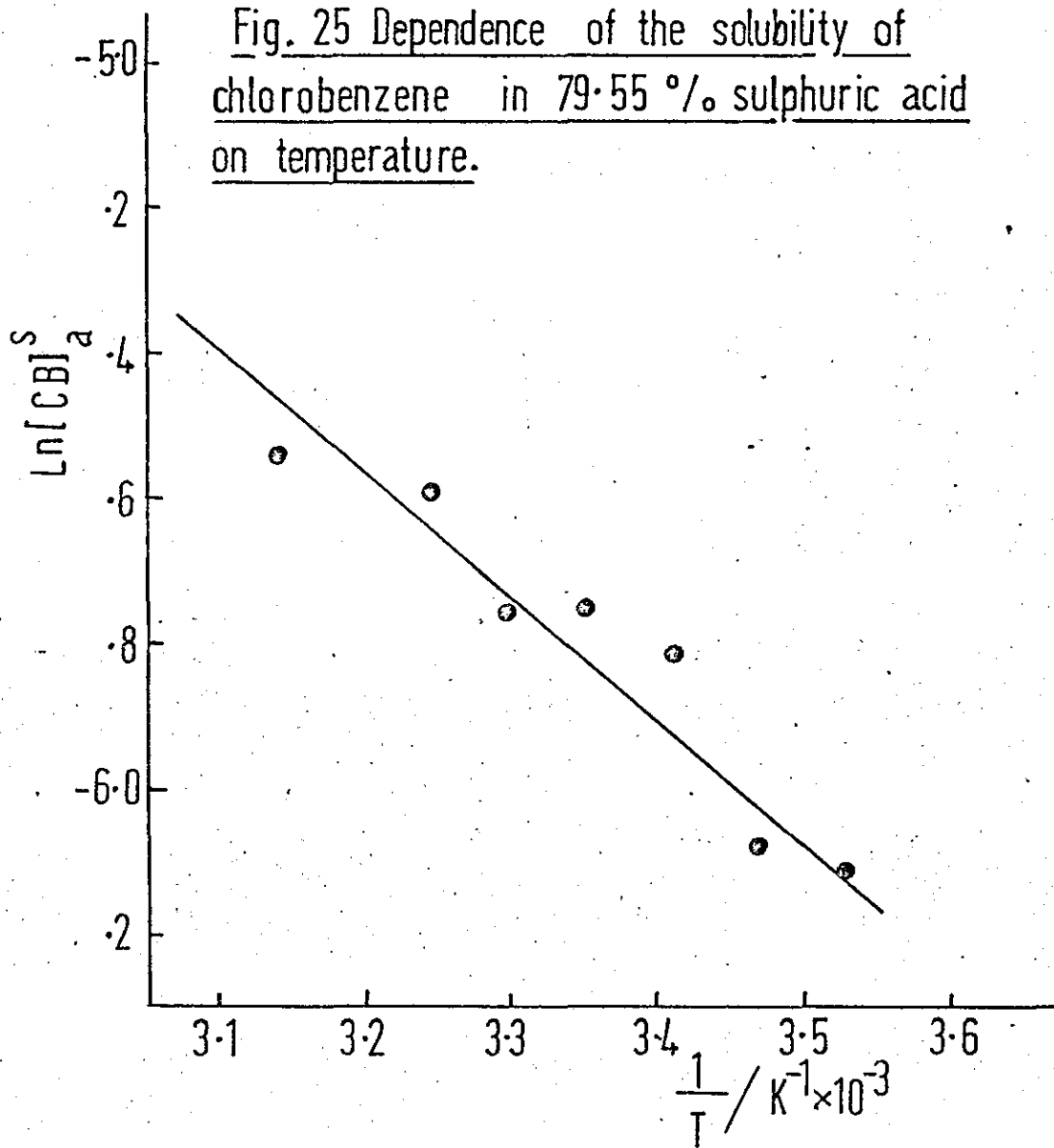


Fig. 25 Dependence of the solubility of chlorobenzene in 79.55 % sulphuric acid on temperature.



varies with each aromatic whereas the other is independent of the substrate. The major contribution to the magnitude of  $E_{k_2}$  is  $\Delta H_{\text{form}}$  and this decreases with increasing acid strength. The extent to which  $\Delta H_{\text{form}}$ , and therefore  $E_{k_2}$ , decreases is independent of the aromatic substrate and therefore affords a means by which the value of  $E_{k_2}$  may be predicted for any aromatic, providing at least one value of

$E_{k_2}$  is known at a particular sulphuric acid strength. Figure 26 shows values of  $E_{k_2}$  for a number of aromatics<sup>32,12</sup> including chlorobenzene in 70.2 and 67.5 per cent sulphuric acid. If a parallel decrease in the value of  $E_{k_2}$  is assumed for each aromatic the predicted  $E_{k_2}$  for chlorobenzene in 79.45 per cent sulphuric acid is ca. 11 kcal mol<sup>-1</sup>, in good agreement with our value.

The activation parameters obtained allow us to estimate the value of  $E_D$ , the diffusivity temperature coefficient for chlorobenzene in 79.80 per cent sulphuric acid, since:

$$E_{\text{overall}} = \frac{1}{2}(E_D + E_{k_2}) + \Delta H_{\text{sol}} \dots\dots\dots 51$$

Insertion of the values into Equation 51 yields a predicted value for

$E_D$  of 3.4 kcal mol<sup>-1</sup>. Another estimate of this value may be obtained from independent experimental data reported by Fasullo<sup>41</sup>.

He gives values of the viscosity of aqueous sulphuric acid mixtures as a function of temperature over a wide range of acid strengths.

The diffusivity is related to the viscosity by the modified Wilke-Chang expression where simply:

$$D = \text{Constant} \times \frac{T}{\eta} \dots\dots\dots 52$$

However, as discussed in Section 1.7 the dependence of diffusivity on viscosity may be nearer -0.8 than -1.0 in this system and therefore a better approximation may be obtained by assuming:

$$D = \text{Constant} \times \frac{T}{\eta^{0.8}} \dots\dots\dots 53$$

Fig.26 Dependence of  $E_{k_2}$  on the sulphuric acid strength for a number of aromatics

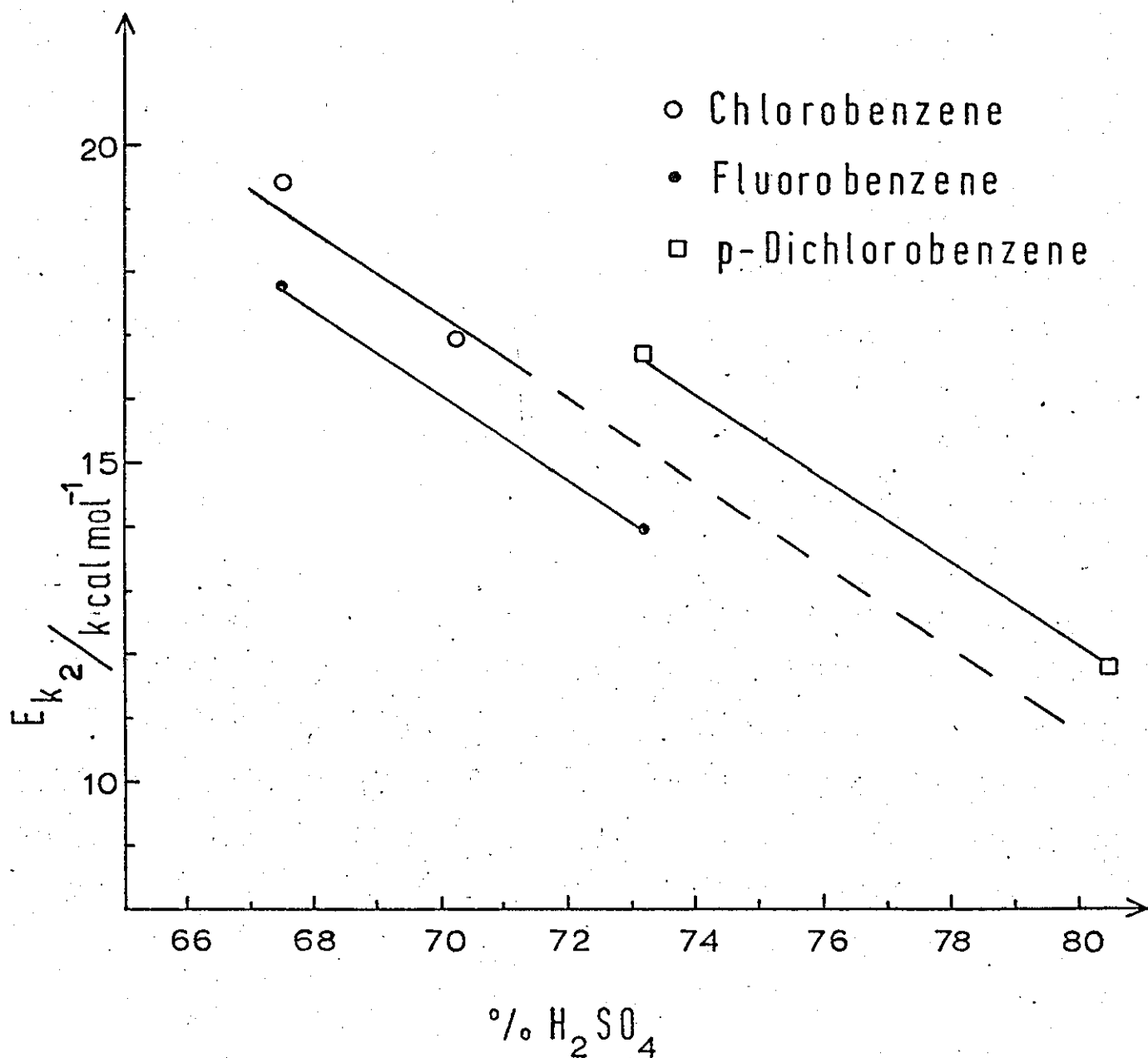




Table 17 shows values of the viscosity of 80 per cent sulphuric acid over the temperature range 4.4 - 60°C together with values of  $\frac{T}{\eta^{0.8}}$  at each temperature. A plot of  $\ln \frac{T}{\eta^{0.8}}$  versus  $\frac{1}{T}$  gives a good straight line which leads to an activation energy of 5.0 kcal mol<sup>-1</sup>. This compares quite favourably with the value of 3.4 kcal mol<sup>-1</sup> above and goes some way towards confirming the validity of Equation 49 for chlorobenzene under these conditions. The magnitude of  $E_D$  is of some interest, and should be commented upon, for it is somewhat higher than the values usually associated with diffusion phenomena generally and <sup>42</sup> which normally fall within the range 1-3 kcal. The value obtained from Fasullo's data may be compared with that for the viscosity activation energy <sup>43</sup> of water, which at 0°C is 5.06 kcal and which is likewise rather high. The anomalous behaviour of water, and we suspect, concentrated sulphuric acid solutions, is explained <sup>43</sup> by the degree of hydrogen bonding that takes place in these strongly associated media. Thus, an additional amount of energy, the so called "structure activation energy" is required to break the hydrogen bonds before flow of the liquid can occur. As the temperature of the solution is raised so the number of hydrogen bonds that have to be broken before flow can occur decreases and a lower activation energy is observed. The result is a non-linear Arrhenius plot over an extended temperature range.

#### 6.6 THE EFFECT OF PRECIPITATION OF NITROPRODUCTS FROM THE ORGANIC PHASE ON THE INITIAL RATE OF NITRATION IN THE STIRRED CELL

There can be little doubt that the poor reproducibility of the stirred cell runs above ca. 81 per cent sulphuric acid strength and the sudden critical dependence on the position of the stirrer are closely bound up with the appearance of a white precipitate at the interface. The precipitate can be assumed to consist of a mixture of mononitro-

TABLE 17.

TEMPERATURE /°C	VISCOSITY / cP	$T/\eta^{0.8}$ /K cP <sup>-0.8</sup>
4.4	35.6	15.9
15.5	24.0	22.7
26.7	16.6	31.7
37.8	11.9	42.9
48.9	8.8	56.6
60.0	6.7	72.8

chlorobenzenes, the products of the nitration, and their precipitation may be expected to have a considerable effect on the rate of mass transfer across the interface. Two factors are important. The first is that the precipitation out of solution of the product will decrease the absorbance measured in the organic phase. The second is that the precipitation of a solid near or at the interface effectively changes the system from a liquid-liquid one to a solid-liquid one and this will affect the rate of mass transfer.

The degree of precipitation is likely to be influenced by the extent to which the organic phase is agitated and the rate of accumulation of product in the organic phase i.e. the rate of chemical reaction. Thus, when the stirrer is moved down from the interface further into the acid the organic phase above it becomes virtually stagnant, precipitation is encouraged and the rate of reaction decreases (Figure 22). When the stirrer is brought up to the interface the process is reversed, the rate of reaction is increased and the precipitate already accumulated in the lower half of the organic phase is rapidly swept into solution. This results in the sudden dramatic increase in absorbance observed under these conditions

(Figure 22). The results of the experiments in which the rate of nitration was determined by the loss of nitric acid method show that a two-fold effect is present since the same irreproducibility in the initial rate was observed as when the rates were determined by the accumulation of nitroproducts method. Thus, the precipitation genuinely affects the rate of nitration observed in the stirred cell as well as the rate of dissolution of the products into the organic phase.

Under the conditions prevalent in the stirred cell the nitro-products, when formed, would be expected to remain at the bottom of the organic phase, near to the interface with the acid phase, because of their rather greater density compared to the substrate (Table 18). A three-layered system may be visualized where the mass transfer of the substrate into the acid phase is severely reduced by the presence of the solid products. This explanation for the results obtained with chlorobenzene at very high rates of reaction accounts for the fact that with toluene the phenomenon was not observed despite comparable rates of reaction having been measured. This is because all three mononitrochlorobenzene isomers are solid at 25°C (Table 18) but only the p-isomer is for toluene, and this accounts for only about one third of the total product. The problem severely limits the use of the stirred cell for the study of the nitration of chlorobenzene and emphasises the ineffectiveness of mechanical agitation in the system.

TABLE 18.

AROMATIC	MELTING POINT /°C	DENSITY /g ml <sup>-1</sup>
Toluene	-95	0.8669
o-nitrotoluene	-9.55	1.1629
m-nitrotoluene	16	1.1571
p-nitrotoluene	54.5	1.1038
Chlorobenzene	-45.6	1.1058
o-nitrochlorobenzene	33.5-35	1.368
m-nitrochlorobenzene	46	1.343
p-nitrochlorobenzene	83.6	1.2979

DISCUSSION

## CHAPTER 7

### FACTORS AFFECTING THE RATE OF MASS TRANSFER IN THE STIRRED CELL

The use of the stirred cell in the study of mass transfer with simultaneous reaction has one principal attraction in that the interfacial area is virtually constant and easily measurable and this allows values of the important parameters  $k_L$  and  $D$  to be estimated by application of Danckwerts' Surface Renewal Theory. Against this advantage, however, may be set the complications of turbulent flow and the effect of contamination of the interface which may appreciably affect the value of the mass transfer coefficient. Nevertheless, Cox and Strachan<sup>1</sup> employed this system for the study of the nitration of toluene and chlorobenzene in mixed acid media with some success. In particular, they obtained what appeared to be a reasonable estimate of  $2.8 \times 10^{-3} \text{ cm s}^{-1}$  for  $K_L$  at  $25^\circ\text{C}$  with chlorobenzene, an aromatic free of any kinetic complications at the sulphuric acid strengths studied. The value of  $k_L$  in the absence of chemical reaction in the stirred cell was, however, some ten times lower than this at  $1.73 \times 10^{-4} \text{ cm s}^{-1}$  and considerably lower than usually observed for the transport of organic liquids through water in stirred cell systems. Interest, therefore, centred on the factors that influence the rate of mass transfer in such systems.

#### 7.1. EMPIRICAL CORRELATIONS

Most of the work on the factors affecting the value of  $k_L$  in the stirred cell has been performed in the absence of chemical reaction by the unhindered observation of the transfer of one phase into another. Typically, Blokker<sup>36</sup> employed a thermostatted cylindrical

transfer cell in which the two phases were independently stirred by counter-rotating paddles situated near to the centre. At the stirrer speed used (120 rev min<sup>-1</sup>) only a slight undulation of the interface was produced. The transfer coefficients were determined either by measuring the change in conductivity of one of the phases or by sampling and analysing one or both of the phases after certain intervals of time. Lewis employed a similar set up but was able to standardise the degree of turbulence by restricting the interface to an annular gap between a central and peripheral baffle.

44

Lewis found that the results of his work on systems, diagrammatically represented in Figure 27 (a), obeyed the empirical law:

$$k_{L(1)} = 1.33 \times 10^{-7} \nu_1 (Re_1 + Re_2 \eta_2 / \eta_1)^{1.65} + 0.0167 \nu_1 \dots 54$$

where subscripts 1 and 2 refer to the two liquid phases,  $\eta$  is the viscosity,  $\nu$  is the kinematic viscosity (denoted by  $\eta/\rho$ , in cm<sup>2</sup>s<sup>-1</sup>) and Re is the Reynolds number (defined by  $L^2N/\nu$ , where L is the tip-to-tip length of the stirrer blades and N is the number of revolutions of the stirrer per second). The correlation has received considerable criticism despite being numerically satisfactory to  $\pm$  40 per cent. The principal argument is with the absence of a term in  $D_1$ , the diffusivity of the transporting species through phase 1.

A more satisfactory correlation<sup>45</sup> for the mass transfer across a clean surface in a stirred cell is:

$$k_{L(1)} = 0.00316 (D_1/L) (Re_1 Re_2)^{0.5} (\eta_2 / \eta_1)^{1.9} (0.6 + \eta_2 / \eta_1)^{-2.4} \dots 55$$

(Sch. 1)<sup>5/6</sup>

Fig.27(a) Diagrammatic representation of the stirred cell system used by Lewis.

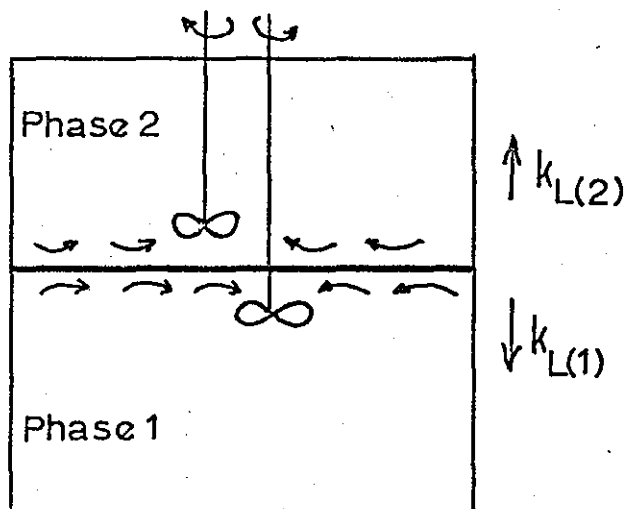
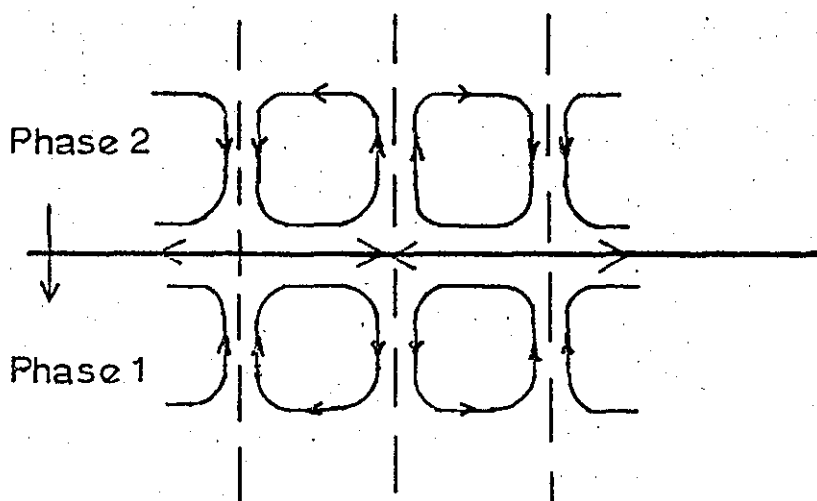


Fig.27(b) Diagrammatic representation of the formation of convection cells.





where Sch. is the Schmidt number defined as  $\nu/D$ . This correlation, which is accurate in predicting values of  $k_L$  to  $\pm 40$  per cent, suggests that  $k_L$  is dependent on  $D^{1/6}$  in the stirred cell and not  $D^{1/2}$  as predicted by Danckwerts' Surface Renewal Theory.

The dependence of  $k_L$  on the diffusivity is a useful indication of the mode of mass transfer in a system. Lewis and Whitman's Film Theory<sup>46</sup> predicts a dependence on diffusivity to the first power across a stagnant film of liquid near to the interface. Under these conditions the rate of mass transfer is governed by:

$$\frac{dq}{dt} = \bar{a} k_L \Delta c \quad \dots\dots\dots 56$$

where  $\frac{dq}{dt}$  is the rate of mass transfer of material,  $\bar{a}$  is the interfacial area and  $\Delta c$  is the difference between the concentration of solute at the interface and in the bulk. The mass transfer coefficient is defined as:

$$k_L = \frac{D}{\Delta x} \quad \dots\dots\dots 57$$

where  $\Delta x$  is the thickness of the laminar sublayer or stagnant film.

If, however, there is an extreme of turbulence and eddies of fresh solution are rapidly swept into the immediate vicinity of the interface, neither the laminar sublayer nor a stationary surface can exist. In this case the diffusion path becomes so short that diffusion is no longer rate-controlling and the rate of mass transfer is governed by:

$$\frac{dq}{dt} = \bar{a} \bar{v}_n \Delta c \quad \dots\dots\dots 58$$

where  $\bar{v}_n$  is the mean velocity of the liquid normal to the interface and equal to  $k_L$ . The latter is now independent of the diffusivity.

The theory of Danckwerts predicts an intermediate dependence between these two extremes of  $D^{\frac{1}{2}}$  and mass transfer is visualised to take place by the continual replacement of surface elements from the bulk of the continuous phase by eddy diffusion. The validity of the Danckwerts model has been proved experimentally for such systems as gas adsorption in packed columns where short contact times of the gas with a turbulent liquid are encountered. In the case of the stirred cell, the dependence of  $k_L$  on  $D^{1/6}$  in Equation 55 suggests that when the surface is uncontaminated the replacement by turbulent flow of elements of liquid in the surface is very important and that molecular diffusion from these elements occurs over a very short distance. On this evidence successful application of Danckwerts theory to the stirred cell data obtained by Cox and Strachan might seem doubtful.

More recent work in this field, however, indicates that the mass transfer coefficient does depend upon the square root of the diffusion coefficient. McManamey et.al.<sup>47</sup> determined the water phase mass transfer coefficient for the diffusion of helium and iso-butane from water to toluene and dekalin in a transfer cell similar to that of Lewis<sup>44</sup>. Much of the early work on mass transfer coefficients was based on rates of mutual saturation of binary liquid systems, and the variations in  $D$  were obtained by changing the liquids, with a consequent alteration in viscosity. Because the diffusion coefficient and viscosity are inter-related, their effects on the

mass transfer coefficient are difficult to separate. McManamey's three component system, with the transfer of solutes with differing diffusivities between two liquid phases, allowed the influence of D to be estimated directly. The use of helium, with a diffusivity of  $6.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , and iso-butane, with a diffusivity of  $1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , allowed a relatively large variation in  $k_L$  to be achieved from which the mean exponent on D was estimated at 0.45. This work lends added weight to the values of  $k_L$  obtained by Cox and Strachan by the application of the Danckwerts equation to their stirred cell system.

The exact dependence of  $k_L$  on the viscosity of each phase is rather more difficult to estimate. It exerts its influence principally through its appearance in the Reynolds and Schmidt number terms in empirical correlations. Equation 55 allows us to make some estimate of the effect of viscosity on the value of  $k_L$  observed in a stirred cell system such as ours, when phase 1 is changed from one of pure water to one of 80 per cent sulphuric acid. If we consider that during this change the physical parameters such as N and L remain constant and phase 2 remains the same i.e. toluene, with a constant viscosity<sup>48</sup>,  $\eta_2$ , of 0.59cP at 20°C, then:

$$k_{L(1)} \propto D_1 \left( \frac{\rho_1}{\eta_1} \right)^{0.5} \left( \frac{1}{\eta_1} \right)^{1.9} \left( 0.6 + \frac{\eta_2}{\eta_1} \right)^{-2.4} \left( \frac{\eta_1}{\rho_1 D_1} \right)^{5/6} \dots\dots 59$$

The variables may be grouped such that:

$$k_{L(1)} \propto D_1^{1/6} \cdot \rho_1^{-1/3} \cdot \left( \eta_1^{-1.6} \left( 0.6 + \frac{\eta_2}{\eta_1} \right)^{-2.4} \right) \dots\dots 60$$

When the values of  $D_1, \rho_1$  and  $\eta_1$  for pure water, or dilute aqueous solutions, and 80 per cent sulphuric acid, shown in Table 19, are

inserted into the proportionality the overall decrease in  $k_L$  due to the change of these parameters is estimated at ca.40. The individual contributions to the decrease due to the variables  $D_1$ ,  $\rho_1$  and  $\eta_1$  are 1.5, 1.2 and 21, respectively which suggests that the principal factor in the determination of  $k_L$  is probably the viscosity. Clearly, this can only be an approximate guide to the individual effects, the dependence of  $k_L$  on  $D_1^{1/2}$  in accordance with the observations of McManamey would mean the estimate of 1.5 is probably somewhat low. Nevertheless, the empirical correlation easily accounts for the low values of  $k_L$  obtained for chlorobenzene and toluene in the absence of chemical reaction compared to those obtained in aqueous systems. Typically, Blokker<sup>36</sup> observed values of 2.60 and  $2.14 \times 10^{-3} \frac{\text{cm s}}{\lambda}$  for the transport of ethyl acetate and isobutanol in water at 25°C, some ten times greater than that observed in 70-80 per cent sulphuric acid.

TABLE 19.

PARAMETER	AQUEOUS MEDIUM	TEMP/°C	80% $H_2SO_4$	TEMP/°C
$D_1/\text{cm}^2\text{s}^{-1}$	$1.0 \times 10^{-5}$ , ref.35	30	$0.8 \times 10^{-6}$ , ref.1.	20
$\rho_1/\text{g ml}^{-1}$	1.0, ref. 48.	20	1.73, ref. 48.	20
$\eta_1/\text{cP}$	0.86, ref. 41.	26.7	16.6, ref. 41.	26.7

An alternative explanation for the lower intrinsic value of  $k_L$  obtained in our stirred cell system compared to Blokker's may be found in the differences in physical set up between the two. The influence of a change in vessel geometry or shape of stirrer is difficult to assess. However, the principal difference between the two systems is the use, by Blokker, of two-counter rotating paddles

for the individual agitation of both phases. The effect of the additional stirrer may well be significant. The effectiveness of stirring in the system is measured by the Reynolds number, which represents the ratio of inertial forces to viscous forces in the liquid, and is dependent on the stirrer intensity,  $f$ , given by  $L^2N$ . It is an important group and is used as an indicator for the existence of turbulent or laminar flow. According to Equation 55  $k_L$  is dependent upon the Reynolds numbers of both phases equally and thus the absence of a stirrer in the organic phase in our system is likely to effect the magnitude of  $k_L$ .  $Re_2$  can never reach zero, since this would lead to a value of  $k_L$  equal to zero, therefore mechanical agitation of the lower phase (phase 1) must induce some degree of agitation in the phase above it due to the shearing forces applied through the interface. The effect of shear manifests itself in the familiar waves and undulations observed in these systems. The results of the experiments with chlorobenzene at high sulphuric acid strengths, where poor agitation of the organic phase was thought to be the cause of a stratification of product and reactant in the organic phase (Section 6.6), suggest, however, that in this system the degree of turbulence transmitted to the organic phase may be rather low. To clarify this point, and therefore determine the extent to which stirring of the organic phase affects the value of  $k_L$ , it is suggested that a series of mass transfer runs be performed with toluene or chlorobenzene in concentrated sulphuric acid utilizing a set up similar to Blokker's, with both phases being individually stirred by counter-rotating paddles.

## 7.2. INTERFACIAL TURBULENCE

Despite the lack of any definitive fundamental theoretical treatment for results obtained from a stirred cell system, the importance of the replacement by turbulent flow of surface elements is unquestionable. In fact, the continual replacement of liquid is readily visible when talc particles are sprinkled on the surface of a liquid. The nature of this interfacial turbulence or convection is of considerable interest to chemical engineers since the movement at the interface and its vicinity changes the resistance to mass transfer and thus the mass transfer coefficient. The effect of interfacial turbulence on the interfacial area, and hence the rate of mass transfer, is also important, although this is not significant when the depths of the phases between which mass transfer takes place are large in comparison to the thickness of the layers subjected to interfacial movement. This is probably true in the case of the stirred cell.

If two liquids are brought into contact with one another in the absence of any external agitation mass transfer will occur. The process will never be uniform, however, and localized areas of lower interfacial tension will appear resulting in a movement of liquid initially parallel to the interface and then moving away from it. The interface is simultaneously being replaced by fresh liquid from the bulk and this leads to the formation of convection or roll cells. Figure 27(b) is a diagrammatic representation of a part of the interface and shows the movement of liquid near to it. The factors that determine the growth and persistence of these roll cells and the speed of the convection process are numerous. The essential prerequisite is, however, the existence of a concentration

(or temperature) gradient leading to an interfacial tension gradient across the interface.

A mathematical treatment of the hydrodynamics of this spontaneous interfacial convection process has been laid out by Sternling and Scriven<sup>49,50,51</sup>. They have considered the conditions under which a fluctuation in the surface tension during mass transfer can build up into a macroscopic eddy. They suggest that surface eddying leading to improved mass transfer will be promoted by:

- (a) Solute transfer from the phase of higher viscosity and lower diffusivity.
- (b) Large differences in  $D$  and  $\nu$  between the two phases.
- (c) Steep concentration differences near the interface.
- (d) A large decrease in interfacial tension with concentration of solute.
- (e) The absence of surface active agents.
- (f) A large interfacial area.

Clearly, in the stirred cell nitration of chlorobenzene or toluene, not all of these factors are important. An explanation for the increased  $k_L$  value obtained when chemical reaction is taking place compared to when it is not is sought, however, and therefore the factors of principal interest are those that might be expected to change when chemical reaction takes place. Three factors may be isolated. The first is the effect of increasing concentration gradient with rate of reaction. At low rates of reaction, or in the absence of it, the concentration gradient of aromatic on the acid side of the interface is small. On increasing chemical reaction  $\left(\frac{dc}{dx}\right)_{x=0}$  becomes steeper as shown in Figure 3(c). It should be pointed out

that the above concentration gradient is that normal to the interface and not parallel with it as indicated by Figure 27(b). However, since the movement of the roll cells is circular, both concentration gradients might be expected to have an influence on the speed of convection.

The second effect is the production of surface active agents, in the form of the nitroaromatic products of the reaction, at the interface. This might be expected to have the opposite effect to the above and mass transfer would be reduced mainly due to a damping of interfacial turbulence by a thin film of nitro-product<sup>36</sup>. To counterbalance this is the effect of the change in interfacial tension with concentration of solute. The third factor, not mentioned above, is the presence of a temperature gradient at the interface due to the high exothermicity of nitration. This might be expected to indirectly increase the value of  $k_L$  by its influence on the viscosity. In the case of the stirred cell the rate of reaction is slow and the rate of heat production low in the bulk of the acid phase. The temperature at the interface may be considerably greater than in the bulk, however. A quantitative assessment of the influence of the above factors is not possible. The overall effect is nevertheless quite clear; chemical reaction improves surface renewal at the interface in the stirred cell and compensates for the intrinsically low values of  $k_L$  observed in the absence of chemical reaction. The phenomenon is entirely consistent with the concept of surface renewal taking place by interfacial convection and the continual replacement of surface elements by eddy currents.



### 7.3. CONCLUSION.

The discussion above accurately reflects the complicated nature of mass transfer in stirred cell systems. Despite empirical correlations and theoretical equations this system still lacks a general treatment and each set up should be considered separately. The exact influence of each variable on mass transfer under all conditions may not be possible. However, indications are that the dependence of  $k_L$  on  $D^{1/2}$  in this system, similar to that observed in the packed column and stirred reactor, permits the use of Danckwerts' Surface Renewal Theory in the interpretation of the results. Considerable care must nevertheless be taken in the elucidation of values of  $k_L$  obtained in the presence of appreciable chemical reaction. The value of  $k_L$  cannot be taken as constant for all rates of chemical reaction. The use of the stirred cell at very fast rates of reaction can lead to problems connected with the accumulation of products near to the interface. The use of a stirred cell in which both liquid phases are agitated may overcome this problem and this is strongly recommended for future work.

## CHAPTER 8

### ZERO-TH-ORDER KINETICS AND THE MECHANISM OF NITRATION.

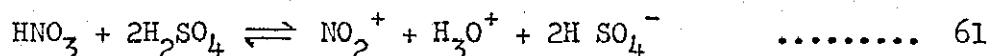
#### 8.1. THE KINETIC FORM OF NITRATION IN ORGANIC SOLVENTS.

Our knowledge of the mechanism of nitration in organic solvents such as nitromethane and acetic acid is largely due to the work of Ingold and his collaborators. They were the first to observe the characteristic kinetic features of the reaction and correctly interpret them in terms of the nitronium ion mechanism. This mechanism was first proposed by Euler in 1903, but it was not until 1946 that existence of the nitronium ion was proved conclusively and its effectiveness as the electrophilic species in nitration clearly established.

#### 8.2. THE EXISTENCE OF THE NITRONIUM ION.

The existence of the nitronium ion has been proved in three ways which do not depend on its behaviour in the nitration process:

(a) A study of the effect of nitric acid on the freezing point of sulphuric acid indicates that the observed depression is approximately four times that of an ideal solute<sup>52</sup>. This points to the existence of an equilibrium whereby nitric acid is transformed into nitronium ions in accordance with the following:



(b) The nitronium ion has been identified in the Raman spectra of nitric acid in sulphuric acid<sup>53,54</sup>. A band at  $1400 \text{ cm}^{-1}$  is attributed to the nitronium ion while a band at  $1050 \text{ cm}^{-1}$  is due to the bisulphate ion, formed simultaneously with the nitronium ion as indicated by the above equilibrium. The intensity of the

bands are strongly dependent on the sulphuric acid strength and are not detectable below acid strengths of 85 per cent.

(c) Nitric acid and perchloric acid react<sup>55</sup> to form solid, salt-like nitronium and hydroxonium perchlorates  $(\text{NO}_2)^+ (\text{ClO}_4)^-$  and  $(\text{H}_3\text{O})^+ (\text{ClO}_4)^-$ . The nitronium ion salt may be obtained pure and its structure has been determined by X-ray crystallography<sup>56</sup>.

### 8.3. THE EFFECTIVENESS OF THE NITRONIUM ION.

The existence of the nitronium ion is not, however, proof of its effectiveness in the nitration process. For this we turn to the results of the kinetic studies performed by Ingold and his collaborators. They observed several characteristic features of the reaction:

(a) The rates of nitration of benzene, toluene and ethylbenzene in solutions of nitric acid in nitromethane<sup>57</sup> were observed to be independent of the concentration of aromatic substrate. i.e. zeroth-order with respect to aromatic. This clearly indicates that nitration proceeds through a slow formation of a reactive intermediate. Under conditions in which benzene and its homologues were nitrated at the zeroth-order rate, the reactions of the halogenobenzenes obeyed no simple kinetic law whereas the nitration of p-dichlorobenzene<sup>58</sup> was fully dependent on the first power of the concentration of aromatic. Nitration in acetic acid<sup>58</sup>, sulpholan<sup>59</sup> and carbon tetrachloride<sup>60,61,62</sup>, showed similar kinetic phenomena and discounts the possibility of the results being explained on the basis of solvent effects. The zeroth-order rate was found to depend on the character of the organic solvent. Since the rate, under these

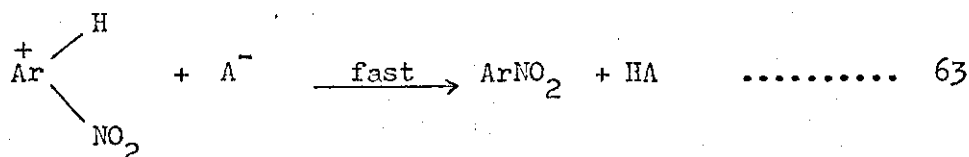
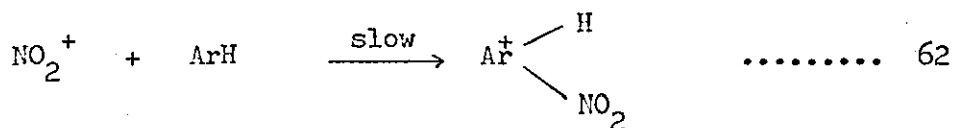
conditions, is dependent upon the heterolysis of nitric acid, involving the generation of ions from neutral molecules, it is accelerated by an increase in the polarity of the medium. Thus, both acetic acid and sulpholan closely resemble each other and are both "slower" solvents than nitromethane. It is not possible to give more than this qualitative description because of the difficulty in assessing the polarity of the medium from its macroscopic physical properties.

(b) Very small amounts of nitrate ions strongly retard the zeroth-order rate without modification of the kinetic form. This is an important observation for it shows that the formation of nitronium ions, which is rate controlling under these conditions, must itself consist of two steps. The first (Equation 1), providing nitrate ions, is easily reversible whereas the second (Equation 2) is poorly reversible, since under zeroth-order conditions the aromatic substrate traps the nitronium ions as soon as they are formed. A pre-equilibrium step must therefore exist and this leads to the postulation of the separate existence of the nitric acidium ion,  $\text{H}_2\text{NO}_3^+$ .

(c) The addition of water has negligible effect on the zeroth-order rate but the addition of sufficiently large quantities causes the zeroth-order kinetics to be displaced by first-order kinetics. This confirms the suggestion that water is not produced in the easily reversible first step but in the second step, with the simultaneous production of the electrophilic species.

The final stage in the nitration of aromatics, reaction of the electrophilic species with the aromatic substrate, is similarly

well understood. The accepted theory likewise involves the postulation of two stages, a slow uptake of nitronium ion being followed by rapid transfer of a proton. Since the rate-determining step is bimolecular the mechanism is labelled S<sub>E</sub>2:



The intermediate cation, the so called Wheland intermediate, is now well substantiated on theoretical grounds<sup>63</sup>.

Thus, through the elegant work of Ingold and his collaborators, the effectiveness of the nitronium ion mechanism in organic solvents is well established.

#### 8.4. THE MECHANISM OF NITRATION IN THE MIXED ACID SYSTEM

Surprisingly, no comparable kinetic evidence for the existence of the nitronium ion mechanism in mixed acid systems, such as used in the industrial mononitration of aromatics, has been reported<sup>13</sup>. This is undoubtedly due to the very low solubilities of aromatics in aqueous sulphuric and nitric acid solutions. Some investigators<sup>64</sup> have suggested that nitronium ions may not exist in the relatively weak mixed acids normally used for the nitration of reactive aromatics such as toluene, benzene and phenol. Buntin et al<sup>65</sup> considered that the nitrosonium ion, NO<sup>+</sup>, may be the active nitrating agent under these conditions. The observation

of the principal kinetic feature of the nitronium ion mechanism in the nitration of toluene and o-xylene in the range 70-80 per cent sulphuric acid is of some importance, therefore. It confirms the effectiveness of the nitronium ion as the electrophilic species under commercial nitrating conditions.

The phenomenon of zeroth-order kinetics is observed at the limit of observation by the stopped-flow technique in the homogeneous system and with virtually saturation concentrations of aromatic in the acid. The process is promoted by a high reactivity and solubility of the aromatic but both factors are severely limited. The possibility of obtaining zeroth-order kinetics with benzene as substrate should be reasonable due to the somewhat higher solubility, although rather high sulphuric acid strengths would be necessary. The observation of the phenomenon with chlorobenzene is less likely due to its low reactivity. The use of very reactive substrates such as mesitylene is counterbalanced by the effect of encounter control on the value of  $k_2'$  obtainable and the low solubilities often encountered. There is a possibility of increasing the solubility possible by increasing the temperature at which runs are performed. This might lead to more accurate values of  $k_1$ .

#### 8.5. THE INDUSTRIAL NITRATION OF AROMATICS.

The onset of zeroth-order behaviour in the homogeneous system results in a suppression of the rate of nitration in the two phase mixed acid system below that predicted assuming first-order kinetics. This suppression comes on top of the already suppressed rate of nitration for reactive aromatics, due to the onset of encounter control, and accounts for the plant operating experience which shows that benzene can be nitrated in a continuous plant

designed for toluene with only very minor changes in conditions<sup>13</sup>. Furthermore, the exact knowledge of the mechanism of nitration in the two phase system allows us to look at earlier work on the subject in a new light. Previous work on the reaction in miniature continuous and batch reactors involved the empirical correlation of rate data due to the lack of any real theoretical model. This work can now be reassessed in terms of Danckwerts' Surface Renewal Theory and the nitronium ion mechanism. In particular, the extensive data of McKinley and White<sup>9</sup> for the nitration of toluene in a continuous flow system could yield much useful information for future plant design.

#### 8.6. CONCLUSION.

The anomalous features of toluene nitration at high sulphuric acid strengths in the stirred reactor and stirred cell have been accounted for by consideration of a changeover in rate determining step in the homogeneous system. This now brings the results of toluene obtained by Cox into line with those of chlorobenzene. Both aromatics may now be suitably treated by Danckwerts' Theory of Mass Transfer. In this respect an important aim of this thesis has been achieved.

Nitration, despite having been studied from a kinetic standpoint for the best part of a century, still remains a rich source of interest for the organic-physical chemist and chemical engineer. Throughout the course of this work several points of interest have been raised connected with nitration generally which suggest further areas of work as follows:

(a) Additional determinations of the value of  $k_1$  would seem desirable. In particular, providing accurate values of  $k_1$  could be obtained, it would be of interest to obtain an estimate of the activation energy for the ionization of nitric acid to nitronium ions. Similarly, an accurate correlation of  $k_1$  with sulphuric acid strength would allow predictions and extrapolations of the value of  $k_1$  to be made at other acid strengths. The values of  $k_1$  obtained from kinetic data could be confirmed by means of a relaxation technique such as the temperature jump method. This would involve the sudden displacement of the equilibrium between nitric acid and nitronium ions. The rate of restoration of the equilibrium may then be followed and will always obey a first-order kinetic law from which the relaxation time may be estimated. This is related to the backward and forward rate coefficients for the equilibrium and may be used to obtain estimates of them.

(b) The problem of simultaneous mononitration and dinitration has received little attention. This is of some industrial significance since dinitro-products are an impurity and should be minimized. McKinley and White<sup>9</sup> observed generally insignificant amounts of dinitrotoluene in their mononitration process. However, in two runs appreciable amounts of dinitro-products were formed coinciding with rather higher nitric acid concentrations in the acid feed. Since, under these conditions, toluene was not observed in the organic product stream they concluded that dinitrotoluene is not produced under steady-state conditions until the mononitration of toluene is substantially complete. Plant experience indicates, however, that substantial dinitration may well occur at the beginning of the run when the nitric acid concentration



is at a maximum. This brings into doubt the consecutive nature of the dinitration process. It would be of interest to establish whether the concentration of nitric acid affects the relative rates of mono and dinitration in a stirred reactor and in fact whether this relative rate agrees with that predicted assuming the individual rates of nitration of aromatic and mononitroaromatic.

(c) The study of the side reactions of nitration, particularly oxidation reactions, has already received attention<sup>66</sup>. Interest was originally aroused by the appearance of colours in both organic and acid phases. Most of the main products of the reactions have been identified and a mechanism postulated for their production. This involves the attack of the aromatic through the oxygen on the nitronium ion to form an aryl nitrite which further reacts to give phenols. The evidence for the existence of these aryl nitrites is, as far as we can see, rather speculative and the mechanism likewise. Nevertheless, the extent to which oxidation takes place and competes with nitration is of some commercial importance and is conveniently monitored by the rate of formation of nitrous acid which is formed in equimolar quantities with the by-products. The ratio of by-products to nitroaromatics formed has been determined for a number of aromatics but requires further study so that the factors that affect the relative ease of oxygen and nitrogen attack of the nitronium ion may be elucidated.

(d) Finally, the effect of a most important parameter,  $a'$ , the interfacial area per unit volume of acid phase, in the nitration of aromatics in stirred reactors, has received little or no interest. Clearly, the optimization of this parameter is important. It would

thus seem desirable to obtain a measure of this parameter via the mean drop diameter under a wide variety of conditions in a stirred reactor. This could be done by means of fast speed cine photography which would also afford a means by which the production, break-up and coalescence of drops could be studied. The effect of the change of organic phase composition, from one of pure substrate to one of nearly pure mononitrated substrate, on the drop size might be investigated.

## APPENDIX

### THE DETERMINATION OF NITRIC ACID IN SULPHURIC ACID BY A COLORIMETRIC METHOD

#### SOLUTION OF IRON REAGENT

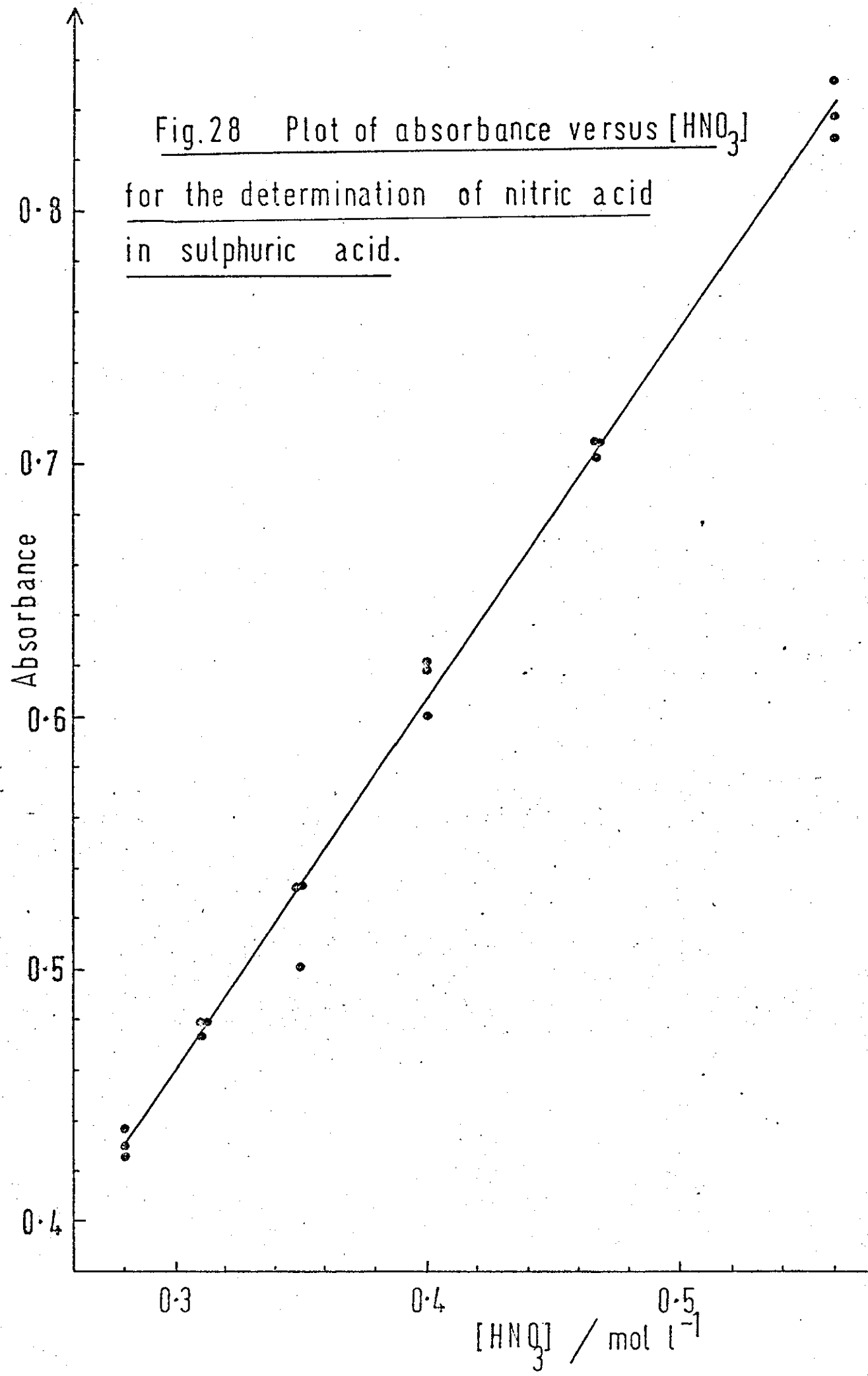
$\text{FeSO}_4 (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$  (20g) dissolved in 100 ml of 10 per cent (V/V) aqueous sulphuric acid and filtered.

#### PROCEDURE

A 0.1 ml quantity of the spent acid was pipetted into 1.0ml of distilled water in a 25 ml conical flask. This was cooled in an ice bath and 1.0ml of the iron reagent run in followed by 12.5 ml of 5:1 (V/V) sulphuric acid with swirling and cooling. The latter was added slowly at first so as not to let the temperature exceed  $25^\circ\text{C}$ . A wine red colour developed which was stable up to 20 minutes. The absorbance was measured at 515nm, as soon as possible after the addition of the acid, against a 5:1 sulphuric acid blank. Figure 28 shows a plot of absorbance versus time for a number of standard solutions of nitric acid in ca.70 per cent sulphuric acid. A linear correlation was observed up to  $0.56 \text{ mol l}^{-1}$  nitric acid, the concentration at which the stirred cell runs were performed.

Fig.28 Plot of absorbance versus  $[HNO_3]$

for the determination of nitric acid  
in sulphuric acid.



## REFERENCES

1. Cox P.R. Ph.D. Thesis, Loughborough University of Technology England, 1971.
2. Ingold C.K. "Structure and Mechanism in Organic Chemistry". G. Bell and Sons Ltd., London, 1969.
3. Deno N.C., Peterson H.J. and Sacher E. J. Phys.Chem. 1961 65 199.
4. Coombes R.G., Moodie R.B. and Schofield K. J.Chem.Soc.(B) 1968 800.
5. Moodie R.B., Schofield K. and Williamson M.J. "Nitro-compounds". Proceedings of the International Symposium, Warsaw, 1963. Pergamon Press, London, 1964 p.89.
6. Deno N.C., Jaruzelski J.J. and Schriesheim A. J.Amer.Chem.Soc. 1955 77 3044.
7. Caldin E.F. "Fast Reactions in Solution". Blackwell, Oxford, 1964.
8. Lewis W.K. and Suen T.J. Ind.Engng. Chem. 1940 32 1095.
9. McKinley C. and White R.R. Trans. A.I.Ch.E. 1944 40 143.
10. Brennecke H.M. and Kobe K.A. Ind.Engng.Chem. 1956 48 1298.
11. Barduhn A.J. and Kobe K.A. Ind.Engng.Chem. 1956 48 1305.
12. Cox P.R. and Strachan A.N. Chem.Engng.Sci. 1971 26 1013.
13. Hanson G., Marsland J.G. and Wilson G. Chem.Engng.Sci. 1971 26 1513.
14. Wilson G. Ph.D. Thesis, University of Bradford, England, 1967.
15. Cox P.R. and Strachan A.N. Chem.Engng.Sci. 1972 27 457.
16. Cox P.R. and Strachan A.N. Chem.Engng.J. 1972 4 253.
17. Danckwerts P.V. Trans. Faraday Soc. 1950 46 300.
18. Danckwerts P.V. Ind.Engng.Chem. 1951 43 1460.
19. Lewis W.K. and Whitman W.G. Ind.Engng.Chem. 1924 16 1215.
20. Higbie R. Trans. A.I.Ch.E. 1935 31 365.
21. Astarita G. "Mass Transfer with Chemical Reaction". Elsevier Pub.Co., Amsterdam, 1967.
22. Danckwerts P.V., Kennedy A.M. and Roberts D. Chem.Engng.Sci. 1963 18 63.
23. Sharma M.M. and Fernandes J.B. Chem.Engng.Sci. 1967 22 1267.
24. Sharma M.M. and Danckwerts P.V. Brit.Chem.Engng. 1970 15 522.

25. Juvekar V.A. and Sharma M.M. Chem.Engng.Sci. 1973 28 825.
26. Joosten G.E.H. and Danckwerts P.V. Chem.Engng.Sci. 1973 28 453
27. Sahay B.N. and Sharma M.M. Chem.Engng.Sci. 1973 28 41.
28. Sahay B.N. and Sharma M.M. Chem.Engng.Sci. 1973 28 2245
29. Mehta V.D. and Sharma M.M. Chem.Engng.Sci 1971 26 461.
30. Cerfontain H. and Telder A. Rec.Trav.Chim. 1965 84 545.
31. Deno N.C. and Perizzolo C. J.Amer.Chem.Soc. 1957 79 1345.
32. Coombes R.G., Crout D.H.G., Hoggett J.G., Moodie R.B. and Schofield K. J.Chem.Soc. (B) 1970 347.
33. Reid R.C. and Sherwood T.K. "Properties of Gases and Liquids". Mc Graw-Hill, London, 1958 p. 283.
34. Perkins L.R. and Geankoplis C.J. Chem.Engng.Sci. 1969 24 1035.
35. Ismail H.A.M. Ph.D. Thesis, Bradford University, England, 1973.
36. Blokker P.C. 2nd International Congress of Surface Activity, Vol. 1. Butterworths, London, 1957, p.503.
37. Deno N.C. and Stein R. J.Amer.Chem.Soc. 1956 78 578.
38. Cerfontain H. Rec. Trav.Chim, 1965 84 491.
39. Kort C.W. and Cerfontain H. Rec.Trav.Chim. 1968 87 24.
40. English F.L. Anal.Chem. 1947 19 (11) 850.
41. Fasullo O.T., "Sulphuric Acid". McGraw Hill, London, 1965 p.302.
42. Caldin E.F. "Fast Reactions in Solution ". Blackwell, Oxford, 1964.
43. Glasstone S. Laidler K.J. and Eyring H. "The Theory of Rate Processes". McGraw-Hill, London, 1941, p.505.
44. Lewis J.B. Chem.Engng.Sci. 1954 3 248, 260.
45. Davies J.T. and Mayers G.R.A. Chem.Engng.Sci. 1961 16 55.
46. Lewis W.K. and Whitman W.G. Ind.Engng.Chem. 1924 16 1215.
47. McManamey W.J., Davies J.T., Woollen J.M. and Coe J.R. Chem.Engng.Sci. 1973 28 1061.
48. "Handbook of Chemistry and Physics". C.R.C. Press, 54th edition, 1973.
49. Sternling C.V. and Scriven L.E. A.I.Ch.E.J. 1959 5 514.
50. Sawistowski H. in "Recent Advances in Liquid-liquid Extraction" Ed. Hanson C. Pergamon Press, Oxford, 1971.

51. Davies J.T. and Rideal E.K. "Interfacial Phenomenon". Academic Press, London, 1963.
52. Gillespie R.J., Graham J., Hughes E.D. and Ingold C.K. and Peeling E.R.A. Nature 1946 158 480.
53. Fénéant S. and Chédin J. Mém. Services. chim.Etat. 1955 40 292.
54. Ingold C.K., Millen D.J. and Poole H.G. J.Chem.Soc. 1950 2576.
55. Goddard D.R., Hughes E.D. and Ingold C.K. J.Chem.Soc. 1950 2559.
56. Cox E.G., Jeffrey G.A. and Truter M.R. Nature 1948 162 259.
57. Benford G. and Ingold C.K. J.Chem.Soc. 1938 929.
58. Hughes E.D., Ingold C.K. and Reed R.I. J.Chem.Soc. 1950 2400.
59. Hoggett J.G., Moodie R.B. and Schofield K. J.Chem.Soc. (B) 1969 1.
60. Coombes R.G. J.Chem.Soc. (B) 1969 1256.
61. Bonner T.G., Hancock R.A. and Rolle F.R. Tetrahedron Lett. 1968 1665.
62. Bonner T.G., Hancock R.A. Yousif G. (in part) Rolle F.R. J.Chem Soc. (B) 1969 1237.
63. Wheland G.W. J.Amer.Chem.Soc. 1942 64 1900.
64. Albright L.F. Ind.Engng.Chem. 1965 57 (10) 53.
65. Buntin C.A., Hughes E.D., Ingold C.K., Jacobs D,I.H. Jones M.M., Minkoff G.J. and Reid R.I. J.Chem.Soc. 1950 2628.
66. Sohrabi T. Ph.D. Thesis, Bradford University, England, 1972.

