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HETEROGENEOUS CATALYSIS OF SUBSTITUTION REACTIONS

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ABSTRACT

The subject of this thesis is the heterogeneous catalysis of the hydrolysis of alkyl halides. A literature survey of this topic and of the heterogeneous catalysis of the hydrolysis of α-halo-acids showed that no systematic study of the phenomenon had previously been undertaken. It also indicated that heterogeneous catalysis of the reaction was only significant in aqueous solutions. The present work consisted of two parts. First, a semi-quantitative study was made of the catalysis of the hydrolysis of ethyl iodide in water by silver nitrate in the presence of a wide range of solids. The hydrolysis was also carried out using Hg_2^{2+}, Hg^{2+}, Pb^{2+}, and Tl^{+} nitrates in the presence of a series of insoluble iodides. For these studies a reaction vessel was designed and built. The effectiveness of the catalysts used has been correlated with the type of complex formed between the reactants and the surface in terms of Pearson's theory of hard and soft acids and bases.

Second, a quantitative study was made of the reaction between silver nitrate and ethyl iodide on a silver iodide surface in water. Initially, the rotating disc technique was used and a second cell was designed and built. However, this work showed that the reaction was surface controlled, and so the disc was abandoned, and a study of the reaction using silver iodide powder was undertaken. The surface area of the powder and the adsorption isotherms of the reactants on it were also measured. The results were interpreted in terms of a Langmuir-Hinshelwood mechanism for the surface reaction.

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Chapter 1

INTRODUCTION

Berzelius,[1] in 1835, was the first chemist to use the term catalysis, in connection with a number of previously unrelated observations. In these observations, the nature of the reaction was influenced by the presence of a substance which was itself unchanged by the process. Since then, catalysis has come to be defined as "the influence on the velocity of a reaction of a substance added to the reaction, the substance itself being chemically unchanged at the end of the reaction".[2] This is a very broad definition, and allows for non-homogeneity of the reaction phase, acceleration and retardation of the velocity, and change in the physical state of the catalyst during a reaction.

Much work has been done on homogeneous catalysis in solution [9] (e.g. acid-base catalysis of various organic reactions) and on heterogeneous catalysis in the gas phase.[9] However, remarkably little work has been done on heterogeneous catalysis by solids in solution, in spite of the fact that heterogeneous catalysis in the liquid phase is widely used in industry, in such processes as catalytic hydrogenation. The industrial approach to the problem seems to be by rule of thumb and "if it works, use it". Very little has been done to understand why "it" is effective. Similarly, in more academic climes, if a heterogeneous catalytic phenomenon is encountered in a solution kinetic study, it has usually been side-stepped in some way - seemingly being a hindrance to the study in hand.

There is, therefore, a great deal to be done in this field before it reaches a state of advancement similar to that reached in the other fields mentioned above.

GENERAL THEORY OF HETEROGENEOUS REACTIONS IN SOLUTION

The overall reaction occurring at a solid/solution interface involves five individual steps:[3]

(i) Transport of reactant species to the interface
(ii) Adsorption on to the solid surface
(iii) Reaction at the surface
(iv) Desorption of products from the surface
(v) Transport of products from the interface

Any one of these may control the overall rate of reaction, by being the slowest. If the transport processes (i) and (v) are slower than the surface processes (ii), (iii), and (iv), then the reaction is said to be transport, or diffusion controlled. If, however, one of the surface processes is the slowest, the reaction is said to be surface controlled. Reactions of intermediate type occur when the rates of the two types of process are similar.

Transport Control

If, at a given point in a solution, the velocity components parallel to the x, y, and z axes are u, v, and w, respectively, then the rate of change of concentration at that point is given by[4]

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) - \left(u\frac{\partial c}{\partial x} + v\frac{\partial c}{\partial y} + w\frac{\partial c}{\partial z}\right) \qquad 1.1$$

$\partial c/\partial t$ is the sum of the rate of change due to diffusion and to convection.

A quantitative approximation to this equation is given by Nernst diffusion theory.[5] Consider a well stirred solution, the bulk concentration of which is constant. At the solid surface in contact with this solution, there is a thin layer of thickness δ, which acts as if it adheres to the surface and through which molecules and ions must diffuse if they are to get to the surface. This is known as the Nernst diffusion layer, or Nernst film.

For a solid of surface area A, in contact with a volume V of solution, of concentration c, Fick's First Law leads to

$$-\frac{dc}{dt} = \frac{DA}{V}\frac{dc}{dy} \qquad 1.2$$

where dc/dy is the concentration gradient normal to the surface, and D is the diffusion coefficient of the solute. Assuming a linear concentration gradient through the Nernst film at the surface

$$\frac{dc}{dy} = \frac{(c - c_1)}{\delta} \qquad 1.3$$

where c_1 is the concentration of the solute at the surface. Thus,

$$-\frac{dc}{dt} = \frac{DA}{V\delta}(c - c_1) \qquad 1.4$$

Diffusion control therefore acts effectively as a first order reaction with a rate constant $k = DA/V\delta$. Nernst assumed that $c_1 = 0$, giving

$$-\frac{dc}{dt} = \frac{DA}{V\delta}.c \qquad 1.5$$

This is reasonable if the surface reaction is fast compared with the rate of diffusion. Thus transport control can be distinguished from surface control by the dependence of its rate on the value of δ, and therefore on the speed of stirring in the solution.

Although the Nernst treatment is only an approximate one, its central tenet, that there exists a concentration gradient in the region of the solution adjacent to and adhering to the solid surface, is sound[6]. The properties and the extent of this region in any system are determined by the diffusion coefficient of the solute, the viscosity of the solution, and the nature of the fluid flow.[7]

In 1942 Levich[8] solved equation 1.1 for the case of a flat horizontal disc rotating about an axis vertical to its plane in an infinite body of liquid. This solution gave a value for δ of

$$\delta = 1.805 \; (D/\nu)^{\frac{1}{3}} \; (\nu/\omega)^{\frac{1}{2}} \qquad 1.6$$

where ν is the kinematic viscosity ($\text{cm}^2.\text{sec}^{-1}$), and ω is the angular velocity of rotation of the disc (rad.sec^{-1}). The theory behind this equation is discussed more fully in Part II of the thesis. It can be seen that if the reaction is transport controlled its rate will be proportional to the square root of the velocity of rotation of the disc, and the technique is therefore of use in determining the rate controlling step of a heterogeneous reaction.

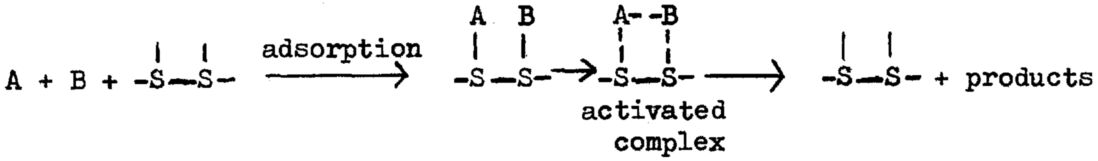
Surface Control[9]

The surface control of a reaction may involve any of the three individual steps (ii), (iii), and (iv) referred to on page 2. Steps (iii) and

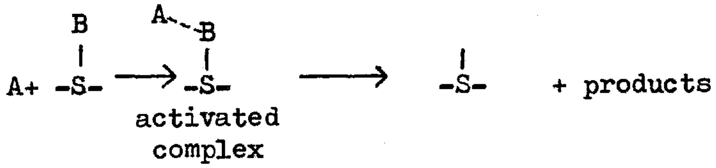
(iv) are usually regarded as a single step-reaction on the surface giving desorbed products.

A general mathematical treatment of the surface control of a heterogeneous reaction in solution has not, to the writer's knowledge, been published. This is presumably because very few solution reactions have been studied, and most of these are transport controlled. For the reaction of gases at a surface, however, the mathematical analysis is well established[9a] and has been very successful in explaining the observed kinetics in many cases. Since the two types of system are very similar, the gas phase treatment will now be briefly considered.

Two distinct models for the reaction between two gases at a surface have been presented. The first, proposed by Langmiur[10] and Hinshelwood[11], assumes that the reaction of two molecules, A and B, at a surface can be represented:



where S is an adsorption site on the surface. It should be stressed that both A and B are adsorbed before reaction occurs - presumably on adjacent sites. The second mechanism, proposed by Rideal,[12] assumes that only one of the reactants is adsorbed on the surface, and that another reacts from the bulk phase. This can be respesented:



It is obviously important to distinguish between these two possibilities in the elucidation of the mechanism of a reaction at a surface. This can be done by a consideration of the kinetic sequences of the two mechanisms. Since a full treatment is presented elsewhere [9,11] only the basic rate equations will be given here.

Langmuir-Hinshelwood Mechanism

The rate of the reaction occurring at the surface is assumed to be given by:

$$\nu = k_o C_A C_B A \qquad 1.7$$

where C_i is the surface concentration of i molecules and A is the surface area.

or, in terms of the fraction of the surface covered, θ, by

$$\nu = k_o \theta_A \theta_B A \qquad 1.8$$

where θ_i is the fraction of surface covered by i molecules

Rideal Mechanism

The rate of reaction is assumed to be given by:

$$\nu = k_o' C_A' C_B A \qquad 1.9$$

where C_B is the surface concentration as above. C_A' is the bulk concentration of A molecules.

In terms of the fraction of the surface covered, θ ,

$$\nu = k_o' \theta_B C_A' A \qquad 1.10$$

The form of equations 1.7 - 1.10, when expressed in terms of the bulk concentrations of A and B, depend on the types of expression assumed for θ_A and θ_B. It should be noted, however, that as the bulk concentrations of A and B increase, θ_A and θ_B will tend to a maximum (on the Langmuir adsorption model $\theta = 1$ for a fully covered surface). When this point is reached, the rate of reaction will become independent of the change of the bulk concentrations of A and B for the Langmuir-Hinshelwood mechanism (equation 1.8) and of the change of the bulk concentration of B molecules for the Rideal mechanism (equation 1.10), i.e. the reaction will tend to zero order with respect to these reactants. The development of equation 1.8 will be considered in Chapter 6.

Redox Reactions

To date, the only general theory of heterogeneous catalysis in solution to be put forward concerns the catalysis by metals of redox reactions in solution of the general type:[14]

$$Ox_1 + Red_2 \rightleftharpoons Red_1 + Ox_2 \qquad 1.11$$

e.g: $2Ce^{4+} + 2Br^- \rightleftharpoons 2Ce^{3+} + Br_2$

With only one definite exception the results, for about 80 reactions, fit the hypothesis that the metal is acting as a simple electron conductor and that the current density-voltage curves of the couples concerned are roughly additive. The extent of catalysis of this type of reaction can therefore be predicted from a knowledge of the electrochemical properties of the couples concerned.

THE SOLVOLYSIS OF HALOGEN-SUBSTITUTED COMPOUNDS[15a]

The heterogeneous catalysis of substitution reactions in solution has not, so far, been investigated systematically. There are, however, many reports of heterogeneous catalysis in the literature,[16] mainly in connection with the solvolysis of alkyl halides and halo-acids. The solvolysis of a typical alkyl halide in the presence of a wide variety of solids was therefore selected for study.

The solvolysis of organic compounds containing halogen atoms is a substitution process[17] of the general type:

$$R - X + Y \longrightarrow R - Y + X \qquad 1.12$$

For example:

$$RCl + H_2O \longrightarrow ROH + HCl$$

$$RCl + OEt^- \longrightarrow ROEt + Cl^-$$

where R is an alkyl group

Ingold & Hughes[18] proposed that there were two possible mechanisms, S_N1 and S_N2. The S_N signifies Substitution Nucleophilic, since the process is essentially that of one, electron rich, nucleophile replacing another at the seat of substitution. The letters 1 and 2 refer to the number of molecules taking part in the rate-determining step. The mechanisms are as follows:

S_N2 This involves two molecules simultaneously undergoing a covalency change and can be represented:

$$Y \curvearrowright R \overset{\curvearrowright}{-} X \longrightarrow Y - R + X \qquad 1.13$$

where the curved arrows indicate the transfer of an electron pair in the making or breaking of a covalent bond. In the transition state, the bonds are described by Ingold[15a] as being partial and partially ionic, differing in length and polarity from the fully formed bonds.

The concurrence of the covalency changes is a major factor in the facilitation of a reaction of this type, since very high activation energies would be necessary otherwise.

SN1 This mechanism involves two stages: a slow heterolysis of the substituted compound followed by a rapid combination of the carbonium ion formed with the substituting agent. The reaction is therefore unimolecular and can be represented generally:

$$R\overset{\curvearrowright}{-}X \xrightarrow{\text{slow}} R^{+} + X^{-} \qquad 1.14$$

$$Y^{-}\overset{\curvearrowright}{\;}R^{+} \xrightarrow{\text{fast}} Y - R \qquad 1.15$$

The ionisation is assumed to proceed through a transition state involving a stretched partial bond, and partial charge transfer.[15a]

The energy of bond breaking is partially compensated by that of solvation, and the activation energy is therefore less than it would be without solvation. Thus a suitable polar solvent is essential to the mechanism.

The Kinetic Criteria of Mechanism

S_N2 If the two reactants are present in small comparable concentrations, the mechanism would be expected to lead to a second order rate equation:

$$\text{Rate} = k_2 \left[Y\right]\left[RX\right] \qquad 1.16$$

There are, however, a number of circumstances in which the rate may appear to be first or an intermediate order. These include one of the reactants being in a constant excess (if the substituting agent is, say, the solvent), or present as a component of a buffered equilibrium, or if the two reactants are not ionically independent (e.g., if they form ion pairs in a non-polar solvent).

S_N1 The mechanism can also lead to first order kinetics, with the overall rate equal to the rate of heterolysis:

$$\text{Rate} = k_1 \left[RX\right] \qquad 1.17$$

This only occurs when the rate of recombination of the ions is negligible compared with the rate of combination with the substituting agent - when the latter is in large excess (e.g., as solvent). Generally, these two rates are comparable and the rate law is of the form:

$$\text{Rate} = \frac{k[RX]}{(1 + \alpha[X]/[Y])} \qquad 1.18$$

where α is the ratio of the specific rates of carbonium ion combination with X and Y. When α is large 1.18 simplifies to:

$$\text{Rate} = k' \frac{[RX][Y]}{[X]} \qquad 1.19$$

If, in some way, $[X]$ is kept constant

$$\text{Rate} = k'' [RX][Y] \qquad 1.20$$

and second order kinetics result.

Some Consequences of the SN1 and SN2 Mechanisms

The detailed consequences of the above mechanisms have been dealt with fully elsewhere[15b], and will not be recounted here. With reference to the system which is the subject of this thesis, the following points are relevant.

The more electron-releasing the alkyl substituent, the more likely the mechanism is to be SN1, since ionisation is the key factor. The electrons are released by the inductive effect and the order of the intensity of the effect for alkyl radicals is

Me < Et ∼ n - Pr and high homologues

and for branched chain molecules

Me < Et < iso - Pr < t - Bu

Thus, one would expect Me and Et and other primary alkyl halides to be more susceptible to attack under an SN2 mechanism, and iso-Pr, t-Bu, and other secondary and tertiary alkyl halides to be more readily ionised, and to react by an S_N1 route. Although there is no sharply defined point at which one mechanism gives way to the other, these predictions have been found to be largely true for the systems examined.[19, 20, 21]

From the above, it can be seen that the effect of introducing a carboxylate ion substituent into the molecule concerned, would be to increase the tendency to follow the S_N1 mechanism. This is because CO_2^- is an electron repelling group and will therefore facilitate the heterolysis. Experimental evidence relating to the solvolysis in water or aqueous alcohol of α-halogeno-acylate ions appears to support this hypothesis.[22,23]

The solvent also plays an important part in the determination of the mechanism. As the solvent becomes more polar, the tendency of the reaction to occur by the S_N1 route increases since the ions formed are more easily solvated and therefore more stable. Formic acid is outstanding in this respect, and will promote unimolecular reaction even of primary alkyl halides, while water, aqueous ethanol, aqueous acetone, dry ethanol, and dry acetone are successively less ionising.

The substituting agent also plays a part in the determination of the reaction mechanism. In general, the more nucleophilic the substituting agent, the more likely the reaction is to go by the S_N2 route. This effect can be used to distinguish the two mechanisms, since the rate of an S_N2 reaction will be dependent on the nucleophilicity of the substituting agent, whereas the rate of a S_N1 reaction will not.

Electrophilic Reagents

The S_N1 heterolysis of an alkyl halide is followed by the solvation and stabilisation of both ions. There are, however, electrophilic reagents which can attract and combine with the displaced group, leaving the carbonium ion to react with the substituting agent. Among such reagents are metal ions, in particular silver and mercuric ions:

$$R - X + Ag^+ \longrightarrow R^+ + AgX_{(s)} \qquad 1.21$$

$$R^+ + Y^- \longrightarrow R - Y \qquad 1.22$$

Kinetic investigations have shown that the rate-determining step of all these[24, 25, 26, 27,28] reactions involves the alkyl halide and the silver ion.

Heterogeneous Catalysis

It has been reported that in reactions of this latter type, the silver halide formed, and the reagent silver oxide if used, catalyse the reaction heterogeneously.[24, 25,27] The reaction taking place at the surface has been pictured as an S_N1 type reaction,[16] the ionisation of the adsorbed alkyl halide occurring with the aid of adsorbed silver ions. The reaction is then completed by the uptake of an anion from solution. However, little is really known about the rate-controlling process at the surface, because the kinetics of the heterogeneous part of the reaction have not been measured alone. It is not even known whether the reaction is surface or transport controlled, nor is any information available about the specificity of the catalyst.

The work reported in this thesis is an attempt to shed further light on these questions. A review of the rather scattered observations on this topic found in the literature is given in the next section.

LITERATURE SURVEY

Two main classes of halogen substituted compounds have been studied in relation to their solvolysis with silver salts. They are alkyl halides, and α- halo-acids. For the sake of convenience, they will be reviewed separately.

Alkyl Halides

Much of the work done has been of a rather fragmentary nature, and the results have therefore been listed in Table 1.1. Some of the more important items from this table will now be discussed.

Donnan and his co-workers[29, 30, 31] studied the reaction of silver nitrate with various alkyl iodides in alcoholic and aqueous alcoholic media. They found that the main reactions occurring were:

$$RI + AgNO_3 + EtOH \longrightarrow ROEt + AgI_{(s)} + HNO_3 \qquad 1.23$$

$$RI + AgNO_3 \longrightarrow RNO_3 + AgI_{(s)} \qquad 1.24$$

$$RI + AgNO_3 + H_2O \longrightarrow ROH + AgI_{(s)} + HNO_3 \qquad 1.25$$

1.23 was considered to be the main reaction occurring in alcohol, and 1.25 likewise in water. 1.24 occurred in both, and all three in water/ethanol mixtures. The distribution of products in pure ethanol was

$$ROEt : RNO_3 = 70 : 30$$

and this was unaffected by the catalysis of the reaction by the ionic nitrates.[30]

The calculated second order rate constant (k_2) was found to increase with increasing initial reactant concentrations (C_o) in ethanol, according

TABLE 1.1

Ref.	Reactants	Solvent	Temp. (°C)	Auto-cat.	Catalysis by added solid	Method of measurement	Order of reaction	Remarks
29	$AgNO_3$ + MeI, EtI, n-PrI, n-BuI, iso-BuI, iso-AmI	dry ethanol	24.5	Not stated	No solid added	Titration for Ag^+ ion	Pseudo-2nd	The 2nd order rate constants depended on the initial concentration of the reactants, especially on the silver nitrate.
30	$AgNO_3$ + EtI	"	"	"	"	Titrn. for Ag^+ & H^+ ions	"	Addition of $EtNO_3$ had no effect on rate. Addition of HNO_3 retarded reaction slightly
30	"	"	"	"	"	"	"	Addn. of $Ca(NO_3)_2$ increased rate. Addn. of NH_4NO_3 increased rate even more. It was concluded that reactant was $AgNO_3$ molecules
30	$AgNO_3$ + EtI, MeI	Aq. EtOH from 0:100 to 100:0 (v/v)	"	Not found	"	"	"	Concluded from Ref. 1 that products must catalyse reaction but were unable to identify catalyst
31	Aglactate + EtI	40:60 v/v H_2O : EtOH	25	Not found	"	"	"	2nd order constants independent of initial concentrations.

TABLE 1.1

Ref.	Reactants	Solvent	Temp. (^oC)	Auto-cat.	Catalysis by added solid	Method of measurement	Order of reaction	Remarks
31	$AgNO_3$ + EtI	CH_3CN	25	Uncertain	No solid added	Titrn. for Ag^+ ion	Pseudo-2nd	2nd order constants depended on initial concentration.
31	$AgNO_3$ + CHI_3	EtOH	"	Not found	"	"	"	Remarks as for Ref. 1.
24	$AgNO_3$ + MeI	H_2O	26	Not stated	4×10^{-3} molar AgI Large effect	"	2nd order const. calc.	
24	" "	EtOH	"	"	4×10^{-3} molar AgI. Not as large as in water.			
32	$AgNO_3$ + EtI	MeOH/EtOH		Not found	No solid added.		2nd order	

TABLE 1.1

Ref.	Reactants	Solvent	Temp. (°C)	Auto-cat.	Catalysis by added solid	Method of Measurement	Order of Reaction	Remarks
33	$AgNO_3$ + MeI, EtI, iso-PrI, neo-PenI	CH_3CN, C_6H_5CN, acetone	25	None found	No solid added	Titrn. for Ag^+ ion	1 w.r.t. RX 1-2 w.r.t. $AgNO_3$	
34	$AgClO_4$ + MeI	benzene	25, 35	uncertain	"	Electrometric titrn. for Ag^+ ion	2nd. $2\frac{1}{2}$ at higher concns.	2nd order contants were dependent on initial concn. of $AgClO_4$. $LiClO_4$ increased rate.
34	" "	"	25		colloidal Ag No effect.			Quantity of solid added not stated.
35	$AgNO_3$ + p-R.C_6H_5.CH_2Br R = H, Me, NO_2	90%(w/w) aq. EtOH	30	Strong	None added	Titrn. for Ag^+ ions	1st, 2nd both calc.	Both constants were dependent on initial concn. of $AgNO_3$.
36	EtI	H_2O	15		colloidal AgI +ve effect	pH		
36	$AgNO_3$ + EtI	H_2O	20	none found		Volhard's titrn. for Ag^+ ion	1st w.r.t. $AgNO_3$	
27	Ag_2O + β-n-octyl bromide, n-PhEtCl	63% aq. EtOH	b.p. of solvent		AgBr added +ve effect	Estimation of bromide remaining		
27	$AgNO_3$ + β-n-octyl bromide	"	35	Found		"		AgOAc gave some initial rate
27	"	"	"		AgBr 1 mole Strong	"		Volume of soln. not stated.
20	$AgNO_3$ + Me, Et, n-Pr, iso-Bu, neo-Pen bromide & chlorides	70% V/V aq. EtOH	63.95 95	Found		Volhard & electrometric titrn. for Ag^+ ion	2nd	

TABLE 1.1

Ref.	Reactants	Solvent	Temp. (^{o}C)	Auto-cat.	Catalysis by added solid	Method of Measurement	Order of Reaction	Remarks
37	$AgNO_3$ + $(CH_3)_2.CCl.(CH_2)_n.CH_3$	EtOH		None found			2, for $n<4$ 1, for $n>9$ 1-2, for n= 4-9	
38	$AgNO_3$ + MeI	H_2O	25	None found		Conductance & titrn.	2nd calc. 1 w.r.t. MeI, 1-2 w. r.t. $AgNO_3$	Calc. 2nd order consts. dependent on initial concn. of $AgNO_3$.
38	$AgClO_4$ + MeI	"	"	"		"	"	Less dependent on initial $[AgClO_4]$ than for $AgNO_3$.
39	$AgNO_3$ + Me → n-Heptyl bromides	70:30 H_2O: acetone		None found				
40	$AgNO_3$ + $(Et)_3CCl$	aq. acetone	Several	None found			Dependent on solvent & temp.	
43	Pr & iso-Pr bromides & iodides	aq. EtOH (small H_2O concns.)	b.p. of solvent		0.17 mole $HgBr_2$ in 150 ml soln. HgI_2 Strong cat. by both solids	Estimation of Br or I remaining		HgI was a better catalyst than HgBr .
46	$AgNO_3$ + Allylchloride	EtOH			0.2 mole AgCl Strong cat.			Volume of solution unstated. Increase in rate of 40-50% in light, & of 20% in dark.

to the relation $k_2 = \text{constant}.C_0^{0.53}$, for equal initial concentration of reactants. This was thought to indicate that one of the products was acting autocatalytically. It was shown that neither nitric acid nor the alkyl nitrate were responsible but the effect of added silver iodide was not investigated.

The reactions in which the alkyl halide was ethyl iodide were first order with respect to the iodide, and between first and second order with respect to the silver nitrate.

It was tentatively concluded from this work that the reacting species was undissociated silver nitrate molecules.

The results obtained by Donnan and his co-workers have recently been re-examined[47] in terms of an ion pair mechanism, for ethanolic and aqueous ethanolic solutions. It was assumed that the silver nitrate is considerably associated in these solvents and that this leads to a transition state of the type

$$NO_3^- \; \overset{+}{R}IAg \qquad 1.26$$

Thus, the rate of the reaction would depend on the concentration of ion pairs in the solution, and not on the stoichiometric concentration of silver nitrate. The degree of association was accurately known in these solutions from conductance data, and this allowed the variation of the measured velocity constant with the initial reactant concentrations to be obtained theoretically. It was calculated that $k_2 = \text{constant } C_o^R$, where R lies between 0.4 and 0.6, in good agreement with the experimentally determined value of Donnan. Also, the predicted value of the increase in rate due to the addition of ammonium nitrate to the reaction solution was in close agreement with the experimental one. It was therefore concluded that the results of Donnan could be explained without recourse to the postulate of heterogeneous catalysis.

An intermediate similar to that in 1.26 was postulated by Hammond etal.[33], for the reaction of ethyl iodide with silver nitrate in acetonitrile. This hypothesis was supported by the fact that silver nitrate gave a higher rate of reaction than silver perchlorate, and when silver perchlorate was used, the addition of lithium perchlorate accelerated the reaction.

The same authors concluded from a literature survey that heterogeneous catalysis is extensive in aqueous media, but in other media its extent varies, and in some cases it may become absent altogether.

Study of the hydrolysis of β-n-octyl bromide and α-phenylethyl chloride[27] in aqueous ethanol led to the suggestion that the reagent was silver ions adsorbed on the surface of the solid present. Both silver oxide and silver bromide together with silver nitrate in solution gave a larger rate of reaction than silver oxide, presumably because of the larger concentration of silver ions at the surface. Also, no change in the measured rate was found on substituting silver acetate for silver nitrate.

This idea was further developed by Dostrovsky and Hughes.[20] They suggested that the reaction at the surface also involved the nitrate ion giving an adsorbed transition state of the type

$$NO_3^- - - - - - R - - - Br - - - Ag^+ \qquad 1.27$$

which is similar to that proposed by Hammond[33] and by Parfitt[47], except that the complex is postulated to be adsorbed on the surface of the catalyst.

Colcleugh and Moelwyn-Hughes[38] recently studied the reaction of methyl iodide with silver nitrate in aqueous solution. The orders of reaction were found to be one in methyl iodide, and between one and two in silver nitrate. Second order rate constants were calculated and found to depend on the initial concentration of silver nitrate, but for a given concentration of the latter, to be independent of the initial concentration of methyl iodide. Further, this variation of rate constant was different if ClO_4^- was substituted for NO_3^-. This was taken as an indication that the anion was was involved in the reaction giving a transition state similar to 1.26. No mention of the heterogeneous catalytic effect was made, but the above data indicates that it could have been present. This conclusion is supported by the fact that the reaction tended to be irreproducible in its later stages.

A study of the reaction of a homologous series of alkyl bromides (Me → n-heptyl) with silver nitrate in aqueous acetone was reported by Melendez-Andreu,[39] who included a comprehensive review of the literature in his paper. He concluded that heterogeneous catalytic effects were only noticeable in hydroxylic solvents. From his own experimental work he found that there was no catalytic activity by the precipitated silver bromide. Systematic variations in the order of reaction, as a function of the initial reactant concentration and the nature of the medium, were found. Differences were also found in the velocity of the reaction on using silver perchlorate instead of silver nitrate. He concluded that there was a gradual variation in the nature of the transition state, as a function of the structure of the organic halide, the nature of the silver salt, and of the medium.

Nicolet and Stevens[43] examined the catalysis by mercuric bromide and iodide of the alcohololysis of propyl and isopropyl bromides and iodides. They found that both these salts were good catalysts, the iodide being the better.

Halo-acids

The results of the work done on the solvolysis of halo-acids are presented in Table 1.2. The more important of these are discussed below.

In 1910, G. Senter[24,25] studied the reactions

$$\mathrm{R.CHX.CO_2H} + \mathrm{AgNO_3} + \mathrm{H_2O} \rightleftharpoons \mathrm{R.CHOH.CO_2H} + \mathrm{AgX_{(s)}} + \mathrm{HNO_3} \tag{1.28}$$

$$\mathrm{R.CHX.CO_2^-} + \mathrm{AgNO_3} + \mathrm{H_2O} \rightleftharpoons \mathrm{R.CHOH.CO_2^-} + \mathrm{AgX_{(s)}} + \mathrm{HNO_3} \tag{1.29}$$

$$\mathrm{R.CHBr.CO_2R'} + \mathrm{AgNO_3} + \mathrm{EtOH} \begin{array}{l} \longrightarrow \mathrm{R.CH(OEt).CO_2R'} + \mathrm{AgBr_{(s)}} + \mathrm{HNO_3} \\ \searrow \mathrm{R.CHOH.CO_2R'} + \mathrm{AgBr_{(s)}} + \mathrm{EtNO_3} \end{array} \tag{1.30}$$

where X is a halogen atom. The stoichiometry of reaction 1.28 had previously been established by Beckurts and Otto[48]. For all three reactions there was a considerable increase in rate produced by the presence of silver bromide, in aqueous solution. Added AgBr produced a smaller acceleration than that produced in situ - this was ascribed to the colloidal nature of the AgBr produced in situ. It was noted that colloidal particles were less stable in alcoholic solution, and it was found that the catalytic effect was much reduced when reaction 1.30 was carried out in alcohol instead of water. Gelatin (0.25%) increased the rate of reaction[41] 1.28 significantly and this was attributed to its prevention of coagulation of the silver bromide formed.

TABLE 1.2

Ref.	Reactants	Solvent	Temp. (°C)	Auto-cat.	Catalysis by added solid	Method of measurement	Order of reaction	Remarks
24	$AgNO_3$ + bromoacetic, bromopropionic, bromobutyric, acids and their salts	H_2O	26	Found	1/300 molar AgBr doubled rate	Titrn. for for Ag^+ ion	2nd	Salts react faster than acids. HNO_3 retards reaction. AgOAc gives a higher rate than $AgNO_3$
24	$AgNO_3$ + bromopropionic acid	50% aq. EtOH. 50% aq. acetone	26	Less marked		"	"	Initial rate is about the same as in H_2O.
25	$AgNO_3$ + Me and Et esters of: bromoacetic, α-bromopropionic, α-bromobutyric, α-bromoisobutyric, α-bromoisovaleric, acids.	EtOH and aq. EtOH	49.9		"	"	"	Very little catalysis by AgBr in alcoholic solution.
41	$AgNO_3$ + bromoacetic acid.	H_2O		Found		"		Gelatin(0.25%) added to the reaction mixture increased catalytic effect.

TABLE 1.2

Ref.	Reactants	Solvent	Temp. (°C)	Auto-cat.	Catalysis by added solid	Method of measurement	Order of reaction	Remarks
42	$AgNO_3$ + chloro and bromo acetic acids and Na salts.	Aq. and aq. EtOH		None found			2nd.	2nd order constants decreased during reaction
26	$AgNO_3$ + Na α-bromopropionate	H_2O		Found	Strong cat. by added AgBr		2nd	A period of induction was noted in the absence of added AgBr.
28	$AgNO_3$ + α-bromopropionic acid, its Me ester, and Na^+ salt	MeOH	64		AgBr added + ve effect	Titrn. for Ag^+ ion		Confirmed Senter's results (Ref.24 and ~~[illegible]~~ 25)
28	Ag_2O + bromopropionic acid its Me ester and Na salt	H_2O	0		"	"		
44	Ag_2O + Na bromoacetate	H_2O	60					Rate increased with quantity of Ag_2O
45	$AgNO_3$ + $AgClO_4$)+ isopropylchloroformate	CH_3CN	25	Not found			2nd	Rates lower with $AgClO_4$ than with $AgNO_3$

Both Senter[24,25] and Euler[42] attributed the diminution of the rates of reaction 1.28 and 1.29 by added nitric acid to the suppression of the formation of the anion, through which the reaction was assumed to occur. This hypothesis was supported by the fact that, at the same concentrations, reaction 1.29 is faster than reaction 1.28, and by the fact that the rate of reaction 1.30 is virtually unaffected by the addition of nitric acid.

Cowdrey, Hughes, and Ingold[28] concluded from their studies that the reagent was silver ions adsorbed on the surface of the solid. When silver oxide was employed instead of silver nitrate, it was shown that if the silver salt of the particular acid was soluble, the rate of reaction was greater using the free acid than the acid salt (cf. silver nitrate). This was attributed to the action of the free acid in first dissolving some of the silver oxide, thus building up a far larger concentration of silver ions than would otherwise have been possible. Using silver oxide, they proved that heterogeneous catalysis by silver bromide occurred, and that the rate of hydrolysis of sodium α-bromopropionate depended on the excess of silver oxide present. Euler and Fahlander,[44] hydrolysing sodium bromoacetate, also showed that the reaction rate increased with the quantity of suspended silver oxide. The function of the silver oxide is apparently twofold:[16] to provide silver ions in solution, and to provide a heterogeneous surface on which the reaction can occur.

More recently, Kevill and Johnson[45] investigated the reaction of silver nitrate and perchlorate with isopropyl chloroformate in acetonitrile. They found that for the perchlorate the corrected second order rate constants increased steadily with increasing perchlorate concentration. This may indicate heterogeneous catalysis, or an increasing degree of association into ion pairs as postulated by Parfitt et al[47], although neither possibility is mentioned by the authors. The observed rate constants using silver perchlorate were always 15 - 20% less than those obtained with the same concentration of silver nitrate. When the appropriate tetraethyl ammonium salts were added (the same concentration in each case), an increase in the rate constant was found for both, being about 10% for perchlorate, and about 60% for nitrate. These facts are consistent with an ion pair mechanism. The authors considered the rate determining step of the reaction to be either nucleophilic attack (presumably by the acid anion) or an electrophilically assisted heterolysis, but not both. These conclusions seem to be at variance with the experimental results.

Hughes[16] has drawn a parallel between the heterogeneous silver ion reaction and the S_N1 mechanism for homogeneous reactions. He assumed that the adsorption of the halide stretches the carbon-halogen bond, and that the adsorbed silver ion then extracts the halogen as an ion. This is consistent with Senter's and others' experimental results, since an electron repelling substituent, such as CO_2^-, would facilitate the ionisation process and accelerate the reaction, whereas electron attracting groups, such as CO_2H, and CO_2Me, should have the opposite effect and thus retard the rate. These effects are opposite to the requirements of an S_N2 mechanism, which would be facilitated by a withdrawal of electrons from the seat of substitution.

Analogous Reactions

So far only those reactions involving silver salts have been discussed. Professor Barreira[58] has suggested, however, that there are similar systems which could be studied by substituting Hg^{2+}, Hg_2^{2+}, Pb^{2+}, Tl^{+}, etc. for Ag^{+}. These metals all have soluble nitrates, and other, insoluble, salts which might exhibit catalytic activity. Apparently, very little work has been done on these systems and what little has been done will now be reviewed.

The only reported case in which heterogeneous catalysis has been investigated was the study of the reaction between ethyl iodide and aqueous hydrogen sulphide, in the presence of metal sulphides. Smith and Semon[49] had stated that the reaction did not occur except in the presence of metal sulphides. They postulated the mechanism:

$$MS + H_2S \rightleftharpoons M(HS)_2 \qquad 1.31$$

$$M(HS)_2 + 2EtI \rightleftharpoons MI_2 + 2EtHS \qquad 1.32$$

Brown and Snyder[50] later reported that the reaction did occur in the absence of metal sulphides, and that the rate decreased with increasing acidity. This they attributed to the equilibrium

$$H_2S \rightleftharpoons H^+ + HS^- \qquad 1.33$$

It was found that the addition of PbS, Sb_2S_5, HgS, Ag_2S, CuS, Bi_2S_3, CdS, SnS_2 all accelerated the reaction, to about the same extent (ca. 6 fold). No information is given concerning the mass of catalyst and volume of solution used in each experiment. Also found to be catalysts were bone black, $Al(OH)_3$, gelatin, and $BaSO_4$. Charcoal, however, was not a catalyst.

The hydrolysis of benzylchloride in aqueous dioxane by mercuric nitrate and perchlorate has also been investigated.[51] The solvent was chosen because the mercuric chloride formed was soluble in it, and thus the solution remained homogeneous during the course of the reaction. The two reactions occurring were, in the case of mercuric nitrate:

$$2PhCH_2Cl + Hg(NO_3)_2 \longrightarrow 2PhCH_2NO_3 + HgCl_2 \qquad 1.34$$

$$2PhCH_2Cl + Hg(NO_3)_2 + 2H_2O \longrightarrow 2PhCH_2OH + 2HNO_3 + HgCl_2 \qquad 1.35$$

Catalysis by added nitrate and perchlorate ion was found, but the distribution of the products was affected by the concentration of the added ion (c.f. Burke and Donnan[30]). The reaction was found to be second order, being rigidly first order in benzyl chloride. The second order constant showed a steady decrease during the course of the reaction, this being attributed to the formation of a chloromercuri-benzyl alcohol complex.

The reaction of alkyl bromides with mercuric nitrate has also been studied.[52] Again the studies were conducted in aqueous dioxane, so that the mercuric bromide formed did not precipitate out.

Kornblum et al[53] have made a thorough study of the hydrolysis of ethyl iodide and other alkyl halides using silver nitrite. No mention was made of a heterogeneous catalytic effect.

HYDROLYSIS OF ETHYL IODIDE BY WATER

To elucidate the kinetics of the reaction of ethyl iodide with silver salts, it is necessary to know its rate of reaction with water alone. For the reaction -

$$\mathrm{EtI} + \mathrm{H_2O} \rightleftharpoons \mathrm{EtOH} + \mathrm{HI} \qquad 1.36$$

Moelwyn-Hughes[54] obtained the following first order rate constants:

At 60°C $k_1 = 1.67 \times 10^{-5}$ sec.$^{-1}$

77°C $k_1 = 7.96 \times 10^{-5}$ sec.$^{-1}$

100°C $k_1 = 5.13 \times 10^{-4}$ sec.$^{-1}$

He derived the relationship

$$\ln k_1 = 21.11 - 21{,}200/RT \qquad 1.37$$

Leffek[55] obtained $k_1 = 1.55 \times 10^{-4}$ sec.$^{-1}$ at 80°C, where equation 1.37 would lead to a value of 1.11×10^{-4} sec^{-1}. At 25°C, 1.37 gives a value of $k_1 = 4.31 \times 10^{-7}$ sec^{-1}.

In 50/50 v/v dioxane-water mixtures, first order rate constants were determined[56] for the reaction 1.36 at 50°C, $k_1 = (1.03 - 1.1) \times 10^{-6}$ sec.$^{-1}$, for initial concentrations of the iodide from 0.15M to 0.07M.

The solvolysis in aqueous ethanol has also been studied[57], but the ethanol and water compete in the solvolysis and no simple rate constants for the hydrolysis are available.

PRESENT WORK

The aim of the work presented here has been twofold: firstly, to examine semi-quantitatively the effect of the addition of a wide range of solids to the aqueous silver nitrate-alkyl halide system, and to analogous systems in which the silver ion has been replaced by other cations. This study has been dealt with in Part I.

Secondly, a more detailed study, initially by means of the rotating disc technique, has been made to shed light on the rate-governing processes of the heterogeneous catalysis of the reaction. This work is presented in Part II.

PART I

SEMI-QUANTITATIVE STUDIES

Chapter 2

METHOD OF MEASUREMENT

Preliminary Experiments

For any kinetic study it is important that a suitable method of measurement is chosen. The main criteria involved are:-

(1) that the measuring system should be accurate and reliable.

(2) that it should in no way interfere with the reaction being studied.

For the hydrolysis of alkyl halides in the presence of silver nitrate:

$$RX + AgNO_3 + H_2O \rightleftharpoons ROH + AgX_{(s)} + HNO_3 \qquad 2.1$$

several methods were considered. Initially the most direct method, that of volumetric analysis for silver ion, was tried. Samples of the reaction mixture were analysed by withdrawing a known aliquot of solution from the reaction vessel and titrating with standard ammonium thiocyanate using ferric alum indicator[59a] (Volhard's method). However, this method was found to be very unreliable because the low concentration of reactants (10^{-2}M for both silver nitrate and the alkyl halide) and the presence of organic material in the solution caused the end points to be obscure and irreproducible. Also tried were analysis by Mohr's method[59b] and by using adsorption indicators[59c] (dichlorofluorescein). However, all the methods proved too unreliable for accurate measurement and some instrumental methods were therefore considered:-

(1) U.V. spectrophotometry - this was discarded immediately because of the precipitate (often colloidal) formed during the reaction.

(2) Conductance of solution - this was rejected because it was felt

unwise to introduce metal surfaces into the reaction solution since they might well catalyse the reaction. Indeed, even though Moelwyn-Hughes[38] had used this method for studying the MeI + $AgNO_3$ system, we did find later that platinum catalysed the EtI + $AgNO_3$ reaction.

(3) Amperometric titrations - these were not used for the reason given under (2) above.

(4) E.m.f. measurements with a silver electrode to follow the change of concentration of the silver ion - these were rejected on the same grounds. Once again, this was justified since in later experiments silver metal was found to be a catalyst.

(5) pH Measurement

Reaction 2.1 produces hydrogen ions stoichiometrically. Thus it may be followed by measuring the pH change. The method is specific to reaction 2.1 and insensitive to a second reaction which is known[15c] to occur, namely:

$$AgNO_3 + RX \rightleftharpoons AgX_{(s)} + RNO_3 \qquad 2.2$$

Also the measuring system would introduce no solid other than glass into contact with the reaction mixture. The disadvantages of this method were:-

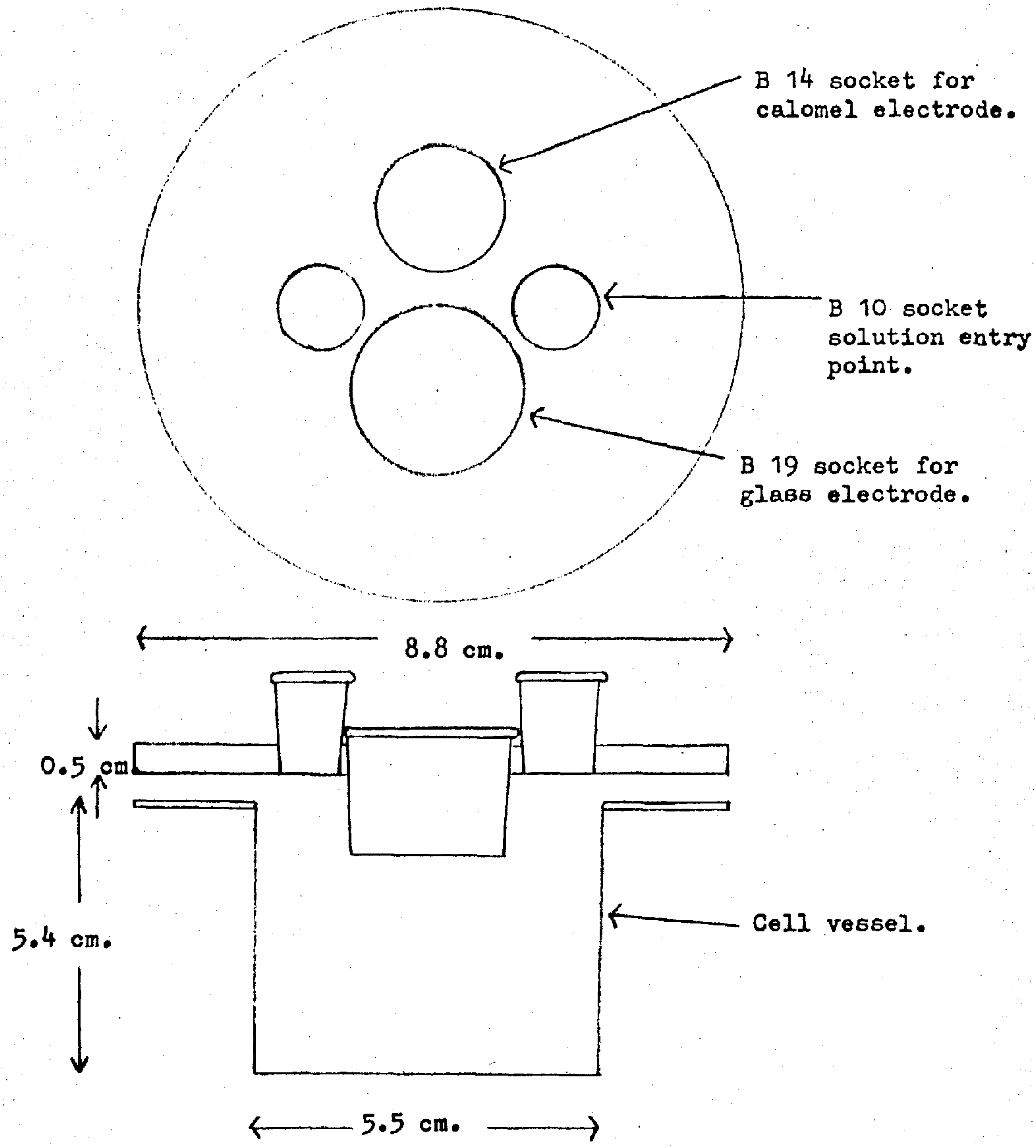
(a) the relative insensitivity of a technique that records the logarithm of the quantity desired

(b) the theoretical difficulties involved in interpreting the pH meter readings.[92] This aspect will be discussed more fully later. On balance, however, it was thought that this was the most suitable method, and it was employed in subsequent experiments.

Design of Cell

During the preliminary investigations by volumetric analysis it had become clear that there was a wide discrepancy between reactions carried out

FIG.2.1 Glass Cell.



in open and in closed containers. This was attributed to evaporation of the volatile organic solute from the reaction mixture in an open vessel. In the light of this evidence a cell was designed with the following design criteria:

(1) A closed container to prevent escape of volatile solute during reaction.

(2) No metal in contact with the reaction solution, to avoid inadvertant catalysis.

(3) Effective stirring, to ensure that the solution was of uniform composition.

The first apparatus built was completely of glass and of ca. 100 ml. capacity, (Fig. 2.1), A glass and a commercial calomel electrode (G 202C, and K 401, respectively, by Radiometer of Copenhagen, Denmark) were inserted through holes in the lid and attached to a Radiometer pH meter 4. The stirring was effected magnetically by an immersible magnetic stirrer made by Rank Bros. of Bottisham. Initially a Teflon covered follower was used, but it was found that bubbles of air stuck to it when the cell was being filled. One covered in glass was therefore substituted. Some kinetic runs were done with this cell, both with and without added catalyst (see later for results) but it was found to suffer from the following defects:-

(1) The kinetics of the 'homogeneous' reaction were found to be irreproducible.

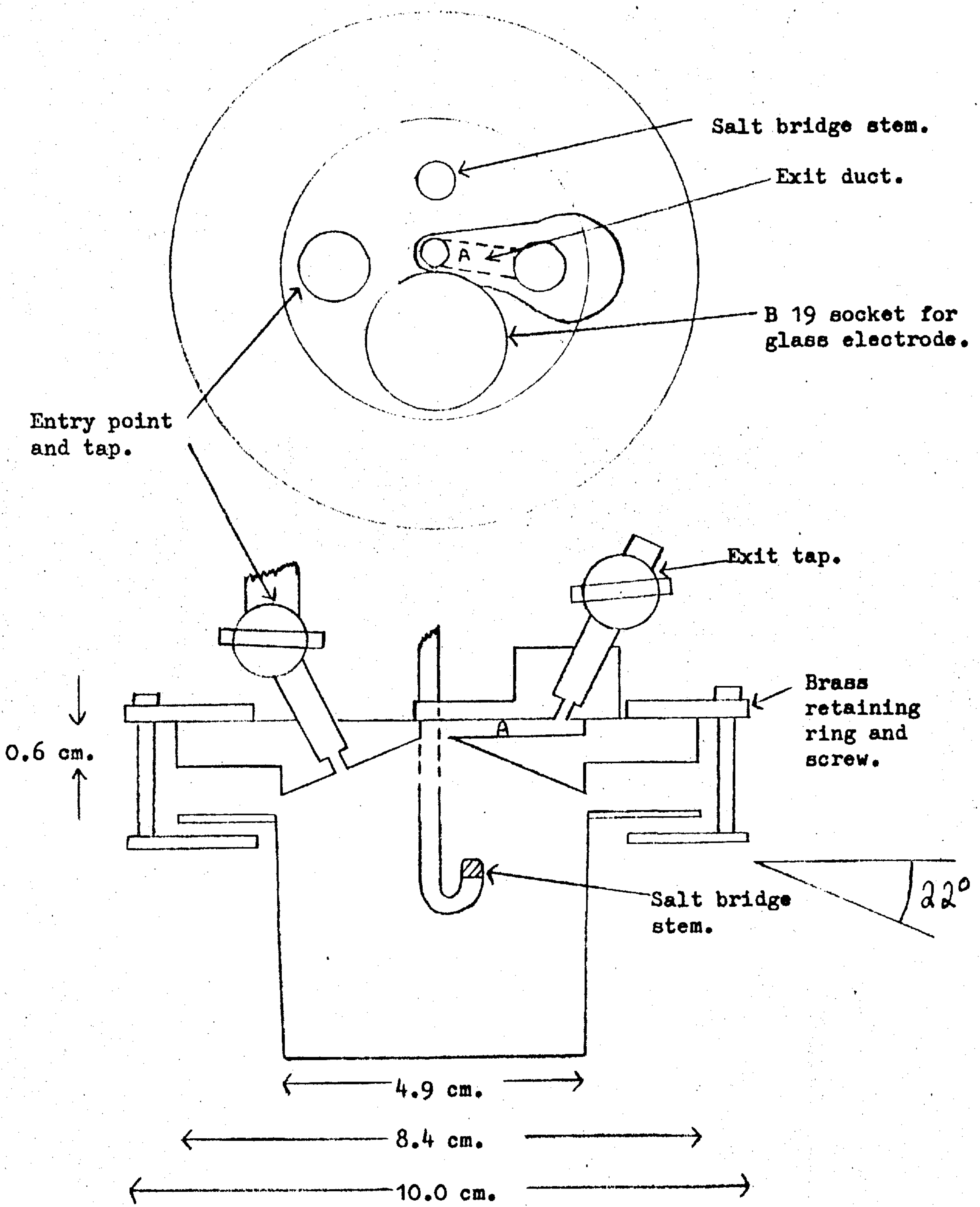
(2) The cell could not be completely filled with liquid, and some air was always trapped inside.

(3) The KCl from the calomel salt bridge was affecting the results obtained owing to the reaction:

$$Cl^- + Ag^+ \longrightarrow AgCl_{(s)} \qquad 2.3$$

These difficulties were overcome by building a cell lid of Perspex (Fig. 2.2) since the machining techniques necessary to avoid the trapping of air could not be used with glass. This cell could be completely filled

FIG.2.2 Cell with Perspex Lid.



with liquid and sealed off from the atmosphere.

The KCl salt bridge was replaced by a KCl/KNO_3 salt bridge, the KNO_3 (0.1M) only being in contact with the reaction mixture. The salt bridge tube (Fig.2.3) was of glass with a porous ceramic plug at each end. The plugs were from a Beckman remote junction glass electrode (150674/RRLB) 0.6 cm. long x 0.5 cm. diameter, fused into a glass tube.

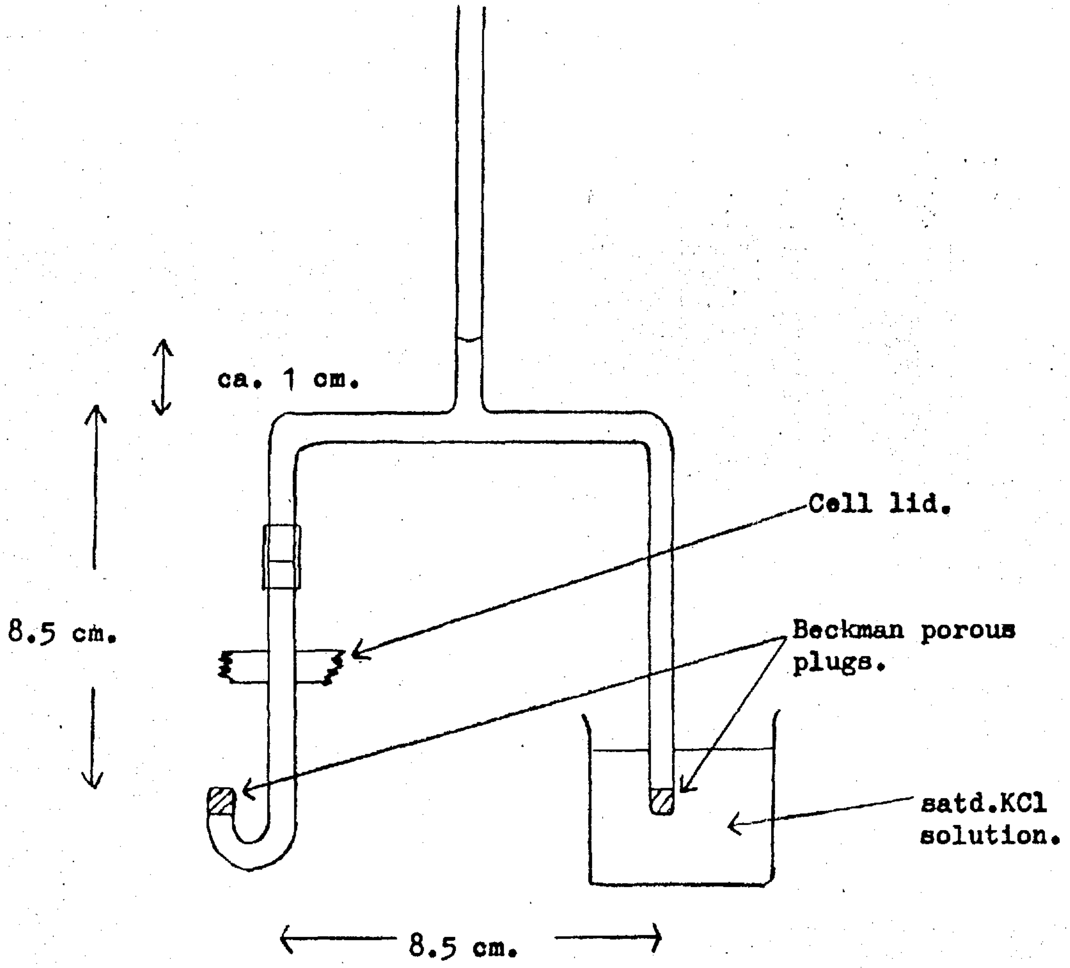
The end of the bridge which dipped into the cell was Araldited to the cell lid. The bridge was in two parts, for convenience of filling, which were joined by a rubber sleeve just above the cell lid. The porous plug in the cell was upturned to give gravitational stability to the liquid junction and the other end of the bridge dipped into a beaker containing satd. KCl solution which was kept at 25°C in the thermostat tank. A head of KNO_3 solution of about 8 - 9 cms. gave a small flow of the solution (about 0.06 ml. per hour) through both plugs, which were kept at approximately the same level. This increased the NO_3^- concentration of the solution by 0.00007 mole/liter in one hour.

Volume of Cell

In order to add the second reactant to the cell as quickly as possible, it was decided to fill the cell to a given, arbitrary mark, ensuring that no air was trapped in the cell. For the initial reactant concentrations to be known accurately it was therefore necessary to know the volume of the cell to this mark. This was measured accurately by weighing.

The glass electrode was fitted into the cell lid, and the salt bridge stem filled with water which was then allowed to bleed until the porous plug surface was wet. The stem was then sealed from the atmosphere and the porous plug surface dried. A magnetic follower was added to the vessel and the lid was screwed into place. The empty cell was weighed. The cell was then

FIG.2.3 Potassium Nitrate Salt Bridge.



filled with degassed doubly distilled water at $25^{\circ}C$ (or $20^{\circ}C$) to the required mark and reweighed. The volume was then calculated from the difference in the two weights and the density of water at the known temperature. Correction was made for the volume of water contained in the barrel of the inlet and outlet taps. The mark on this cell was taken at the top of the outlet tap's barrel. The volume of the cell was found to be 91.5 ± 0.05 ml.

Technique of Filling

The filling technique was as follows. The glass electrode was placed in its socket in the cell lid and the salt bridge filled with KNO_3 solution. The external porous plug of the bridge dipped into a saturated KCl solution into which also dipped the calomel electrode. The glass electrode and the salt bridge stem were immersed in 0.05 M potassium hydrogen phthalate solution and this solution and the saturated KCl solution thermostatted at $25^{\circ}C$. The electrodes were standarised at pH 4.008.[92a] The electrodes were then carefully washed in distilled water and dried, and the cell lid transferred to the vessel into which a known aliquot of silver nitrate of known strength and a magnetic follower had already been placed. The lid was fastened in place by eight brass screws, screwing into a brass ring underneath the flange of the vessel. The whole cell was then thermostatted for about thirty minutes in the water bath. The ethyl iodide solution of known strength was contained in a dropping funnel which was also thermostatted in the bath for the same length of time. The dropping funnel was then connected to the cell by means of a B 14 (Quickfit) cone and socket, and the iodide solution run into the cell, the outlet tap of which was open. The solution was added until it filled the outlet duct up to the tap. Both taps were closed, the magnetic stirrer started, and the change of pH with time followed. The time which elapsed between the start of the addition of the ethyl iodide solution and the taking of the first reading was 1.5 to 2.0 minutes. The time was measured with a Pye stop-clock (which was calibrated against a calibrated electric clock).

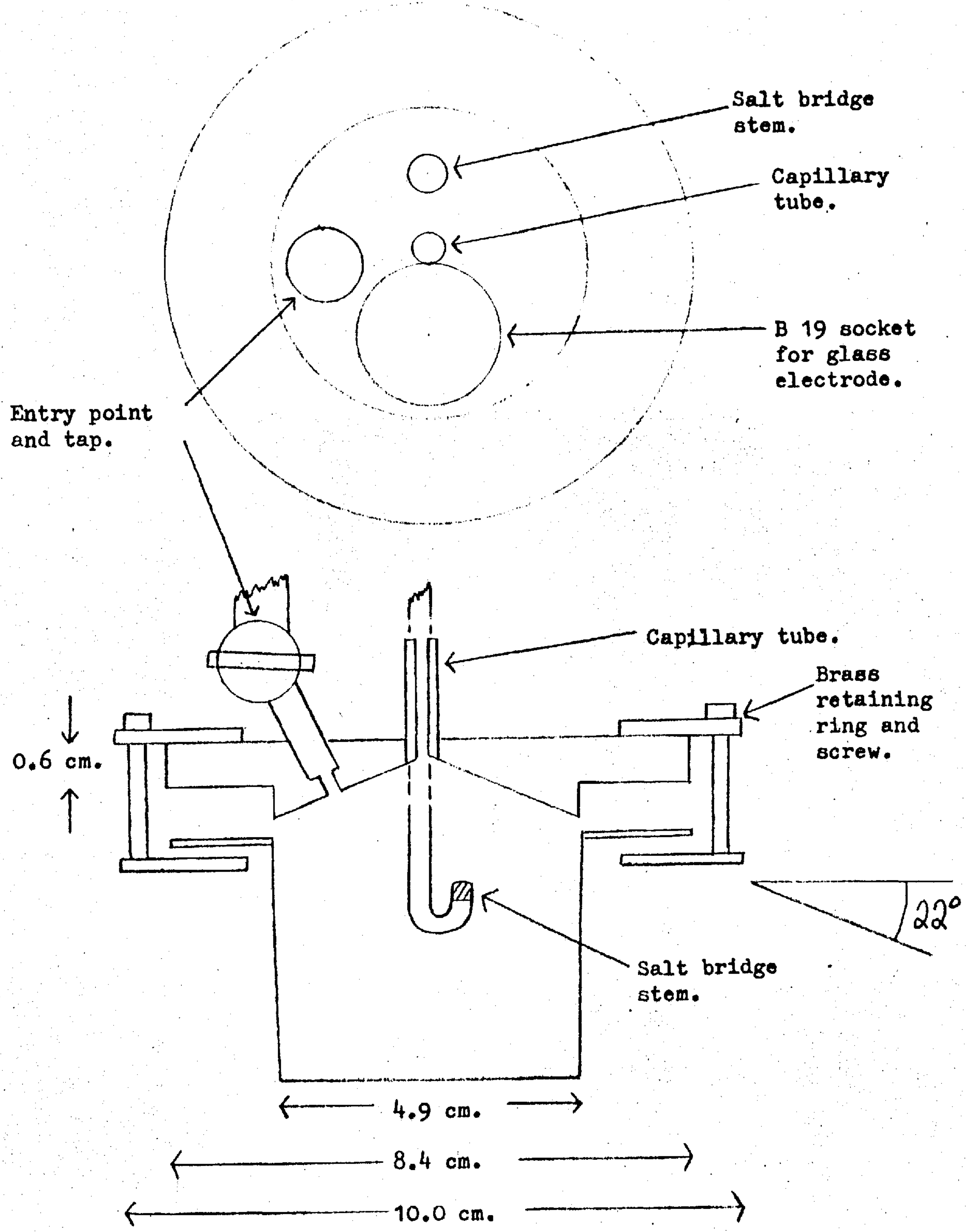
Operating Conditions:

A series of runs was done to establish the best operating conditions. The criteria considered were the reproducibility of the rates of the 'homogeneous' reaction, and the stability and accuracy of the electrodes in known buffer solutions. It was found to be best to leave the cell open, by means of the inlet or outlet tap (to allow for expansion or contraction effects during the reaction) and to have a small hydrostatic pressure of potassium nitrate solution at the cell-bridge liquid junction so that there was a slow leakage of potassium nitrate solution into the reaction solution (not more than 0.06 ml./hour).

The results obtained were found to be independent of the concentration of potassium nitrate in the bridge within the range 0.1 M to 1.0 M. At 0.01 M, however, the measured rate of reaction appeared to be twice that using 0.1 M. It was thought that this was a liquid junction potential effect, and some calculations were made to attempt to verify this, but they were not conclusive (see Appendix). In subsequent experiments potassium nitrate solutions of 0.1 M or greater were always employed. It was found that the addition of 0.01 M KNO_3 to the reaction mixture reduced the rate of reaction from 0.58×10^{-6} moles $litre^{-1} min^{-1}$ to 0.53×10^{-6} moles $litre^{-1} min^{-1}$, and 0.1 M reduced it to 0.50×10^{-6} moles $litre^{-1} min^{-1}$. From this it can be seen that the amount of KNO_3 introduced into the reaction solution by the bridge would have a negligible effect on the rate of reaction.

A further effect was the dependence of the pH reading on the rate of stirring. It was found that an increase in the rate of stirring lowered the pH reading. This effect amounted to ~0.05 - 0.1 pH units between a

FIG.2.4. Cell with Modified Perspex Lid.



quiescent and a well stirred solution at a pH of 5. As the pH fell the effect seemed to decrease and it could be removed by the addition of a small amount (0.01 mole/liter) of potassium nitrate to the reaction solution. The effect was also absent when the pH of stirred buffer solutions was measured. It is uncertain whether the effect is due to the glass electrode or the liquid junction, or both. Later work indicated that both were involved.

As a result of this series of runs another modification was made to the cell. It was found that silver iodide precipitate was being removed from contact with the solution during the run, and this was affecting the measured velocity of reaction. The precipitate was becoming trapped in the outlet duct (Region A in Fig. 2.2) The duct and outlet tap were therefore replaced by a capillary tube - see Fig. 2.4. The modification overcame this difficulty, precipitate not being trapped in the capillary. Using this cell the 'homogeneous' reaction was found to be reproducible to ± 3%, over the first tenth of the reaction. This was considered satisfactory for the investigation of catalysis by various solids.

All the work detailed above, except that involving volumetric analysis, and all later work with this apparatus was carried out in a water bath maintained at 25°C. The temperature was kept constant to ± 1/100°C by means of a mercury contact thermometer (Electromethods 20 - 30°C in 1/10°C divisions) connected, through a make and break relay (Ether type 213 B) to a radiant immersion heater (Electrothermal "Red Rod", 3kW). The water in the bath was stirred continuously.

Purification of Reagents and Preparation of Reaction Solutions

Ethyl Iodide

Ethyl iodide was chosen for study because it was found to react at a convenient rate, and was readily available and easy to handle. It was noticed, however, that the sample used for the preliminary experiments turned brown in a matter of weeks. It has been reported [60,61] that in the presence of U.V. light ethyl iodide decomposes to give iodine, ethane, and ethylene even if in solution, and if oxygen is also present, to give iodine and acetaldehyde. It was decided to try to purify the liquid by distillation. With conventional apparatus, the brown colouration disappeared after one distillation (a fraction boiling 73 - 5°C being collected) the distillate being colorless. There was, however, no change in the measured refractive index of 1.5147 ± 0.005 at 19.5°C (N_D^{15} = 1.5168 [62]). After four such distillations, a sample of crude ethyl iodide and the distillate were both subjected to vapour phase chromatography, using a Perkin-Elmer F11 Gas Chromatograph. (Column - 2 metres x $\frac{1}{8}$" o.d. stainless steel. Packing - Carbowax 1500 on Chromosorb W. Detector - flame ionisation). The results, as shown on the chromatograms, indicated a reduction in the amount of impurity present, but that the distillate was not pure enough for use. A fractionating column, 12 inches long and containing a glass spiral, was therefore added to the distillation apparatus, and a middle fraction, boiling 74 - 74.5°C, was collected. Approximately the first 20% and the last 40% distilling over were rejected. A chromatogram of this liquid showed it to be virtually 100% pure. The peak due to the impurity, had almost vanished, and this degree of purity was considered sufficient for all further work.

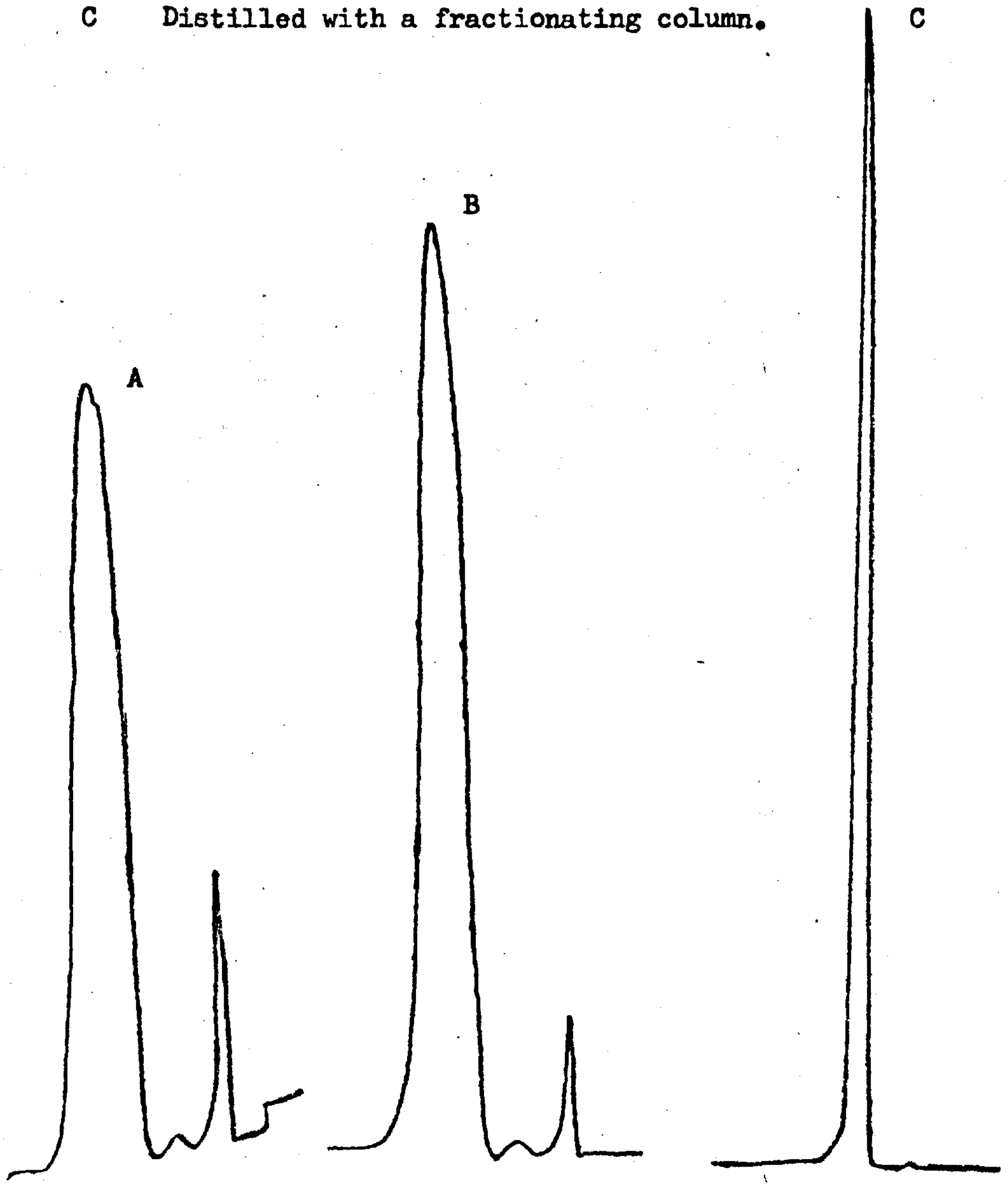
Four to five hours before every run, a sample of ethyl iodide was freshly distilled. A known volume of this (usually about 0.03 - 0.05 ml.) was

FIG.2.5 Vapour Phase Chromatograms of Ethyl Iodide Specimens.

A Undistilled EtI

B Distilled without a fractionating column.

C Distilled with a fractionating column.



immediately added to 250 ml. degassed doubly distilled water in a graduated flask. The addition was made by injecting it below the surface of the water using a micro-syringe (made by Burroughs Wellcome and measuring to 0.0001 ml). The mixture was then made up to the graduation mark with degassed doubly distilled water, a magnetic follower added, and the flask tightly stoppered. Dissolution of the iodide was then effected by stirring the mixture for 2 - 3 hours.

Silver Nitrate

Analar silver nitrate was used throughout. To prepare a reaction solution, crystals of silver nitrate were dried in an oven at 110°C for 2 hours, and after cooling, were weighed out and dissolved in water in a graduated flask to give a solution of known concentration. The crystals were kept in a tightly stoppered bottle in the dark when not in use. Crystals were not redried or stored in a desiccator to prepare another solution, fresh once-dried crystals being used every time a solution was prepared. The solution was generally sufficient for about five runs, and was kept in between runs in a stoppered graduated flask in the dark. The solution was always degassed at a vacuum pump before being used in a run.

Distilled Water

Initially singly distilled water, obtained from a Manesty type OOB (E) still, was used for the experiments, but this led to some irreproducibility in the kinetics of the 'homogeneous' reaction. This was probably because of deposit from the distillation of hard water getting into the distillate. This water was therefore redistilled from a solution containing potassium permanganate and sodium hydroxide in a conventional laboratory still. In this way water of conductivity of $\sim 1 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$ and free from deposit was obtained.

Salt Bridge Solution

This was prepared by dissolving a known weight of Analar potassium nitrate in doubly distilled water.

Chapter 3

RESULTS OF THE SEMI-QUANTITATIVE STUDIES

A The System Silver Nitrate + Ethyl Iodide

At 25°C, the following initial rates were found:-

Table 3.1

$[AgNO_3]_0$	0.001	0.001	0.002
$[EtI]_0$	0.001	0.002	0.001
10^7 Rate (mole liter^{-1} min.$^{-1}$)	5.47 ± 0.18	11.8	11.9
10^3k_2 (liter mole^{-1} sec.$^{-1}$)	9.1 ± 0.3	9.8	9.8

The 'homogeneous' reaction is therefore first order in each reactant, the second order rate constants being given in the bottom line of Table 3.1. This is consistent with the slow step of the reaction being an electrophilically assisted heterolysis of the alkyl halide, i.e.

$$EtI + Ag^+ \xrightleftharpoons{\text{solvent}} AgI\ (s) + Et^+\ (\text{solvated}) \qquad 3.1$$

as proposed by Ingold and others.[15,16]

In the experiments discussed below, the initial concentration of silver nitrate and ethyl iodide were 0.001M and the temperature was 25°C.

Effect of pH

The usual initial pH of the reaction solution was in the range 5.0 - 5.5. When the initial pH was decreased to 3.53 by the addition of dilute nitric acid to the reaction solution, the initial rate was 3.6 x 10^{-7} mole liter^{-1}min^{-1}.

Thus, a 30 fold increase in the hydrogen ion concentration of the solution caused a decrease in the initial rate of only 30%.

Effect of potassium nitrate

The following initial rates were measured for the reaction in the presence of potassium nitrate:-

Table 3.2

$[KNO_3]$ (mole liter^{-1})	Ionic Strength (mole liter^{-1})	10^7 x Measured Rate (mole liter^{-1} min.$^{-1}$)
0	0.001	5.47 ± 0.18
0.01	0.011	5.3 ± 0.1
ca 0.1	0.101	4.75 ± 0.25

According to the Bronsted-Bjerrum theory,[9b] a reaction between two singly charged ions of opposite sign would result in a decrease in rate, in going from an ionic strength of 0.001 to one of 0.101, of a factor of almost two. A reaction between an ion and a molecule, however, as postulated in the present case, should have zero primary salt effect. The results in Table 3.2 are clearly more nearly in agreement with the latter theory than the former. The small decrease observed can be explained by a second order ionic strength effect inasmuch as activity coefficients can be expressed by equations of the type:-

$$\log_{10} f_{ion} = -Az^2_{ion}\sqrt{I} + b_{ion}I \qquad 3.2$$

$$\log_{10} f_{molecule} = b_{molecule}I \qquad 3.3$$

The terms in I, but not those in $\sqrt{I}$, are still present when the transition state (T.S.) theory[9c] is applied to the present case, i.e.

$$\log k - \log k_o = \log f_{Ag+} + \log f_{EtI} - \log f_{T.S.} \qquad 3.4$$

$$= (b_{Ag+} + b_{EtI} - b_{T.S.})\, I \qquad 3.5$$

$$= \Delta b\, I \qquad 3.6$$

Normally b coefficients are of the order of 0.1 and the figures in Table 3.2 lead to a value of Δ b of ca. 0.6 $\pm$ 0.3. Thus the ionic strength effect observed is consistent with the mechanism postulated.

Effect of stirring speed

When the solution was stirred much more slowly than usual, the initial rate of reaction was 5.25×10^{-7} mole liter^{-1} min.$^{-1}$. However, the precipitate formed was more colloidal than usual, and the rate accelerated after this initial period.

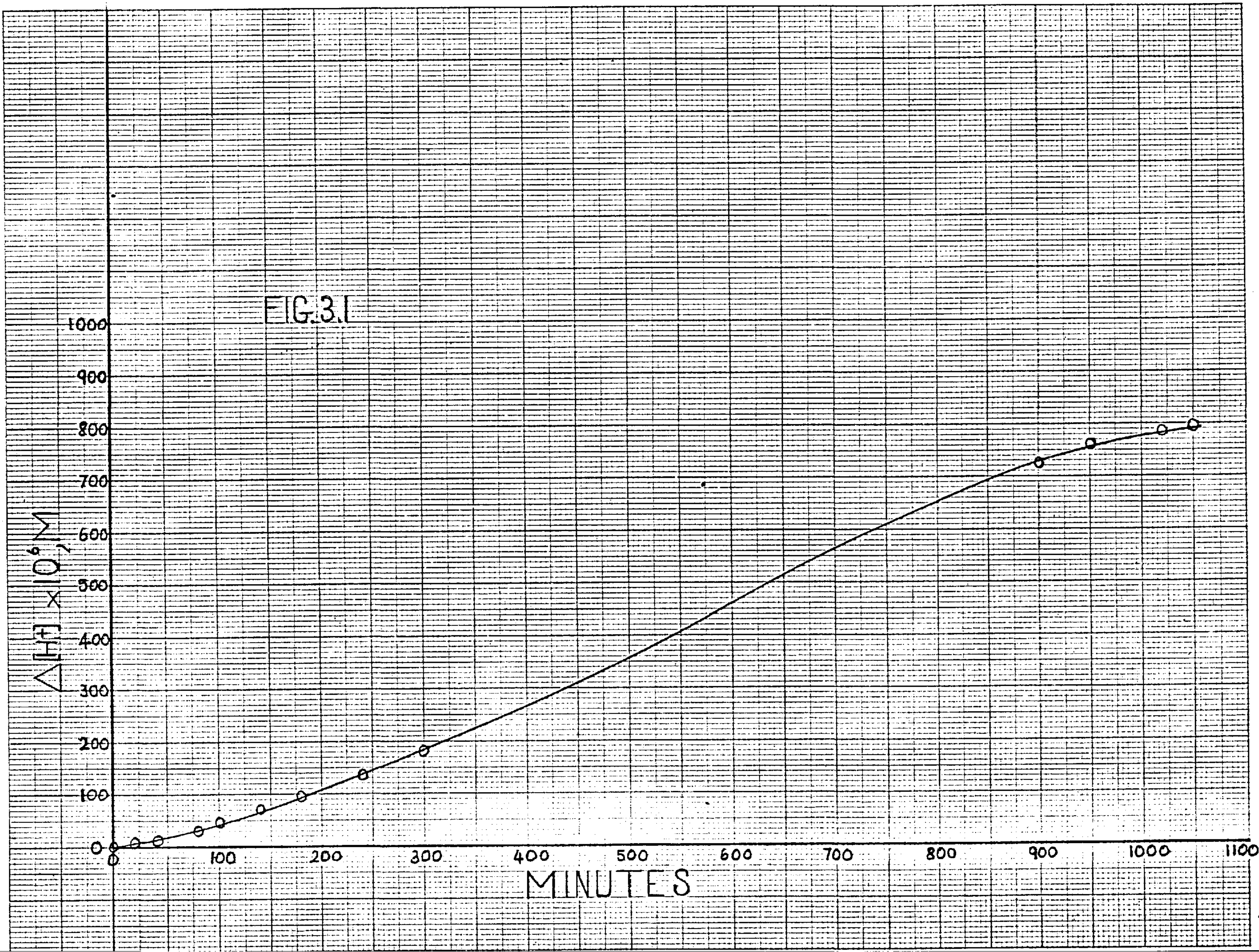
Effect of silver iodide coagulation, and reproducibility

The reaction was found to be rather irreproducible after the first 10% of reaction had occured. It was noted qualitatively that there was a correlation between the state of the precipitate formed during the reaction, and the rate. For instance, if the precipitate coagulated fairly early in the reaction, the rate was lower than average, whereas if it remained in a colloidal state, the rate was higher than average. Because of this, and also because of the effect of pH, only the initial rate of reaction was measured. Fig. 3.1 shows the course of a typical reaction followed to completion.

Effect of distilled water

The above rates of reaction were measured in doubly distilled water. Rather irreproducible results had been obtained using singly distilled water. This was attributed to some of the hard water deposit from the Manesty still getting into the distillate, and for all catalytic work, therefore, doubly distilled water was used.

FIG.3.1



$\Delta[H^+] \times 10^6$, M
1000
900
800
700
600
500
400
300
200
100
0
0
100
200
300
400
500
600
700
800
900
1000
1100
MINUTES

CATALYSTS

A range of catalysts was added, from insoluble silver salts and insoluble iodides, to precipitated metals and inert powders. The initial concentration of silver nitrate and ethyl iodide were always 0.001M, and the temperature was 25°C. In an effort to attain comparability between catalysts 0.01 mole of catalyst was added to the 90 ml. of reaction mixture in each run. However, owing to the varying states of subdivision encountered (especially with the precipitated metals) no great stress should be placed on the order of effectiveness. The full list of catalysts used, with the initial rates of reaction is given in Tables 3.4,5,6,7. Graphs of the rates of formation of hydrogen ions with respect to time are given in Figs. 3.2 - 3.13. Estimates of the effectiveness of a given catalyst are based on the initial rate of reaction recorded with that catalyst.

An interpretation of the results presented in this chapter is included at the end of the chapter.

Preparation of catalysts

No special care was taken in the purification of the catalysts used in this work. If there were any obvious possibility of contamination of a catalyst surface (e.g. silver powder covered with a layer of silver sulphide), then steps were taken to purify the sample. Some catalysts were used straight from the bottle in which they were supplied by the manufacturer, others were washed, and others were freshly prepared. The following list details the preparation of each catalyst used.

Silver iodide was freshly prepared by adding 10 ml. of ca. 1M potassium iodide solution to an equal volume of ca. 1M silver nitrate solution, slowly and with stirring. The precipitate was washed 4 - 5 times in 250 ml. distilled water, by decantation. It was added to the reaction solution without being dried, being kept in a minimum of water. Silver iodide, from BDH, was ground up with a pestle and mortar before use.

The following precipitates were freshly prepared in a manner similar to that used for silver iodide, the appropriate sodium or potassium salt being substituted for potassium iodide or the appropriate nitrate substituted for silver nitrate: silver bromide, silver chloride, silver thiocyanate, silver oxide (using potassium hydroxide), silver phosphate, silver sulphate* (using sulphuric acid), silver cyanide, silver sulphite, silver ferricyanide, silver arsenate**, lead iodide, thallous iodide, mercuric iodide.

Silver succinate was prepared by digesting silver oxide in warm acetic acid and adding succinic acid to the warm solution. The precipitate was filtered off and washed with distilled water.

Cuprous iodide was also freshly prepared.[65] The precipitate was filtered off on a sintered glass filter, and washed in distilled water.

The following catalysts were obtained from a manufacturer (whose name is in brackets) and were used without purification or washing: silver chloride (BDH), this was ground up before use; silver sulphide (BDH)

* The precipitate was filtered off and washed with distilled water until the effluent was neutral to universal indicator paper.

** This precipitate was filtered off before washing, because it was very finely divided.

silicon (BDH), silica (BDH), boron nitride (BDH), animal charcoal (BDH), barium sulphate* (BDH), mercurous iodide (BDH), cuprous iodide (BDH), thallous iodide (BDH), lead (100 mesh to dust, BDH), precipitated silver (Hopkin & Williams), colloidal silver (Hopkin & Williams), precipitated gold, platinum and palladium (all Johnson Matthey).

Powdered glass was prepared by crushing Pyrex glass tube in a pestle and mortar, washing in cleaning mixture (chromic-sulphuric acid) and in distilled water anddrying in an oven at 110°C.

Powdered Perspex was obtained as shavings from a block of Perspex. The shavings were washed in carbon tetrachloride, acetone, and then carbon tetrachloride again.

The stainless steel used was in the form of turnings, which were washed in acetone and dried before use, as was the Teflon.

(i) Results of Runs Using Insoluble Silver Salts

A list of catalysts used, with initial rates of reaction, is given in Table 3.4, and graphs of the rate of change of hydrogen ion concentration in Figs. 3.2 - 3.5.

Silver halides, silver sulphide, and silver thiocyanate.

For the insoluble silver halides a gradation of catalytic activity was found: AgI > AgBr > AgCl, when the precipitates were freshly prepared. However, the age of a catalyst seemed to affect its activity. Thus, silver iodide power from BDH was a much more moderate catalyst than freshly

* The barium sulphate used was washed and left to stand for three hours in contact with dilute sulphuric acid. The precipitate was then filtered off and washed with distilled water.

Table 3.4

The Effect of Insoluble Silver Salts on the $AgNO_3$ + EtI System

Run	Catalyst	Source	Initial Rate x 10^{+7} (mole $liter^{-1}min^{-1}$)	Corrected* Initial rate x 10^7 (mole $liter^{-1}$ min^{-1})
0	None	-	5.47 ± 0.18	-
1	AgI	freshly prepared	ca. 900	-
2	AgI	B.D.H.	ca. 380	-
3	AgBr	freshly prepared	ca. 460	-
4	AgCl	freshly prepared	ca. 290	-
5	AgCNS	freshly prepared	ca. 300	-
6	Ag_2S	B.D.H.	ca. 550	-
7	Ag_2O	freshly prepared	apparently no reaction	-
8	AgCN	freshly prepared	apparently no reaction	-
9	$Ag_3Fe(CN)_6$	freshly prepared	ca. 200	-
10	Ag_2SO_3	freshly prepared	ca. 65	Corrected Rate not computed
11	Ag_2SO_3	freshly prepared	ca. 140	
12	Ag_2SO_4	freshly prepared	ca. 420	37
13	Ag_2Succ	freshly prepared	11.2	ca. 140
14	Ag_3PO_4	freshly prepared	0.14	35
15	Ag_3AsO_4	freshly prepared	25	105 - 108

Mass of catalyst = 0.01 mole
Volume of solution = ca. 91.5 ml.
Initial $[AgNO_3]$ = initial [Et I] = 0.001M
Temperature = 25°C.

* This is the rate adjusted to 0.001M Ag^+ after computation.

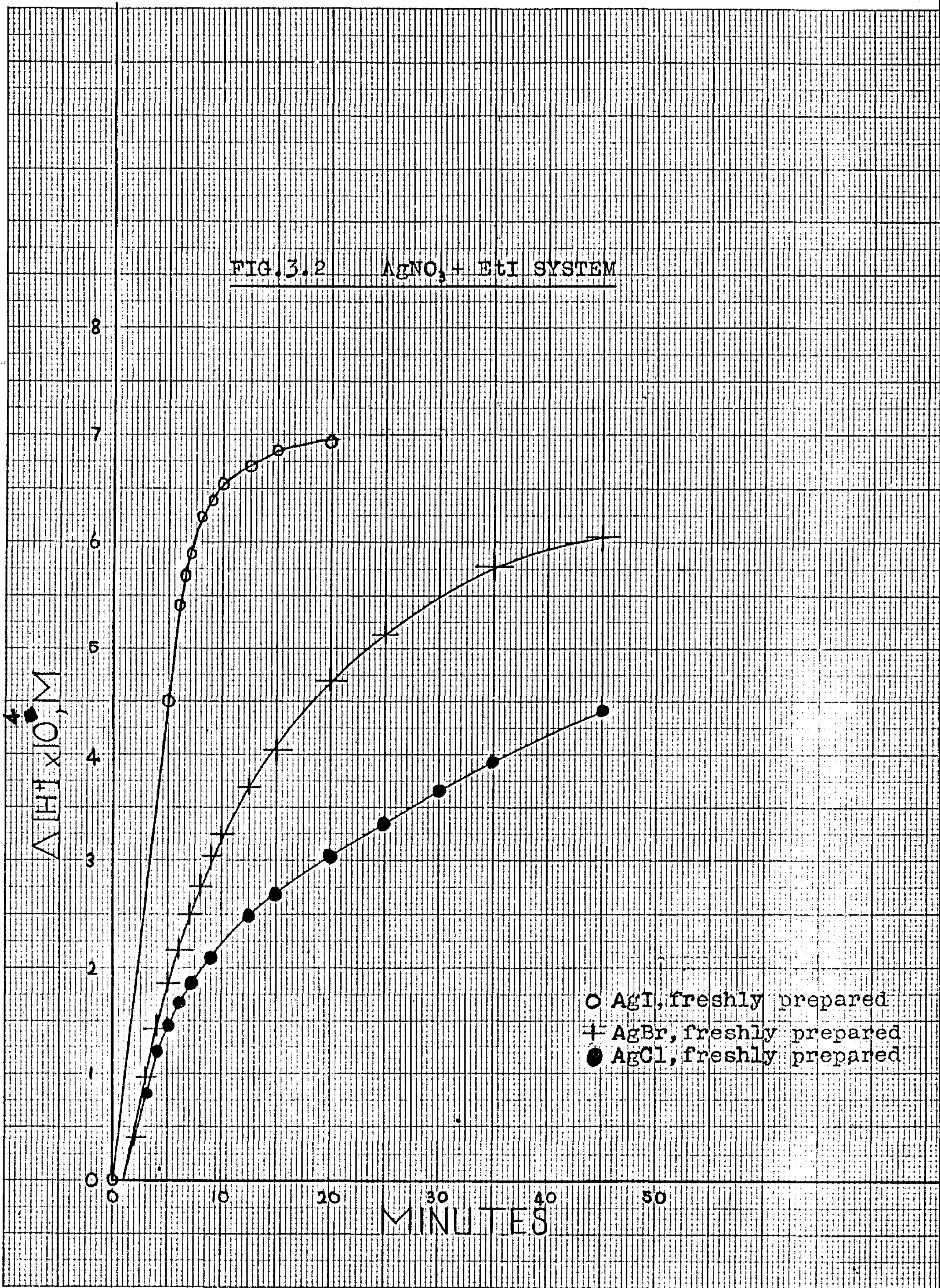


FIG.3.2 $AgNO_3$ + EtI SYSTEM

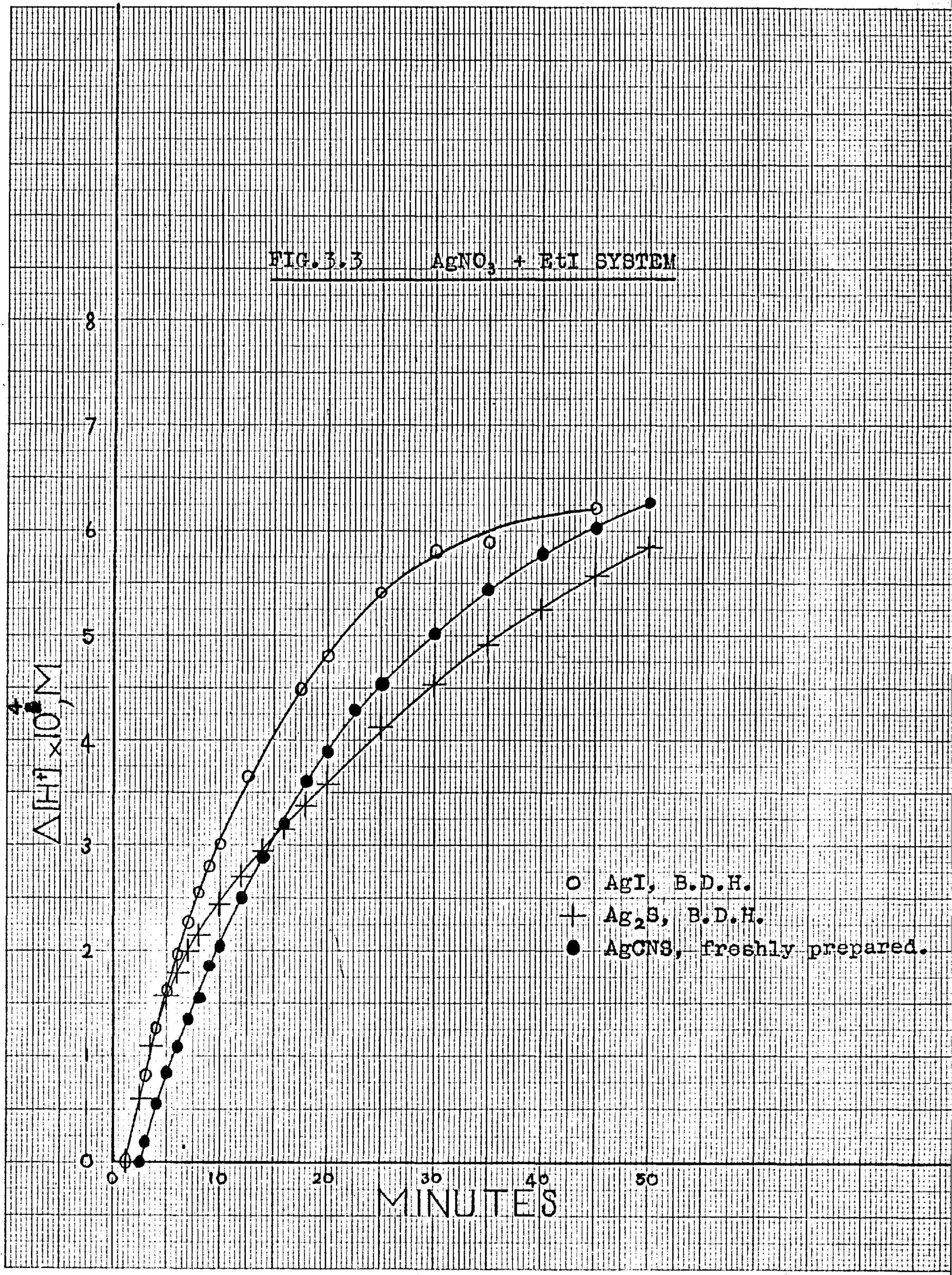


FIG. 3.3 $AgNO_3$ + EtI SYSTEM

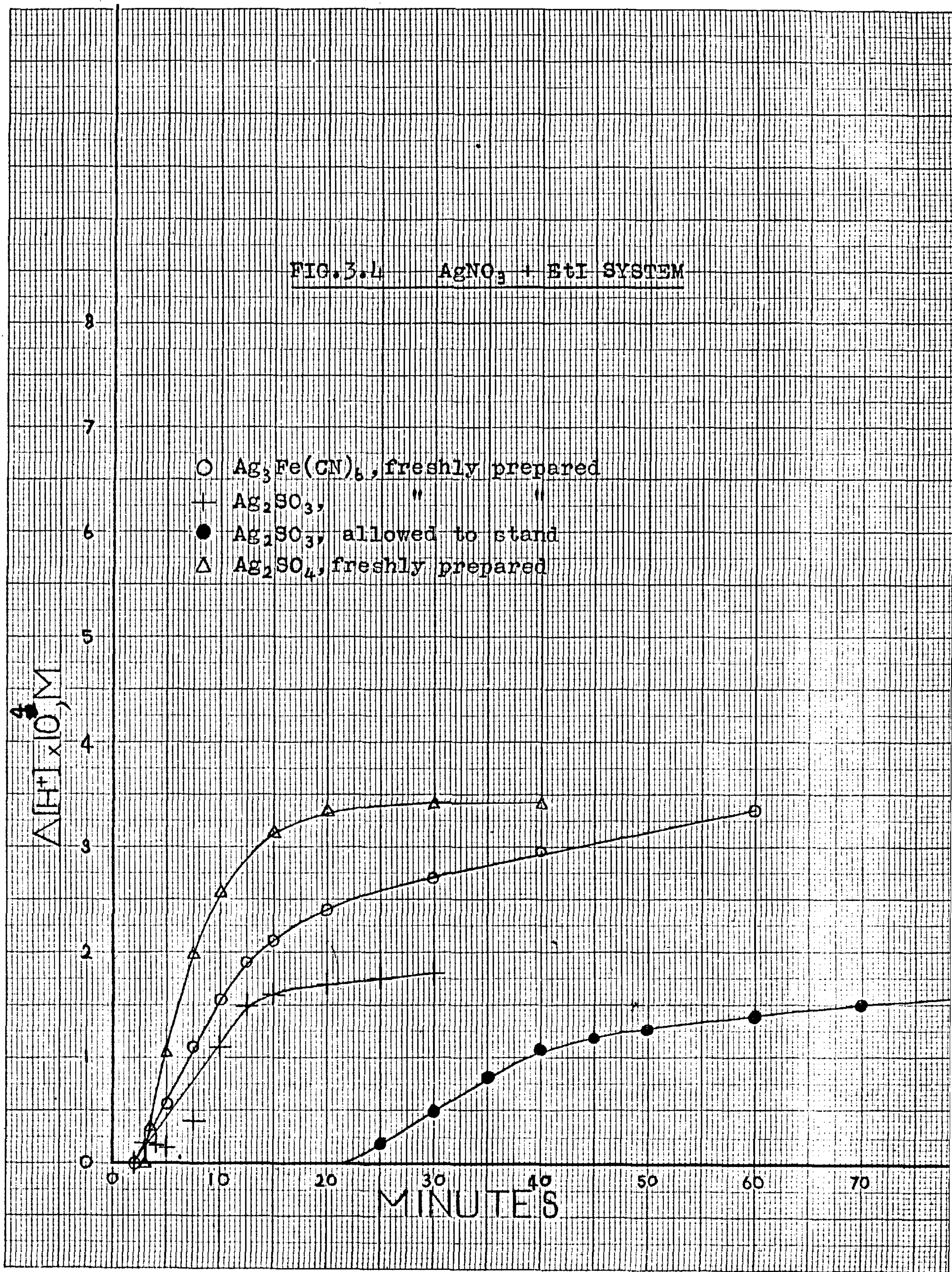


FIG.3.4 AgNO$_3$ + EtI SYSTEM

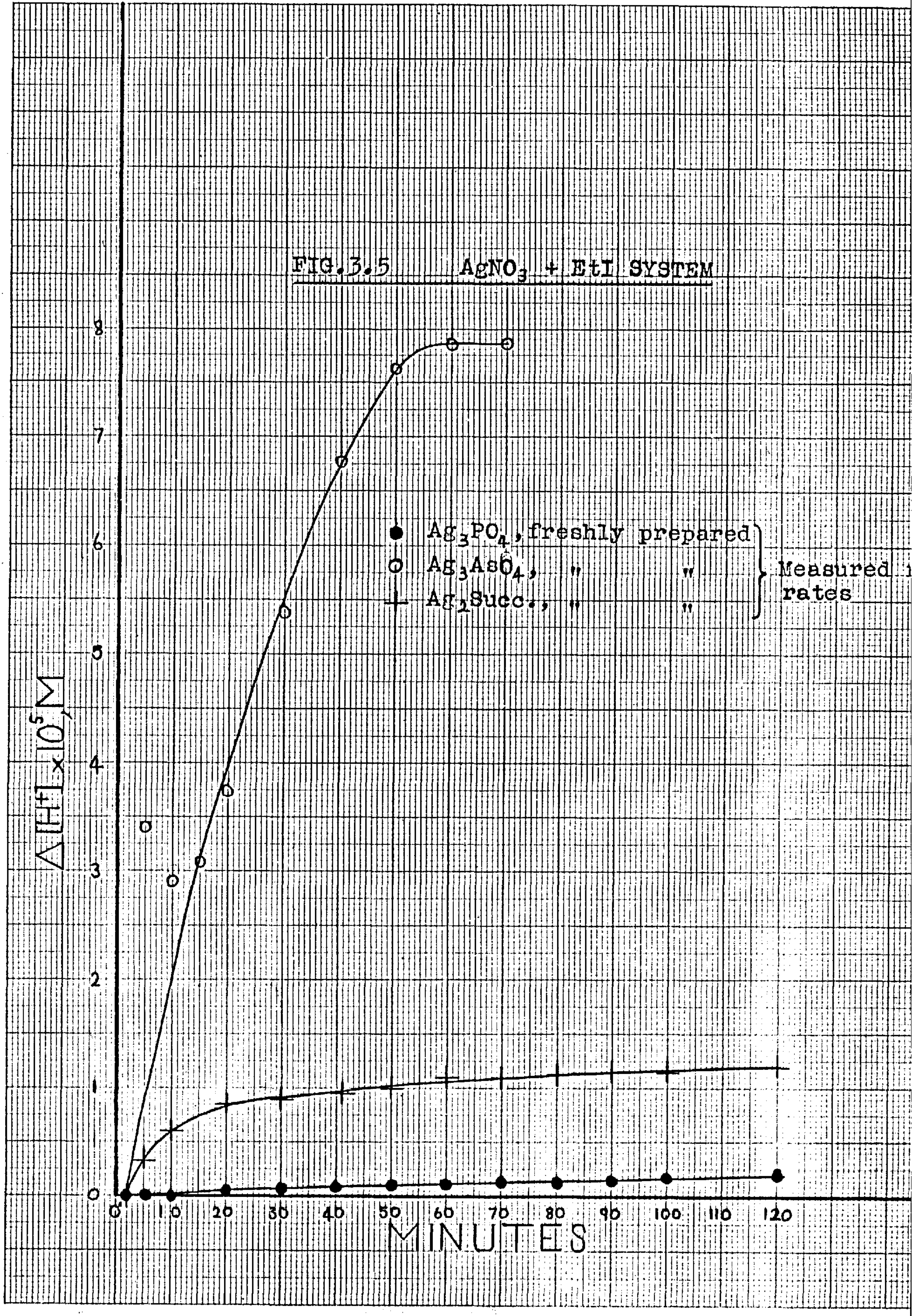


FIG. 3.5 $AgNO_3$ + EtI SYSTEM

prepared silver iodide, being less effective than freshly prepared silver bromide (although this could have been a result of the surface area per gram being smaller). Silver sulphide and silver thiocyanate also appeared to be very good catalysts, the former being better than the bromide, and the latter about as good as silver chloride.

For the other insoluble silver salts the results obtained are rather more difficult to interpret. This is because they are all slightly soluble, and being salts of weak acids tended, on dissolution, to react with the hydrogen ions formed. Thus the measured change of pH with time and therefore measured rate of reaction are not directly related to the real rate. The actual change of hydrogen ion concentration due to the reaction under study can only be calculated from the measured change with a knowledge of the constants of the various equilibria involved.

Consider an insoluble silver salt, AgX, whose solubility product,[66] K_s equals $[Ag^+][X^-]$. Let the association constant[66] of the acid, HX, be

$$K_1 = [HX]/[H^+][X^-] \qquad 3.7$$

If the salt is insoluble we can assume initially for our reaction that, pH = 5, pAg = 3, so that,

$$[HX]/[X^-] = 10^{-5}K_1 = 1/a \text{, (say)} \qquad 3.8$$

$$\frac{[X^-]}{[HX]+[X^-]} = \frac{a}{1+a} \qquad 3.9$$

For HX to be negligible, $a \gg 1$. In this case, the formation of HX from X^- under the stated conditions can be neglected, and the measured change of pH equals the actual change of $[H^+]$ due to the reaction. A similar situation obtains at the end of the reaction, except that $1/a = 10^{-3}K_1$, but the same conditions apply. If a is not much greater than 1, the situation is much more complex (see succinate, phosphate, arsenate, and sulphate).

Similarly for a diprotic acid, H_2Y

$$K_1 = \frac{[HY^-]}{[H^+][Y^{2-}]} \quad ; \quad K_{12} = \frac{[H_2Y]}{[H^+][HY^-]} \qquad 3.10$$

Knowing K_1, K_{12}, and $[H^+]$; $[Y^{2-}]/([HY^-] + [Y^{2-}])$, and $[HY^-]/([HY^-] + [H_2Y])$ can be found, so that in the same way as for a monoprotic acid it can be seen whether or not the acid equilibria are affecting the hydrogen ion concentration.

A further difficulty is that the silver ion concentration may be affected by two factors:-

(1) The solubility product may be such that an appreciable amount of silver ion dissolves into the solution.

(2) Complex ion formation may occur removing silver ion effectively from solution by means of equilibria such as:

$$Ag^+ + X^- \rightleftharpoons AgX \qquad 3.11$$

$$AgX + X^- \rightleftharpoons AgX_2^- \qquad 3.12$$

$$AgX + Ag^+ \rightleftharpoons Ag_2X^+ \qquad 3.13$$

where X^- is an anion generated by the solid.

The following complex ions are known to exist:-[66]

For silver iodide: Ag_3I^{2+}, $Ag_2I_6^{4-}$, Ag^+I^-, AgI_2^-, AgI_3^{2-}, AgI_4^{3-}, $Ag_3I_8^{5-}$

For silver chloride: Ag^+Cl^-, $AgCl_2^-$, $AgCl_3^{2-}$, $AgCl_4^{3-}$, Ag_2Cl^+, Ag_3Cl^{2+}

For silver bromide: Ag^+Br^-, $AgBr_2^-$, $AgBr_3^{2-}$, $AgBr_4^{3-}$, $AgBr_5^{4-}$, $Ag_2Br_6^{4-}$.

For silver thiocyanate: $Ag(SCN)_2^-$, $Ag(SCN)_3^{2-}$, $Ag(SCN)_4^{3-}$, Ag^+SCN^-.

For silver sulphite: $Ag(SO_3)^-$, $Ag(SO_3)_2^{3-}$, $Ag(SO_3)_3^{5-}$.

Their equilibrium constants have been measured, and from these data the silver ion concentration can be calculated.

Calculations have been performed to determine the effect of the equilibria discussed above on the pH and pAg of the reaction solution in the case of AgI, AgCl, AgBr, Ag_2S, AgCNS, $Ag_3Fe(CN)_6$, Ag_3PO_4, Ag_3AsO_4, Ag_2SO_4, Ag_2SO_3, AgCN, and Ag_2Succ.* They show that for AgI, AgBr, AgCl, Ag_2S, and AgCNS, the pH and the pAg are unaffected by the presence of the solid in the reaction mixture, and thus the measured rates can be compared directly. Also, for AgCN the calculations show that the pH and pAg are unaffected. However, it was found that an alkaline solution of pH 8.5 was formed on adding AgCN to the reaction mixture, and there was subsequently no change of pH with time. This was attributed to the fact that on making AgCN the solubility product of AgOH ($10^{-7.5}$) had been exceeded and this had been precipitated as well. The maximum concentration of KCN and $AgNO_3$ possible, if this is to be avoided, are 10^{-4} mole/liter. It was found to be too difficult to collect the required quantity of AgCN (0.01 mole) made this way and the investigation was not pursued.

Silver Sulphite.

Two runs were done with silver sulphite present. The initial rates were 65×10^{-7} and 140×10^{-7} mole liter^{-1}min.$^{-1}$. For the run giving the lower rate, the precipitate had been left standing in water for 2 hours before being used, and had turned slightly brown in this time. The other precipitate was

---

* The values of the association and stability constants used in all these calculations and in the following discussion have been taken from the Chemical Society Special Publication (1964) 'Stability Constants'.

made less than half an hour before being used.

The precipitate dissolves in pure water to give a solution containing 3.3×10^{-4} mole liter^{-1} at equilibrium. Although the extent to which it dissolves in the reaction solution is difficult to calculate, at pH5 and pAg3, $[HSO_3^-]/[SO_3^{2-}] = 10^{2.2}$ and $[Ag(SO_3)^-]/[SO_3^{2-}] = 10^{2.5}$, and this would tend to enhance the dissolution. It can be seen that both the pH and the pAg are affected by the presence of the precipitate, and so the measured rate of reaction is not directly related to the real rate. Even so, catalysis was occurring, although it was not necessarily heterogeneous.

Silver Sulphate.

In the first run the pH was constant (2.48), owing to insufficient washing of the precipitate before use. With a more thoroughly washed precipitate (the washings of which were neutral to universal indicator paper), the initial rate was 418×10^{-7} mole liter^{-1}min.$^{-1}$, the measured pH falling from 4.4 to 3.4 before becoming constant.

In pure water silver sulphate dissolves to the extent of 1.58×10^{-2} mole liter^{-1}. At pH 5 $[HSO_4^-]/[SO_4^{2-}] = 10^{-3}$ and at pH 3 the ratio $= 10^{-1}$, so that both the silver ion concentration and the pH of the solution are affected markedly by the dissolution of the solid. However, the real rate of the reaction being studied can be derived from the measured rate in the following way. Consider:

$$Ag_2SO_4(s) \xrightarrow{\text{dissolution}} Ag^+, SO_4^{2-}, HSO_4^-, H_2SO_4 \tag{3.14}$$

$$AgNO_3 + EtI + H_2O \longrightarrow AgI(s) + EtOH + HNO_3 \tag{3.15}$$

For the dissolution of silver sulphate

$$K_s = [Ag^+]^2 [SO_4^{2-}] \qquad 3.16$$

$$= \frac{[Ag^+]^2 \left([SO_4^{2-}] + [HSO_4^-] + [H_2SO_4]\right)}{\dfrac{[SO_4^{2-}] + [HSO_4^-] + [H_2SO_4]}{[SO_4^{2-}]}} \qquad 3.17$$

Substituting, from 3.10, for $[HSO_4^-]$ and $[H_2SO_4]$, and assuming 3s moles of silver sulphate dissolve

$$K_s = \frac{(a - x + 6s)^2 \cdot 3s}{1 + K_1[H^+] + K_1K_{12}[H^+]^2} \qquad 3.18$$

where x = the concentration of hydrogen ions formed by reaction 3.15 in time t

= the concentration of silver ions used up by reaction 3.15 in time t

a = the initial concentration of silver ion in solution due to the silver nitrate.

Also, the measured hydrogen ion concentration is given by

$$[H^+] = [H^+]_{\text{initial}} + [H^+]_{\text{formed in reaction 3.15}} - [H^+]_{\text{used by sulphate ion}}$$

$$= (b + x - [HSO_4^-] - 2[H_2SO_4]) \qquad 3.19$$

where b = the initial concentration of hydrogen ions in solution.

Substituting for $[HSO_4^-]$ and $[H_2SO_4]$ in 3.19 from 3.10.

$$[H^+] = \left(b + x - \frac{3K_1s[H^+]\left(1 + 2K_{12}[H^+]\right)}{1 + K_1[H^+] + K_1K_{12}[H^+]^2}\right) \qquad 3.20$$

It can be seen that, in principle, 3.18 and 3.20 can be solved for s and x , where x is a measure of the rate of reaction 3.15. However, in practice this is extremely difficult and is best done by assuming a value for s , and using an iterative procedure. Since 3 s is so large compared with x , it can be assumed initially to be 1.58×10^{-2} mole $liter^{-1}$.

This procedure was used to evaluate the real rate of reaction 3.15, the Atlas computer of London University being used to carry out the iteration. The values of K_s and K_1 used in the calculation were 1.585×10^{-5}, and 97.7 respectively. The calculation was done twice, first with $K_{12} = 1 \times 10^{-3}$, and then with $K_{12} = 2.69 \times 10^{-9}$ (the two values being taken from 'Stability Constants'). The values of x and s obtained were the same each time, showing that the reaction $H_2SO_4 \longrightarrow H^+ + HSO_4^-$ was complete in the reaction solution.

The rate obtained by plotting Δx against time was 1170×10^{-7} mole $liter^{-1}$ min^{-1} (see Fig. 3.6). Corrected to 0.001M silver ion, the initial rate of reaction was 37×10^{-7} mole $liter^{-1} min^{-1}$. Thus silver sulphate does catalyse the reaction, but it is a poor catalyst in comparison with the silver halides.

Silver succinate.

The measured initial rate of reaction was 11.2×10^{-7} mole $liter^{-1} min^{-1}$. However, the solubility of silver succinate in water is 6×10^{-4} mole $liter^{-1}$ at 25°C. Also, at pH 5, $[HSucc^-]/[Succ^{2-}] = 10^{0.35}$, and $[H_2Succ]/[HSucc^-] = 10^{-0.8}$, and at pH 4 these ratios are $10^{1.35}$ and $10^{0.2}$ respectively. Now

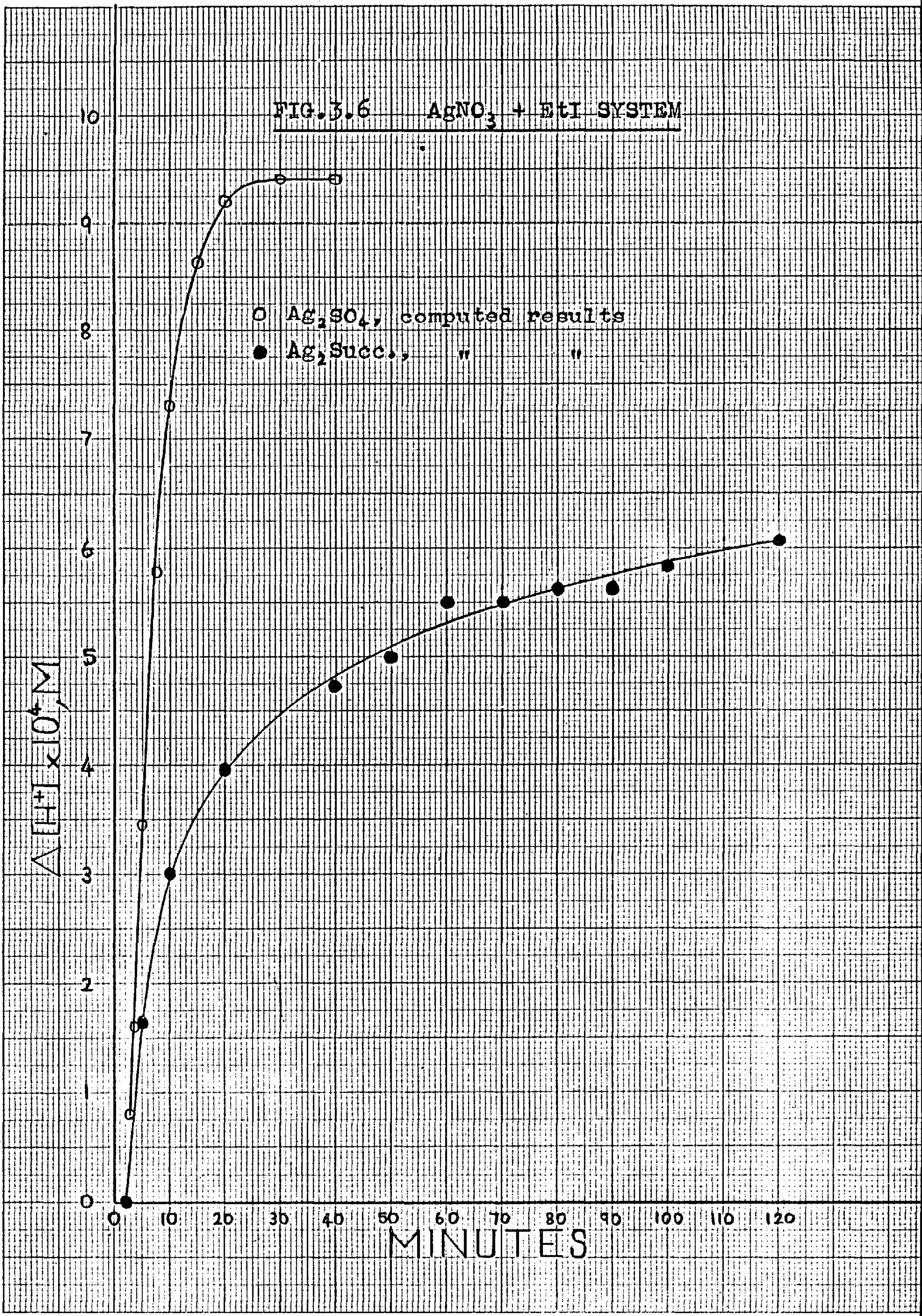


FIG. 3.6 $AgNO_3$ + EtI SYSTEM

the measured pH fell from 4.46 to 4.33, so both the pH and pAg were affected considerably by the presence of the solid. Using equations 3.18 and 3.20, the rate of reaction 3.15 was calculated.

Because of the uncertainty of the values of K_1 and K_{12}, two sets of data were used. If the values $K_s = 8.64 \times 10^{-10}$, $K_1 = 4.325 \times 10^5$, and $K_{12} = 1.609 \times 10^4$ were used, Δx for complete reaction was 1.3×10^{-3} mole liter^{-1} . Since 0.001 M $AgNO_3$ and 0.001M EtI were used, the maximum value of Δx must be 1×10^{-3}. These data were therefore discarded. Values of $K_s = 8.64 \times 10^{-10}$, $K_1 = 1.622 \times 10^5$ and $K_{12} = 1 \times 10^4$ gave $\Delta x = 0.61 \times 10^{-3}$ which is reasonable. The rate of reaction calculated from these values was 550×10^{-7} mole liter^{-1}min^{-1}, or adjusted to 0.001M silver ion, 140×10^{-7} mole liter^{-1}min^{-1}. Hence considerable catalysis occured. The graph of the computed rate of reaction is given in Fig. 3.6

Silver phosphate.

The measured initial rate of reaction was 0.14×10^{-7} mole liter^{-1}min^{-1}, the pH falling from 5.50 to 5.275 in 150 minutes. The solubility of silver phosphate is approximately 10^{-4} mole liter^{-1}, and at pH 5, $[HPO_4^{2-}]/[PO_4^{3-}] = 10^{7.36}$, $[H_2PO_4^-]/[HPO_4^{2-}] = 10^{2.2}$, and $[H_3PO_4]/[H_2PO_4^-] = 10^{-2.85}$ (for $K_1 = 10^{12.36}$, $K_{12} = 10^{7.22}$, $K_{13} = 10^{2.15}$). Thus both the pH and pAg are affected by the presence of the phosphate in solution. It is evident that the only phosphate species that need be considered at this pH is $H_2PO_4^-$. Consider s moles of silver phosphate dissolving:

$$Ag_3PO_4 + 2H^+ \rightleftharpoons 3\,Ag^+ + H_2PO_4^- \qquad 3.21$$

If 3.21 and 3.15 are treated in a manner similar to that used for the sulphate equation, then the following equations result:

$$K_sK_1K_{12} = \frac{(a - x + 3s)^3 s}{[H^+]^2} \qquad 3.22$$

$$[H^+] = (b + x - 2s) \qquad 3.23$$

where the symbols a, b, and x are as before. These equations may also be solved by iteration, and a solution was sought using the Atlas computer.

The values $K_s = 1.445 \times 10^{-16}$, $K_1 = 2.29 \times 10^{12}$, and $K_{12} = 1.585 \times 10^7$ gave Δx for the reaction = 1.25×10^{-2} mole liter^{-1} and were discarded. The values $K_s = 1.0 \times 10^{-20}$, $K_1 = 2.29 \times 10^{12}$, and $K_{12} = 1.585 \times 10^7$ gave Δx for the reaction = 1.089×10^{-3} mole liter^{-1}, and were used to evaluate the real rate of reaction 3.15. This was 110×10^{-7} mole liter^{-1}min^{-1} (Fig 3.7), or corrected to 0.001M silver ion, 35×10^{-7} mole liter^{-1}min^{-1}, hence silver phosphate is comparable with silver sulphate in its catalytic effectiveness. The results also showed that for a change of pH from 5.5 to 5.275, the number of moles liter^{-1} of silver phosphate in solution changed from 7.1×10^{-4} to 1.05×10^{-3}, indicating the sensitivity of the solubility of silver phosphate to pH, in this range.

Silver arsenate.

The measured initial rate of reaction was 25×10^{-7} mole liter^{-1}min^{-1}, the pH falling from 3.95 to 3.72 in 60 minutes. The solubility of silver arsenate in water is ca. 1.4×10^{-6} mole liter^{-1} at 20°C. However, at pH 4 $[HAsO_4^{2-}]/[AsO_4^{3-}] = 10^6$, $[H_2AsO_4^-]/[HAsO_4^{2-}] = 10^3$, and $[H_3AsO_4]/[H_2AsO_4^-] = 10^{-1.7}$ ($K_1 = 10^{10}$, $K_{12} = 10^7$, and $K_{13} = 10^{2.3}$), so that, as for phosphate, the pH is affected by the presence of the solid in solution. Only the species $H_2AsO_4^-$ need be considered, and equations 3.22 and 3.23 apply. These were solved for:

FIG.3.7 $AgNO_3$ + EtI SYSTEM

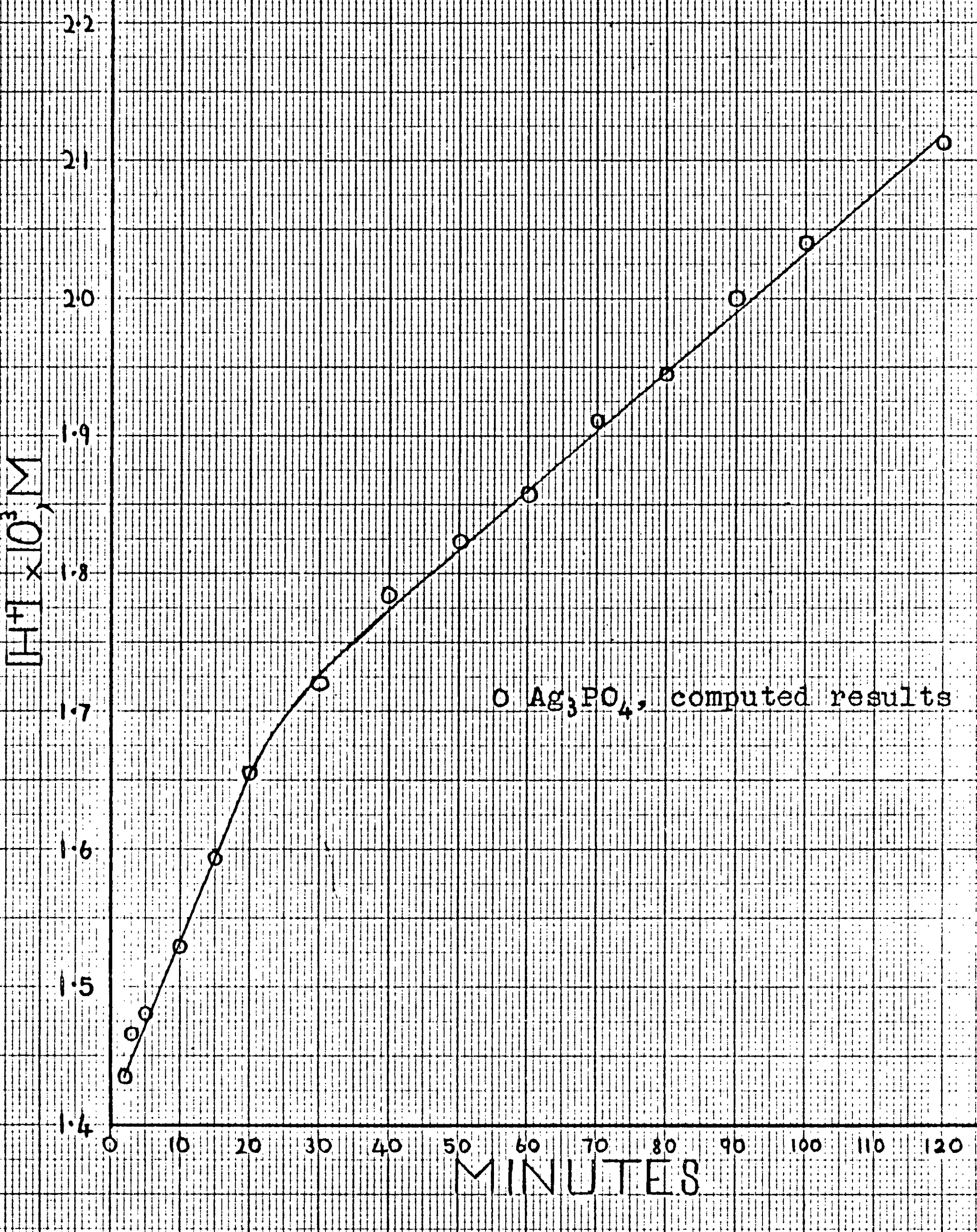


Table 3.3

	K_s	K_1	K_{12}	Δx_{total}
(i)	1.0×10^{-22}	1.622×10^{9}	1.0×10^{7}	1.88×10^{-4}
(ii)	1.0×10^{-22}	3.162×10^{11}	1.0×10^{7}	1.0×10^{-3}
(iii)	1.122×10^{-20}	1.622×10^{9}	1.0×10^{7}	0.88×10^{-3}
(iv)	1.122×10^{-20}	3.162×10^{11}	1.0×10^{7}	3.0×10^{-3}

The values of Δx_{total} are the computed values of the change of x corresponding to the total change of measured pH. (ii) and (iii) were chosen as the most reasonable, (i) and (iv) being rejected as too small and too large respectively.

The calculated rates were (Fig 3.8):

	Rate	Rate corrected to 10^{-3}M silver ion
(ii)	307×10^{-7} mole $liter^{-1} min^{-1}$	105×10^{-7} mole $liter^{-1} min^{-1}$
(iii)	370×10^{-7} mole $liter^{-1} min^{-1}$	108×10^{-7} mole $liter^{-1} min^{-1}$

Thus considerable catalysis occurred.

Silver ferricyanide.

This salt also showed marked catalysis (initial rate = 200×10^{-7} mole $liter^{-1} min^{-1}$). Very few data on the solubility product and equilibrium constants were available, but values of $K_s = 2.3 \times 10^{-24}$ and $K_1 < 1$ indicate that the pAg and pH should not be affected by the presence of the salt.

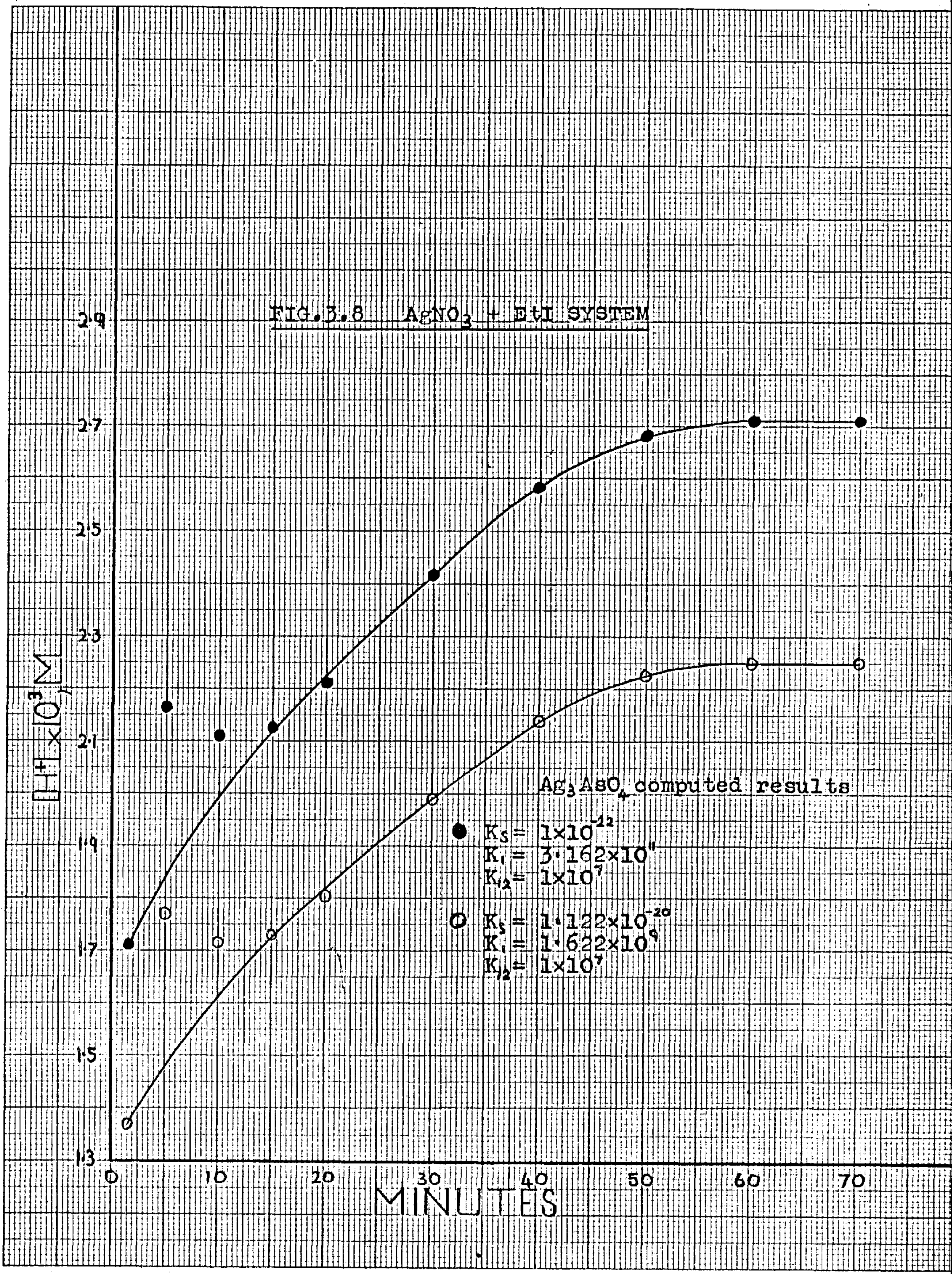


FIG. 3.8 AgNO$_3$ + EtI SYSTEM

An interpretation of the results given in Table 3.4 is presented at the end of the chapter.

(ii) Results of Runs Using Insoluble Iodides

The reaction was carried out in the presence of the following insoluble iodides: HgI_2, Hg_2I_2, PbI_2, CuI, and TlI. An attempt was made to prepare SnI_2, but this failed because of the hydrolysis of the $SnCl_2$ used.

Hg_2I_2, HgI_2, and PbI_2 all appeared, from the measured rates of reaction, to be good catalysts, in the order $Hg_2I_2 > HgI_2 > PbI_2$. CuI gave a solution in which the pH rose instead of falling, and TlI gave a solution of approximately constant pH (5.25). Initial rates of reaction are given in Table 3.5 and graphs of change of hydrogen ion concentration with time are given in Figs. 3.2,3,9, and 10.

Mercurous Iodide.

Consider the equilibrium -

$$2Ag^{+} + Hg_2I_2(s) \rightleftharpoons Hg_2^{2+} + 2AgI\ (s). \qquad 3.24$$

The equilibrium constant $K = a_{Hg_2^{2+}} / a^2_{Ag+}$ 3.25

since the activities of the solids are unity. If we neglect activity coefficients

$$K = \frac{[Hg_2^{2+}]}{[Ag^{+}]^2} \qquad 3.26$$

Table 3.5

The Effect of Insoluble Iodides on the $AgNO_3$ + EtI System.

Run	Catalyst	Source	Initial Rate x 10^7 (mole liter^{-1} min^{-1})
0	none	-	5.47 ± 0.18
1	AgI	freshly prepared	Ca. 900
2	AgI	B.D.H.	ca. 380
3	Hg_2I_2	B.D.H.	ca. 350
4	HgI_2	freshly prepared	ca. 150
5	PbI_2	freshly prepared	ca. 100
6	PbI_2	freshly prepared	
7	CuI	freshly prepared	No measurable rate
8	CuI	B.D.H.	
9	TlI	B.D.H.	pH of solution constant with time
10	TlI	freshly prepared	

Mass of Catalyst = 0.01 mole

Volume of Solution = ca. 91.5 ml.

Initial $[AgNO_3]$ = Initial $[EtI]$ = 0.001M

Temperature = 25°C.

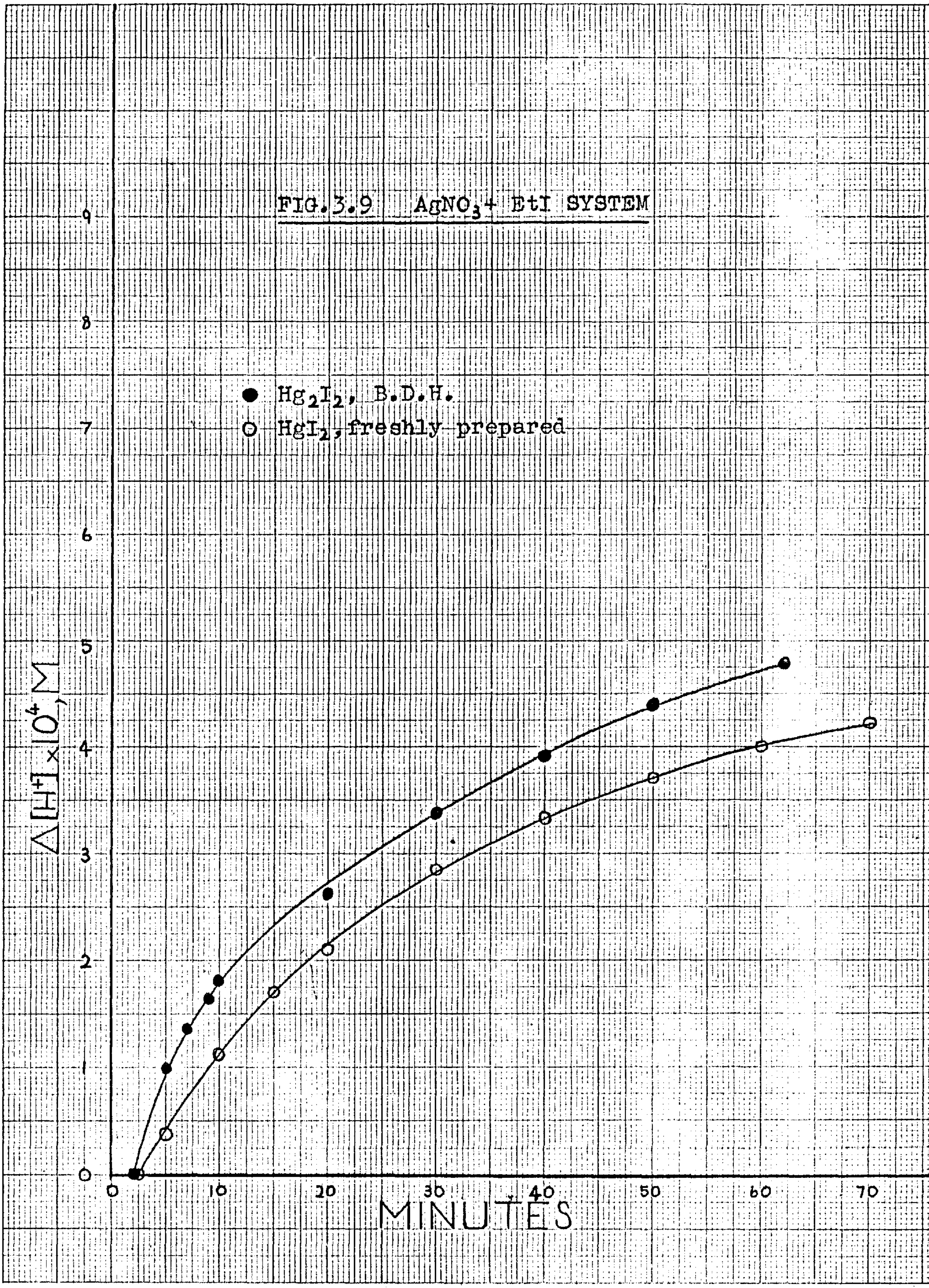
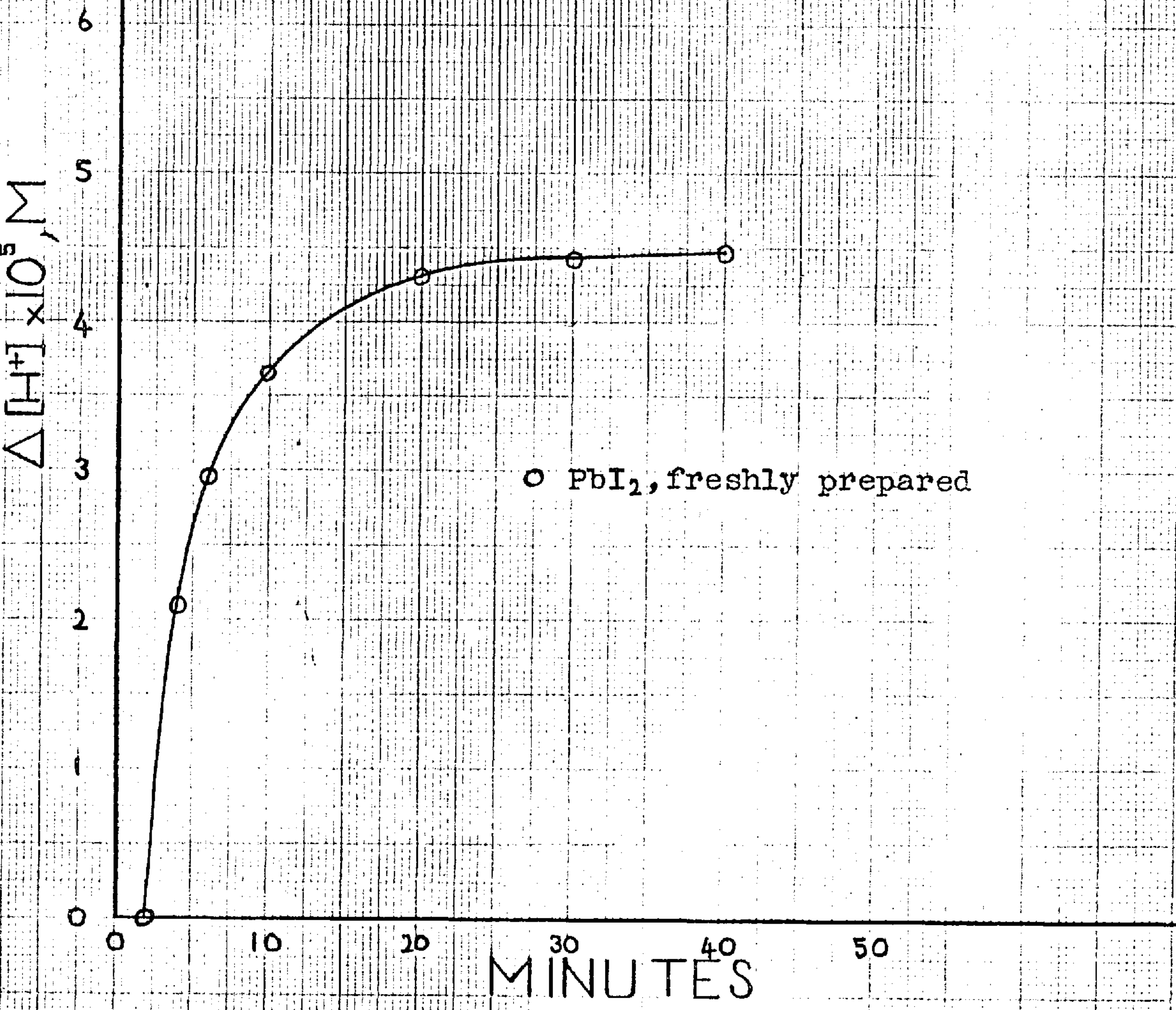


FIG. 3.9 $AgNO_3$ + EtI SYSTEM

FIG.3.10 AgNO$_3$ + EtI SYSTEM



$$= \frac{[Hg_2^{2+}]\,[I^-]^2}{[Ag^+]^2\,[I^-]^2} = \frac{K_s\,(Hg_2I_2)}{K_s^2\,(AgI)} \qquad 3.27$$

$$= 10^4$$

Therefore, the equilibrium 3.24 lies on the right, and the reaction being followed is really

$$Hg_2(NO_3)_2 + 2EtI + 2H_2O = Hg_2I_2(s) + 2EtOH + 2HNO_3 \qquad 3.28$$

in the presence of silver and mercurous iodides as catalysts.

(All values for K_s in this section are taken from 'Stability Constants').

For the reaction:

$$2\,Ag^+ + Hg_2^{2+} = 2Ag + 2Hg^{2+} \qquad 3.29$$

The value of ΔG° was calculated to be 5.6 kcal. from the standard potentials of the couples concerned,[67] i.e.

$$Ag^+ + e \rightleftharpoons Ag \qquad \Delta G^\circ_{Ag} = -E^\circ_{Ag}F \qquad 3.30$$

$$2Hg^{2+} + 2e \rightleftharpoons Hg_2^{2+} \qquad \Delta G^\circ_{Hg} = -2E^\circ_{Hg}F \qquad 3.31$$

$$\Delta G^\circ = 2\Delta G^\circ_{Ag} - \Delta G^\circ_{Hg} \qquad 3.32$$

Thus at unit activity the reaction would not occur. The value of ΔG for the reaction cannot be evaluated because the activities of the ions concerned are not known.

Mercuric Iodide.

For the equilibrium:

$$HgI_2(s) + 2Ag^+ \rightleftharpoons Hg^{2+} + 2AgI(s) \qquad 3.33$$

$K = 10^{20.34}$. The equilibrium therefore lies entirely on the right, and the reaction being followed was

$$Hg(NO_3)_2 + 2EtI + 2H_2O = HgI_2(s) + 2EtOH + 2HNO_3 \qquad 3.34$$

in the presence of mercuric and silver iodides as catalysts.

Lead Iodide.

$K = 10^{21.6}$ for the equilibrium

$$PbI_2(s) + 2Ag^+ \rightleftharpoons 2AgI(s) + Pb^{2+} \qquad 3.35$$

and therefore it lies completely on the right. Thus the reaction being followed was:

$$Pb(NO_3)_2 + 2EtI + 2H_2O = PbI_2(s) + 2EtOH + 2HNO_3 \qquad 3.36$$

For the reaction:

$$2Ag^+ + Pb^{2+} = 2Ag + Pb^{4+} \qquad 3.37$$

$\Delta G^\circ = 42.4$ kcal, so that this will not occur.

Cuprous Iodide.

The equilibrium:

$$Ag^+ + CuI(s) \rightleftharpoons Cu^+ + AgI(s) \qquad 3.38$$

lies on the right, K being $10^{4.7}$. The following reaction:-

$$Cu^+ + Ag^+ \rightleftharpoons Cu^{2+} + Ag \qquad 3.39$$

will also occur ($\Delta G^\circ = -14.9$ k cal). This was borne out by the fact that, after the reaction had been followed for some time, the solid contained black particles of precipitated silver. The reason for the rise of pH was the reaction:

$$2Cu^+ + NO_3^- + 3H^+ \rightleftharpoons 2Cu^{2+} + HNO_2 + H_2O \qquad 3.40$$

for which $\Delta G^\circ = -36.2$ kcal. It is not known whether any hydrolysis of the ethyl iodide occurred.

Thallous Iodide.

For the equilibrium:

$$\text{TlI(s)} + \text{Ag}^+ \rightleftharpoons \text{Tl}^+ + \text{AgI(s)} \qquad 3.41$$

$K = 10^{8.8}$, and the equilibrium therefore lies on the right. Thus, any reaction occurring would be of the type -

$$\text{TlNO}_3 + \text{EtI} + \text{H}_2\text{O} = \text{TlI(s)} + \text{EtOH} + \text{HNO}_3 \qquad 3.42$$

in the presence of silver and thallous iodides as catalysts. However, from the measured pH which was constant with time (at 5.25), reaction 3.42 does not occur at a measurable rate under the conditions used.

E.m.f. Measurements.

An attempt was made to substantiate the above hypotheses by measuring the silver ion concentration in a solution of silver nitrate in contact with the appropriate precipitate. This was done by using a silver electrode and measuring the e.m.f. of the cell:

$$\text{Calomel} \left| \begin{array}{c}\text{KCl}\\ \text{satd.}\end{array} \right| \begin{array}{c}\text{KNO}_3\\ 0.25\text{M}\end{array} \left| \begin{array}{l}\text{Ag}^+\text{, precipitate}\\ 0.001\text{M}\end{array} \right| \text{Ag.} \qquad 3.43$$

However, in the case of mercuric iodide, reaction 3.29 will go from right to left, and for mercurous iodide:

$$2\text{Ag} + \text{Hg}_2^{2+} \rightleftharpoons 2\text{Ag}^+ + 2\text{Hg} \qquad 3.44$$

ΔG° is about zero, so that a silver electrode cannot be used in contact with solutions containing these ions.

However for lead and thallium:

$$2\text{Ag} + \text{Pb}^{2+} \rightleftharpoons 2\text{Ag}^+ + \text{Pb} \qquad \Delta G^\circ = 42.6 \text{ kcal} \qquad 3.45$$

$$\text{Ag} + \text{Tl}^+ \rightleftharpoons \text{Ag}^+ + \text{Tl} \qquad \Delta G^\circ = 26.2 \text{ kcal} \qquad 3.46$$

and therefore the silver electrode can be used in solutions containing these ions.

Lead Iodide.

First, 0.01 mole of freshly prepared lead iodide was equilibrated with water at 25°C, and sufficient silver nitrate solution added to made $[AgNO_3] = 10^{-3}M$. The solution was stirred, and the change of e.m.f. of cell 3.43 with time was followed. The e.m.f. was measured using a Radiometer pH meter 4 as a potentiometer. The initial e.m.f. of the cell was -214 mV and a fluctuation of ± 2 mV. was found over a period of 20 minutes. In still solution, with the precipitate having sunk to the bottom of the vessel, the e.m.f. was -219 mV. Thus, from the Nernst equation,[68] we calculate:-

$a_{Ag^+} = 9.3 \times 10^{-14}$ - stirring

$a_{Ag^+} = 7.6 \times 10^{-14}$ - no stirring

Taking $f_{Ag^+} = 0.94$, we have:

$C_{Ag^+} = 9.9 \times 10^{-14}$ mole liter^{-1} - stirring

$C_{Ag^+} = 8.1 \times 10^{-14}$ mole liter^{-1} - no stirring

Since reaction 3.35 goes virtually to completion, we can take $[Pb^{2+}]$ equal to $5.0 \times 10^{-4}M$. K for equilibrium 3.35 is $10^{21.6}$, so that the value of the silver ion concentration, calculated from an equation similar to 3.27, is 3.5×10^{-12} mole liter . The difference between the calculated and measured values cannot be explained in terms of complex ion formation, since the concentration of PbI^+ and similar species is negligible. The difference is attributed to the fact that the silver electrode is rather erratic in its response below a silver ion concentration of ca. 10^{-6} mole liter^{-1}.

In an attempt to measure the rate of disappearance of silver ions, a second experiment was performed in which the precipitate was added to the stirred solution of silver nitrate. The first e.m.f. measurement was made 1 minute after the lead iodide had been added, but again the e.m.f. recorded was -216 mV, and it drifted to -209 mV in 70 minutes. This corresponds to a change in activity from 8.9×10^{-14} to 1.1×10^{-13}, and was thought to be due to equilibration.

It appears, therefore, that the dissolution of lead iodide and the removal of silver ions from solution occurred quickly, in comparison with the rate of hydrolysis of ethyl iodide.

Thallous Iodide.

Using cell 3.43, 0.01 mole of TlI (from B.D.H.) was equilibrated with water at 25°C, and then an aliquot of silver nitrate solution added to make $[AgNO_3] = 10^{-3}$ M. The solution was stirred and the change of e.m.f. with time followed. Three minutes after the addition of the silver nitrate solution, the e.m.f. was -71 mV, and after 30 minutes it was -162mV and still falling, but at a lower rate. Thus:

$C_{Ag+} = 2.5 \times 10^{-11}$ mole liter^{-1} after 3 minutes

$C_{Ag^+} = 7.4 \times 10^{-13}$ mole liter^{-1} after 30 minutes

For equilibrium 3.41, $K = 10^{8.8}$, and since the equilibrium lies far to the right, we may assume $[Tl^+]$ equals 1×10^{-3} mole liter^{-1}. The value of the silver ion concentration in the solution at equilibrium, calculated from an equation similar to 3.27, is therefore 1.6×10^{-12} mole liter^{-1}. This is in fair agreement with the measured values.

On removing the silver electrode, wiping it and replacing it in the solution, e.m.f.s of -168 and -172 mV were recorded and in both cases the readings became slowly less negative, the solution being unstirred. The effect was probably due to re-equilibration of the electrode with the solution. However, the measured decrease in the silver ion concentration indicates that thallous iodide is slower than lead iodide in removing the silver ions from solution, although the process would still be virtually complete before the ethyl iodide hydrolysis had started.

These two e.m.f. experiments thus confirm the conclusions reached earlier in this section from equilibrium constant calculations alone.

(iii) Results of Runs Using Metal Powders

Four metal powders, Pt, Pd, Ag, and Au were tried as catalysts. Their order of effectiveness (see Table 3.6 and Fig. 3.11) was found to be - Pt > Pd > Ag > Au, but since the rates were rather similar, this order might be misleading. It was found on remeasuring the rate of reaction in the presence of silver, for example, that it was 9.0×10^{-7} mole liter^{-1} min^{-1}, compared with 7.6×10^{-7} mole liter^{-1}min^{-1} for the first run. This variation was probably due to lack of uniformity in the state of subdivision of the sample used. The measured rates did show, however, that the metals were not very good catalysts, when compared with silver iodide, precipitated Pt giving only a four fold increase in rate.

For all the catalysts, except silver, the rate of reaction decreased slightly after the first two or three readings and in the case of gold the reaction rate became lower than the 'homogeneous' rate; i.e. inhibition was apparently occurring. For Pt and Pd, however, the rate was still greater than the homogeneous rate. With Ag, the rate showed a tendency to increase slightly after the first few readings.

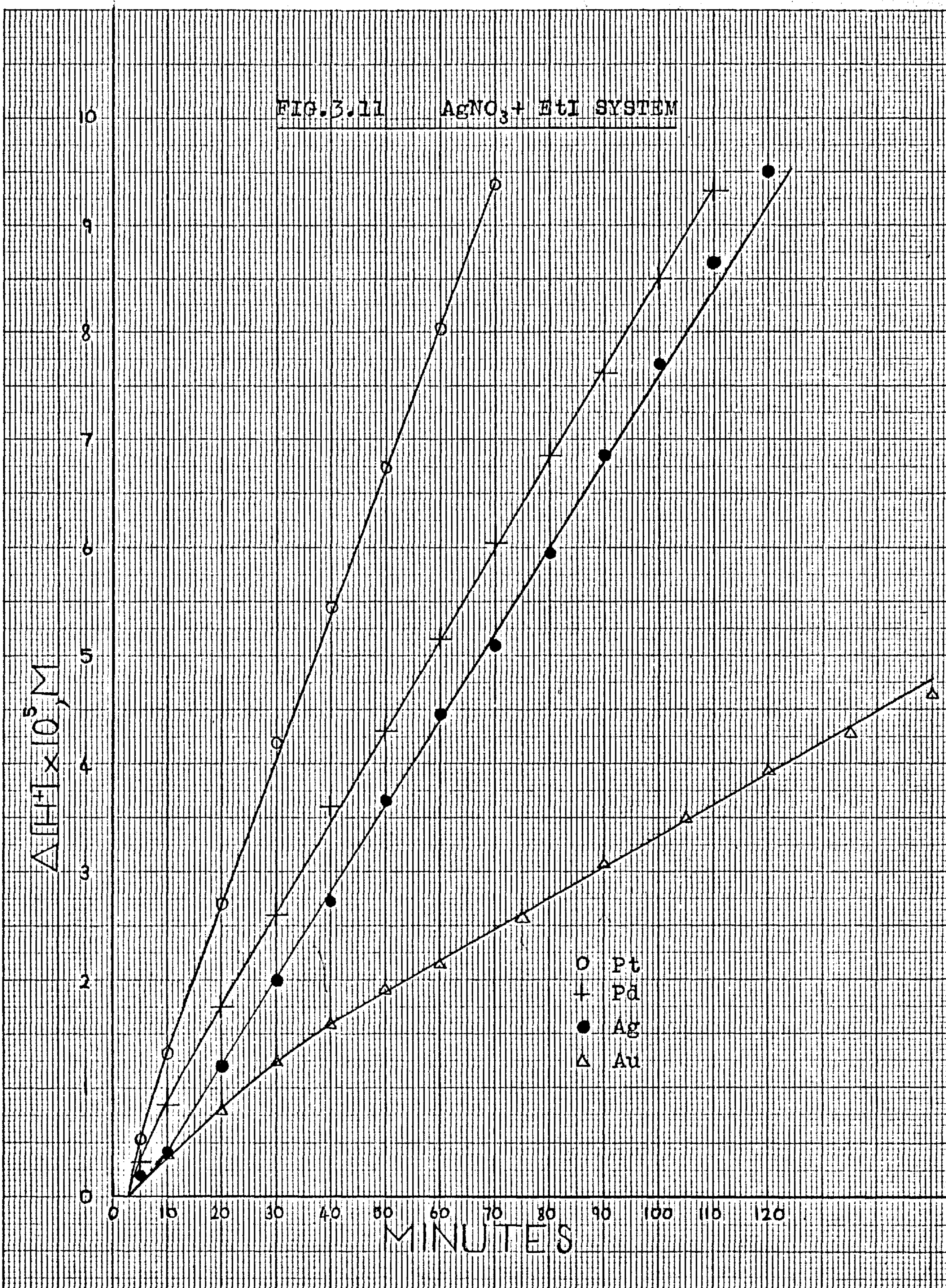


FIG.3.11 $AgNO_3$+ EtI SYSTEM

Since no reaction of the type

$$Au + Ag^{+} \rightleftharpoons Au^{+} + Ag$$

could occur in the reaction solutions, there was no possibility of interference with the pH or pAg by the catalyst. The measured rate could therefore be interpreted as the real rate.

Colloidal silver was also added to the reaction solution but it gave a pH of 8.5, which fell only slightly, and no rate measurement could be made.

Microscopic Examination:

The silver and platinum powders were examined under a Cooke microscope with a display screen. The magnification was 400. The images of the particles were projected on a screen, and were measured by comparison with a stage micrometer. It was found that the particle size was ca. 6×10^{-3} cm for silver, and from 2×10^{-3} to 6×10^{-3} cm for platinum. The particles of both metals were far from being spherical. These data, however, gave an approximate value, for the surface area of platinum added, of 110 cm^{2}. Calculations based on this value (see Appendix.) showed that the reaction was not diffusion controlled, the calculated rate of diffusion of both reactants to the surface being at least 40 times greater than the measured rate of reaction.

Table 3.6

The Effect of Metals on the $AgNO_3$ and EtI System.

Run	Catalyst	State	Initial Rate x 10^{7} (mole liter^{-1} min^{-1})
0	none	-	5.47 ± 0.18
1	Au	precipitated	5.2
2	Pt	precipitated	18
3	Pd	precipitated	15.5
4	Ag	precipitated	7
5	Ag	precipitated	9.6
6	Ag	colloidal	Solution alkaline (pH 8.5)

Re. Table 3.6

Initial $[AgNO_3]$ = Initial $[EtI]$ = 0.001M
Mass of catalyst = 0.01 mole
Volume of solution = ca. 91.5 ml
Temperature = 25°C.

The results presented in Table 3.6 are interpreted at the end of the chapter.

(iv) Results of Runs Using Miscellaneous Catalysts.

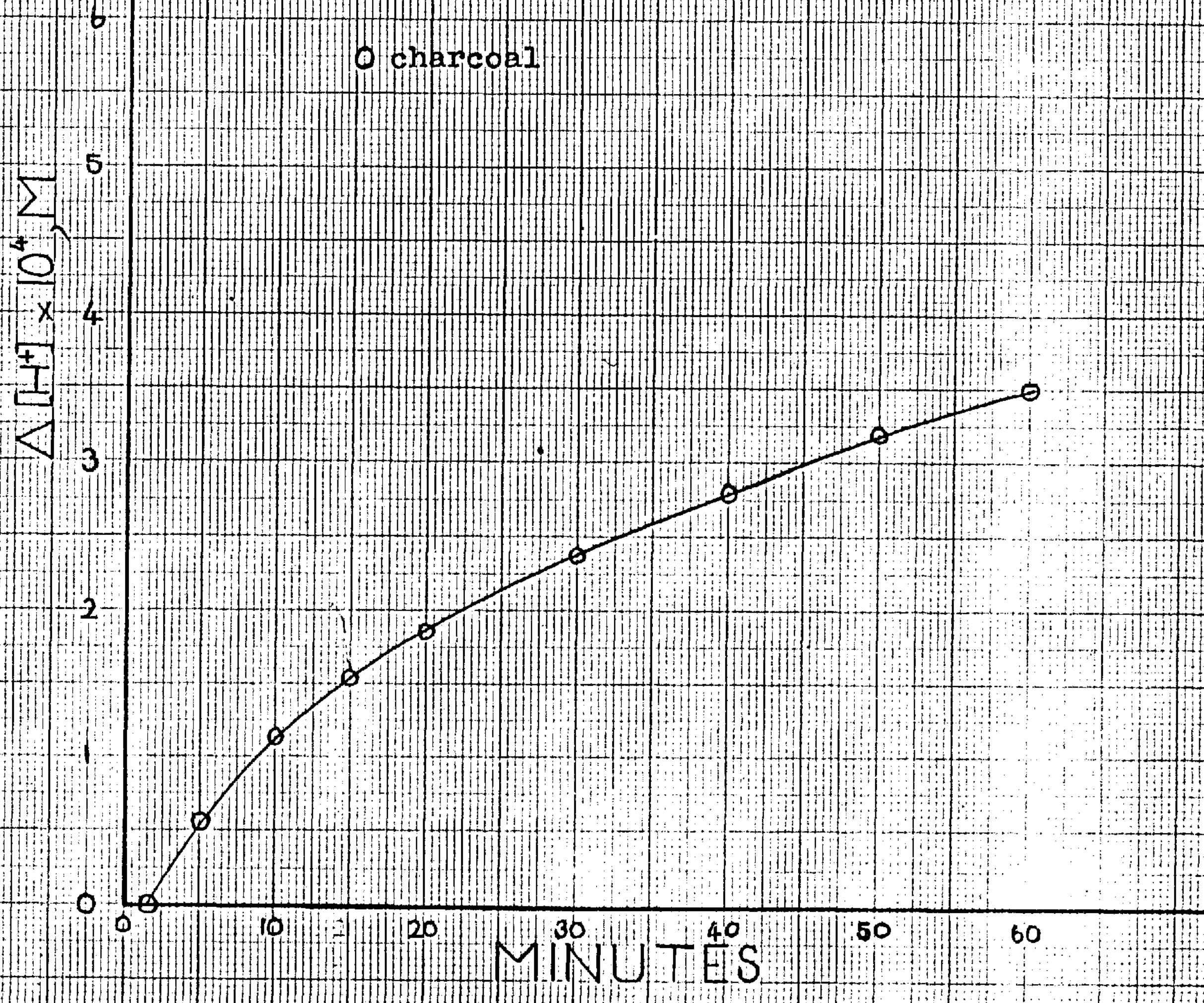
A list of catalysts used, with initial rates of reaction, is given in Table 3.7, and graphs of the rate of change of hydrogen ion concentration in Figs. 3.12 and 3.13.

Since the cell walls in contact with the solution were of Perspex and glass, the effect of these two materials was investigated. Neither was found to affect the rate of reaction, thus showing that the cell itself was catalytically inert.

In the rotating disc work (Chapter 5) Teflon and stainless steel were to be used, and their effect on the reaction rate was investigated, by adding lathe turnings to the reaction mixture. Neither had any effect on the rate.

Two runs with silicon gave similar rates, of 10×10^{-7} mole $\text{liter}^{-1}\text{min}^{-1}$. Its effectiveness is thus comparable with that of the noble metals, as can also be seen from the similarity of the rate curve (Figs. 3.11 and 3.13). However, work carried out recently by another worker in this laboratory (Mrs. M. D. Archer) indicated that the silicon powder supplied by B.D.H. contained an appreciable amount of iron, which may have been the catalytic agent.

FIG. 3.12 $AgNO_3$ + EtI SYSTEM



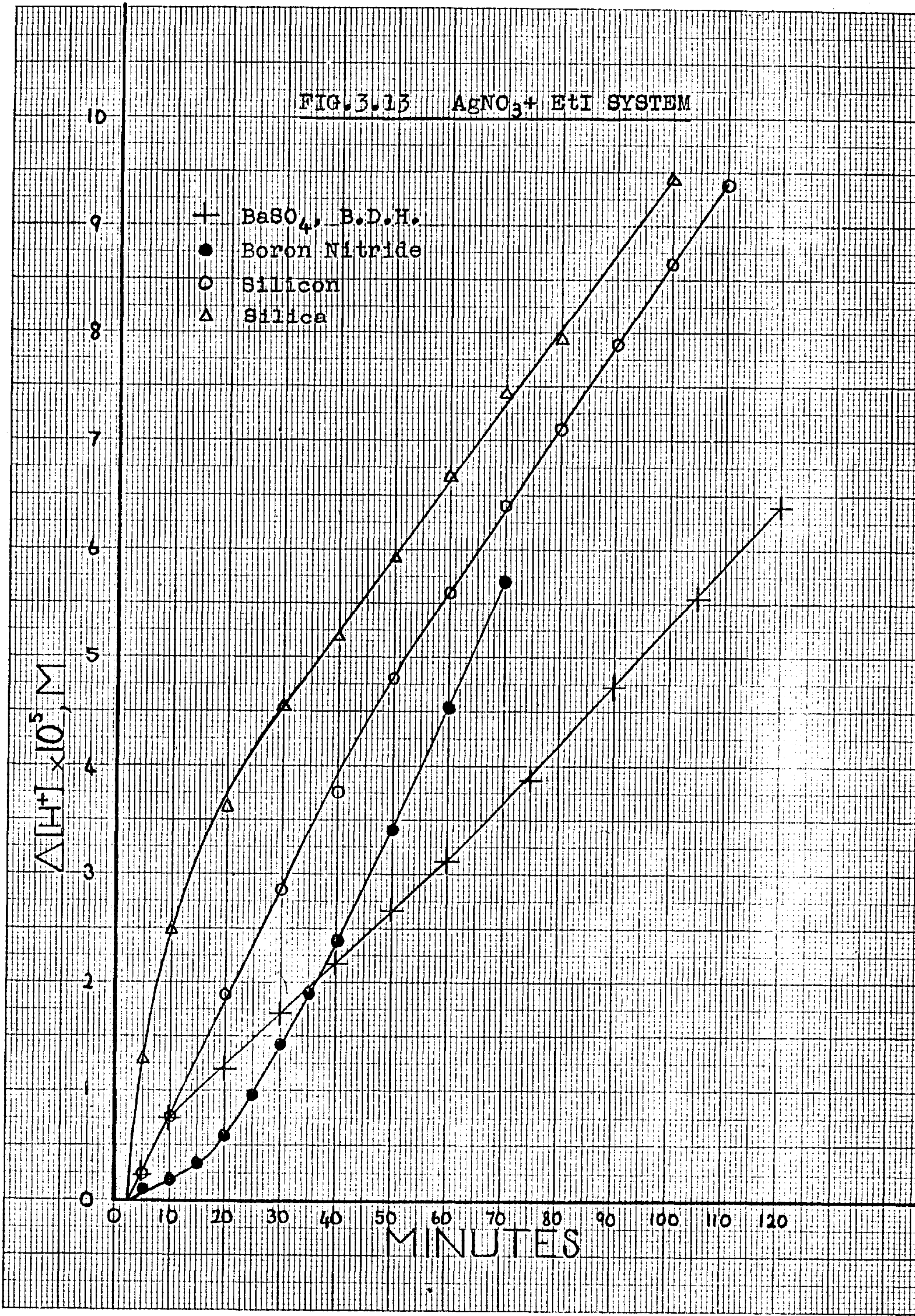


FIG.3.13 AgNO$_3$+ EtI SYSTEM

Finely divided charcoal is a catalyst for many different types of reaction. For the present reaction its effectiveness was of the same order as Ag_2SO_3, HgI_2, and PbI_2, giving a rate of ca. 140×10^{-7} mole $liter^{-1}$ min^{-1}. It was the only catalyst in this section whose effect was comparable with the insoluble silver salts and the insoluble iodides.

Boron nitride, with a structure similar to that of carbon,[70] was the only catalyst used which showed an initial retardation of rate. However, after the first three or four readings the rate increased to a constant value of 9.6×10^{-7} mole $liter^{-1}$ min^{-1} (Fig. 3.13).

Silica gave an initial rate of 52×10^{-7} mole $liter^{-1}$ min^{-1}. After 3 or 4 readings the rate changed (Fig. 3.13) to 6.7×10^{-7} mole $liter^{-1}$ min^{-1}, which is very close to the 'homogeneous' rate. Once again, traces of iron in the supplied material could have affected the result.

Barium sulphate was added as an example of a typical insoluble salt with no ions in common. It gave a slightly alkaline solution, thought to be due to hydroxyl ions adsorbed on the surface of the powder. This was found to be difficult to remove, and only when the powder was stirred for several hours in a dilute solution of sulphuric acid were the last traces removed. A run using barium sulphate so treated and subsequently washed in distilled water and filtered, gave an initial rate of ca. 10×10^{-7} mole $liter^{-1}$ min^{-1}. After about ten minutes, however, the rate fell to 4.8×10^{-7} mole $liter^{-1}$ min^{-1}. The higher initial rate may have been due to desorption from the precipitate, of excess hydrogen ions which had not been removed during washing. This supposition is supported by the fact that the initial pH of solution was ca. 4.5, whereas it was usually 5.0 - 5.5.

Table 3.7

The Effect of Miscellaneous Catalysts on the $AgNO_3$ + EtI System.

Run	Catalyst	State	Initial Rate x 10^7 (mole $liter^{-1} min^{-1}$)
0	None	-	5.47 ± 0.18
1	Glass	powdered	5.2
2	Perspex	powdered	5.2
3	Teflon	turnings	6.2 'Homogeneous' rate measured under the same conditions was 6.0
4	Stainless Steel	turnings	6.0
5	Charcoal	powdered	140
6	Boron Nitride	powdered	2.5
7	SiO_2	powdered	52
8	Si	powdered	10
9	$BaSO_4$	powdered	10

Initial $[AgNO_3]$ = Initial [EtI] = 0.001M

Mass of catalyst = 0.01M

Volume of solution = ca. 91.5 ml.

Temperature = 25°C.

The results presented above are interpreted at the end of the chapter.

Silver Perchlorate.

Two 'homogeneous' runs were done in which silver nitrate was replaced by silver perchlorate. The latter, from G.F. Smith & Co., was not purified, and a solution was prepared such that the initial concentration of silver ion in the reaction mixture would be ca. 0.001M. Since the salt was damp, the silver ion concentration in this solution was measured by means of the cell:

$$\text{Calomel} \left| \begin{matrix} \text{KCl} \\ \text{satd.} \end{matrix} \right| \begin{matrix} KNO_3 \\ 0.25M \end{matrix} \left| AgClO_4 \right| \text{Ag} \qquad 3.47$$

At $25^{\circ}C$, the e.m.f. was 0.407 V. Allowing for the activity coefficient of the silver ion by means of the Güntelberg equation,[68b] and for the dilution of this solution to give the reaction solution (25ml to 91.5 ml), the initial silver ion concentration in both runs was 8.47×10^{-4} mole liter^{-1}. The rate of reaction in these runs was 4.1×10^{-7} mole liter^{-1} min^{-1}.

Assuming the reaction to be first order in silver ion (as for silver nitrate), the rate of reaction corrected to 0.001M silver perchlorate is 4.85×10^{-7} mole liter^{-1} min^{-1}. This is somewhat lower than the 'homogeneous' rate measured with identical concentrations of ethyl iodide and silver nitrate. Since both silver salts are completely dissociated, the nitrate and perchlorate ions must be involved in the mechanism of the homogeneous reaction. It has been suggested that the silver and say, the nitrate ions give rise to a transition state of the type $NO_3^- \overset{+}{EtIAg}$, with the nitrate ion participating in the transition complex as formulated by Kornblum.[53] The experimental results leading to this postulated transition state were obtained in acetonitrile[33] and in aqueous alcohol.[29,30,31] Since the nitrate ion is a stronger nucleophile than the perchlorate ion, the results of the present work would also be consistent with such a transition state.

A recent paper[47] has reinterpreted work by Burke and Donnan, done in aqueous alcoholic media, in terms of an ion pair concept which led to the type of transition state described above. Theory was found to be in close agreement with experiment. It would thus appear that this approach is a valid one in homogeneous solutions of this type. It has not yet been determined, however, whether the anion takes any part in the reaction at the surface, i.e. in the heterogeneous part of the reaction.

SECOND REACTION

A reaction of the general type

$$MNO_3 + RX \longrightarrow MX(s) + RNO_3 \qquad 3.48$$

is known to occur,[15c] and the extent to which it does occur is obviously of importance in interpreting the observed rates of the reaction under study. In the preliminary studies involving the $AgNO_3$ + EtI system, two methods of detecting any $EtNO_3$ present were used:

(1) U.V. spectrophotometry.

(2) spot tests.

(1)

A sample of Eastman Kodak unpurified ethyl nitrate was dissolved in water (solubility 1.3 gm/100 ml) and its u.v. spectrum plotted in the region 200 - 350 mμ, using a Hilger and Watts Ultrascan spectrophotometer. This showed an absorption peak in the region 200 - 210 mμ. Finer resolution was not possible because of the limitations of the instrument. Both ethyl alcohol and ethyl iodide have absorption peaks in this region, ethyl iodide having another peak at 250 mμ, and so this method could not be used for the detection of ethyl nitrate in the reaction mixture.

It was found that spectra of the reaction products gave very large absorption peaks in the 210 mμ region, much larger than indicated by the estimated concentrations of ethyl iodide, ethyl alcohol, and ethyl nitrate. This was attributed to the nitric acid present - a comparison spectrum of 10^{-3}M nitric acid giving the same peak. A new peak also arose at 300 mμ, appearing mostly as a shoulder to the peak at 210 mμ, and this was enhanced by the removal of ethyl nitrate and ethyl alcohol by distillation. A comparison spectrum of a solution of ethyl nitrate (0.0006M) in nitric acid (10^{-3}M) was made, but showed no peak at 300 mμ. The origin of this peak is not understood.

To summarise, the u.v. absorption method was not suitable for the detection and estimation of the second reaction.

(2)

With the aid of a spot test the presence of ethyl nitrate could, in principle, be qualitatively established. The presence of silver nitrate and nitric acid, which would interfere, would necessitate separation of the ethyl nitrate from the bulk of the reaction products first. This was conveniently done by distillation, at atmospheric pressure; the first fraction collected containing the ethyl nitrate (b.p. 88 - 9°C) and ethyl alcohol (b.p. 78°C) and any remaining ethyl iodide (b.p. 72°C), but not the silver nitrate or nitric acid.

The spot test for nitrate was based on the reaction of nitric acid with diphenylamine, or NN′ diphenylbenzidine to give the intensely blue quinoidimonium salt.[71] Using NN′diphenylbenzidine, the limit of detection was 0.07 μg nitric acid. When the spot test was applied to the ethyl iodide solution before reaction it gave a negative indication but produced a positive response with the first distilled fraction of the reaction products.

To check the interference of silver nitrate, nitric acid and ethyl alcohol, a blank solution was made up containing the approximately expected concentrations of these three substances in the reaction solution. This was distilled in the same way as the reaction mixture, and the first fraction collected. The spot test gave no indication of nitrate present, thus proving that there was no interference from the silver nitrate and nitric acid.

The presence of nitrate in the products and its absence in the reactant ethyl iodide solution was therefore attributed to the formation of ethyl nitrate during the reaction. An estimate of the extent of the second reaction was made by using Feigl's figure of the limit of detection[71] of $\sim 6 \times 10^{-5}$ mole/liter. Distillation of the reaction products and subsequent dilution of the reaction products ten times gave an indication which was only just visible. Thus $1 - 5 \times 10^{-5}$ mole/liter of ethyl nitrate appeared to be present in the reaction products, i.e. 1 - 5% of the reactants had reacted by this path. More accurate evidence was forthcoming by the indirect method below.

(3) E.m.f. Measurements

Consider the two reactions involved:

$$AgNO_3 + RX + H_2O \rightleftharpoons AgX(s) + ROH + HNO_3 \qquad 3.49$$

$$AgNO_3 + RX \rightleftharpoons AgX(s) + RNO_3 \qquad 3.50$$

Only if 3.50 is negligible will the change in concentration of nitric acid be equal to the change in concentration of silver ion:

i.e. $-\Delta[Ag^+] = \Delta[H^+]$

A homogeneous run was, therefore, carried out, in which both the concentration of silver ions and the pH were measured initially and at equilibrium. The reactants were 0.001M silver nitrate and 0.001M ethyl iodide.

The cell used for the silver ion determination was:

$$\text{Calomel} \left| \begin{matrix} KCl \\ \text{satd.} \end{matrix} \right| \begin{matrix} KNO_3 \\ 0.25M \end{matrix} \left| \; Ag^+ \; \right| Ag \qquad 3.51$$

and it was calibrated by means of a stock 0.00367M solution of silver nitrate. This gave $E_{cal} = 0.2435V$ at 25°C., allowance having been made for the silver ion activity coefficient.

The pH of the solution was measured in the way already described (see Chapter 2). The pH at zero time was calculated by an extrapolation of the measured initial rate. The final pH of the reaction solution was measured with the solution both well stirred and quiescent.

The following results were recorded:

Table 3.8

	pH	$[H^+]$	$\Delta[H^+]$	E.m.f.(mV)	$[Ag^+]$	$-\Delta[Ag^+]$
Initially	5.20	8.46×10^{-6}		410	9.97×10^{-4}	
Finally (stirring)	3.12	7.586×10^{-4}	7.50×10^{-4}			
Finally (no stirring)	3.15	7.079×10^{-4}	6.99×10^{-4}	343	2.66×10^{-4}	7.31×10^{-4}

All concentrations are in mole liter^{-1}.

It can be seen that the maximum discrepancy between $-\Delta[Ag^+]$ and $\Delta[H^+]$ was ca. 4.5%. This represents the maximum extent of the second reaction.

We may conclude, therefore, that for the $AgNO_3$ + EtI reaction, the second reaction can, to a first approximation, be neglected in considering the kinetics of the main reaction.

B Other Systems

Because of the difficulties encountered in using insoluble iodides as catalysts in the $AgNO_3$ + EtI system, the silver ion was replaced by other cations, and the catalytic influence of the insoluble iodides on these reactions was investigated. The nitrates used were $Hg(NO_3)_2$, $Hg_2(NO_3)_2$, $Pb(NO_3)_2$, and $TlNO_3$. Only those iodides less soluble than the iodide of the nitrate being used were employed as catalysts, to avoid the difficulty which had arisen with silver nitrate. It was assumed for all these cases that the reaction causing the change of pH would be analogous to the silver nitrate reaction:

$$M(NO_3)_n + nEtI + nH_2O \longrightarrow MI_n(s) + nEtOH + nHNO_3 \qquad 3.52$$

No attempt was made to show that this was the reaction being studied, or to verify its stoichiometry. It was further assumed that there was the possibility of occurrence of:

$$M(NO_3)_n + nEtI \longrightarrow MI_n(s) + nEtNO_3 \qquad 3.53$$

and tests to ascertain the extent of this reaction are described later.

In all the catalysed runs 0.01 mole of catalyst was used and the initial concentration of ethyl iodide was 0.001M. For $TlNO_3$, the initial concentration was 0.001M, and for $Pb(NO_3)_2$, $Hg(NO_3)_2$, and $Hg_2(NO_3)_2$ it was 5×10^{-4}M. The volume of the reaction mixture was ca. 91.5 ml.

The details of preparation of the catalysts are given in part A of this chapter.

An interpretation of the results in this section is presented at the end of the chapter.

(i) Lead Nitrate.

To make up the lead nitrate solution, A.R. lead nitrate (undried) was used, and the strength of the solution calculated from the mass of nitrate used. A 'homogeneous' run was carried out with 0.0005M $Pb(NO_3)_2$ and 0.001M EtI. In 120 minutes the pH drifted from 5.06 to 5.18, and it was concluded that the rate of reaction 3.52 was too small to be measured. During this time, however, a thin white, opalescent precipitate had formed in the cell, and this was attributed to reaction 3.53. The precipitate became thick and white after being left for a day, (PbI_2 is a yellow solid). An attempt was made to repeat this experiment in a conical flask, to provide material for analysis, but this time no precipitate was formed. The reason for this is not understood.

The insoluble iodides added to the reaction mixture were freshly prepared silver and lead iodide and B.D.H. mercurous iodide and thallous iodide. The initial rates of reaction are given in Table 3.9 and graphs of the rate of change of hydrogen ion concentration in Figs. 3.14 and 3.15. The order of effectiveness was $AgI > PbI_2 > TlI > Hg_2I_2$, the latter giving no measurable rate.

Of the metals used, powdered platinum gave a constant pH (4.82), and lead gave a pH which rose from 7.7 to 9.3 in 40 minutes. The run was repeated with lead previously washed in dilute nitric acid and then water. The pH was then almost constant with time at 7.45.

With precipitated silver the initial rate of reaction was 5.2×10^{-7} mole liter^{-1} min^{-1}. This fell after the initial period to an almost constant value of about 0.3×10^{-7} mole liter^{-1} min^{-1}. (Fig. 3.14).

The most effective catalyst, apart from AgI, was charcoal. This gave an initial rate of $\sim 50 \times 10^{-7}$ mole liter^{-1} min^{-1}. Again the rate decreased and became linear, after the initial period, at ca. 3×10^{-7} mole liter^{-1} min^{-1}.

Table 3.9

The Effect of Selected Catalysts on the $Pb(NO_3)_2$ + EtI System

Initial $[Pb(NO_3)_2] = 5 \times 10^{-4}$ M
Initial [EtI] = 0.001M
Mass of catalyst = 0.01 mole.
Volume of solution = 91.5 ml.
Temperature of reaction = 25°C

Table 3.9

The Effect of Selected Catalysts on the $Pb(NO_3)_2$ + EtI System

Run	Catalyst	Source	Initial Rate x 10^7 (mole $liter^{-1}$ min^{-1})
0	none	-	ca. 0
1	AgI	freshly prepared	ca. 850
2	PbI_2	freshly prepared	30.6
3	TlI	B.D.H.	1.6
4	Hg_2I_2	B.D.H.	1.9
5	Pt	Johnson Matthey	-
6	precipitated Ag	Hopkin & Williams	5.2
7	powdered Pb	B.D.H.	-
8	Charcoal	B.D.H.	50

An attempt was made to correlate the change of $[H^+]$ with the change of $[Pb^{2+}]$ during a run when AgI was the catalyst. This was to establish, as for silver nitrate, whether reaction 3.53 played any significant part in the kinetics of the system. The change of pH was measured, as usual, with a glass electrode, the initial pH of the components of the solution being measured individually and the change of pH throughout the reaction being followed, to a final constant value. A lead rod, ca. 0.5 cm in diameter, was used as the lead electrode, the e.m.f. of the cell:

$$\text{Calomel} \left| \begin{matrix} \text{KCl} \\ \text{satd.} \end{matrix} \right| \begin{matrix} KNO_3 \\ 0.25M \end{matrix} \left| Pb(NO_3)_2 \right| Pb \qquad 3.54$$

being measured to give $[Pb^{2+}]$.

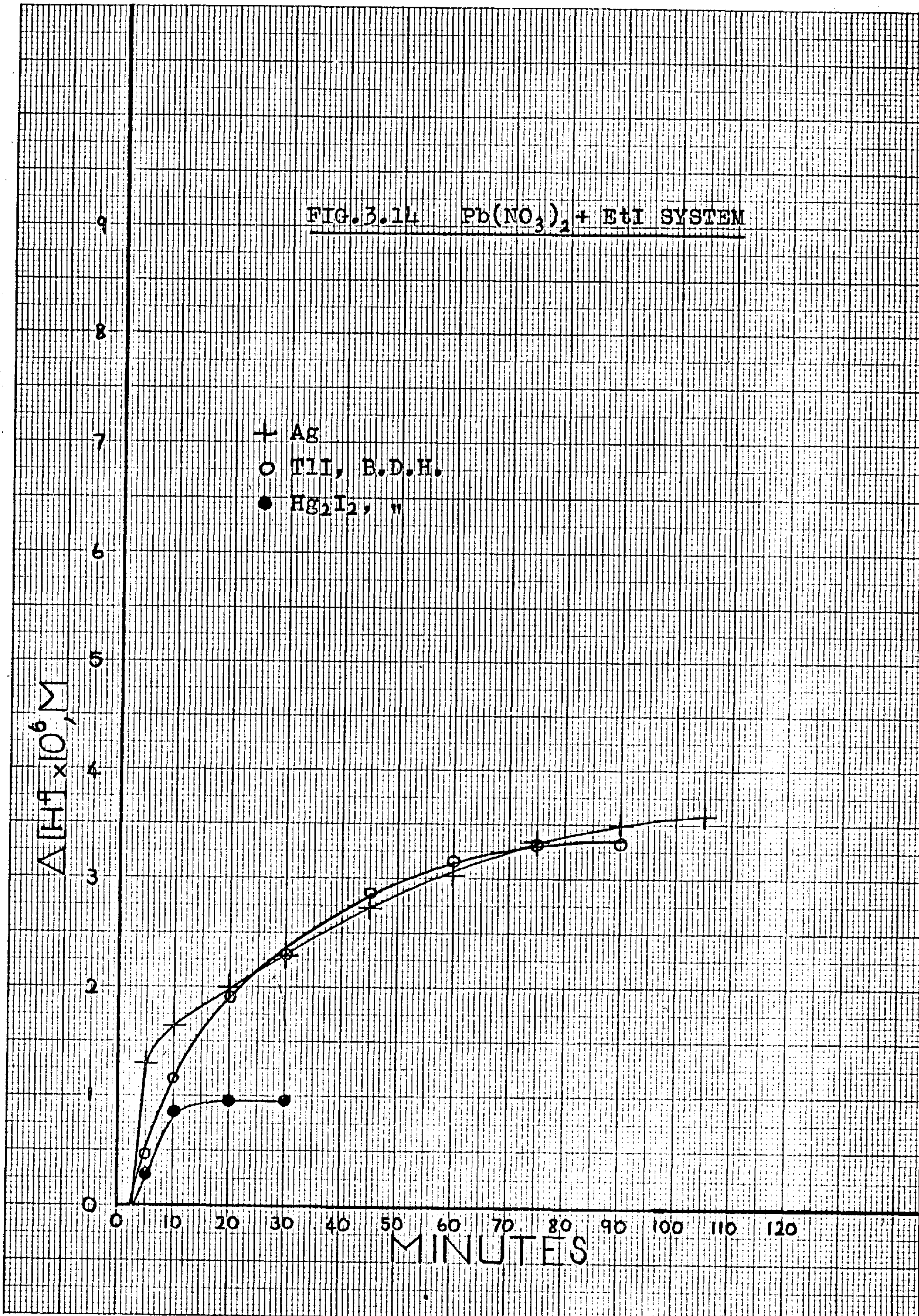


FIG. 3.14 $Pb(NO_3)_2$ + EtI SYSTEM

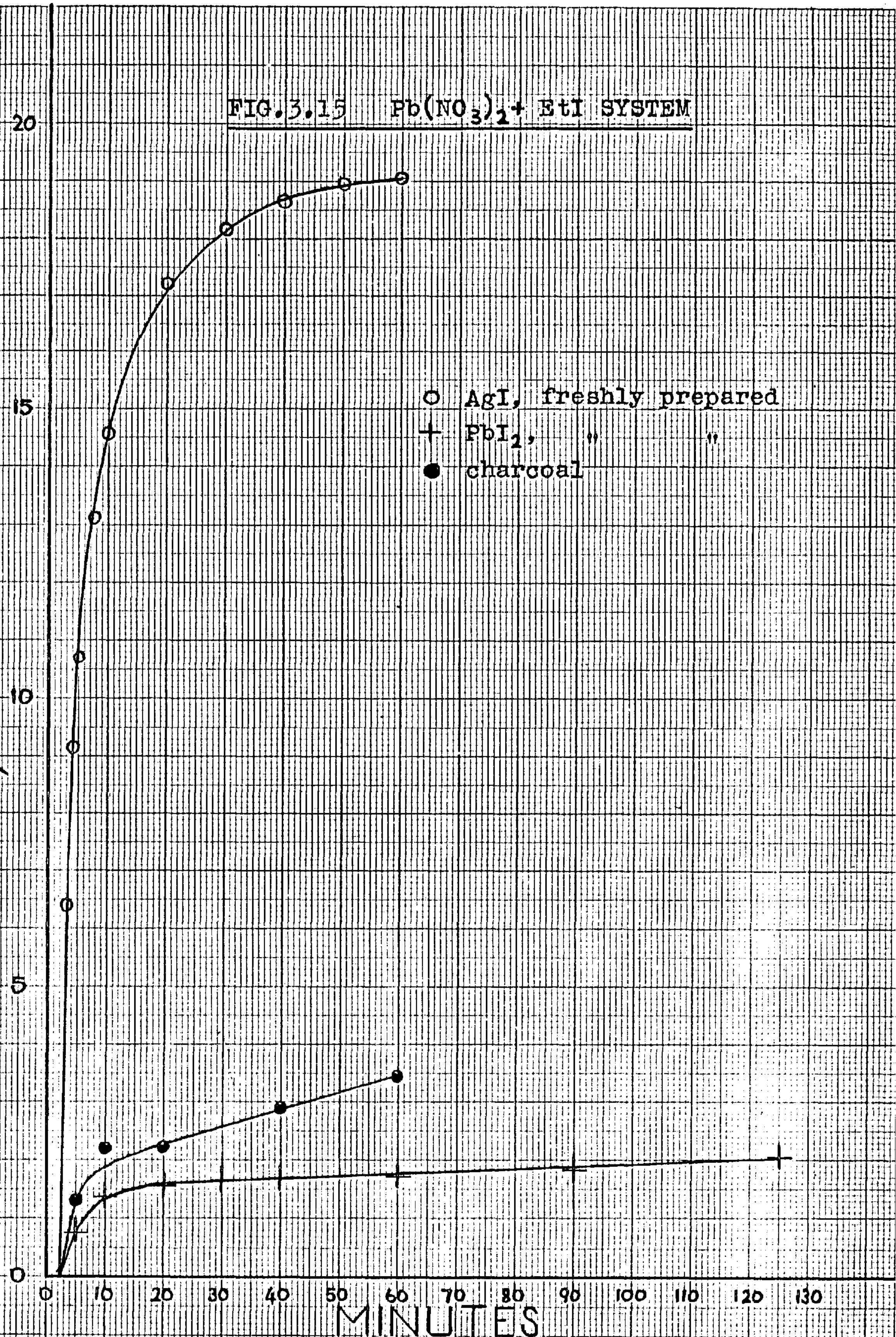


FIG. 3.15 $Pb(NO_3)_2$ + EtI SYSTEM

However, this electrode did not give reproducible readings of the e.m.f. of the cell and was abandoned. A Pt wire was then coated with lead from a $Pb(NO_3)_2$ solution (0.01M), using a lead anode and passing 0.2 mA for 1 hour. A dark grey matt deposit was formed on the wire. On using the electrode to measure the e.m.f. of the cell an unsteady reading was obtained, and patches of bright Pt could be seen on the wire. The attempt to measure the cell's e.m.f. was therefore abandoned.

(ii) Mercuric Nitrate.

A fresh sample of Hopkin & Williams G.P.R. mercuric nitrate, guaranteed to contain $\nless$ 99% $Hg(NO_3)_2$, was used to make up the solution, by weight. It was acidified to ca. 10^{-3}M nitric acid to prevent decomposition to mercuric oxide. This gave, for the reactions, a lower initial pH and a smaller change of pH, and consequently a greater error in the rate measurements.

The following initial rates were found for the 'homogeneous' reaction (Fig. 3.16):

Table 3.10

Run	$[Hg(NO_3)_2]_0$	$[EtI]_0$	Initial Rate x 10^{7} (mole liter^{-1} min.$^{-1}$)
1	5×10^{-4} M	0.001M	250
2	5×10^{-4} M	0.001M	140
3	5×10^{-4} M	0.002M	250
4	0.001M	0.001M	750

During the reaction a red precipitate formed (HgI_2 is red). This was in the form of a finely divided powder which stuck to the glass in the cell. The stirring was not effective enough to disperse the precipitate uniformly throughout the solution.

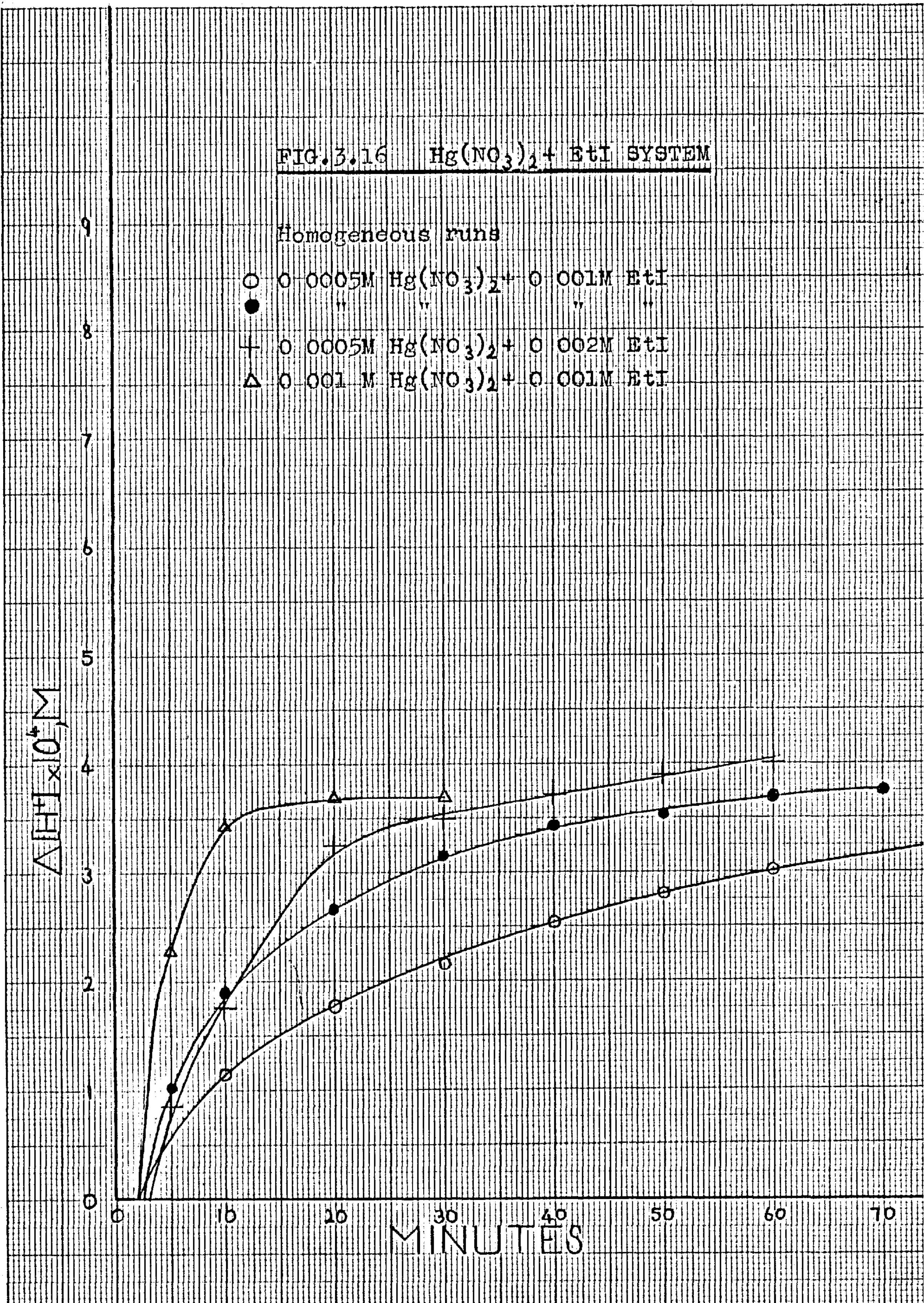


FIG.3.16 $Hg(NO_3)_2 + EtI$ SYSTEM

The initial rate of the homogeneous reaction appears to be very irreproducible. (see runs 1 and 2, Table 3.10). This was because the rate was measured over a period in which about 10% of the ethyl iodide present had reacted, and a corresponding amount of mercuric iodide had formed. Assuming the mercuric iodide catalysed the reaction (see below) and comparing the system with the silver nitrate system, it is expected that this would lead to considerable irreproducibility. With silver nitrate the initial rate was measured before the amount of precipitate became significant, i.e. when only 1 - 2% of the ethyl iodide present had reacted. In addition, the nature of the precipitate in the mercuric nitrate system accentuated the irreproducibility.

As a result, it would be unwise to attempt to deduce a rate law from these values.

The insoluble iodides added to the reaction mixture were freshly prepared silver and mercuric iodides, and B.D.H. mercurous iodide. The initial rates are given in Table 3.11, graphs of the rate of change of hydrogen ion concentration in Fig. 3.17. The order of effectiveness was $AgI > Hg_2I_2 > HgI_2$, although the mercuric iodide was rather aggregated initially in the cell, and for comparable surface areas may be as good a catalyst as mercurous iodide.

Powdered Pt gave an initial rate of 230×10^{-7} mole liter^{-1} min^{-1}, which is not significantly different from the 'homogeneous' value, and two runs with charcoal gave rates of ca. 500×10^{-7} mole liter^{-1} min^{-1} (Fig. 3.18).

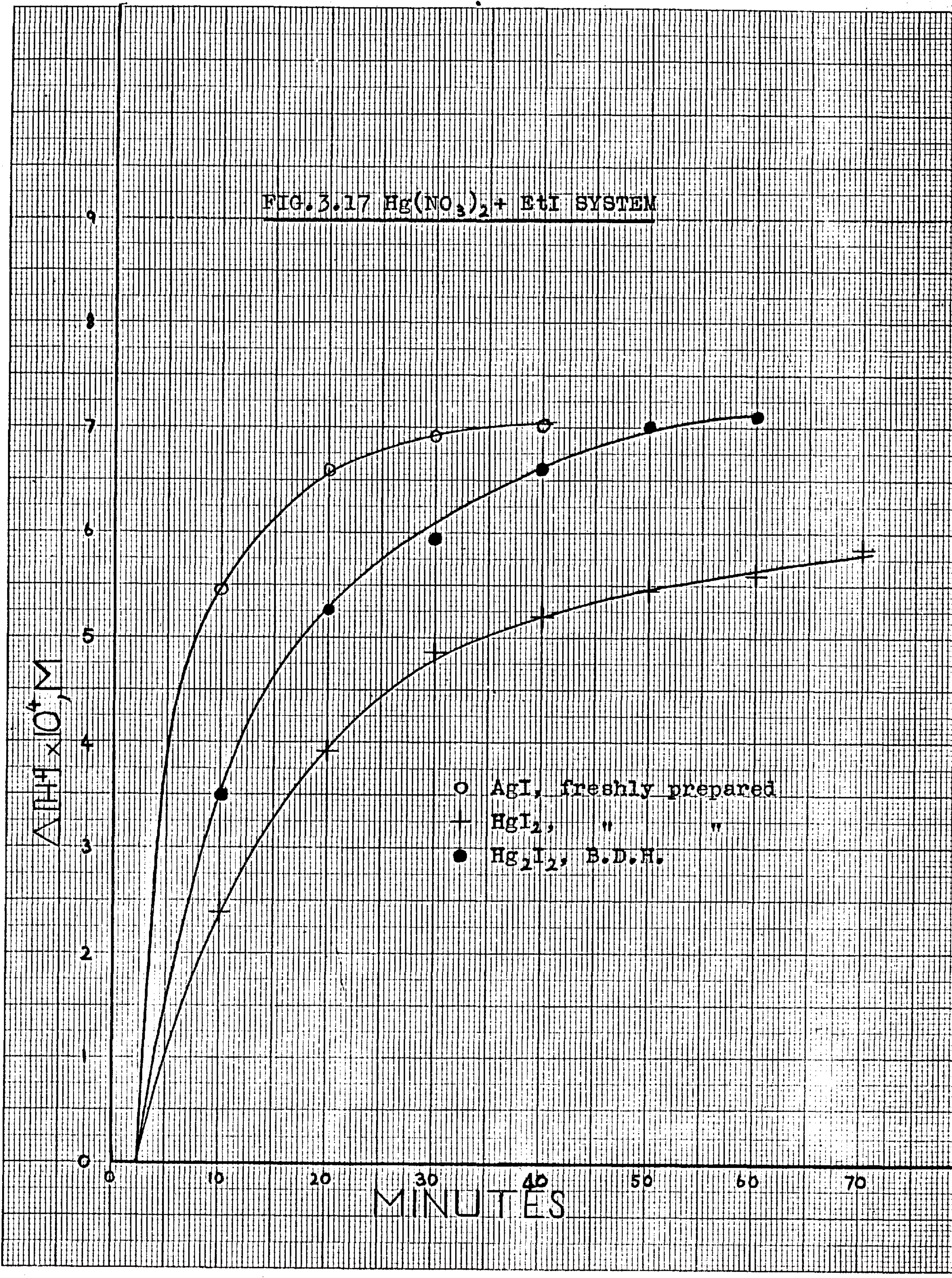


FIG. 3.17 $Hg(NO_3)_2$ + EtI SYSTEM

FIG.3.18 $Hg(NO_3)_2$ + EtI SYSTEM

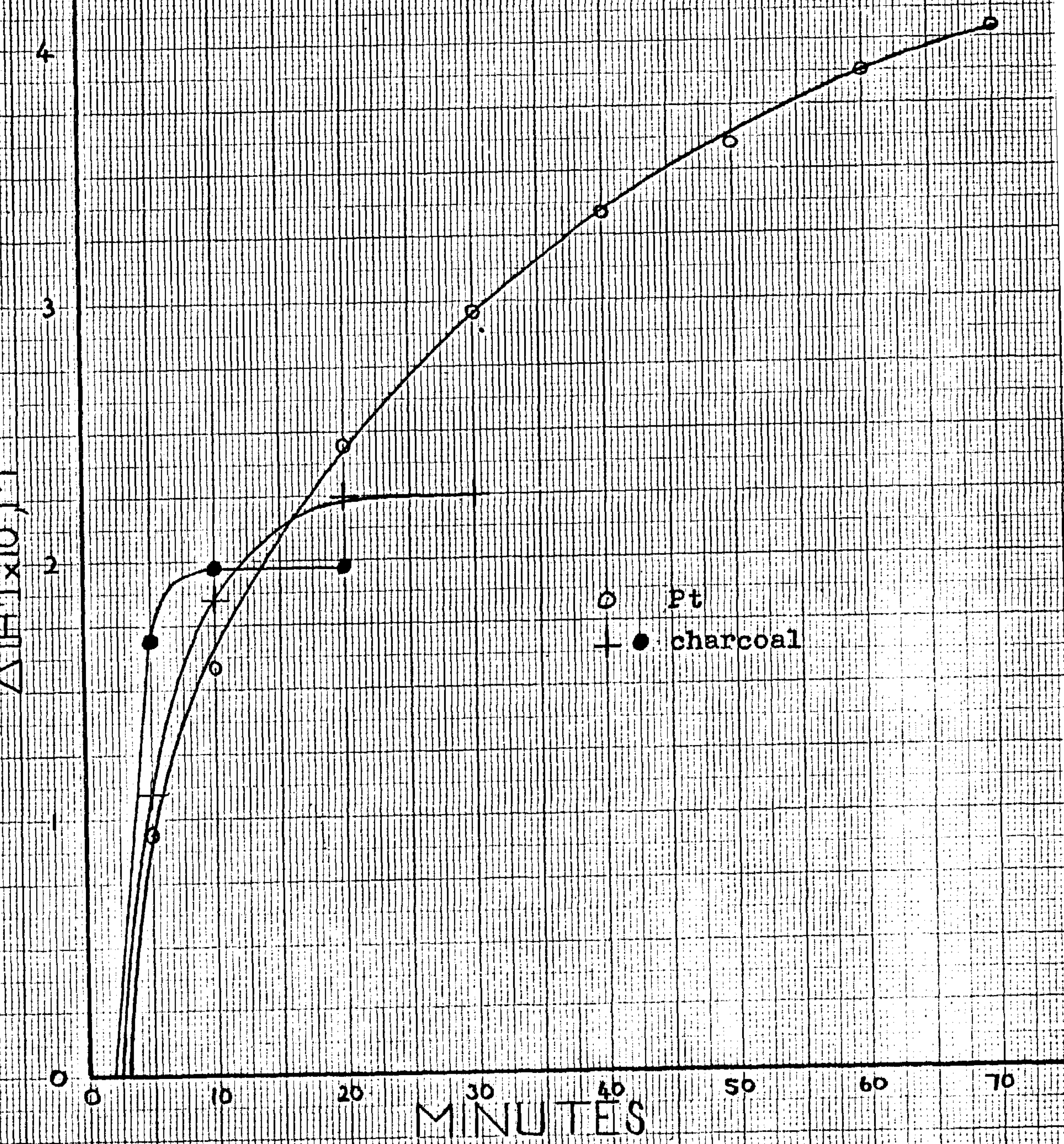


Table 3.11

The Effect of Selected Catalysts on the $Hg(NO_3)_2$ + EtI System

Run	Catalyst	Source	Initial Rate x 10^7 (mole liter^{-1}min^{-1})
0	none	-	ca. 200
1	AgI	freshly prepared	ca. 730
2	Hg_2I_2	B.D.H.	ca. 450
3	HgI_2	freshly prepared	ca. 320
4	powdered Pt	Johnson Matthey	ca. 230
5	charcoal	B.D.H.	ca. 570
6	charcoal	B.D.H.	ca. 440

Initial $[Hg(NO_3)_2]$ = 5 x 10^{-4} M
Initial [EtI] = 0.001M
Mass of catalyst = 0.01 mole
Volume of solution = ca. 91.5 ml.
Temperature = 25°C.

(iii) Mercurous Nitrate.

The mercurous nitrate solution was prepared by dissolving a known weight of undried A.R. mercurous nitrate in water containing ca. 10^{-3} M nitric acid to stabilise the solution. The solution was stood over mercury to prevent oxidation to mercuric nitrate. As with mercuric nitrate the problem of a small pH change was encountered.

For the 'homogeneous' reaction the following rates were measured:

Table 3.12

Run	$[Hg_2(NO_3)_2]_0$	$[EtI]_0$	Initial Rate x 10^7 (mole liter^{-1} min.$^{-1}$)
1,2,3	0.0005M	0.001M	75 ± 15
4	0.0005M	0.002M	110
5	0.001M	0.001M	150

The precipitate formed during the reaction was much less coagulated than with mercuric nitrate. It was very finely divided (no individual particles could be seen) and a dirty yellow color (Hg_2I_2 is yellow). A dark colored precipitate settled after stirring had ceased in runs 1 and 2 (Table 3.12).

From the above rates of reaction it appears that the rate law is:

$$\text{Rate} \propto [Hg_2(NO_3)_2]\,[EtI]^{\frac{1}{2}} \qquad 3.55$$

Insufficient data are available at present to interpret this law.

Of the insoluble iodides, only freshly prepared silver iodide and B.D.H. mercurous iodide could be used. The results are given in Table 3.13.

Powdered platinum gave a rate curve (Fig.3.19) the first three points of which were rather scattered. However, the later points appeared to coincide with the points produced by a 'homogeneous' run, so the degree of catalysis was very slight.

Mercury, when added to the reaction mixture, gave an initial rate of ca. 100 x 10^{-7} mole liter^{-1} min.$^{-1}$, but in the later stages appeared to retard the reaction (Fig. 3.20). Towards the end of the reaction the mercury became very dirty and was broken into small droplets which would not coalesce.

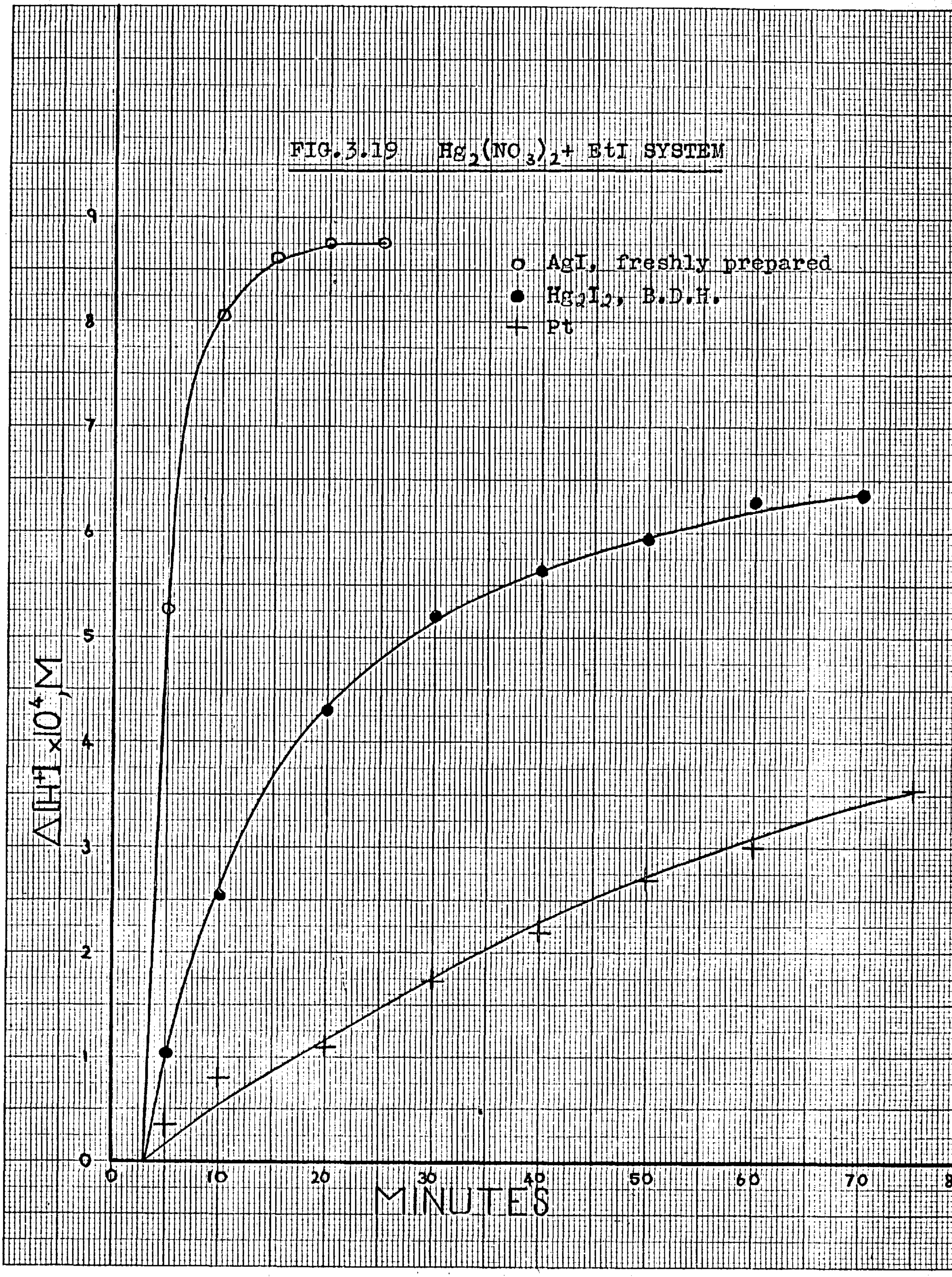


FIG.3.19 $Hg_2(NO_3)_2$ + EtI SYSTEM

FIG. 3.20 $Hg_2(NO_3)_2$ + EtI SYSTEM

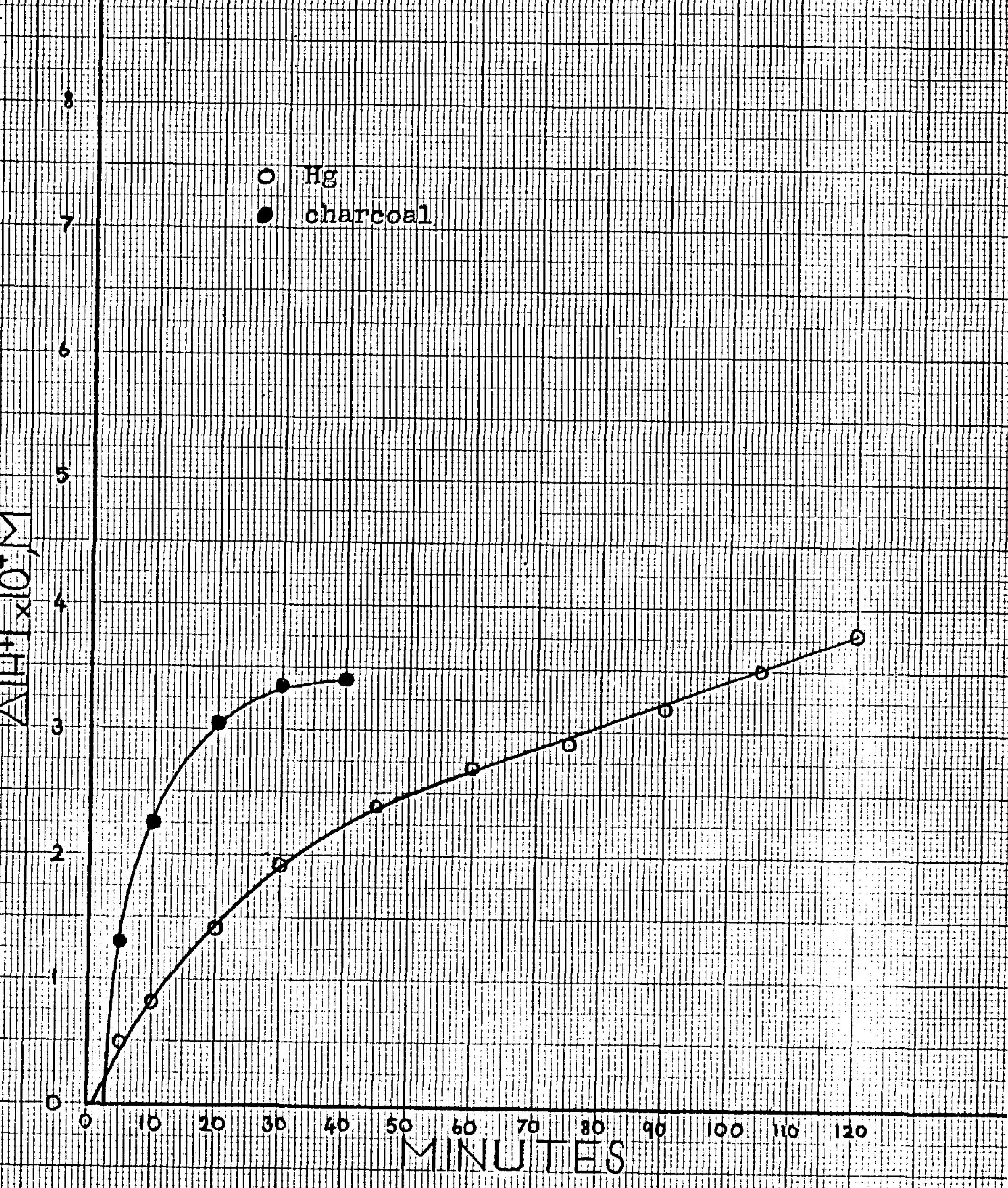


Table 3.13

The Effect of Selected Catalysts on the $Hg_2(NO_3)_2$ + EtI System

Run	Catalyst	Source	Initial Rate x 10^7 (mole $liter^{-1}$ $min.^{-1}$)
0	none	-	ca. 75
1	AgI	freshly prepared	ca. 2100*
2	Hg_2I_2	B.D.H.	ca. 460
3	powdered Pt	Johnson Matthey	ca. 75
4	mercury	not known	ca. 100
5	charcoal	B.D.H.	ca. 680
6	charcoal	B.D.H.	ca. 625

Initial $[Hg_2(NO_3)_2]$ = $5 \times 10^{-4}M$
Initial $[EtI]$ = 0.001M (*0.0012M)
Mass of Catalyst = 0.01 mole
Volume of Solution = ca. 91.5 ml.
Temperature = 25°C.

Once again AgI and charcoal proved to be the best catalysts.

An attempt was made to correlate the change of hydrogen ion concentration occurring during a run with the change of mercurous ion concentration. As for silver and lead, this was to determine whether reaction 3.53 played any significant part in the kinetics of the system. Although the homogeneous reaction was fast enough, mercury was chosen as a catalyst for the reaction because it served as an electrode as well. The cell used to measure the $[Hg_2^{2+}]$ was:

$$\text{Calomel} \;\Big|\; \begin{matrix}\text{KCl}\\ \text{satd.}\end{matrix} \;\Big|\; \begin{matrix}KNO_3\\ 0.25M\end{matrix} \;\Big|\; Hg_2^{2+} \;\Big|\; Hg \qquad 3.56$$

The mercury was connected to the potentiometer by means of a platinum wire, sheathed in glass almost to its tip, which dipped into the mercury far enough not to expose any platinum to the solution. The e.m.f. of a stock solution of $Hg_2(NO_3)_2$ was measured, to obtain the initial concentration of the reaction solution.

A run ($Hg_2(NO_3)_2$ + EtI) was done using an aliquot of this stock solution (diluted to give $[Hg_2(NO_3)_2]_0 = 0.0005M$) and about 1 ml. of mercury in the cell. The mercury was stirred into the reaction mixture during the run, and at equilibrium was found to be too dirty to use as an electrode. Clean mercury was therefore added to the cell and used to measure the equilibrium mercurous ion concentration. In evaluating the change in the mercurous ion concentration, activity coefficients were considered.

The pH was measured with a glass electrode assembly, as usual. The initial pH of the reaction solution was obtained by extrapolating to zero time the rate when the first reading was taken. The value agreed well with the measured pH of a solution similarly made up, but without any ethyl iodide present (measured 2.70, extrapolated 2.699)

The measured values were, at 25°C:

Table 3.14

	pH	$[H^+]$	$\Delta[H^+]$
Initial	2.699 ± 0.005	$(2.00 \pm 0.023) \times 10^{-3}$	
Final	2.603 ± 0.005	$(2.495 \pm 0.029) \times 10^{-3}$	$(4.95 \pm 0.52) \times 10^{-4}$
	E.m.f.	$[Hg_2^{2+}]$	$\Delta[Hg_2^{2+}]$
Initial	466.2 ± 0.5 mV	$(4.14 \pm 0.07) \times 10^{-4}$	
Final	441.7 ± 0.5 mV	$(1.92 \pm 0.07) \times 10^{-4}$	$-(2.22 \pm 0.14) \times 10^{-4}$
E_{cal}	243 mV		

(All concentrations are in mole liter^{-1})

Now, if for every Hg_2^{2+} ion used, $2H^+$ ions are formed

$$-2\Delta\left[Hg_2^{2+}\right] \equiv \Delta\left[H^+\right] \qquad 3.57$$

From Table 3.14

$$2\Delta\left[Hg_2^{2+}\right] = (4.44 \pm 0.28) \times 10^{-4}\ \text{mole liter}^{-1}$$

$$\Delta\left[H^+\right] = (4.95 \pm 0.52) \times 10^{-4}\ \text{mole liter}^{-1}$$

It can be seen that the calculation is very sensitive to slight errors in the measurement of pH, and also to the value of E_{cal}. Within the limits of experimental error, however, the change of hydrogen ion concentration is equivalent to the change of mercurous ion concentration, and therefore there is no real reason for considering reaction 3.53 for the mercurous nitrate and ethyl iodide system.

(iv) Thallous Nitrate

The thallous nitrate solution was prepared from a fresh sample of B.D.H. thallous nitrate, specified to be not less than 98% pure. The molarity of the solution was calculated from the weight of solid used.

A 'homogeneous' run gave no measurable rate of reaction, the pH drifting from 5.04 to 5.97 in 118 minutes. However, during this time, a whitish, very finely divided precipitate formed in the cell (TlI is a yellow solid). An attempt was made to repeat the experiment in a conical flask to provide material for analysis, but no precipitate was formed the second time. The reason for this is not understood.

To test whether the drift of pH was due to adsorption of hydrogen ions on the surface of the precipitate, the pH of a stirred solution of 0.01 mole of thallous iodide powder (B.D.H.) in 90 ml. of water at 25°C was measured. No comparable drift was noted, but the surface area and condition of the solid were probably different.

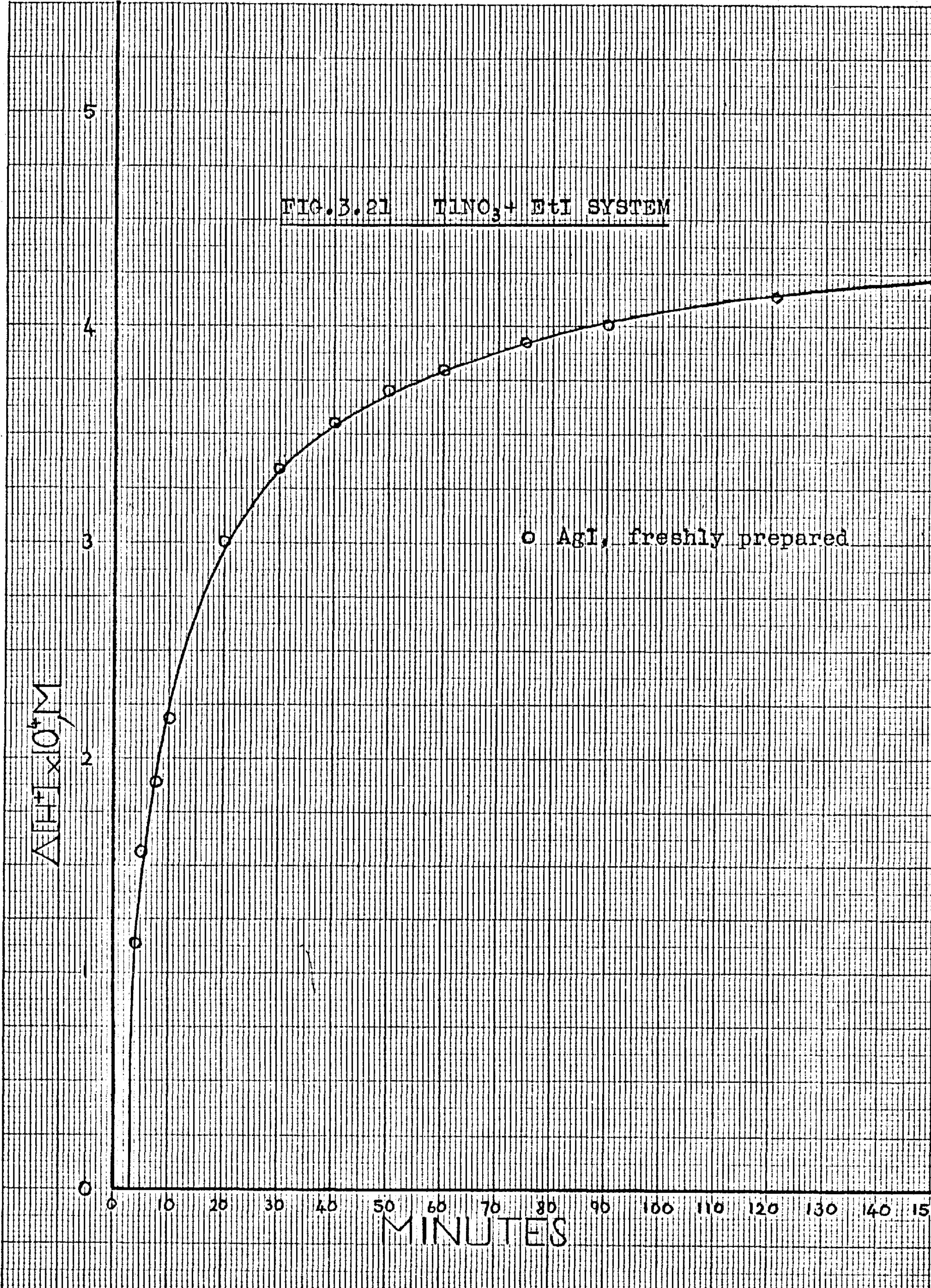


FIG.3.21 $TlNO_3$+ EtI SYSTEM

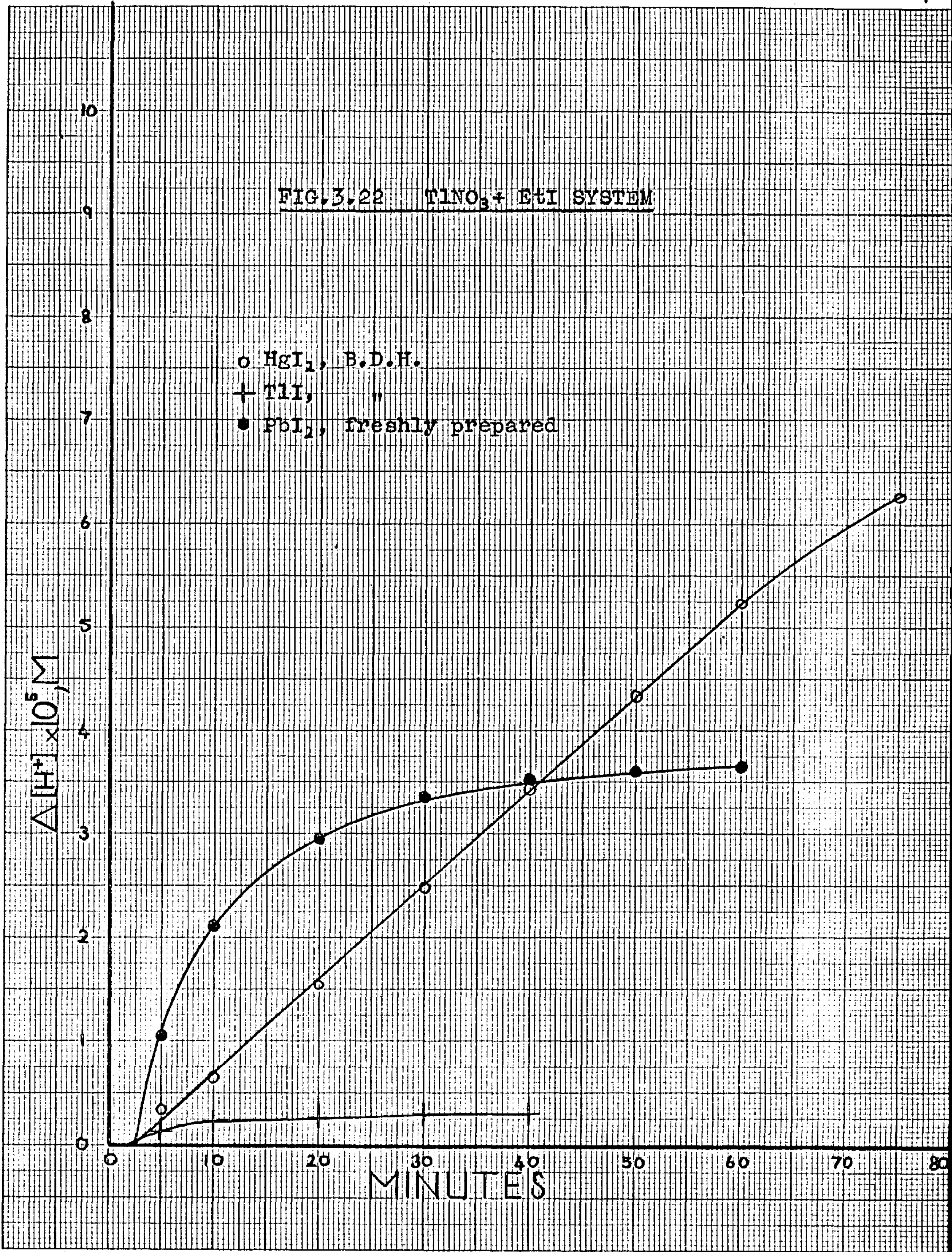


FIG.3.22 $TlNO_3$+ EtI SYSTEM

The insoluble iodides tried as catalysts were: B.D.H., TlI, CuI, HgI_2 , and Hg_2I_2; freshly prepared - PbI_2 and AgI. The rates of reaction are given in Table 3.15, and graphs of the rate of change of hydrogen ion concentration in Figs. 3.21 and 3.22. The order effectiveness of the catalysts was $AgI > PbI_2 > HgI_2 > TlI$; there was no measurable rate of reaction with CuI and Hg_2I_2, a slow rise of pH being noted in both cases.

The only other catalyst tried was charcoal, but no reaction occurred, the pH again rising slowly.

Table 3.15

The Effect of Selected Catalysts on the $TlNO_3$ + EtI System

Run	Catalyst	Source	Initial Rate x 10^7 (mole liter^{-1} min.$^{-1}$)
0	none	-	ca. 0
1	AgI	freshly prepared	ca. 1140
2	PbI_2	freshly prepared	ca. 40
3	HgI_2	B.D.H.	8.8
4	TlI	B.D.H.	4.5
5	CuI	B.D.H.	No apparent reaction
6	Hg_2I_2	B.D.H.	
7	charcoal	B.D.H.	No apparent reaction

Initial $[TlNO_3]$ = Initial $[EtI]$ = 0.001M
Mass of Catalyst = 0.01 mole
Volume of Solution = ca. 91.5 ml
Temperature = 25°C.

INTERPRETATION OF THE RESULTS PRESENTED IN THIS CHAPTER

It is obvious that the results of this exploratory study cannot be interpreted in a quantitative manner, since they are only semi-quantitative themselves. They can, however, be discussed in the light of a theory which is itself only qualitatively expressed at present. This is Pearson's theory of hard and soft acids and bases.[99]

In Pearson's view, an extension of the acid-base concept proposed by Lewis,[103] acids and bases are subdivided into the catagories: hard and soft. The definitions of the four classes are:

(a) soft base - a base in which the valence electrons are easily polarised or removed.

e.g. CN^-, I^-, $S_2O_3^{2-}$

(b) hard base - one which holds its valence electrons much more tightly.

e.g. OH^-, F^-, NO_3^-

(c) soft acid - an acid in which the acceptor atom is of large size, of small or zero positive charge, or has several valence electrons which can easily be removed or distorted.

e.g. Cu^+, Ag^+, Hg^{2+}

(d) hard acid - an acid of small size, high positive charge and with no valence electrons which are easily polarised or removed.

e.g. H^+, Na^+, Ca^{2+}, Al^{3+}

With these definitions a general principle can be stated:[99,100] hard acids prefer to coordinate with hard bases and soft acids with soft bases.

According to Pearson, the base or acid strength with respect to the hydrogen or hydroxide ion respectively is also a factor which influences the ease of coordination. However, this is a secondary characteristic and will not take precedence over the principle stated above. For instance, the S^{2-} and I^- ions, both of which are soft bases, will coordinate better with soft acids such as Ag^+ and Hg_2^{2+} than they will with hard acids like Al^{3+} and Ca^{2+}. However, S^{2-} will coordinate better with a soft acid than I^- because it is more basic (with respect to H^+).

The bonding theory which leads to these generalisations has been discussed elsewhere,[100] and will not be presented here. The various effects involved have not yet been combined to give quantitative expression to the concepts of 'hardness' and 'softness'. However, it seems that the main factors involved are (i) the σ bonding tendency of the acid or base, i.e. whether it forms ionic or covalent bonds; electronegativity and polarisability are important properties here, (ii) the π bonding tendency of the acid or base, i.e. whether it has empty d orbitals, say, capable of accepting π electrons, or whether it has full d orbitals capable of donating π electrons, (iii) the possibility of stabilisation of the resultant complex by dispersion forces in the case of covalent bonding. Solvent effects also seem to play a part, but to a much smaller extent than (i), (ii) and (iii).

We may discuss the results of the present work in the light of this theory. Let us assume, for the heterogeneous reaction, that cations from solution will be adsorbed on anion sites, while the ethyl iodide will be adsorbed on cation sites, so that, for the reaction $AgNO_3$ + EtI, on AgI(s), say, we will have complexes of the type $(EtI : Ag)^+$ and $(Ag^+ : I^-)$ on adjacent sites. The formation of Et^+ and then EtOH is assumed to occur through the interaction of these two acid-base complexes.

(1) The Silver Nitrate - Ethyl Iodide System

(i) Catalysis by a Series of Insoluble Silver Salts

We may correlate the experimental results with the Pearson theory by examining the influence on the reaction of a series of insoluble silver salts. It may be assumed for this series that the formation of the complex $(EtI : Ag)^+$ does not change throughout the series and that what is being examined is the variation in the formation of the $(Ag^+ : X^{n-})^{(n-1)-}$ complex, where X^{n-} is the anion of the solid under consideration. Silver is a soft acid, with an outer electron configuration in the unipositive state of $4d^{10}$, and an ionic radius of 1.26 Å. It would therefore be expected to coordinate best with soft bases. The anions of the insoluble silver salts used (Table 3.4) may be classified as follows:

Soft	Medium	Hard
I^-	$\leftarrow Br^-$	Cl^-
CNS^-	$\leftarrow SO_3^{2-}$	PO_4^{3-}
S^{2-}	$AsO_4^{3-} \rightarrow$	SO_4^{2-}
		$(Succ^{2-})$

The arrows in the medium group indicate the tendency of the ions towards softness and hardness.

The gradation of experimentally determined effectiveness was (for equimolar amounts of catalyst):

$AgI > Ag_2S > AgBr > AgCl \sim AgCNS > Ag_2SO_3 \sim Ag_2Succ > Ag_3AsO_4 > Ag_3PO_4 \sim Ag_2SO_4$.

It is immediately noticeable that the softest anions provided the best catalytic surfaces (according to the measured initial rates of reaction), and that the hardest anions provided the worst catalytic surfaces. Thus, there appears to be a correlation between the affinity of the silver ion for the surface and the effectiveness of the surface as a catalyst. The gradations AgI $>$ AgBr $>$ AgCl and $Ag_3AsO_4 > Ag_3PO_4$ are as expected. It is expected that Ag_2S would be a better catalyst than AgI, since S^{2-} is soft and a strong base, whereas I^- is only soft. In fact, for the B.D.H. catalysts, Ag_2S was a better catalyst than AgI.

It might appear that the position of AgCl in this scheme is anomalous, in that Cl^- is hard and a weak base and yet seems to be a good catalyst. There are two explanations of this. First, as Pearson has pointed out, although the relative rates within a group of the periodic table are comparable, those between different groups are not. Second, although Pearson classifies Cl^- as hard along with SO_4^{2-}, etc. it does seem to be much softer than the latter - a hypothesis supported by the well known ability of the chlorine atom to form covalent bonds, and also its ability to act as though it were to some extent electropositive, as $Cl^{\delta+}$. Both of these properties point to the fact that chloride is much more polarisable, and therefore much softer, than sulphate. Also the chloride ion has empty d orbitals which may accept some d electron density from the Ag^+ ion.

The position of the succinate ion appears also to be rather anomalous. According to Pearson's classification, the acetate ion is hard and therefore it would be expected that the succinate ion is also hard. Silver succinate would thus be expected to be a poor catalyst. That it is quite a good catalyst may be the result of its being quite a strong base.

To summarise: there is a marked correlation between the ease of coordination of the silver ion with the anion sites and the effectiveness of the corresponding insoluble silver salt as a catalyst in the reaction between silver nitrate and ethyl iodide.

(ii) Catalysis by Precipitated Metals

According to Pearson's theory, bulk metals may be regarded as soft acids. Therefore, from the point of view of the adsorption of ethyl iodide on the surface, the metals examined should have been good catalysts, since the iodide group is a soft base. The fact that they were not may, however, be understood in terms of the poor adsorption of silver ions on these surfaces. As pointed out by Pearson, the formation of a metal-metal bond would occur only if the system were stabilised by means of electron-donating ligands, which are absent in this case.

(iii) Catalysis by Miscellaneous Catalysts

Barium Sulphate

Both the cation and anion sites are classified as hard, and therefore poor coordination of the reactants with the surface sites would be expected. The material was not a catalyst, and the correlation agrees with that found in section (i).

Charcoal

Charcoal has a graphite structure, with sp^2 hybridisation of the carbon atoms, and the electrons in the unhybridised p orbitals forming a mobile system of the metallic type. Thus a concentration of electron density can be built up at the site of an adsorbed cation. Similarly, for an anion the concentration of negative charge at a particular site can easily be reduced. Charcoal would therefore be expected to be soft towards both acids and bases. It was found to be a good catalyst, although not as good as the insoluble silver salts, in agreement with the correlation in section (i).

Boron Nitride

Boron nitride also has a graphite structure with sp^2 hybridisation of both B and N, and with π electron density. In contrast with charcoal however, this π density is localised, so that the variation in the density of electronic charge at a given site is expected to be much smaller than is possible for charcoal. The direction of polarisation will be $\overset{\delta+}{>B} - \overset{\delta-}{N<}$. Thus boron nitride should show some tendency towards softness for both acids and bases, but far less than charcoal. It was found that boron nitride approximately doubled the rate of reaction, again supporting the correlation found in section (i).

Silicon

Silicon has a diamond lattice structure and would therefore be expected to be hard for both acids and bases. Thus no catalysis would be expected. That it occurred may have been due to the iron impurity in the sample.

Silica

It would be expected that silica, with a diamond-like structure, and no π electron density, would be hard towards bases. Towards acids, it should be softer because of the lone pairs on the oxygen atoms. It was found that it did catalyse the reaction, but not to any great extent.

Summary.

There is a definite correlation between the hardness and softness of the surfaces examined and their effectiveness as catalysts for the $AgNO_3$ + EtI reaction. For the series of insoluble silver salts, the salts with soft anions were good catalysts while those with hard anions were poor catalysts. The same correlation existed for the miscellaneous catalysts, although here the various materials had to be soft to both acids and bases to be effective catalytically. This latter is the reason why the metals, although soft towards bases, were poor catalysts - they adsorbed silver ions only very poorly. The reasons behind this correlation will be discussed later in the section.

(2) Catalysis in the $Hg(NO_3)_2$ + EtI, $Hg_2(NO_3)_2$ + EtI, $Pb(NO_3)_2$ + EtI, and $TlNO_3$ + EtI Systems

The approximate heterogeneous rates of the above reactions in the presence of a series of insoluble iodides, charcoal, and precipitated silver are given in Table 3.16.

Charcoal was a good catalyst for the Hg_2^{2+}, Hg^{2+}, and Pb^{2+} systems, being second only to silver iodide in effectiveness. For the Tl^+ system it was not a catalyst, and for the Ag^+ system it was, compared with silver iodide, a moderate catalyst. Since all the metal ions involved are soft (except [illegible] Pb^{2+} which is somewhat harder), they should all coordinate easily with the charcoal surface. However, the divalent cations should cause a far greater polarisation of the electron density of the surface, and therefore facilitate the formation of the (EtI : $\overset{\delta+}{C}$) complex to a greater degree than is possible with Ag^+ and Tl^+. Thus

Table 3.16

Systems	Catalysts						
	Hg_2I_2	HgI_2	PbI_2	AgI	TlI	Charcoal	Ppted. Silver
$Hg_2(NO_3)_2$ + EtI	ca. 385			ca. 2025		ca. 650	
$Hg(NO_3)_2$ + EtI	ca. 250	ca. 120		ca. 530		ca. 300	
$Pb(NO_3)_2$ + EtI	1.9		30	ca. 850	1.6	ca. 50	5.2
$AgNO_3$ + EtI				ca. 900		ca. 135	
$TlNO_3$ + EtI	0	8.8	40	ca. 1140	4.5	0	

The figures given above are $10^{7} \times$ initial rates of the heterogeneous reaction in mole $liter^{-1} min^{-1}$.

Initial $[MNO_3]$ = Initial $[EtI]$ = 0.001M

Initial $[M(NO_3)_2]$ = 5×10^{-4}M

Mass of catalyst = 0.01 mole

Volume of solution = ca. 91.5 ml.

Temperature of reaction = 25°C.

charcoal should be a more effective catalyst for the systems containing divalent cations, as has been found. For lead it appears that the formation of the (Pb^{2+}: $C^{\delta-}$) complex occurs less readily.

All the cations used, both as nitrates and iodides, in these experiments are soft acids except for Pb^{2+} which was somewhat harder. Iodide ions and covalent iodides are soft bases, and therefore all the insoluble iodides, with the possible exception of PbI_2, should have been good catalysts for all the systems. The theory did not, however, predict an order of effectiveness. It was found in general that all the iodides did catalyse the reactions, the only exceptions being Hg_2I_2 and CuI in the $TlNO_3$ system. In the two systems ($TlNO_3$ and $Pb(NO_3)_2$) in which PbI_2 was tried, it was a good catalyst, and it appears that in these environments the Pb^{2+} ion is of similar softness to the Tl^+ ion. The $TlNO_3$ and $Pb(NO_3)_2$ systems gave similar orders of catalytic effectiveness of the insoluble iodides, and this suggests that this order is largely determined by the complex formed between the ethyl iodide molecules and cation surface sites $(EtI : M)^{n+}$ (c.f. charcoal). This hypothesis is supported by the fact that, for all the systems, silver iodide was the best catalyst. From consideration of the charge number and ionic radius, it seems that the silver ion is the softest of the cations used, and the complex above would be formed most easily on a silver ion site, and thus a silver iodide surface.

We may also compare the rates of reaction of the various systems on a given catalyst. This procedure has the advantage that the surface area of a given catalyst should be fairly reproducible from run to run, and should thus allow comparison of the rates of heterogeneous reaction of different systems to be made. However, no clearly defined order emerges from an examination of the columns of Table 3.16, which is reasonable, since all the catalyst surfaces and cations are soft, and no order of softness has yet been determined.

It is probable that in this case the order of the cations on an individual catalyst will be determined by secondary factors, e.g. the crystal faces exposed for reaction, the suitability of interionic distances on the surface, the acid strengths of the various cations. A determination of the adsorption isotherm of each reactant on each catalyst would shed more light on the problem.

Discussion

So far, we have noted a correlation between the type of coordination which occurs between the two reactants and the surface, and the effectiveness of that surface as a heterogeneous catalyst for the reaction. The reasons for this correlation will now be briefly discussed.

The variation in the effectiveness of the series of insoluble silver salts has been correlated with the $(Ag^+ : X^{n-})^{(n-1)-}$ complex. It appears that the greater the affinity of the silver ion for the surface site (i.e. the more strongly it is adsorbed) the more effective is the catalyst. This may be because:

(i) As the affinity of the silver ions for the surface increases, so does the surface concentration of these ions for a given bulk concentration. This leads to a rate of surface reaction which increases with increasing affinity.

(ii) The hydration of the silver ion is affected by its adsorption on the surface, and it is reasonable to suppose that as the strength of its adsorption on the surface increases, the degree of hydration of the adsorbed ion decreases, thus facilitating electrophilic attack on the adsorbed ethyl iodide molecule.

(iii) The adsorption of the silver ion on the surface brings it into close proximity with the ethyl iodide molecule for a longer interval of time than would be the case for a collision in the bulk solution, and this increases the probability that reaction between the two species will occur. Presumably the more strongly the ion is adsorbed the longer it remains on the surface, and so the greater is this probability.

For the adsorption of the ethyl iodide molecule to give the $(EtI : M)^{n+}$ complex, no clearly defined order of effectiveness of catalyst surfaces has so far been established. However, it may be reasonably assumed that factors (i) and (iii) above operate for this complex as well, while (ii) is clearly less important. Further, the more strongly ethyl iodide is adsorbed, the more the bond between the iodine and the ethyl group will be weakened, and the more likely will be the occurrence of heterolysis.

PART II

QUANTITATIVE STUDIES

Chapter 4

THE ROTATING DISC

INTRODUCTION

The rotating disc system is at present unique, in that it allows the introduction into a reaction solution of a heterogeneous surface of known area under precisely defined conditions of fluid flow and mass transport. It is therefore well suited to the study of heterogeneous catalysis in solution, and in this particular case to the study of the heterogeneously catalysed hydrolysis of ethyl iodide by silver nitrate in water. The particular catalyst whose effect is to be studied will be introduced into the reaction mixture as the active surface of a rotating disc. The theoretical basis of the method will now be discussed.

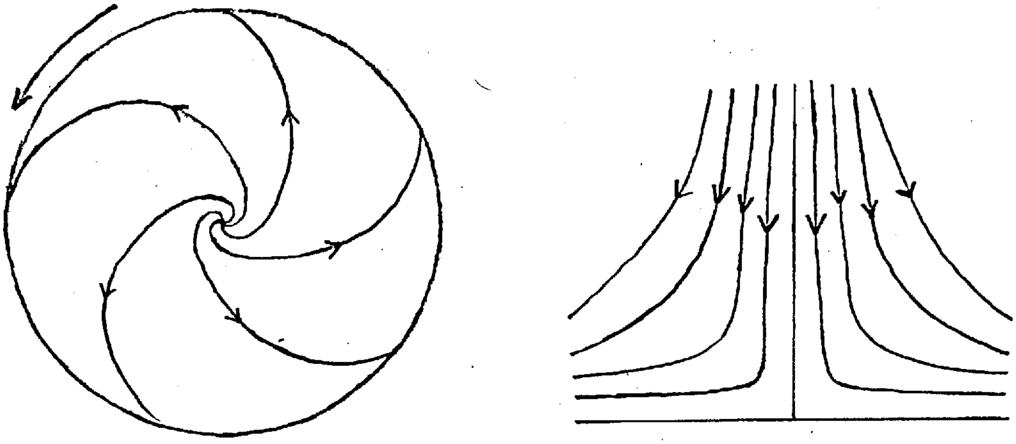
THEORY

The theory of the fluid flow and mass transport phenomena associated with the rotating disc system have been dealt with by Levich,[72,8] and by Riddiford.[73] The main equations and their underlying assumptions will be presented here.

Fluid Flow

The system comprises an infinite horizontal lamina rotating with a constant angular velocity about a perpendicular axis in a fluid of infinite extent. The pattern of flow is shown in Fig. 4.1. Attention

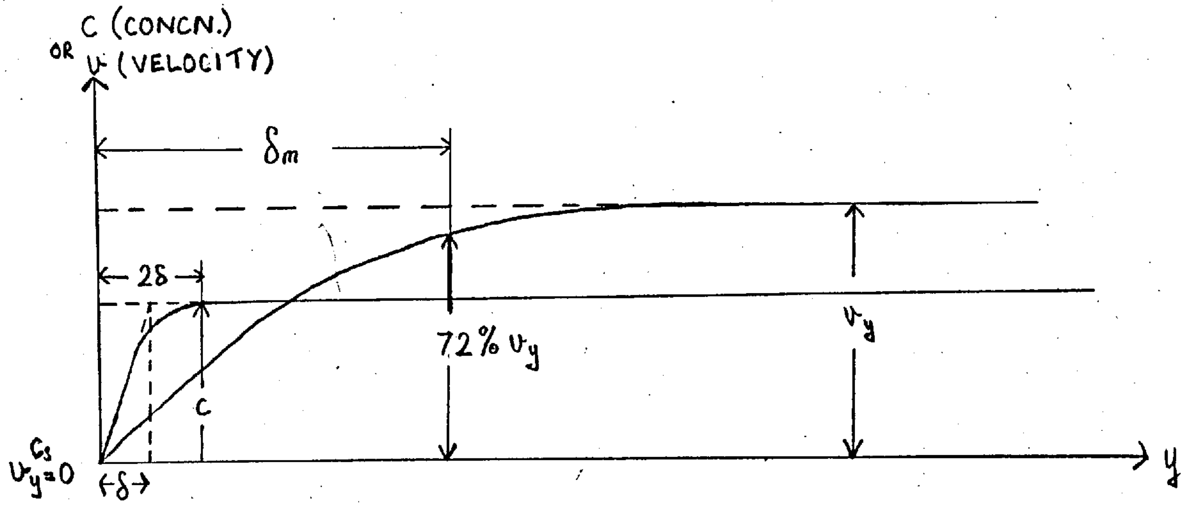
FIG.4.1. Pattern of Flow at a Rotating Disc.



Plan

Elevation

FIG.4.3 Fluid and Transport Boundary Layers.



will be restricted to that part of the system below the lamina since the upper half is a mirror image.

The general form of the Navier-Stokes equation[93] for the dependence of the fluid velocity vector υ_m on the coordinates of the system is, for an incompressible fluid,

$$\frac{d\,\upsilon_m}{dt} = -\text{grad}\,\frac{P}{\rho} + \nu\,\text{div grad}\,\upsilon_m + \frac{f_m}{\rho} \qquad 4.1$$

where P is the pressure

ρ is the density

ν is the kinematic viscosity

f_m is any volume force - e.g. gravity - acting upon the element of fluid

Also,

$$\text{div}\ \upsilon_m = 0 \qquad 4.2$$

because matter is conserved.

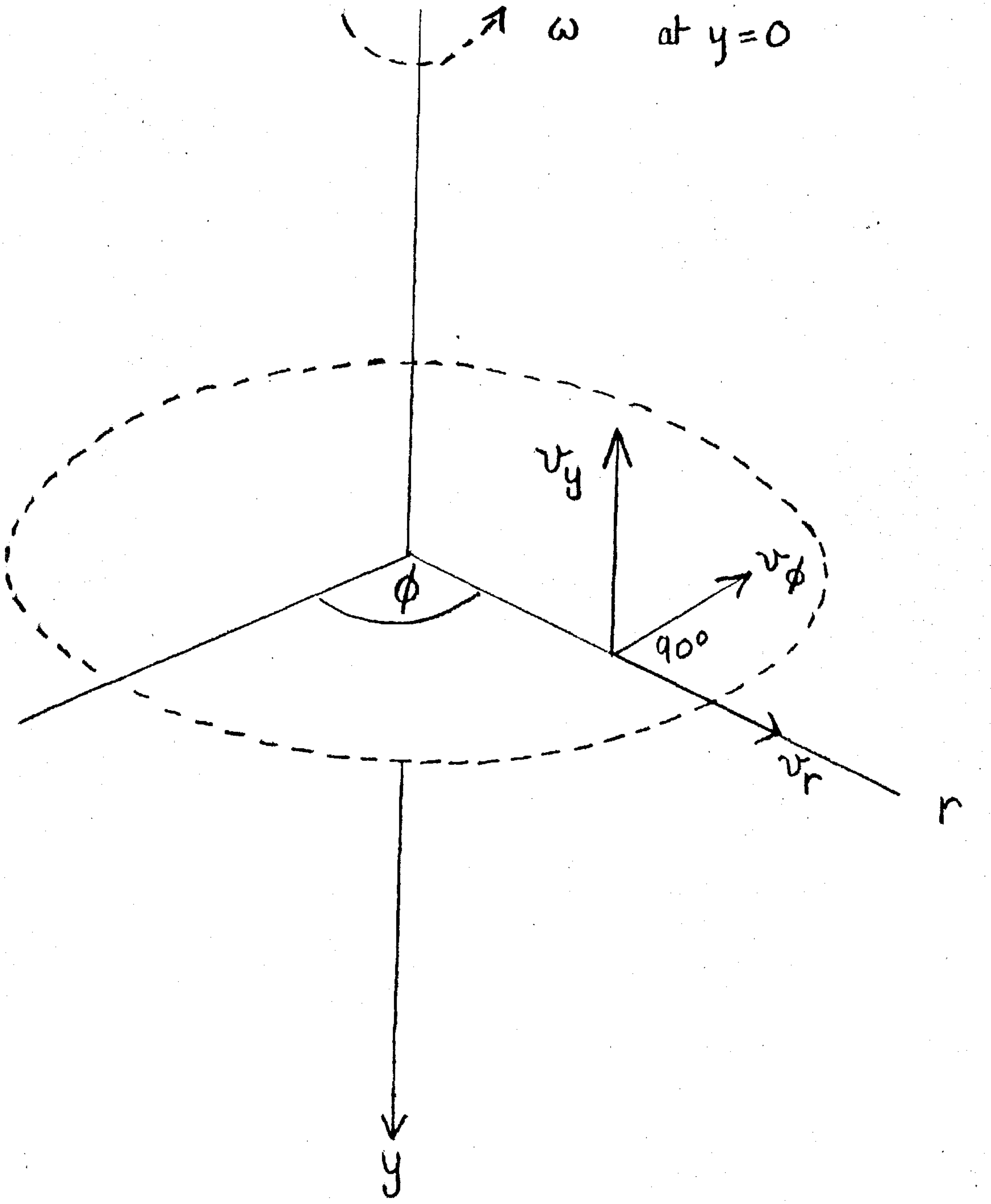
The above equations may be expressed in polar coordinates[74] y, r, ϕ, where y is the distance from the lamina measured normal to its surface, r is the distance from the axis of rotation in the plane of the lamina (y = 0), and ϕ is the angular component in the plane of the lamina. The corresponding fluid velocity components are then υ_y, υ_r, and υ_ϕ (see Fig. 4.2). These equations may now be solved by making the following assumptions:-

a) for the non-turbulent, stationary state, $d\upsilon_m / dt = 0$,

b) by axial symmetry, the flow cannot depend explicitly on ϕ, i.e. υ_y is independent of ϕ,

c) υ_y must be independent of r,

FIG.4.2 Fluid Velocity Components.



d) since the fluid is incompressible and the lamina horizontal P is a function of y only,

e) by considering angular velocities which generate forced convection of sufficient intensity, natural convection may be ignored ($f_m = 0$).

The boundary conditions for the solution of the resultant equations may be established by considering that, close to the lamina, the fluid acquires radial and tangential motion, being thrown out horizontally, there being no slip at $y = 0$. To balance this horizontal outflow, there must be an axial inflow, of negative sign, which must be constant at sufficiently great distances from the lamina since, as y tends to infinity, v_r and v_ϕ must tend to zero.

The solution of the equations[75,76] indicates that there is a layer of liquid in contact with, and dragged around by, the disc. This is known as the fluid boundary layer, of thickness, δ_m. Levich[72] considered that its boundary lay at a point where v_ϕ is only 5% of its value at the disc surface, and v_y has a value which is 80% of its value at an infinite distance from the disc.

The distance of this boundary from the lamina is given by

$$y = \delta_m = 3.6 \, (\nu / \omega)^{\frac{1}{2}} \qquad 4.3$$

where ν is the kinematic viscosity in $cm.^2 sec.^{-1}$

ω is the angular velocity in $rad. sec.^{-1}$

Riddiford[73], however, assumed the percentages for v_ϕ and v_y to be 10 and 72 respectively which gave,

$$y = \delta_m = 2.8 \, (\nu / \omega)^{\frac{1}{2}} \qquad 4.4$$

Note that the thickness of the layer is independent of the radial coordinate, r . However, Millsaps and Pohlhausen[77] concluded that, if the small influence of the flow towards the lamina were considered, the thickness of the fluid boundary layer is a function of the Reynolds number:

$$Re = r^2 \omega / \nu \qquad 4.5$$

They showed that the thickness is essentially constant when Re exceeds 100.

Mass Transport

Let us now consider the transport of a species A_j towards the surface of the rotating infinite lamina.[8a,b] The general equation of this transport is:

$$j_m = C_j v_m - D_j \text{ grad } C_j + U_j C_j \text{ grad } \psi \qquad 4.6$$

where j_m is the flux of Aj

D_j is the diffusion coefficient of Aj

v_m is the fluid velocity vector

ψ is the potential

U_j is the electrical mobility of Aj, equal to $D_j Z_j F/RT$

which leads to

$$\frac{\partial C_j}{\partial t} = \text{div } (D_j \text{ grad } C_j) - v_m \text{ grad } C_j - \text{div}(U_j C_j \text{ grad } \psi) \qquad 4.7$$

This may be expressed in polar coordinates in the steady state when $\partial C_j/\partial t = 0$. The following assumptions are then made:

a) the fluid flow conforms to the conditions described above

b) Aj is uncharged (i.e. $U_j = 0$)

c) Dj is not a function of Cj

d) Cj is independent of ϕ and r. Levich[8a] has said that the physical significance of this is that the radial motion of the fluid cannot carry Aj beyond the lamina, which is true for an infinite lamina.

The problem now reduces to the solution of an equation of a one-dimensional transport normal to the lamina, i.e.

$$Dj\left(\frac{d^2Cj}{dy^2}\right) = v_y \frac{dCj}{dy} \qquad 4.8$$

Levich[8a,b] stated that the solution of this equation converged rapidly for $y > \delta$ where

$$\delta = 1.80\ (Dj/\nu)^{1/3}\ (\nu/\omega)^{1/2} \qquad 4.9$$

Dj being ca. $10^{-5}\ cm^2 sec^{-1}$. He thus regarded δ as the thickness of the <u>transport boundary layer</u> - the distance measured normal to the lamina in which there is a concentration gradient.

Gregory and Riddiford[78] showed that a more accurate solution to to the equation gave the point of convergence as $y = 2\delta$, for values of Dj/ν between 0 and 4×10^{-3}, and they consider this to be the thickness of the transport boundary layer. This, too, is independent of r, giving a 'uniformly accessible surface'.

It may be noted that the thickness of the transport boundary layer is related to that of the fluid boundary layer by the factor $(Dj/\nu)^{\frac{1}{3}}$, which is of the order of 0.1. The two boundary layers are depicted schematically in Fig. 4.3.

Thus the fluid body may be divided into two regions, the bulk of solution in which transport is purely convective, and the transport boundary layer in which transport occurs by a combination of diffusion and convection, the former predominating at the surface. The maximum (limiting) rate of mass transport of Aj to unit area of the surface is given by:

$$j_{m,lim} = \frac{DjCj(\infty)}{\delta\, I(\infty)} \qquad 4.10$$

where Cj (∞) is the concentration of Aj in bulk solution and $I(\infty)$ is an integral of the form:

$$I(\zeta) = \int_0^{\zeta} \exp\left[-\zeta^3 + 0.885 \left(\frac{D_j}{\nu}\right)^{1/3} \zeta^4 - 0.394 \left(\frac{D_j}{\nu}\right)^{2/3} \zeta^5 --- \right] \qquad 4.11$$

$$\text{and } \zeta = y/\delta \qquad 4.12$$

As D_j/ν approaches zero, $I(\infty)$ approaches 0.895. It can easily be seen from this that the rate of a transport controlled reaction is a function of $(\omega)^{1/2}$, because of 4.9 and 4.10.

Although the equation for the limiting current density is irrelevant to the present work, it will be given here because of the discussion in the following section. From 4.10, 4.12 and 4.9

$$i_{lim,j} = \pm \left(\frac{0.554}{I(\infty)}\right) z F D_j^{2/3} \nu^{-1/6} \omega^{1/2} C_j(\infty) \qquad 4.13$$

Equation 4.7 has also been solved for a solution containing three ion species,[8a] one of which is at very low concentrations. It gives an equation identical to 4.10 for the limiting flux of the latter species. The values of Dj and ν, however, refer to the solution and not to the pure solvent.

CONFORMITY TO THEORY OF THE PRACTICAL DISC

At the present time there is a certain amount of controversy in the literature about the extent to which various practical designs of rotating disc conform with theoretical requirements. Riddiford[73] has summarised the work done so far, with the exception of experiments done in this laboratory by Johnston.[79] The present study in which large catalytic effects were sought, has been guided, so far as the practical design goes, by the above. The factors influencing the design of the experimental system will now be discussed.

The theory predicts that for streamlined flow an infinite plane lamina rotating at a constant angular velocity about a vertical perpendicular axis, in a fluid of infinite volume, will offer a 'uniformly accessible surface'. This implies that the thickness of the fluid and transport boundary layers are dependent only on the y coordinate (with the possible exception of a small region at the center of the disc - see below). For the practical disc this necessitates:

1) Streamlined flow

Since the basic assumption of the theory is that the system is in the steady state, i.e. $dU_M/dt = 0$, it is vital that the flow of liquid in the practical system should be streamlined. This will obtain provided that the maximum value of the Reynold's number, Re = $r^2\omega/\nu$ - the value at the periphery of the disc - is less than the critical value for the onset of turbulence. From the work of Theodorsen and Regier,[80] Riddiford[73] suggested that this value is approximately 2×10^5. Levich,[72a] however, stated that streamlined flow is sustained up to 10^5 only for very well balanced and centered discs, and is usually sustained only up to 10^4. Johnston,[79a] in this laboratory, found the Levich equation (4.13) to be obeyed up to 1400 r.p.m. for a 7.6 cm. disc of type D (Fig. 4.4), which leads to a Reynolds number of ca. 2.0×10^5 at the periphery of the disc.

A lower limit to the functional range of Re is imposed by two factors. Firstly, as mentioned in the theory section, δ_m is a function of Re and therefore of r below Re = 100. This implies that the rotation speed must be high enough that the area at the center of the disc, for which Re $<$ 100, contributes a negligible fraction to the total mass transport. However, for disc E (Fig. 4.4) results[81] were in agreement with theory (Equation 4.13) when the value of Re, corresponding to the periphery of the active region, was less than 20. This indicates that the transport boundary layer is unaffected at these values

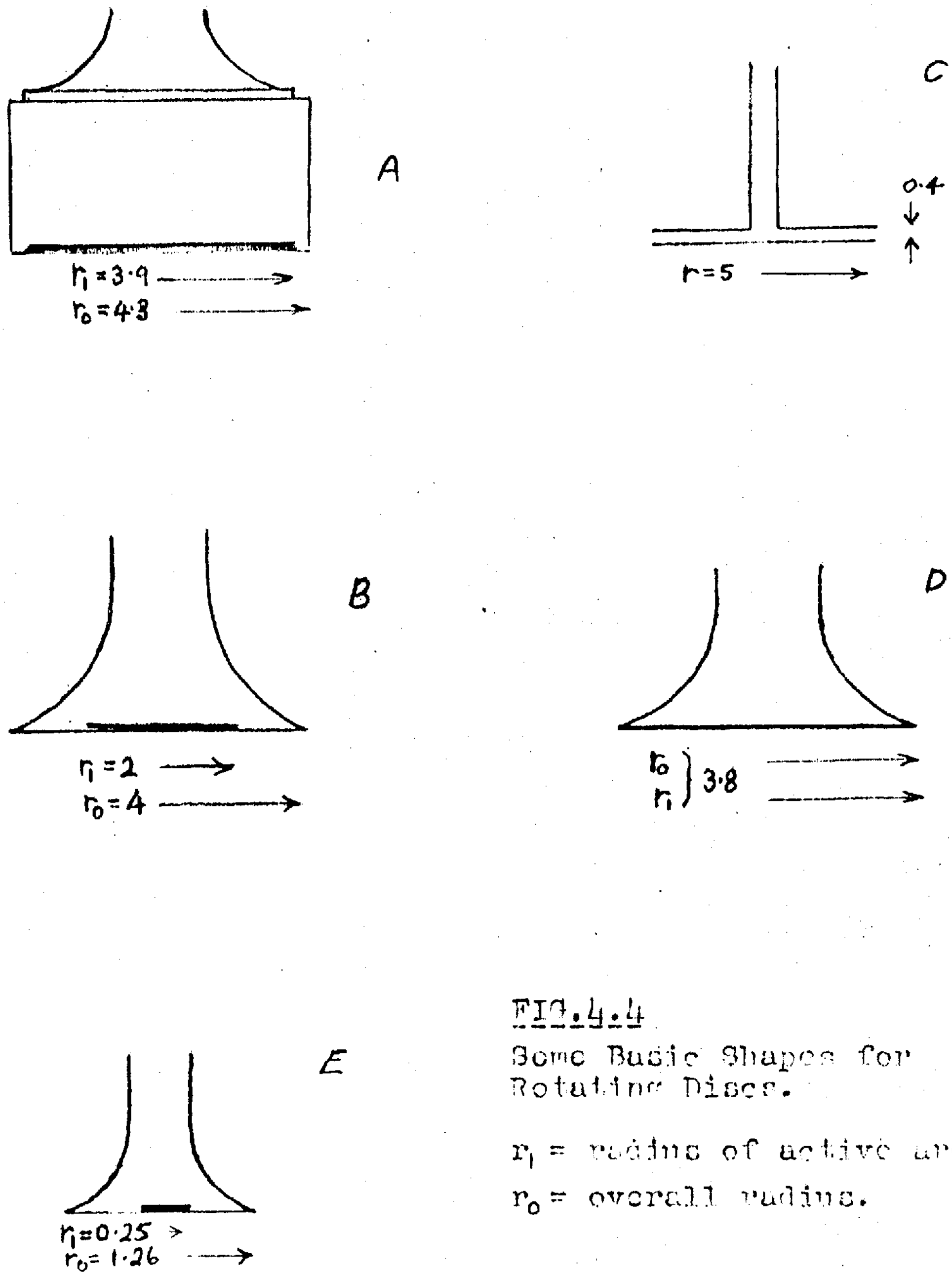


FIG.4.4

Some Basic Shapes for Rotating Discs.

r_1 = radius of active area.

r_0 = overall radius.

of Re.

The second reason for imposing a minimum on the value of Re is that at low speeds the ratio δ_m/r may become so large that natural convection can no longer be disregarded in comparison with forced convection. This situation has been treated by Kholpanov,[82] and is considered to lead to positive deviations from theory.

2) The finite radius, r_0, of the disc should be very much larger than the thickness of the fluid boundary layer, from the fluid flow requirements, i.e.

$$r_0 \gg 2.8\,(\nu/\omega)^{\frac{1}{2}}$$

For aqueous solutions at room temperature, and a rotation speed of 100 r.p.m., δ_m is of the order of 1 mm., and if the disc radius is large compared with this it will obviously be so for the transport boundary layer.

If a disc has an active central region from $r = 0$ to r_1, surrounded by an inert annulus from r_1 to r_0 then the requirements are that $r_0 \gg \delta_m$, $r_1 \gg \delta$. With disc E (Fig 4.4) Blurton and Riddiford[81] obtained limiting currents in agreement with theory when these ratios were as low as 12 and 10 respectively.

3) The active surface of the disc must be flat. Available evidence[73,79] shows that its roughness must be negligible in comparison with δ_m, and it would seem wise to ensure that this applies with respect to δ, also. The effect of roughness on the fluid flow seems to be the induction of turbulence at lower values of Re than would otherwise be possible. In the case of copper discs dissolving in sulphuric acid[84] and of silver plating on silver discs,[79b] this led to enhanced mass transport, although

for the electro-deposition of nickel[85] no enhancement of the overall rate was found when 56 artificial asperities of the order of $0.1\delta_m$ in height were introduced. In the case of copper, the effect was ascribed to local turbulence at inert spots on the surface which gave rise to fairly isolated irregularities, and for silver, to needles of silver growing through the diffusion layer. In the last case, the asperities left a streamlined spiral wake, but apparently did not greatly disturb the laminar flow at the surface.

4) Edge effects

With the simplest form of disc, a thin foil rotating on a narrow shaft (Fig. 4.4,C), the finite thickness of the edge presents a surface to the fluid which contributes to the active area and must be taken into account. The most effective means of removing this difficulty seems to be the use of a disc whose lower side is active for $r = 0$ to r_1, and inert from r_1 to r_0. ($r_1 < r_0$), i.e. an active central area surrounded by an inert annulus.

Unless the former is of appropriate shape a second edge effect arises due to the interaction between the liquid above the disc surface at y = 0, and that below. Riddiford[73] considered that this effect was responsible for positive intercepts found in the dependence of i_{lim} on $\omega^{\frac{1}{2}}$ observed by a number of workers.[86,87,88,89]

Johnston[79c] has examined the effect of the shape of the former, using discs A, B, and C (Fig. 4.4), on the limiting current in the system $0.2M\ KNO_3 + 0.936 \times 10^{-4} M\ Ag^+$ with a silver disc. He concluded that, for large discs (r = 2 to 4 cm), i_{lim} was independent of the shape of the disc, whether the disc had an annulus or not, and whether it was on a cylindrical or trumpet shaped former. It is these large discs that are employed in the present work.

The third edge effect arises from the fact that there must always be some disturbance of the flux towards the edge of the working surface, because at this point, the transport boundary layer thickness diminishes to zero. It is here that the normal concentration profile of the transport boundary layer gives way to what Jahn and Vielstich[90] term 'spherical diffusion'. This effect can be minimised by ensuring that the radius of the working surface is very much greater than the thickness of the transport boundary layer.

5) Theory requires that the lamina shall rotate in an infinite volume of solution. Thus all the bounding surfaces, the liquid/air boundary, and the walls of the containing vessel should be <u>effectively</u> at an infinite distance from the disc. Gregory and Riddiford[78] reported that this condition was satisfied when all the above surfaces were more than 0.5 cm. from the disc. Johnston[79d] found, using a trumpet shaped disc (see Fig. 4.4, D) of 7.6 cm. diameter, that a vessel of 10 cm. diameter gave a higher value of i_{lim} than a 12.5 and a 16.5 cm. vessel. The 12.5 cm. vessel also gave a slightly higher value than the 16.5 cm, but the difference was barely within experimental error.

Concerning the clearance of the disc from the bottom of the vessel, Johnston[79d] found that, if this was less than about 1 cm., limiting currents tended to be irreproducible. There was no significant effect on i_{lim} when the disc was raised so that its surface was only 1 to 2 mm. below the surface of the liquid.

6) If the center of the disc does not coincide with its axis of rotation, the disc will sweep out an area greater than its geometric area. This will also be the result of any slight misalignment of the rotation shaft. This effect is, however, only of importance in the case of discs with a small active area. Butler[91] has calculated that for a disc 0.05 cm. diameter a 'whip' of 1×10^{-3} inches would cause the disc to sweep out an area only 1% greater than its geometric area.

DESIGN OF CELL AND DISCS

In the design of a cell for the study of the $AgNO_3$ + EtI system the following design criteria were considered:

1) all the criteria listed in Chapter 2.

2) the criteria discussed in the previous section.

One of the criteria listed under (1) was that there should be no metal in contact with the reaction solution. It had, however, previously been established (Table 3.6) that stainless steel was not a catalyst for the reaction, so the non-catalytic surfaces of the discs shown in Figs. 4.10 and 4.11 were of this material. Apart from this, the two sets of criteria are compatible, and were considered together in the design of the cell.

Since the discs were to be used as catalytic surfaces only (i.e. not as electrodes), it would have been difficult to test whether the system conformed to theoretical requirements. This led to a design in which a generous margin of safety was allowed at any point where the conformity of practice to theory was not sharply defined. For example, although Riddiford[78] had stated that the walls of the vessel were effectively at infinity if at a distance greater than 0.5 cm. from the disc;

Johnston's findings[79d] indicated that the diameter of the vessel should be approximately twice that of the disc. The present design was therefore based on Johnston's results.

To maximise the catalytic effect, discs of approximately 6 cm. diameter were to be used. This led to a cell of about 800 ml capacity, the glass vessel being 14 cm in diameter by 5 cm. deep. The vessel was flanged in order to fit to the Perspex lid, the two being sealed together by means of an O-ring (16cm. in diameter). The lid and the vessel were clamped together by means of two brass rings, one on top of the lid, and the other beneath the flange of the vessel with a rubber cushion between it and the glass. The rings were screwed together by 8 brass screws and wing nuts placed at intervals around their edges (Fig. 4.5). The rings were about 2.5 cm. wide, the outer diameter being 20 cm.

Between the flange of the vessel and the lid was fitted a detachable Perspex ring (Fig. 4.6). This was triangular in cross-section, and about 1 cm. deep. When the lid of the cell was tightened down on to the vessel, it pushed the ring down against the walls of the vessel, and thus sealed the bulk of the vessel from the air gap left between the lid and the glass flange by the O-ring seal. This facilitated reproducible filling of the vessel.

The Perspex lid was 17.5 cm. in diameter, and 1.25 cm. thick (Fig. 4.5). Araldited into it were (i) a reference electrode stem identical with that in the small cell (Fig. 4.5 E), (ii) 3 B19 sockets (Fig. 4.5 A, B, C), (iii) 1 B34 socket in the center of the lid (for the disc shaft) (Fig. 4.5 D), (iv) a stop tap for sealing the cell

FIG.4.5 Plan of Lid of Rotating Disc Cell with Upper Brass Ring.

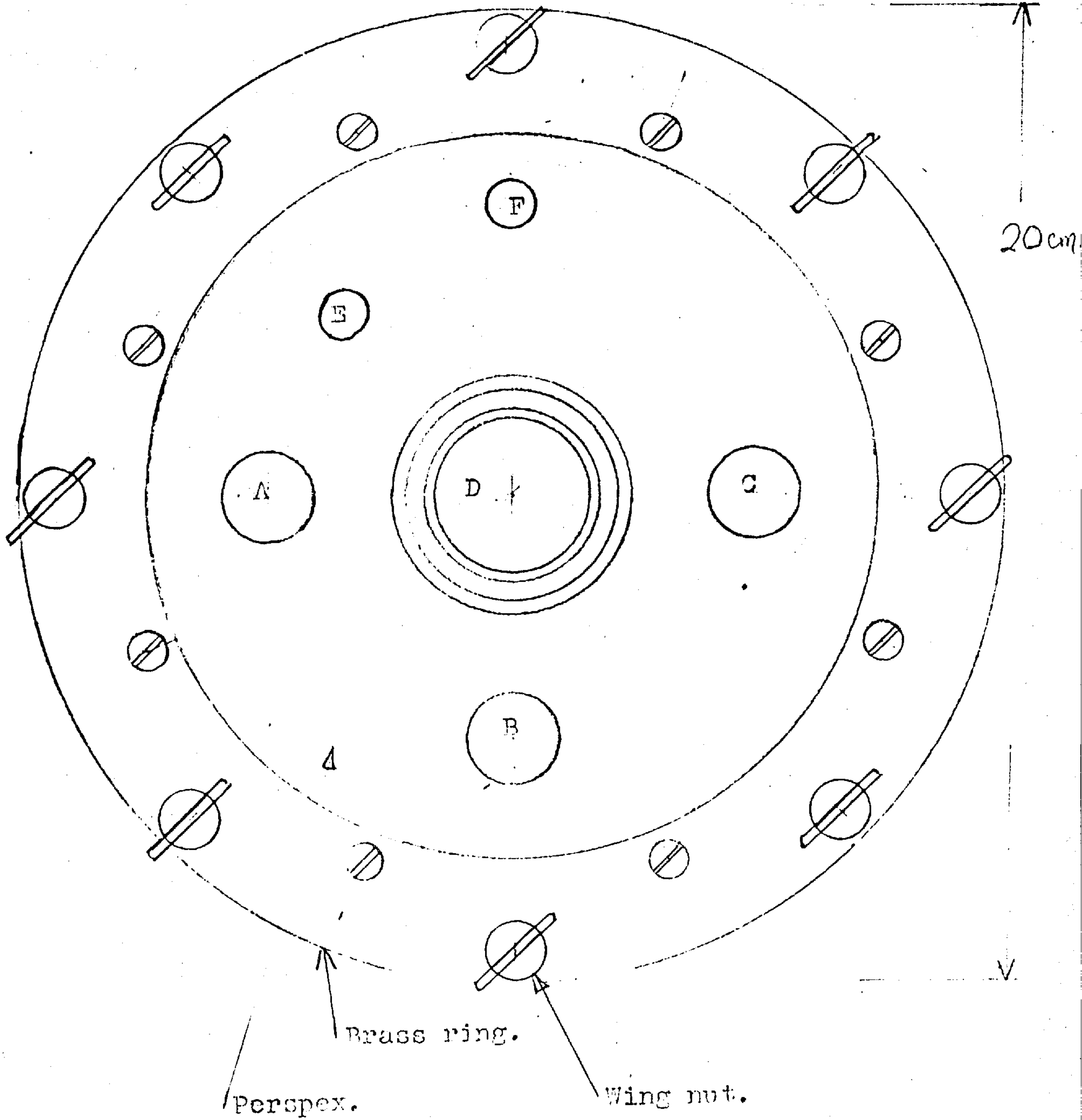


FIG.4.6 Perspex Ring.

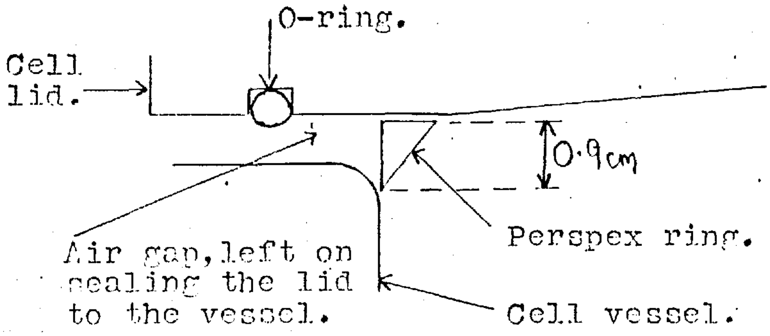
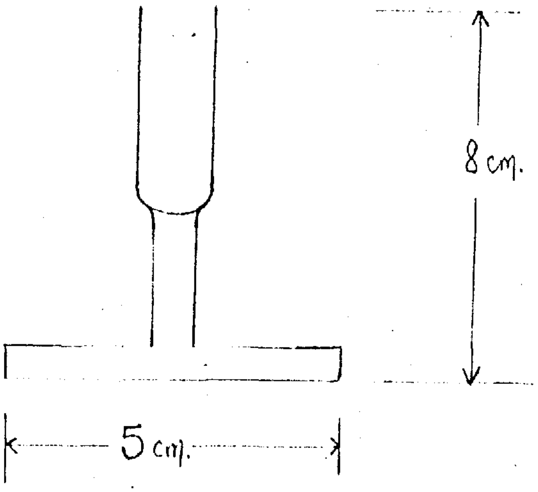


FIG.4.12 Glass Stirrer.



from the atmosphere at atmospheric pressure after the filling was complete (Fig. 4.5 F). The underside of the lid had a 1° slope (above the horizontal) to facilitate the removal of air bubbles during filling (if the cell was to be filled completely with liquid). Of the three B 19 sockets, one was to accommodate the entry of a glass electrode into the cell (Fig. 4.5, A), a second to allow the addition of the ethyl iodide solution to the cell (Fig. 4.5, C), and the third was a spare.

The discs were attached to the motor shaft (see Fig. 4.7) by means of three grub screws which threaded through holes at the top of the disc sleeve into indentations in the shaft at A. The shaft was sealed to the cell by means of an assembly of brass and glass (Fig. 4.8). It consisted of a glass tube 11 cm. long which had a B 34 cone at one end, to connect to the B 34 socket in the lid, and a B 34 socket at the other end. Into this socket a brass sealing device fitted to form an airtight seal (Fig. 4.9). The device was of the shape of a B 34 cone externally, and it contained a rubber O-ring which fitted closely, in the region B to C, to the spinning shaft carrying the rotating disc (Fig. 4.7). This device could be dismantled to allow the lubrication of the O-ring with vacuum grease. When connected to the cell and the shaft, the glass and brass assembly sealed the cell, the disc, and the shaft up to the O-ring, from the atmosphere. The glass tube had a side arm with a tap. This was to facilitate the filling of the cell.

All the Quickfit joints were sealed with P.T.F.E. sleeves, to make them airtight without using vacuum grease.

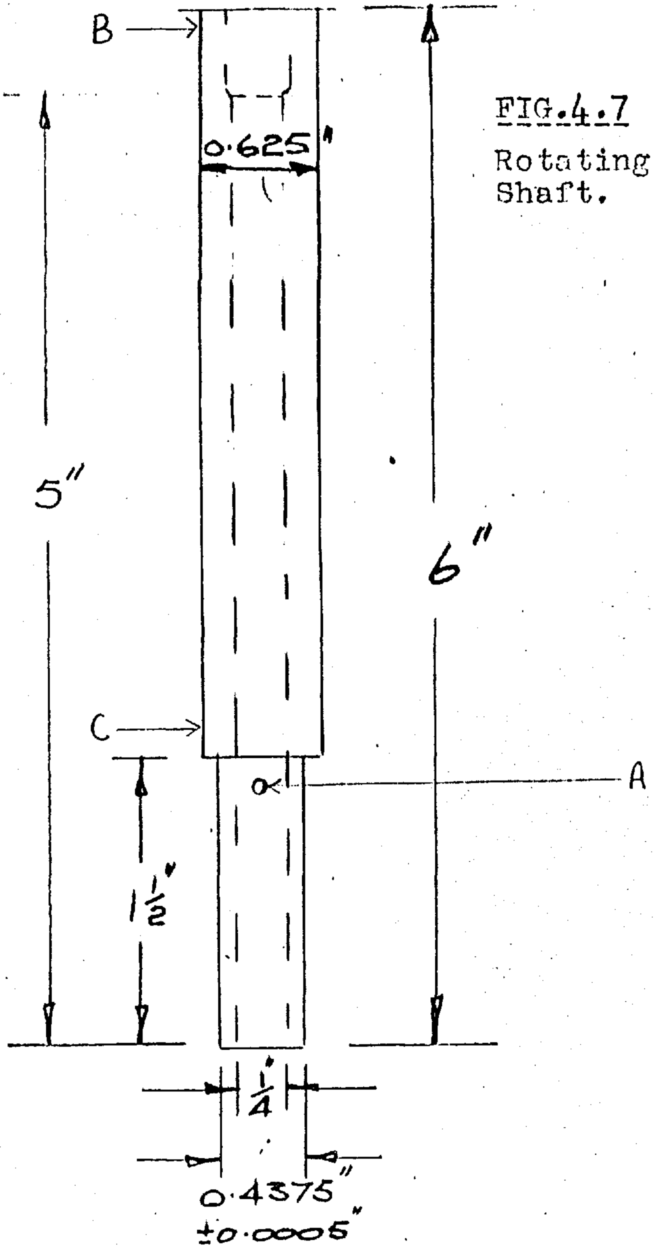


FIG.4.7

Rotating Disc Shaft.

FIG. 4.8

Assembled Rotating Disc Apparatus.

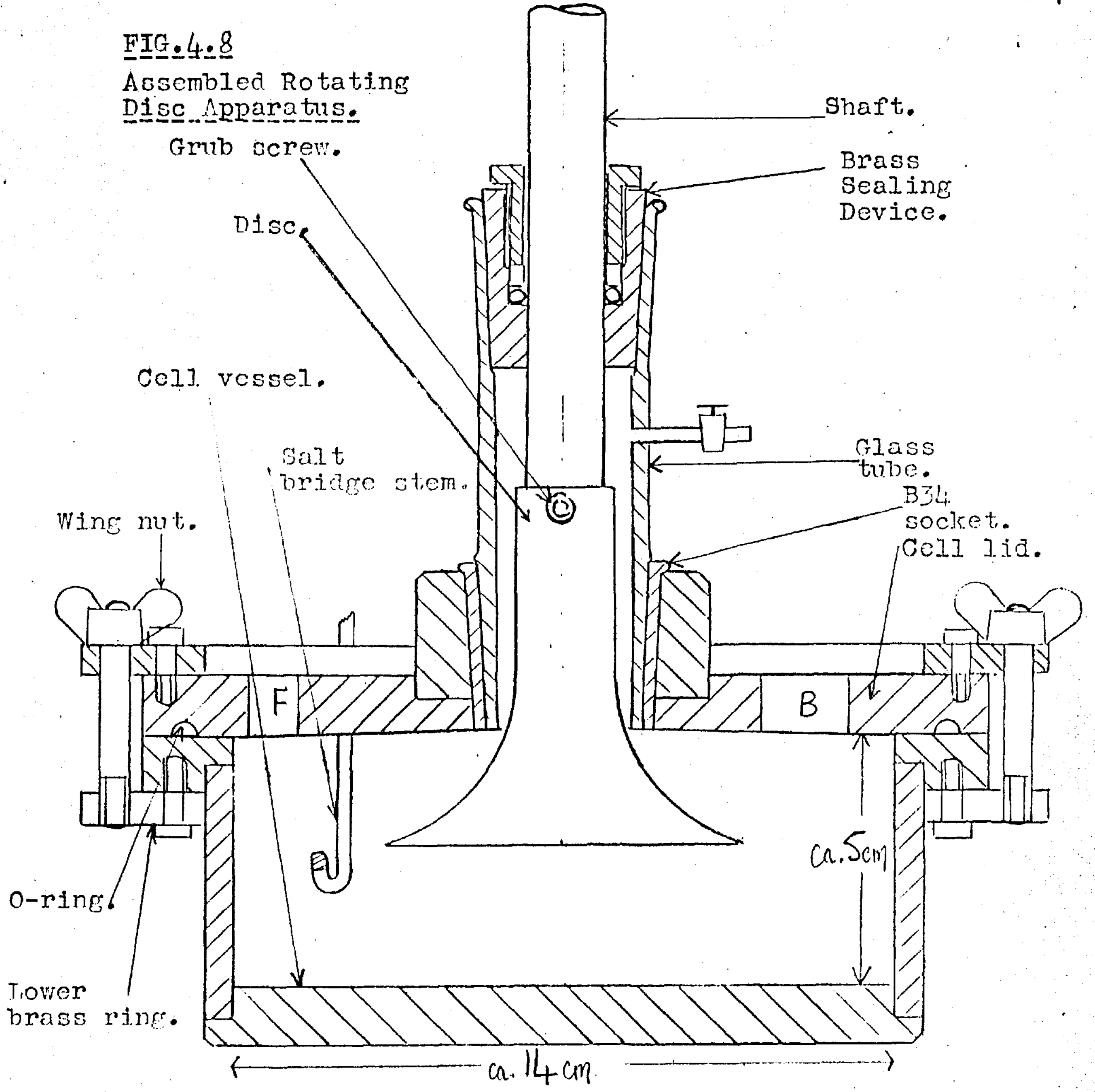
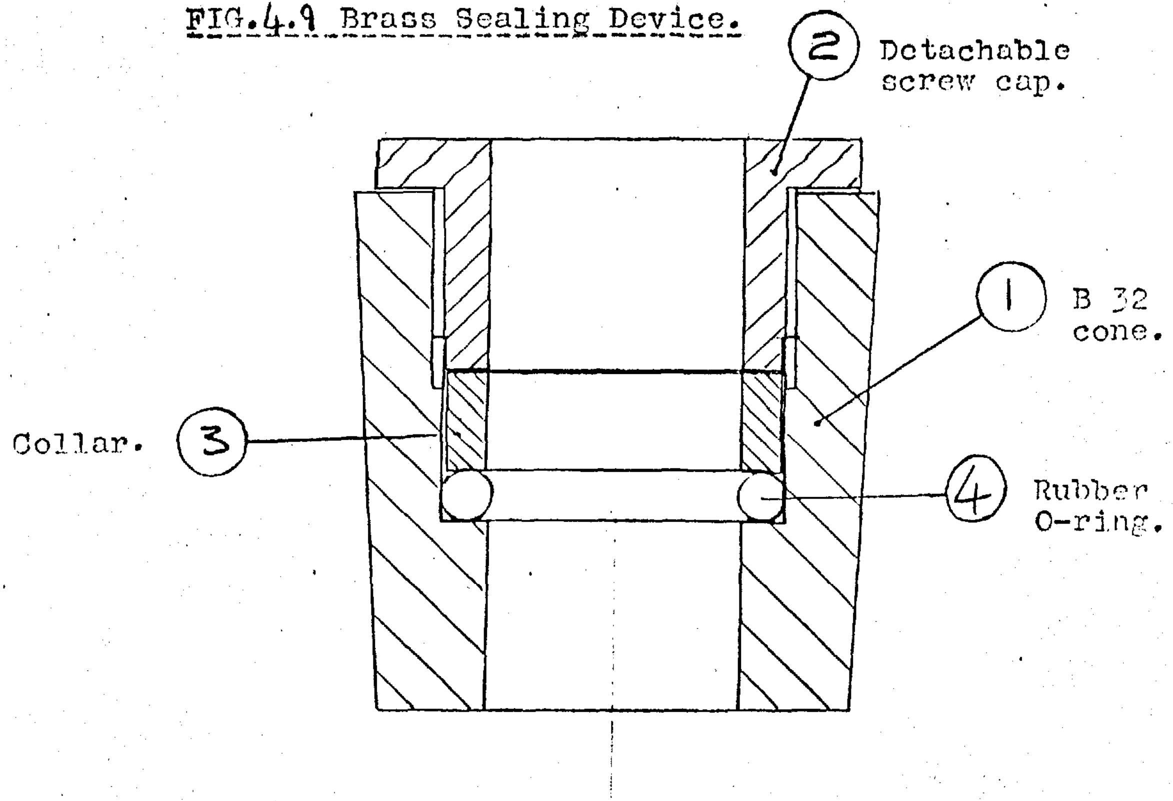


FIG.4.9 Brass Sealing Device.



pH Measuring System

The pH measuring system was identical with that used in the small cell. Because of the inaccuracies inherent in the measurement of pH,[92] it was planned to calibrate the measuring system for this quantitative study. This was to have been done by measuring the pH of standard solutions of nitric acid and potassium nitrate at the appropriate concentrations, the solution being stirred at various rotation speeds by a blank disc. However, the results obtained using the system (Chapter 5) did not warrant this accuracy, and the calibration was not performed.

Discs

Three basic discs were used during the experiments. It was decided to use trumpet shaped discs, as recommended by Riddiford.[73] It was found that the shaft on which they were to be mounted had a 'whip' of $\sim 2 \times 10^{-3}$ inches, but this could not be reduced.

In order to determine the best operating conditions (see Chapter 5) a series of runs was done using a blank disc with no active surface. This comprised a Perspex spinner mounted on a Hostaflon sleeve, and was similar in shape and size to the silver chloride disc (Fig. 4.10). It was not very well centered on the shaft, and precessed quite noticeably, but this was ignored because of the lack of active surface.

A second disc (Fig. 4.10) incorporated an active surface of silver chloride. A 6 cm. disc of fused silver chloride (Johnson Matthey) was Araldited into a spinner of Teflon, with an annulus of Teflon (outer diameter 7.8 cm) around the silver chloride surface. The Teflon spinner was mounted on a stainless steel sleeve (Perspex, Teflon, and stainless

FIG.4.10 Silver Chloride Disc.

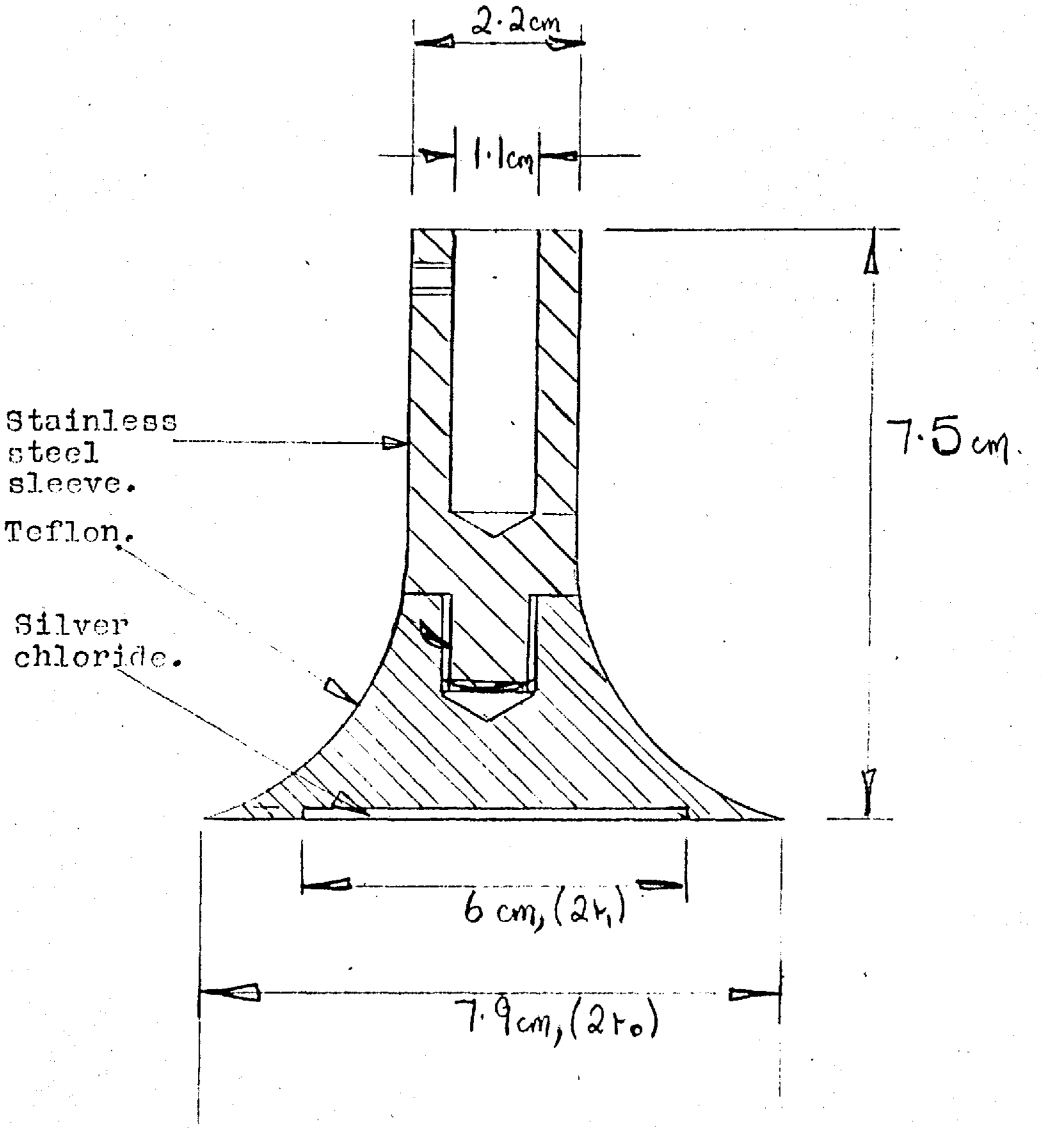
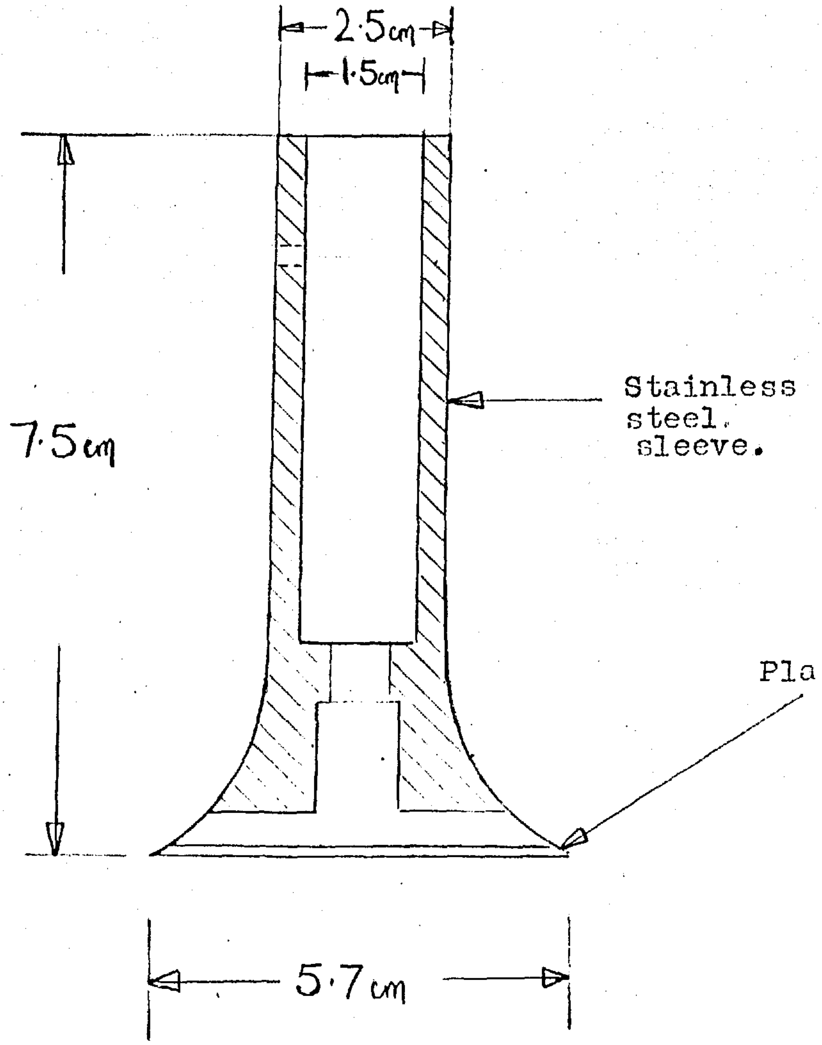


FIG.4.11 Platinum Disc.



steel had all previously been shown not to catalyse the reaction between ethyl iodide and silver nitrate).

The third disc (Fig. 4.11) was made completely of stainless steel, the bottom, active, surface being platinum. There was no inert annulus surrounding the platinum, ($r_1 = r_0 = 2.85$cm). This disc did not have as great a radius on the upper surface as the other two. It and the silver chloride disc were much better centered than the blank disc.

The method of preparation of the discs for individual runs will be given in the experimental section (Chapter 5).

The cell is shown completely assembled in Fig. 4.8 with the glass electrode, and the stop tap on the cell lid omitted because of lack of space. The cell vessel depicted in this diagram is actually of Perspex which, because it was a better fit to the lid, did not require a Perspex ring (Fig. 4.6), or a rubber ring between the lower brass ring and the vessel. In fact, however, this vessel was not used, the glass vessel being preferred because of ease of cleaning and because the walls were more transparent.

Rig and Motor

The shaft to which the discs were attached, together with the motor that drove it and the platform which supported the cell, were mounted on a steel baseplate. For ease of apparatus assembly, the height of the platform was adjustable in relation to the shaft and disc. The whole assembly could be raised or lowered on an angle iron framework, enabling the cell to be partially immersed in a water bath thermostatted at 25°C (for details see Chapter 2).

The rotating disc was driven through a 10:1 reduction gear by a special d.c. motor coupled with a Servomex M.C. 43 controller. The speed of rotation of the motor, indicated directly on a dial, could be varied continuously from 0 to 7000 r.p.m. and could be set to ~ ± 1%. The purpose of the reduction gear was to allow the motor to run at high speeds for low speeds of rotation of the disc, since the motor tended to turn rather unevenly at low speed.

TECHNIQUE OF FILLING

The cell was so large, and was designed in such a way, that its volume could not be measured in the manner of the small cell (see Chapter 2). Instead its volume was determined by adding known volumes of water from a measuring cylinder. It was found that the B 34 cone and socket arrangement for the shaft and disc allowed the volume of liquid added to the cell to vary by as much as ± 5 ml, the cell still being 'full', i.e. the surface area of liquid in contact with air being at a minimum. The capacity of the cell was measured for each of the discs to be used, and was found to be 790 ml for the blank disc, 760 ml for the silver chloride disc, and 780 ml for the platinum disc.

The simplest way of adding the ethyl iodide solution to the cell was to pour it in, through a nozzle attachment, from the graduated flask in which it had been prepared. Some 20 calibration experiments with a 250 ml. 'A' grade flask showed that the volume delivered in this way was 249.5 ± 0.07 ml.

The procedure adopted was to add the silver nitrate first, by means of 'A' grade pipettes, to make up the volume:

(volume of cell - 250 ml.)

If the cell was not to be filled to the lid, then the volume of silver nitrate solution added was:

(total volume of solution - 250 ml.)

The ethyl iodide solution was then poured in as described. The method of preparation of the reaction solutions was identical to that in Part I.

The sequence of filling operations was as follows. The electrodes were first standardised in 0.05 M phthalate solution at 25°C. For this, the cell lid, with glass electrode in place, and with the reference salt bridge filled with 0.25 M potassium nitrate solution, was placed on an auxiliary vessel containing the buffer solution and was fastened into place by means of the brass rings. The outer end of the salt bridge dipped into saturated potassium chloride solution in a 100 ml beaker which was attached to the cell lid by a wire ring which fastened to one of the wing nuts. This cell and beaker were then placed in the thermostat tank, a calomel electrode dipped into the potassium chloride solution, and the whole left for 30 minutes to attain the temperature of the tank. The electrodes were then standardised.

During the period of thermal equilibration, the silver nitrate solution was pipetted into the cell vessel. If the reaction was to occur in the presence of potassium nitrate, a known weight of the salt was added from a weighing bottle prior to the addition of the silver nitrate solution. The Perspex ring was then fitted loosely into place.

After the pH standardisation, the standardisation cell was taken out of the tank, and the lid removed. The electrodes were washed in distilled water, and they and the underside of the lid were dried carefully with Kleenex tissue. (The underside of the lid was always slightly damp from condensation). The rotating disc sleeve was then passed through the B 34 socket from the underside of the lid and steel rods slipped through the holes at the top of the sleeve so that the disc would hang from the lid while the cell was being fastened together, the rods resting on the top of the B 34 socket. This was done to prevent the catalytic surface of the disc coming into contact with any other surface, thereby incurring the risk of contamination or mechanical damage. The lid was secured to the vessel by means of the brass rings, the beaker of potassium chloride solution attached as before, and the cell placed on the platform of the rig. The shaft sealing assembly had previously been greased with silicone grease and fitted on to the shaft and secured as high up as possible. The steel holding rods were then removed and the disc sleeve slipped up the shaft to point A (Fig. 4.7) and secured with steel grub screws. The level of the disc surface in the cell was then adjusted, by raising or lowering the platform, so that it was approximately the same height above the cell bottom (~3 cm.) for each run. The sealing assembly was slid down the shaft so that its B 34 cone secured into the B 34 socket in the cell lid. The disc and shaft were now sealed from the atmosphere. The whole apparatus was lowered into the thermostat tank and allowed to acquire the temperature of the water, as was the flask of EtI solution. To the B 19 entry socket (Fig. 4.5,C) was attached a glass cylinder (the entry attachment), approximately 10.5 cms. long and 1.5 cm. in diameter, by means of a B 19 extended cone. The cylinder extended 1.5 cm. below the cone, and was topped by a B 19 socket. Its purpose was to provide a small head of liquid during the addition of the ethyl iodide solution to ensure that the cell filled completely, with no air pockets trapped against the lid.

After about 30 minutes of thermal equilibration the graduated flask was removed from the tank and dried. The Servomex was switched on, and the disc was rotated at the required velocity. The tap on the lid of the cell and that on the shaft sealing assembly were both opened. The stopper in the neck of the flask was removed and the nozzle substituted. The clock was started and the ethyl iodide solution was poured into entry attachment, the flask being emptied. A B 19 stopper was then placed in the socket of the entry attachment, and both taps closed, to seal off the contents of the cell from the atmosphere. The change of pH with time was recorded, the velocity of rotation of the shaft being checked for constancy at regular intervals during the run.

Chapter 5

RESULTS OF EXPERIMENTS USING THE ROTATING DISC

PRELIMINARY EXPERIMENTS

Before any quantitative work involving the discs with catalytically active surfaces was done, a series of 15 runs was carried out with the blank disc (Chapter 4) to establish the best operating conditions. The criteria were

(i) reproducibility of the 'homogeneous' rate

(ii) independence of this rate from the velocity of rotation of the disc.

The results are presented in Table 5.1. They show that the above criteria are best satisfied when the cell is full of liquid, and when the solution contains 0.02 mole liter^{-1} of potassium nitrate. All succeeding runs were done under these conditions. The rate of the 'homogeneous' reaction, for comparison with the catalysed rates to be measured, was taken, from runs 11 and 12, to be (0.50 ± 0.01) x 10^{-6} mole liter^{-1} min.$^{-1}$

The effect of adding potassium nitrate to the reaction was to reduce the rate of reaction, whether the cell was full or not, independent of the velocity of rotation of the disc. The reason for this is twofold. First, the presence of the salt caused coagulation of the silver iodide formed, reducing the surface area available for catalysis. A correlation between the rate of reaction and the state of subdivision of the precipitate supported this hypothesis. Secondly, the secondary salt effect

Table 5.1

Run No.	Rate of Reaction x 10^6 (mole liter^{-1} min.$^{-1}$)	Time Interval over which rate was measured (mins.)	Concn. of KNO_3 in Cell(M)	Cell Full	Velocity of Rotn. of disc (R.P.M.)	Linearity of Rate
1	0.427 0.517	20-50 60-90	0.02	No	400	Two separate linear portions, meeting at 50 min
2	"	"	"	"	"	"
3	0.44	20-55	0.02	No	400	Linear from 0-120 mins.
4	0.44 0.48	10-50 50-90	0.02	No	400	Linear 10-50, & 50-90 with different slopes
5	0.50	20-75	0.02	No	100	
6	0.49	0-20	0	No	400	Rate accelerated rapidly after 20 minutes
7	0.50	0-20	0	No	400	Rate accelerated rapidly but did not reproduce run 6
8	0.39 0.73 0.56	0-10 30-50 10-30	0 0 0	No No No	100 300 400	Rate did not appear to be related to the velocity of rotation of the disc.
9	0.53	20-50	0	No	100	Linear from 10 to 50 mins., accelerating after 50 mins.
10	0.525	0-20	0	No	100	Linear 0-20 mins. Much greater acceleration than for run 9.
11	0.51	20-90	0.02	Yes	400	Linear 20-105
12	0.495	30-90	0.02	Yes	100	Linear 20-120
13	0.65	0-90	0	Yes	400	
14	0.65	0-90	0	Yes	400	
15	0.53 0.59	2-20 30-90	0	Yes	100	Linear 0-20, 30-105 mins. with different slopes

Initial $[AgNO_3]$ = Initial $[EtI]$ = 0.001 M for all runs.
Temperature = 25°C.
Volume of full cell = ca. 800 ml.

With the cell full the liquid/air interface was negligible, but with it not full this area was ca. 150 cm^2.

of 0.02 M potassium nitrate would have been, according to the theory presented in Chapter 3, to reduce the rate by about 0.2×10^{-7} mole liter^{-1} min.$^{-1}$

The effect of filling the cell also seems to be connected with the state of the precipitate. A much more reproducible rate was obtained when the cell was full (runs 13 and 14) than when it was empty (runs 6 and 7), indicating that the precipitate was formed more reproducibly in the former case. This may have been due partly to the swirling of the solution which occurred when the cell was not full, but which was absent when the cell was full. This hypothesis is supported by the fact that, at 100 r.p.m., there was little change in the rate on filling the cell (runs 9 and 15, 5 and 12) whether KNO_3 was present or not. At 400 r.p.m. the effect of filling the cell was to increase the rate of reaction (runs 4 and 11, 7 and 13), possibly indicating that the effect of the swirling of the solution was to coagulate the precipitate.

When the cell was not full, a reduction in the rate of rotation of the disc caused an increase in the rate of reaction, the effect being less marked in the presence of potassium nitrate (runs 4 and 5, 6 and 9). This is in agreement with the hypotheses above. When the cell was full, however, a reduction in the rate of rotation caused a decrease in the rate of readtion (runs 11 and 12, 13 and 15). This may have been due to the solution becoming non-uniform at the lower rotation speed because of a settling out of the precipitate formed. The effect was very slight in the presence of potassium nitrate, however, and can be neglected in this case (runs 11 and 12).

EXPERIMENTS USING CATALYTICALLY ACTIVE DISCS

To explain the course taken by this series of experiments, each result obtained will be followed by a short discussion, which will indicate what the next experiment was to be.

In all the runs reported in this section, the temperature was 25°C and the initial concentration of silver nitrate and ethyl iodide in the reaction solution was 0.001M. The solution was always (except where stated) 0.02M with respect to potassium nitrate and the cell was always full. All the rates quoted are in mole liter^{-1} min.$^{-1}$

1) Platinum Disc

A 5.7 cm. diameter stainless steel disc, with a platinum undersurface was used (Fig. 4.11). The platinum had a bright, smooth machined finish, and was washed in acetone and much distilled water before the run. The stainless steel was wiped before use with a Kleenex moistened with carbon tetrachloride.

Two runs were done, both at 400 r.p.m., the second one because the disc had rotated rather eccentrically during the first. A new Hostaflon insert cured this fault for the second run. The measured rates were 0.49×10^{-6} and 0.50×10^{-6}, thus showing no measurable catalytic effect.

2) Silver Disc

A disc with a silver surface was prepared by plating the above platinum disc by means of the cell[69]:

disc	$KAg(CN)_2$,	KNO_3	KNO_3	$KAg(CN)_2$,	KNO_3	Pt	5.1
	0.065M	0.05M	1M in agar	0.065M	0.05M		

The KNO_3 was added to the silver plating solution to reduce the electrical resistance and permit larger currents to pass. The disc was made the cathode, and an average current of 17mA was passed for 16 hours. The solution in the cathode compartment was stirred during plating.

The stainless steel of the disc was protected from the plating process by previously covering it, to the edge of the platinum, with Perspex solution (I.C.I. Plastics Division) which dried to form a hard impermeable coat. It did not, however, seal to the metal at the edge of the coat, and this was done by means of polystyrene cement. This composite coating had the advantage that it could be peeled off easily after the plating. The platinum surface was cleaned as in (1) before the plating process.

After plating, the disc was washed twice in a small quantity of 0.880 ammonia followed by a large quantity of distilled water. The Perspex and polystyrene were removed and the disc rewashed in distilled water. The measured rate of reaction at 400 r.p.m. with this disc was 0.49×10^{-6}, indicating once again the absence of catalysis.

Discussion

From microscopic studies (Chapter 3), the surface area of silver and platinum powder added to the reaction mixture in the small cell appeared to be ca. 110 cm^2. The geometric area of the disc used was 27 cm^2. Allowing for the difference in volume of the two cells (90 ml. compared with 780 ml.), the reduction in catalytic activity using the disc would be ca. 1:36. Now powdered Pt increased the rate by about 300% and Ag by ca. 100%, so the increases in rate caused by the discs were expected to be 8% for Pt, and 3% for silver. Thus, although no observable effect would be anticipated for the silver disc, the platinum disc should give a measurable increase in rate. That it did not may have been due to (i) inaccuracy of the surface area measurement, (ii) contamination of the Pt surface, (iii) a difference in the catalytic activity per $cm.^2$ between the powder and the disc.

3) Silver chloride disc

The construction of this disc is described in Chapter 4. A cut was taken across the face of the disc, using a clean unlubricated tool, on a lathe, to expose a new surface. The disc was then stored in tissue in the dark until use. Before the run the upper surfaces of the disc were wiped with a tissue moistened in carbon tetrachloride. The measured rate was 0.48×10^{-6} at 400 r.p.m., being in agreement with the 'homogeneous' rate, within experimental error.

Discussion

It was thought that this failure to catalyse the reaction might be due to contamination of the silver chloride surface, since freshly prepared silver chloride powder (Table 3.4) increased the rate 58 fold.

A fresh cut across the catalytic surface was therefore taken, and the surface washed in acetone followed by distilled water. The upper surface was treated as above. The measured rate, at 400 r.p.m., was 0.49×10^{-6}.

For a third run, a fresh surface of silver chloride was exposed by washing the disc for 3-4 minutes in 0.5M sodium thiosulphate solution. The disc was then washed in water, and the upper surface cleaned as before. The measured rate of reaction, at 400 r.p.m., was again 0.49×10^{-6}.

Discussion

Three possible reasons for the lack of catalytic activity of the disc were considered:

(i) the surface area of the silver chloride disc was insufficient to give rise to a measurable increase in rate,

(ii) the surface of the fused silver chloride was far less active, per unit area, than the silver chloride powder used in the semi-quantitative studies,

(iii) the disc surface had been badly contaminated during each run, despite the cleaning and precautions taken.

Before investigation of these possibilities, the effect of a silver sulphide disc upon the reaction was studied.

4) Silver sulphide disc

A disc with a silver sulphide surface was prepared using the 5.7 cm. platinum disc and the method described in section 5(c). The disc was first plated with silver and then sulphidised with a 0.1M solution of sodium sulphide (B.D.H. recrystallised). This solution was slightly cloudy and was filtered before use. A current of 4-6 mA was passed for $4\frac{1}{2}$ hours and the surface of the disc became a uniform blue-black colour. The Perspex and polystyrene covering on the stainless steel was stripped off, and the disc washed and stored in distilled water before use. It was noted that part of the disc surface did not wet properly before the run was done. This area increased after the run from about a tenth to about half of the disc's surface. The rate, using this disc, at 400 r.p.m., was again 0.49×10^{-6} .

The possible reasons for the lack of activity of this disc were thought to be similar to those put forward to explain the lack of activity of the silver chloride disc. Since silver iodide had been found to be the best catalyst for the reaction, a disc of this material was then made and its effect on the rate of reaction studied in more detail.

5) Silver iodide disc[69]

(a) The 5.7 cm. diameter Pt disc was plated with silver using cell 5.1, and a current of 19mA for about 24 hours. The stainless steel was protected this time by insulation tape sealed at the edge with polystyrene cement. After plating, the silver was washed with 0.880 ammonia followed by distilled water. The disc was then anodically iodised in a 0.1M solution of potassium iodide, with a fresh 1M KNO_3 agar salt bridge. A current of 7mA was passed for 25 hours in the dark, the solution being stirred all the time. The surface appeared to be a fairly uniform greenish colour after being washed in distilled water, in which it was then kept until used. The upper surface was stripped of its covering and cleaned with a tissue moistened with carbon tetrachloride. The measured rate of reaction, at 400 r.p.m., was 0.505×10^{-6}.

Discussion

A possible reason both for the rate and for the green colour was that during the iodisation the potential at the disc surface had risen high enough for iodine to be formed, which might have poisoned the catalytic surface. A check was made on the identity of the material on the surface of the disc by measuring its potential (with a Radiometer pH meter 4 used as a potentiometer) against a saturated calomel electrode, an experiment which gave $E_{disc} = -0.082V$ at 21.8°C. The calculated potential for a Ag/AgI electrode in 0.1M KI solution at 25°C is -0.085V.[67] Thus it appears that the surface coating was silver iodide.

(b) To ensure that iodine was not being formed, the disc was then stripped down to the platinum, replated with silver as before, a current of 16.5mA being passed for 17 hours. It was iodised in the presence of light, but this time the potential at the disc surface was monitored continually, using the cell:

Disc	KI	KNO_3	KCl	Calomel	5.2
	0.1M	0.25M	Satd.		

The potassium nitrate salt bridge was a U-shaped glass tube with a Beckman porous plug (similar to those used for the reaction cell) at each end, filled with 0.25M potassium nitrate solution. One plug was placed as close as possible to the disc surface to minimise ohmic drop in the circuit.

The measured e.m.f. of cell 5.2 was:

0.330V, when no current was flowing in the iodising circuit, initially and after 5 hours.

0.293V, when a current of 7mA was flowing in the iodising circuit, initially.

0.242V, when a current of 7mA was flowing in the iodising circuit, after the iodisation had proceeded for 5 hours.

The iodisation was stopped after 5 hours to prevent iodine being formed, and the disc treated as in the last run before use. The silver iodide surface appeared to be more yellow than in (a). A kinetic run with this disc again gave a measured rate of reaction of 0.49×10^{-6} at 400 r.p.m.

Discussion

The calculated e.m.f. of cell 5.2 at 25°C, taking $E^{o}_{Ag/AgI}$ = −0.1518V,[67] E_{cal} = 0.2445V, and f_{I^-} = 0.7543, is E = 0.333V. This agrees well with the measured value and indicates that silver iodide was indeed being formed on the surface. Even when current was passing, though, the potential was not nearly positive enough to liberate iodine:

$(E^{o} = 0.5355V \text{ for } I_2 + 2e \rightleftharpoons 2I^{-})$

To check whether the rotating disc had any catalytic activity, a run was done with it by a coworker in the laboratory (Mrs. M.D. Archer) to catalyse the reaction

$$Co(NH_3)_5Br + H_2O \longrightarrow Co(NH_3)_5OH + HBr \qquad 5.3$$

which had previously been shown to be catalysed by silver iodide powder. The disc increased the rate of reaction by 215% at 400 r.p.m. and by 150% at 200 r.p.m., showing that the catalytic effect was proportional to $\omega^{\frac{1}{2}}$. The reaction was therefore transport controlled. A rough calculation using equations 1.5 and 1.6 indicated that the surface of the disc possessed only 10-20% of the catalytic activity expected for a transport controlled reaction, so that a large part of the surface was contaminated.

A similar calculation was made for the $AgNO_3$ + EtI reaction, with $D = 1.8 \times 10^{-5}$ cm.^{2} sec.$^{-1}$, $A = 30$ cm.^{2}, $V = 800$ cm.^{3}, $\delta = 0.5 \times 10^{-3}$ cm., and $c = 10^{-3}$M. This gave $-dc/dt$ = ca. 8.1×10^{-5} mole liter^{-1} min.$^{-1}$ Thus even if the disc had been 90% contaminated the measured rate would have been ca. 8×10^{-6}, i.e. 16 times greater than the 'homogeneous' rate. It follows that the rate of the $AgNO_3$ + EtI reaction was not transport but surface controlled, and it therefore seemed likely that there was insufficient surface present on the disc to give a measurable increase in rate.

Before any surface area measurements were attempted, to verify the above hypothesis, other possible causes of the lack of activity of the disc were examined. These were:

1) Contamination of the disc surface. This possibility could only be eliminated by the most stringent precautions during the preparation of the disc. Two possible sources of contamination were the agar bridge used in the plating process, and the silicone grease which lubricated the shaft sealing assembly.

2) Leakage of electrical charge from the disc surface during a run. It was postulated that a high charge density at the silver iodide surface was necessary for catalysis to occur. No attempt had been made so far to isolate the disc electrically, and this may have been the cause of the lack of catalytic activity.

3) The possible difference in the catalytic activity/cm.^{2} between electro-deposited and powdered silver iodide. If the reaction were transport controlled this would be irrelevant, but for surface control it could be critical.

What little information is available concerning the structure of electro-deposited silver halides pertains to silver chloride and bromide. Huber[102] concluded, from electron microscopy studies on anodically deposited films of these materials, that silver halide films formed in this way were 'locked' surfaces, i.e. they were non-porous. In addition, work on electroplated silver chloride by Sowerby[101] shows that a low index face is exposed.

Studies on the exchange of isotopic iodine between $CH_3{}^{131}I$ and silver iodide precipitates[96] prepared in various ways indicated that the surfaces acted uniformly, i.e. the phenomenon of active sites was absent. So far, however, the relationship between the catalytic activity of a silver iodide surface and its structure has not been investigated.

(c) In order to test (1) above, the disc used in (b) was stripped down to the platinum and then replated and iodised as in (a). The agar bridge was replaced for both processes by a 2M potassium nitrate solution in a U-shaped glass tube. At each end of the tube a capillary was introduced to reduce the flow of liquid through the tube. In addition, the upper surface of the disc was protected with Perspex cement sealed at the edge by polystyrene cement, instead of the insulating tape used in (a) and (b).

The disc was yellow when newly iodised, but on being stored in distilled water for a day before use it became somewhat more green.

A run with this disc, in the absence of potassium nitrate from the reaction solution (to avoid any impurities introduced with this salt), gave a rate at 400 r.p.m. of 0.60×10^{-6} (compared with 0.65×10^{-6} for the 'homogeneous' rate under these conditions).

The disc, shaft, and shaft sealing assembly were then washed in triethylamine to remove silicone grease, and then in distilled water. The run was repeated, the silicone grease being replaced by Apiezon M. The rate was 0.72×10^{-6}.

Discussion

It had been thought that the potassium nitrate added to the reaction solution might be inhibiting the reaction in some way, but this does not appear to have been the case. No explanation can be advanced for the apparently low result of the first run, except that the reaction is rather irreproducible in the absence of potassium nitrate (Table 5.1). Little attention should be paid to the results of the second run, since silver salts have a well known affinity for amino-compounds, and there might have been an interaction between the disc surface and the triethylamine (the disc was greener after the washing in triethylamine). It would seem prudent, however, to use Apiezon M instead of silicone grease for future work.

The runs reported in this section indicate that contamination of the surface is probably not the reason for the lack of activity of the silver iodide discs.

(d) The hypothesis (2) of the leakage of electrical charge being the cause of the lack of activity of the discs was tested in two ways.

Firstly, the 5.7 cm. platinum disc was replated and iodised as in (c), a yellow surface being formed. A run was done in which the disc was isolated electrically (the resistance between the disc and the shaft to which it was attached, measured before the run with an Avometer, was greater than 1 megohm). The rate, at 400 r.p.m., was 0.495×10^{-6}.

Secondly, a silver iodide disc was made by sticking, with Perspex cement, a piece of silver foil to the undersurface of the blank disc. A connection was made to the disc by soldering a piece of wire to the silver, and it was iodised anodically as in (c) until electrical connection failed because the area around the solder had been completely converted to the iodide. The solder was then removed, leaving an unplated area of ca. 1 cm^2. at the side of the disc. The colour of the disc was green. At 400 r.p.m., the rate was 0.51×10^{-6}.

Discussion

These two runs strongly suggested that the inactivity of the discs was not due to charge on the silver iodide surface leaking away to earth.

(e) Two experiments were carried out to compare the catalytic activity/gm. of electro-deposited and powdered silver iodide (3). In the first, the silver iodide from the surfaces of the discs used in (a), (b), and (c) was powdered in a glass beaker with a glass rod, and 1.28 gm. added to the reaction mixture in the small cell (initially 0.001M in $AgNO_3$ and EtI, and 0.02M in KNO_3). The initial rate of reaction was 2.4×10^{-6}, some 5 times the 'homogeneous' rate.

Discussion

This result shows that the powder was a catalyst. However, 2.4 gm. of B.D.H. silver iodide powder had given rise to a rate of 38×10^{-6} (Table 3.4) indicating that the powder used in this run was far less active. This was at least partly due to a much smaller surface area/gm., as could be seen from the size of the particles in the cell.

In the second experiment, a disc was prepared from B.D.H. silver iodide powder. The powder was ground up, washed in hot dilute nitric acid (to remove any silver present), and then in distilled water, and dried at 80°C. Prior to washing it had looked a greenish colour, similar to the electroplated discs (a) and (b). The blank disc was stripped of its silver iodide coat (section d), and a layer of Perspex cement applied to the plane under-surface and a thick layer of the powder spread over it. After drying at room temperature, the excess silver iodide was shaken off, and that adhering to the disc was smoothed using a clean wet spatula. The surface appeared yellow, and very uneven. A run with the disc gave a rate, at 400 r.p.m., of 1.21×10^{-6}, which fell to 0.98×10^{-6} on reducing the velocity of rotation to 100 r.p.m., and fell further, to 0.87×10^{-6}, on restoring the velocity of rotation to 400 r.p.m. Clearly the catalytic activity was decreasing with time.

The surface of the disc was smoothed further by rubbing it wet against a plane glass surface. A run, at 100 r.p.m., gave a rate of 0.92×10^{-6} which fell to 0.81×10^{-6} on increasing the rotation velocity to 400 r.p.m., confirming the independence of the rate of reaction from the speed of rotation.

Discussion

It appears from the above that:

(i) either the reaction is not transport controlled, or

(ii) the surface was too rough to act in accordance with theory, in which case it would be acting in a manner similar to the powder.

It is not possible to compare the activity of this disc with that of the electrodeposited ones, since the surface of this disc was so rough that its area was probably much greater than that of those used in (a), (b), (c), and (d).

The results obtained so far with the silver iodide discs all strongly suggest that the reaction is surface controlled, and that the reason for the lack of activity of the discs is that there was insufficient surface present to cause a measurable increase in the rate of reaction. Thus, a determination of the surface area of silver iodide powder was now essential.

(f) The surface area of silver iodide powder was estimated in two ways.

(i) A rough estimate was made using the microscopic technique reported in Chapter 3. The size of the particles of B.D.H. silver iodide fell into two distinct ranges, the smaller particles being ca. 10^{-3} cm. across, and the larger ones ca. 3×10^{-2} cm. The ratio of small to large was about 20:1. Assuming the particles to be spherical the surface area per gram of powder is 34 cm^2.

(ii) A determination was made by means of the exchange of ^{131}I between the surface and a solution of potassium iodide (reported fully in Chapter 6), which gave a value for the surface area of $19m^2 \pm 1m^2$ per gm. for B.D.H. silver iodide powder, the particle size of which was less than 76μ.

Discussion

The results of (ii) above agree to an order of magnitude with the result of exchange experiments and B.E.T. determinations by other workers on other silver iodide samples.[96] It appears from these results that the particles measured in (i) were really aggregates of crystals, which would break up to the individual crystals in solution (Chapter 6). Thus this value for the surface area bore no relation to the real surface area in solution.

From a value of $19m^2/gm.$ it can be calculated that the increase in rate which would be expected in the experiments with a 5.7cm. silver iodide disc would be 0.026%. This value is obtained from a comparison with the increase in rate produced by a known surface area of silver iodide powder (Chapter 6, Table 6.1). Thus even if the surface area determination was in error by two orders of magnitude, the increase in rate would be barely detectable.

Conclusions

The results reported in this chapter show that the silver nitrate and ethyl iodide reaction occurring at a surface is controlled by the surface processes and not by the transport of reactants to the surface.

The possibility of complete contamination of the surface, and the leakage of electrical charge from the surface, as reasons for the lack of activity of the discs, have been discounted. The possibility of the difference of catalytic activity between electro-deposited and powdered silver iodide remains but, in view of the small surface area of the disc (section f), cannot be tested at present. An obvious possibility for future work here is the investigation of the relationship between the type of surface and its catalytic activity, a topic which has been studied in the heterogeneous catalysis of some gas reactions.

Logically, the next step of the present investigation is an examination of the kinetics of the reaction between silver nitrate and ethyl iodide at a silver iodide surface, using AgI powder. The method and results of this work are reported in Chapter 6.

Chapter 6

QUANTITATIVE STUDIES USING SILVER IODIDE POWDER

The rotating disc studies related in Chapter 5 yielded no quantitative information concerning the mechanism of catalysis, except that the reaction was surface controlled. A series of experiments was therefore undertaken with silver iodide powder in order to elucidate the kinetics and mechanism of the reaction at the surface. For this study, a batch of silver iodide was specially prepared, and its surface area was measured.

Preparation of Silver Iodide Powder

About 200 grams of B.D.H. silver iodide powder were purified for use in this series of experiments. The powder was first ground up, in a pestle and mortar, as finely as possible. It was thoroughly washed in hot dilute nitric acid to remove any silver on the surface (it had looked rather black in parts before grinding). It was then washed thoroughly in distilled water and dried in the oven at 80°C for eight hours. After this it was reground using a glass pestle and mortar (to prevent contamination with any catalytically active material). Finally, it was sieved, using a series of mechanical sieves, to separate it into batches of particle size: less than 76μ(200 mesh), 76-250μ(60 mesh), 250-600μ(25 mesh), and greater than 600μ. In this way, it was hoped to obtain powder of a fairly uniform particle size which could be used in a series of quantitatively comparable runs, and whose surface area could be determined. It was found that most of the powder was in the 'less than 76μ' batch, and this was the powder used for the series of kinetic runs described below. It was stored in a tightly stoppered bottle in the dark.

SURFACE AREA DETERMINATION

The surface area of $<76\,\mu$ silver iodide powder, prepared as above, was measured by means of $^{131}I^-$ ion exchange between the solution and the surface.

Theory[94]

At equilibrium:

$$\frac{\text{Moles of } ^{131}I^- \text{ on the surface}}{\text{Moles of } ^{131}I^- \text{ in solution}} = \frac{\text{Total moles of } I^- \text{ on the surface}}{\text{Total moles of } I^- \text{ in solution}}$$

The number of moles of $^{131}I^-$ in solution is proportional to the radioactive count of the solution, so that,

$$\frac{a - b}{b} = \frac{\text{Total moles of } I^- \text{ on the surface}}{\text{Total moles of } I^- \text{ in solution}} \qquad 6.1$$

where a is the radioactive count in unit time of a solution containing $^{131}I^-$ ions before exchange

b is the radioactive count in unit time of a solution containing $^{131}I^-$ ions when exchange equilibrium is reached

If the number of moles of I^- in solution is known, therefore, the number of moles on the surface, and the surface area, can be determined.

A practical difficulty arises here, because the $^{131}I^-$ may also exchange with I^- ions below the surface of the powder, and give an erroneously large value for the surface area. The amount of exchange occurring at different times is therefore determined, since the surface exchange should occur faster than the exchange with the crystal interior (a process which involves diffusion in the solid). A plot of the amount of exchange against time should therefore show when the former process is complete.

There is also the problem of adsorption of the I^- ions by the solid. If this is extensive, the number of moles of I^- in solution at exchange equilibrium must be determined directly, for substitution in equation 6.1. Also, the calculated number of moles of I^- on the surface must be corrected for the number of moles adsorbed before the surface area can be calculated.

Experimental

A standard solution of 5×10^{-3} M potassium iodide was prepared, containing sufficient $^{131}I^-$ ions (0.1mc from the Radiochemical Center, Amersham) to give a count of about 140000 (all values of counts given will be per 1000 seconds). 50 ml of this solution was placed in each of six tubes fitted with ground glass sockets and stoppers. 1 gm of $<76\mu$ AgI powder was added to each of five of these, and to the sixth was added 1 gm of 250 - 600μ powder. All the tubes were shaken vigorously by hand for one minute and then tumbled mechanically for various lengths of time. After tumbling, the mixture was centrifuged, and an aliquot of the solution counted. This was done by pipetting, using a micro-syringe, 0.4 ml. on to an aluminium planchet. The liquid was evaporated off under an infra-red lamp and the residue was counted using a Geiger-Müller end window tube (MX/123 + probe unit, Ekco type N558b) with a dead time of 300 μsec., and an Ekco type N530E scalar. The E.H.T. source was 600 V, and the discriminator voltage 5 V. The standard solution was counted in the same manner. The values so obtained were corrected for background count, and dead time, and are presented in Table 6.1. The decay of the iodine isotope during the period of the experiment (ca 6 hours) was calculated to be less than 5%, and was neglected. The concentration of iodide ions in the solution after exchange was not measured, and has been assumed for the purpose of the calculation to be 5 x 10^{-3} M (this is reasonable since a similar experiment using ^{110}Ag was carried out, and the total silver ion concentration in solution after exchange was found to be the same as before). The number of I^- ions on the surface was calculated from equation 6.1.

Table 6.1

Sample	Mass (gm)	Period of Tumbling (Min.)	Count per 10^3 sec.	Corrected count per 10^3 sec.	Calculated No. of I^- ions/gm.
Stock soln.			142,800	148,915	
<76μ AgI	0.9997	0	125,948	130,623	1.85 x 10^{19}
"	0.9985	15	102,085	105,037	4.44 x 10^{19}
"	1.0008	30	91,080	93,366	8.96 x 10^{19}
"	1.0049	60	80,450	82,167	12.23 x 10^{19}
"	0.9988	180	69,850	71,079	16.48 x 10^{19}
250-600μAgI	0.9966	15	122,222	126,608	2.25 x 10^{19}

The values in the last column of Table 6.1 were plotted against time (Fig. 6.2). Point A on this graph shows the point at which the surface exchange reached equilibrium. (It is thought that the one minute point is relatively high because the mixture was shaken vigorously for the whole of its period of agitation). The line of smaller slope then represents the exchange of $^{131}I^-$ within the interior of the crystals, the line of steeper slope representing the sum of this process and the surface exchange. Thus, by extrapolating the former to zero time we may obtain a value which represents the total number of I^- ions on the surface. This value, from

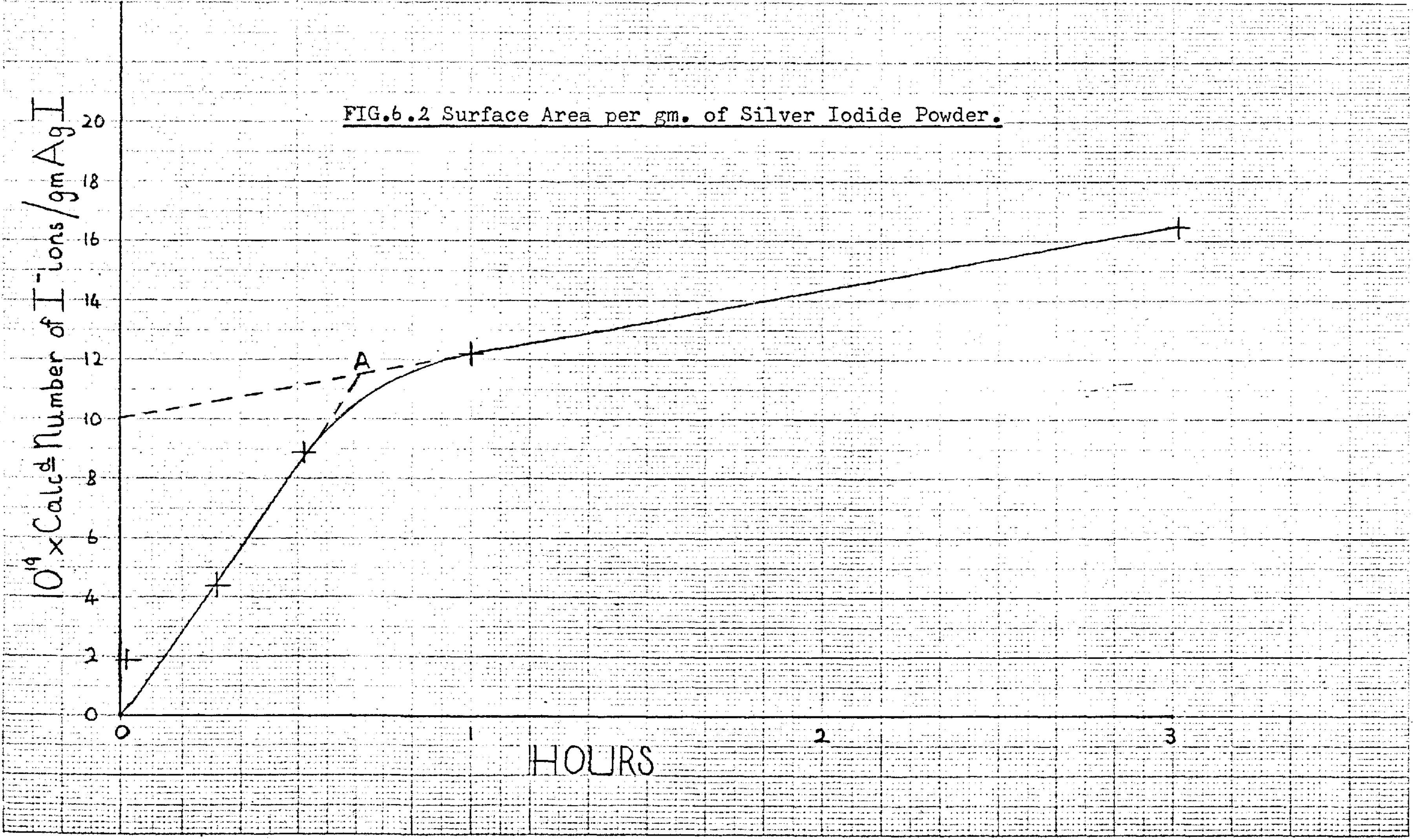


FIG.6.2 Surface Area per gm. of Silver Iodide Powder.

Figure 6.2, is $(10.1 \pm 0.4) \times 10^{19}$ ions/gm. Assuming a 1 : 1 correspondence of silver and iodide ions on the surface, and taking the ionic radii of silver and iodide as 1.26Å and 2.16Å respectively,[70] the surface area of powder = $19.8 \pm 0.8 m^2 gm^{-1}$. This agrees, to an order of magnitude, with measurements made by other workers on silver iodide powders[96] using the same technique and $^{131}I^-$, and to two orders of magnitude with B.E.T. measurements by the same workers.

From a comparison of the run done with 250 - 600μ powder with those using <76μ powder, it appears that the surface area/gm is approximately half that of the finer powder. This value is not a reliable one, however, because measurements were made at one time period only, and a series of separate determinations should be made.

A determination of the surface area using the same technique and ^{110}Ag was attempted. The value obtained for the surface area was $3.3 \times 10^2 m^2 gm^{-1}$, so that about 70% of the silver iodide present appeared to be on the surface. This is quite unreasonable, and it was clear that considerable exchange of silver ions between the solution and the interior of the crystals had occurred. That silver ions diffuse through the crystal much more quickly than halide ions is evident from the fact that the transport number of the silver ion in solid silver halides is very nearly unity.[97,98]

KINETIC EXPERIMENTS

Apparatus

The apparatus was basically that used in the rotating disc studies. The sole difference was that the rotating disc was replaced by a glass paddle (Fig. 4.12), which was attached to the shaft by means of a rubber sleeve. Thus the solution could be stirred at a known velocity. The paddle was placed in the cell in the same manner as the rotating discs (see Technique of Filling, Chapter 4), except that, when the cell was being fastened up, it rested on the bottom with the sleeve leaning against the inside of the B 34 socket in the lid, instead of being suspended from the socket.

The silver iodide powder was put into the cell at the same time as the potassium nitrate crystals, and the silver nitrate solution was then added. The whole mixture was stirred for up to 90 minutes at 400 r.p.m. before the addition of the ethyl iodide solution. This procedure was found necessary because adding the solution to the powder in the vessel caused some coagulation of the latter into small lumps. These lumps were broken up during the stirring. It was, however, found to be impossible to prevent a small proportion (ca. 5%) of the powder from floating on top of the solution.

Except for the above, the filling of the cell was exactly as detailed in Chapter 4.

Results

The results of the series of experiments are given in Table 6.2. All the runs were carried out at 25°C and in the presence of 0.02M potassium nitrate. The volume of solution was 800 ml.

Table 6.2

Run	$[AgNO_3]_o$ (M)	$[EtI]_o$ (M)	Stirring Speed (r.p.m.)	Type of Powder	Mass added (gm.)	Initial Rate x 10^6 (mole liter^{-1} min.$^{-1}$)	Initial Heterogeneous Rate x 10^6 (mole liter^{-1} min.$^{-1}$)
1	0.00101	0.001	400	none	-	0.548	
2	"	"	"	none	-	0.533	
3	0.001	"	600	<76μ	1.25	1.71	1.17
4	"	0.002	"	"	"	3.30	2.22
5	0.002	0.001	"	"	"	2.58	1.50
6	0.004	"	"	"	"	4.40	2.24
7	0.002	0.002	"	"	"	4.80	2.64
8	0.0005	0.0005	"	"	"	0.534	0.40
9	0.001	0.001	"	"	2.5	2.85	2.31
10	"	"	"	"	0.625	1.02	0.48
11	"	"	400	"	"	1.04	0.50
12	"	"	600	250-600μ	5.0	3.33	2.79

The initial heterogeneous rates of reaction are derived from the measured rates by subtracting the rate of the appropriate 'homogeneous' reaction. The values subtracted were:

Table 6.3

$[AgNO_3]_o$ (M)	$[EtI]_o$ (M)	Value subtracted x 10^6 (mole liter^{-1} min.$^{-1}$)
0.001	0.001	0.54
0.002	"	1.08
0.001	0.002	1.08
0.002	"	2.16
0.0005	0.0005	0.135

In Table 6.3 only the first value was measured experimentally, the rest being calculated on the assumption (Chapter 3) that the 'homogeneous' reaction was first order in both silver nitrate and ethyl iodide.

It should be noted that values subtracted in Table 6.2 to give the heterogeneous rate may be inaccurate. The reason for this is that if a significant proportion of the reactants are adsorbed on the surface of the powder, their concentrations in solution will be smaller than their initial concentrations. Thus, the corrections for the 'homogeneous' rate will be smaller than the values given in Table 6.3, and the values of the heterogeneous rates will be correspondingly larger. The best way to minimise this error in future experiments is to use a smaller surface area of catalyst, and to reduce the 'homogeneous' rate by working at low temperatures.

A second error arises from the state of the catalyst. Some catalyst (ca. 5%) remained floating on top of the solution during a run, and the state of subdivision of the powder in the solution is not well known.

It has been assumed in this series of runs that if two solutions were stirred for the same length of time before the addition of the ethyl iodide solution to the cell, the state of subdivision of the powder would be the same.

Conclusions

A plot of the initial rate of reaction from runs 3,9, and 10 (Table 6.2) is given in Fig. 6.1. It can be seen that the rate of the heterogeneous reaction is directly proportional to the mass of catalyst, and therefore to the surface area present. This would be expected whether the reaction was surface or transport controlled, since the rate equations for both involve a surface area term. Runs 10 and 11, however, confirm the conclusion reached in Chapter 5 that the heterogeneous reaction is surface controlled.

From runs 3,4,5,6, and 8 (Table 6.2), the rate law for the reaction at the surface appears to be

$$\text{Rate} \propto [AgNO_3]^{0.5}\,[EtI] \qquad 6.2$$

However, if runs 4,5,and 7 are considered, the apparent rate law is

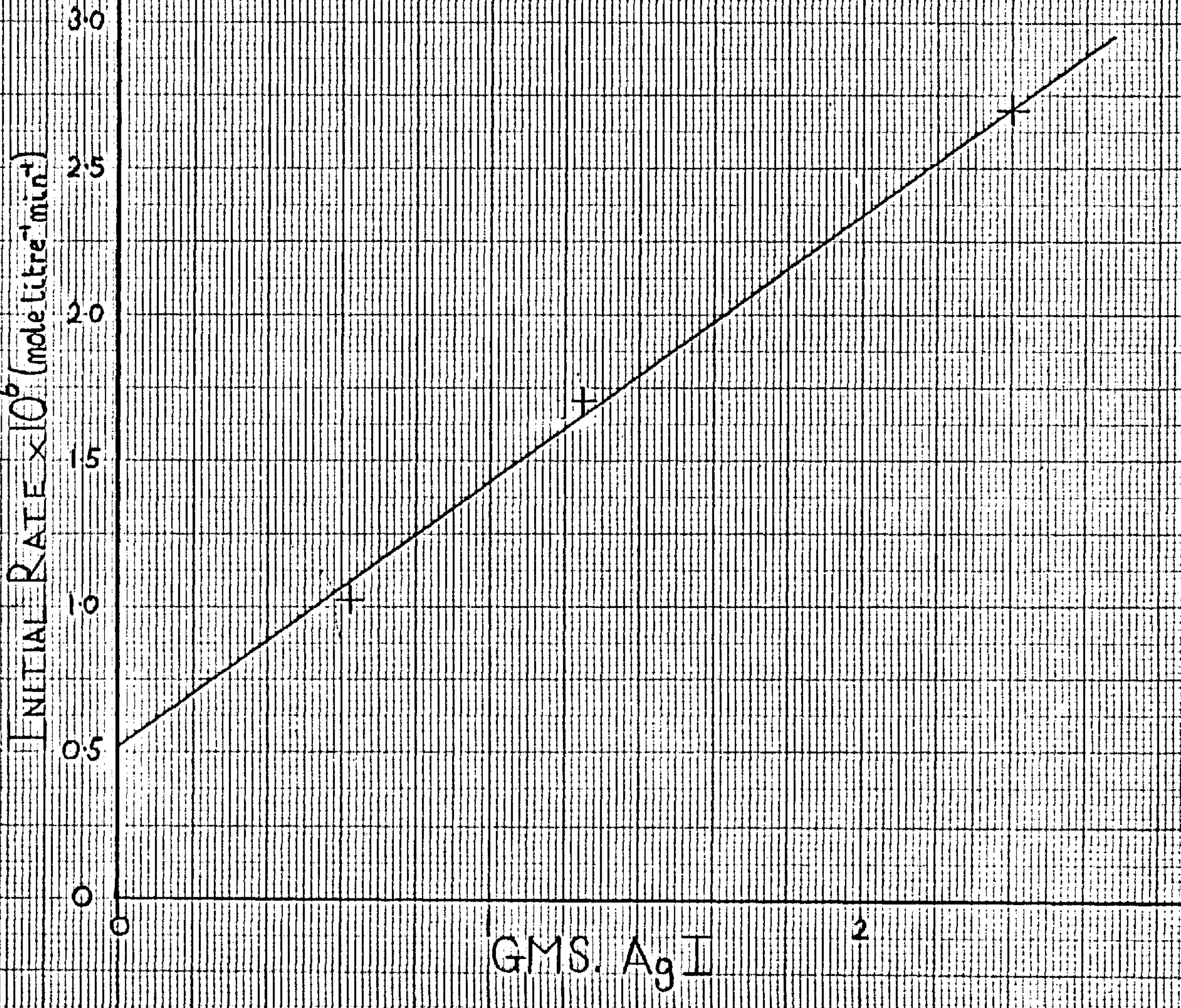
$$\text{Rate} \propto [AgNO_3]^{0.25}\,[EtI]^{0.82} \qquad 6.3$$

Thus, the indices decrease as the concentrations at which the relation was determined increases. According to the Rideal mechanism[12] the index of only one reactant concentration should decrease with increasing concentration, and the other should remain equal to unity (Equation 1.10).

On the other hand, the Langmuir-Hinshelwood[11] mechanism predicts that, if both reactants are fairly strongly adsorbed on the surface, the order of reaction for both will tend to zero as the concentration in the bulk phase increases (Equation 6.4). The above results are consistent with

FIG. 6.1 $AgNO_3$ + EtI SYSTEM.

Influence of mass of AgI added on the initial rate



the latter mechanism, and not the former.

Consider, therefore, the Langmuir-Hinshelwood mechanism for the reaction at the surface. Let us assume that both reactants are fairly strongly adsorbed on the surface (a postulate confirmed by later adsorption experiments), so that the rate of reaction is given by[11]

$$\nu = k_o\left(\theta_{Ag^+}\right)\left(\theta_{EtI}\right)A \qquad 6.4$$

where θ_{Ag^+} is the fraction of the surface covered by Ag^+ ions

θ_{EtI} is the fraction of the surface covered by EtI molecules

and A is the surface area (m^2). ν is in mole min^{-1}, and k_o is in mole min^{-1} m^{-2}. This rate is related to the measured rate of the heterogeneous reaction (Table 6.2) which is given by

$$\frac{d\left[H^+\right]}{dt} = \nu^1 = \frac{1000}{V}\, k_o^1 \left(\theta_{Ag^+}\right)\left(\theta_{EtI}\right) \qquad 6.5$$

In equation 6.5, V is the volume of the reaction solution in cm^3, and ν^1 and k_o^1 are in mole $liter^{-1}min^{-1}$. Comparing 6.4 and 6.5 we see that

$$\nu = \nu^1 \times V/1000 \qquad 6.6$$

$$k_o^1 = k_oA \qquad 6.7$$

The values of θ_{Ag^+} and θ_{EtI} may be derived from a Langmuir adsorption isotherm in two ways.

(i) If we assume that the surface available for adsorption of silver ions is independent of that available for the adsorption of ethyl iodide and vice versa, i.e. that each species cannot be adsorbed on the adsorption sites of the other, the equations leading to a Langmuir isotherm are, for unit area of surface:

$$k_{Ag^+} C_{Ag^+} (1 - \theta_{Ag^+}) = k^1_{Ag^+} \theta_{Ag^+} \qquad 6.8$$

and $$k_{EtI} C_{EtI} (1 - \theta_{EtI}) = k^1_{EtI} \theta_{EtI} \qquad 6.9$$

where k_{Ag^+} and k_{EtI} are the rate constants for the condensation of the respective species on to the surface and $k^1_{Ag^+}$ and k^1_{EtI} are the rate constants for the corresponding evaporation. The surface reaction itself is assumed to be the slow step and its rate is neglected in equations 6.8 and 6.9.

From 6.8 $$\theta_{Ag^+} = \frac{k^{11}_{Ag^+} C_{Ag^+}}{1 + k^{11}_{Ag^+} C_{Ag^+}} \qquad 6.10$$

where $$k^{11}_{Ag^+} = k_{Ag^+} / k^1_{Ag^+}$$

Similarly from 6.9,

$$\theta_{EtI} = \frac{k^{11}_{EtI} C_{EtI}}{1 + k^{11}_{EtI} C_{EtI}} \qquad 6.11$$

Substituting 6.10 and 6.11 in 6.4

$$v = \frac{k_o A \, k^{11}_{Ag^+} \, k^{11}_{EtI} \, C_{Ag^+} C_{EtI}}{\left(1 + k^{11}_{Ag^+} C_{Ag^+}\right)\left(1 + k^{11}_{EtI} C_{EtI}\right)} \qquad 6.12$$

Rearranging,

$$\left(1 + k^{11}_{Ag^+} C_{Ag^+}\right) \left(1 + k^{11}_{EtI} C_{EtI}\right) = \frac{K \, C_{Ag^+} C_{EtI}}{v} \qquad 6.13$$

Where $K = k_o k^{11}_{Ag^+} k^{11}_{EtI} A$. Expanding the brackets and neglecting powers of the concentration greater than 1, 6.13 becomes

$$\frac{C_{Ag^+} C_{EtI}}{v} = \frac{k^{11}_{Ag^+}}{K} \left(C_{Ag^+} + \frac{k^{11}_{EtI}}{k^{11}_{Ag^+}} C_{EtI} \right) + \frac{1}{K} \qquad 6.14$$

Thus, by plotting $C_{Ag^+} C_{EtI}/\nu$ against $C_{Ag^+} + nC_{EtI}$ where n is probably about unity, we may test the assumption that the two species are adsorbed independently. This assumption seems to be reasonable since it is unlikely that a silver ion will be adsorbed on a silver ion site or an iodide group on an iodide ion site.

(ii) If we assume that the surface available for adsorption of the silver ion is not independent of the adsorption of the iodide ion, and vice versa, the equations leading to the Langmuir isotherm are, for unit area surface:

$$k_{Ag^+}C_{Ag^+}(1 - \theta_{Ag^+} - \theta_{EtI}) = k^1_{Ag^+}\,\theta_{Ag^+} \qquad 6.15$$

$$k_{EtI}C_{EtI}(1 - \theta_{Ag^+} - \theta_{EtI}) = k^1_{EtI}\,\theta_{EtI} \qquad 6.16$$

leading to

$$\theta_{Ag^+} = \frac{k^{11}_{Ag^+}C_{Ag^+}}{1 + k^{11}_{Ag^+}\,C_{Ag^+} + k^{11}_{EtI}C_{EtI}} \qquad 6.17$$

$$\theta_{EtI} = \frac{k^{11}_{EtI}C_{EtI}}{1 + k^{11}_{Ag^+}\,C_{Ag^+} + k^{11}_{EtI}C_{EtI}} \qquad 6.18$$

Substitution of 6.17 and 6.18 in 6.4 and rearrangement gives:

$$\left(\frac{C_{Ag^+}\,C_{EtI}}{\nu}\right)^{\frac{1}{2}} = \frac{k^{11}_{Ag^+}}{K^{\frac{1}{2}}}\left(C_{Ag^+} + \frac{k^{11}_{EtI}}{k^{11}_{Ag^+}}\,C_{EtI}\right) + \frac{1}{K^{\frac{1}{2}}} \qquad 6.19$$

We may therefore plot $C_{Ag^+} + nC_{EtI}$ against $(C_{Ag^+} C_{EtI}/\nu)^{\frac{1}{2}}$. Figs. 6.3 and 6.4 show plots of $C_{Ag^+} + nC_{EtI}$ against $C_{Ag^+} C_{EtI}/\nu$ and $(C_{Ag^+} C_{EtI}/\nu)^{\frac{1}{2}}$ respectively for values of $n = 0.5,\ 1.0,\ 1.5$.

FIG.6.3

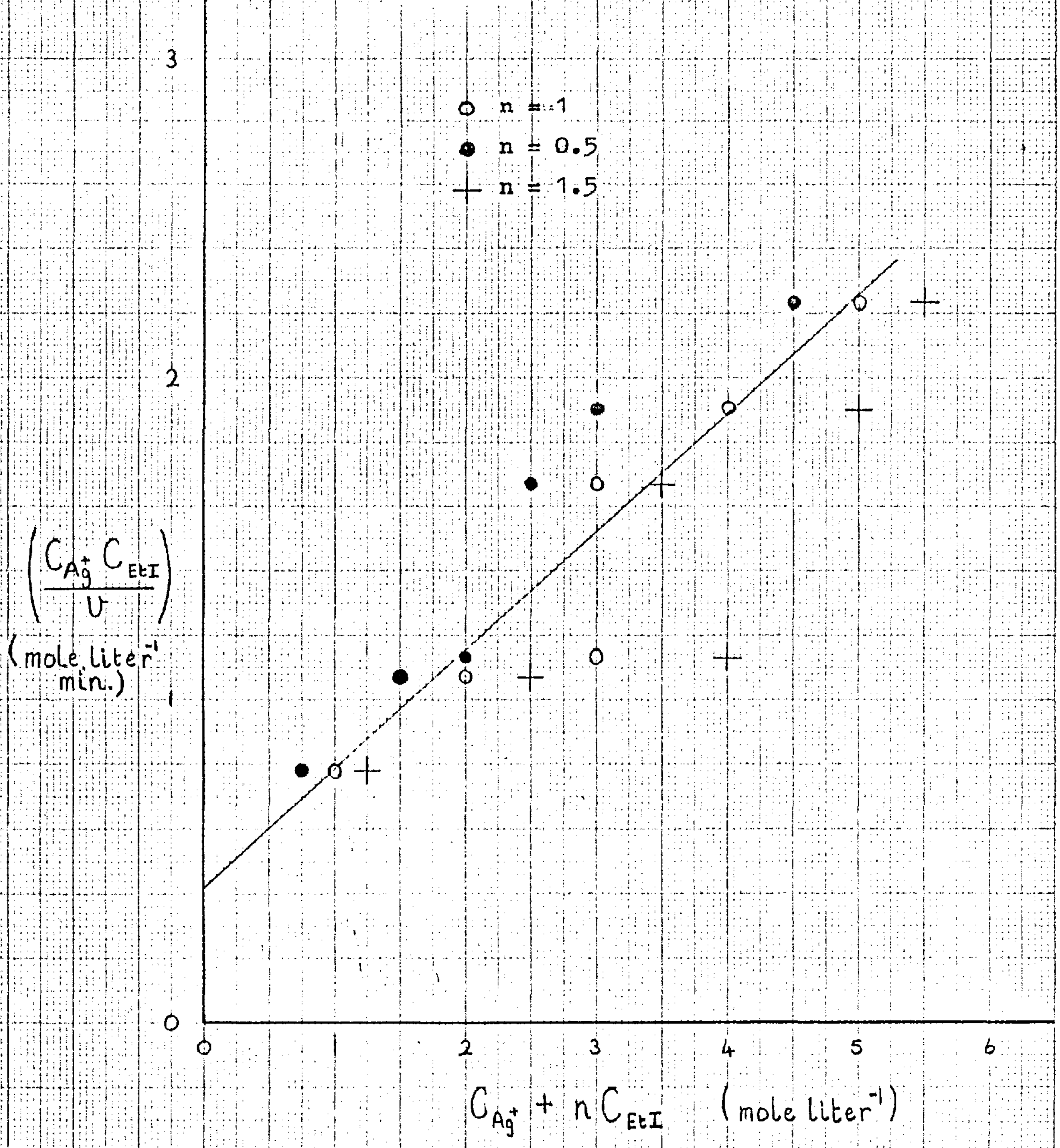
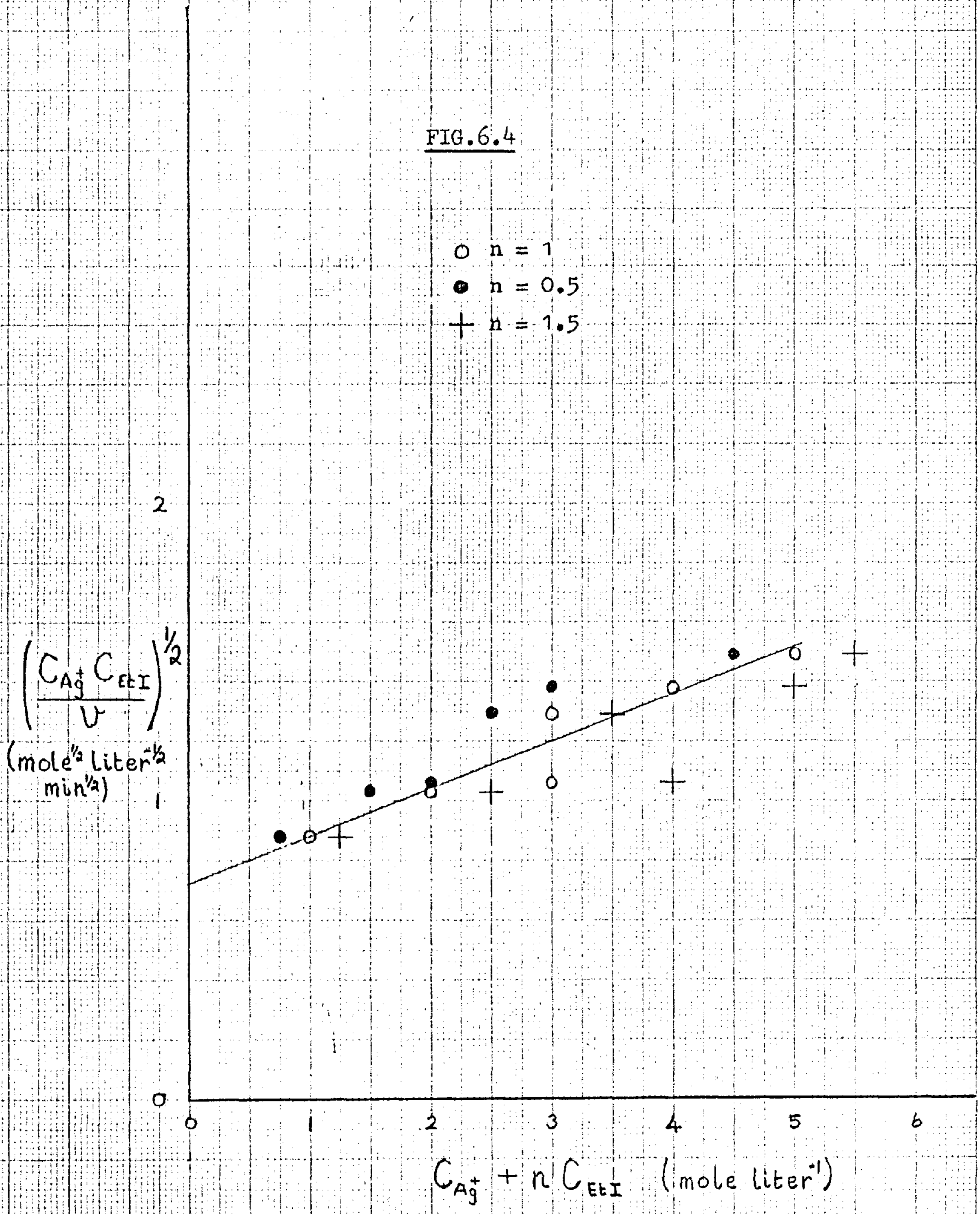

○ n = 1
● n = 0.5
+ n = 1.5
3
2
1
0
$\left(\frac{C_{Ag^+} C_{EtI}}{v}\right)$
(mole liter^{-1} min.)
0
2
3
4
5
6
$C_{Ag^+} + n C_{EtI}$ (mole liter^{-1})

FIG.6.4


○ n = 1
● n = 0.5
+ n = 1.5
$\left(\frac{C_{Ag^+} C_{EtI}}{v}\right)^{1/2}$
(mole$^{1/2}$ liter$^{-1/2}$ min$^{1/2}$)
2
1
0
0
1
2
3
4
5
6
$C_{Ag^+} + n\,C_{EtI}$ (mole liter^{-1})

From an examination of these plots it appears that the best linear fits are obtained when $n \simeq 1$. The fit appears to be rather better in Fig. 6.4 than in Fig. 6.3 but the results are by no means conclusive. This indicates that the adsorption of each species is not independent of the other. A possible explanation is that an ethyl iodide molecule can adsorb on to a site which was an iodide ion originally, but which has adsorbed a silver ion from solution, or that there is some steric hindrance to the adsorption of a silver ion by an ethyl iodide molecule sitting on an adjacent site. The results obtained are only indicative, however, and measurement over a wider range of concentrations must be made before any firm conclusions can be drawn.

The approximate values of $k^{11}_{Ag^+}$, k^{11}_{EtI}, and k_o, the rate constant, when $n = 1$ may be calculated from Figs. 6.3 and 6.4 and are given in Table 6.4. The values of k_o refer to a velocity measured in the presence of 1 m^2 of silver iodide surface in 1 liter of solution.

Table 6.4

Mechanism	Fig.	$k^{11}_{Ag^+}$ (liter mole^{-1})	k^{11}_{EtI} (liter mole^{-1})	k_o (mole min.$^{-1}$ m.$^{-2}$)
Independent adsorption	6.3	0.86	0.86	0.13
Non-independent adsorption	6.4	0.22	0.22	1.58

In order to test which model for θ_{Ag^+} and θ_{EtI} is the correct one, adsorption isotherms should be measured for each species in the presence of the other. This task will be greatly complicated by the simultaneous occurrence of the reaction being studied, and may be impossible to execute with any accuracy. However, useful information may also be obtained from the individual adsorption isotherms.

ADSORPTION ISOTHERMS

An attempt was made to determine the adsorption isotherm of silver ions on $<76\mu$ silver iodide powder. The purpose of this was to verify the assumption that silver ions were strongly adsorbed on this surface, and to determine the value of $k^{11}_{Ag^+}$ in the absence of ethyl iodide.

The determination was carried out by adding a known amount of silver ions to a known volume of solution containing a known surface area of silver iodide powder (the $<76\mu$ powder used in the kinetic runs), allowing the system to equilibrate, and measuring the concentration of silver ions remaining in solution.

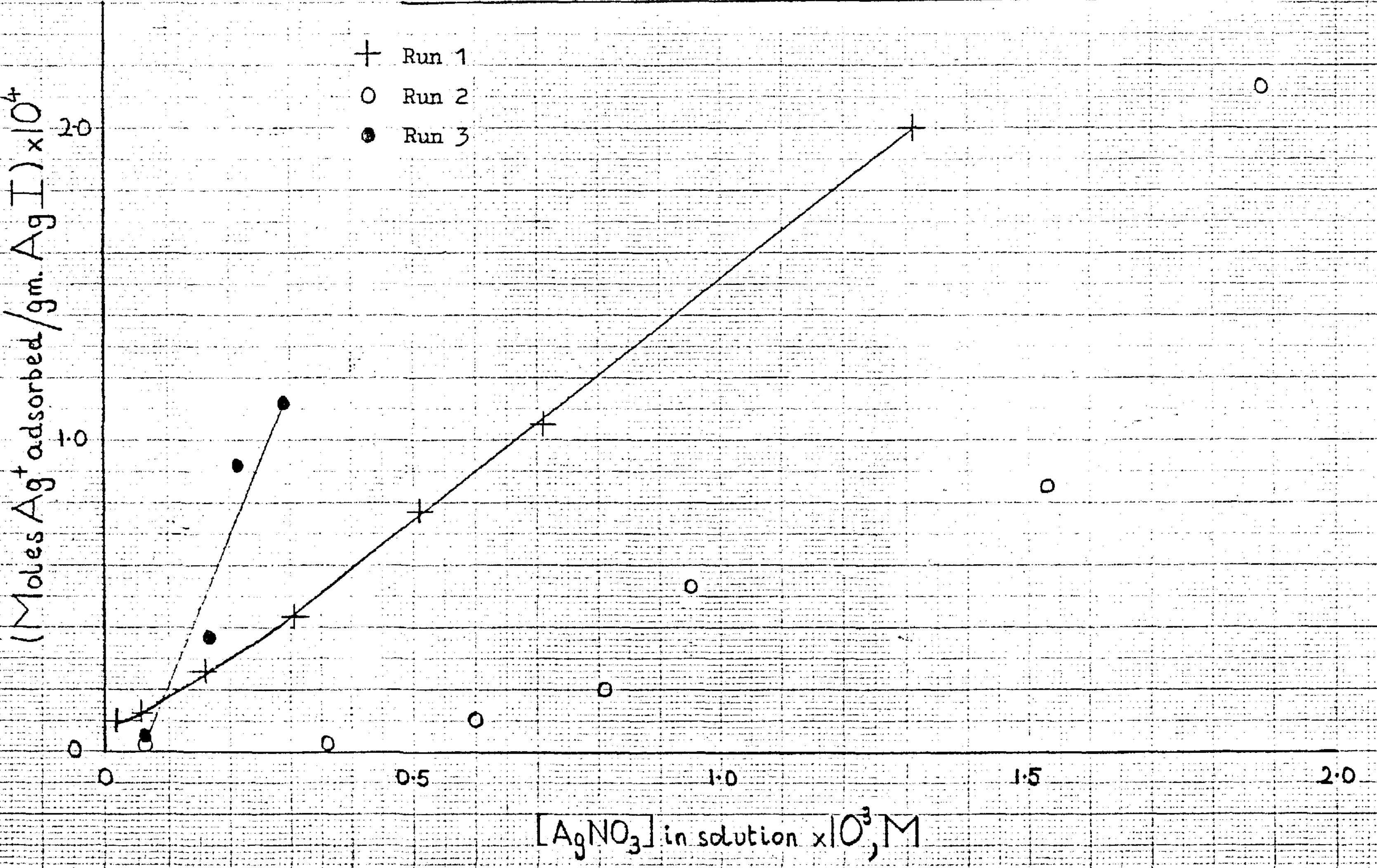
This latter was done in two ways:

(1) measurement of the e.m.f. of cell 3.43,

(2) spectrophotometric determination of complexed silver ion.[63] The complexing agent used was bromopyrogallol red in the presence of 1 - 10 phenanthroline.

Fig. 6.5 shows a plot of the number of moles of silver ion adsorbed against the equilibrium concentration of these ions in solution. Run 1 was carried out with 1 gm. of silver iodide powder which had been shaken vigorously with a small volume of water prior to the determination in

FIG.6.5 Adsorption Isotherms of Silver Ions on Silver Iodide Powder.



order to break up the particles. During the experiment the powder was stirred into contact with the solution using the paddle as in the kinetic runs. The initial volume of solution was 500 ml. , and this increased to 700 ml. during the addition of the silver nitrate solution. The silver ion concentration was measured by means of method (1). This method was also used in run 2, but the powder (again 1 gm) was not pre-shaken. During the determination, the mixture was shaken to equilibrate it, instead of being stirred, and the volume change was from 400 - 600 ml. In these two runs the successive additions of silver nitrate solution to the mixture were made by means of an 'A' grade burette. In run 3, a series of 6 separate mixtures of 50 ml. of solution and 0.25 gm. of powder were made up, each with a different initial concentration of silver ions. These mixtures were shaken vigorously by hand first, and then tumbled mechanically for a period of 3 - 4 hours. They were then centrifuged, and a sample of the solution analysed spectrophotometrically for silver ion. All the solutions used in runs 1,2, and 3 were 0.02 M with respect to potassium nitrate (as were the solutions in the kinetic runs). Runs 1 and 2 were carried out at 25°C, and run 3 at room temperature (ca. 20°C).

The results of the three isotherms are completely irreproducible, although runs 1 and 3 gave approximately linear plots. The reason for the irreproducibility was probably that the dry powder, which was made up of aggregates of single crystals (see the microscopy measurements in Chapter 5) broke up only slowly in solution so that the surface available for adsorption increased with time. Thus, the greatest adsorption occurred in run 3, where the most vigorous shaking took place. The deviations from linearity here are explained by the difference in the vigour of the shaking of the separate mixtures. Run 1 shows the most linear plot, although this may have been fortuitous (see later). In run 2, there is an almost random scatter of points, indicating that the powder was strongly aggregated initially, and only began to break up after some time. It is recommended that, in future determinations, the powder should be shaken vigorously in solution for several hours before the adsorbate is added. Only in this way can complete break-up of the aggregates be ensured, and reproducible results obtained. The results obtained show that the powder used in the kinetic runs was not completely broken up (although the amount of surface present was probably reproducible from run to run, and fairly constant during the initial period of a run). The value quoted for k_o is therefore lower than the true value.

Runs 1 and 3 show a fit to the Freundlich isotherm[64]

$$x = M k.C^n \qquad 6.20$$

where

x is the number of moles adsorbed

C is the concentration in solution at equilibrium

M is the mass of powder added

k is a constant

with n = 1. The difference in slope is due to the fact that if the powder is not completely broken up into its individual crystals, the value of M which fits equation 6.20 will be smaller than the mass of powder added to the solution.

It is apparent that the powder used in run 1 was not completely broken up, and this is also true for the powder used in the kinetic experiments

(Table 6.2). Thus, for these latter no accurate estimates of the amount of silver ion on the surface, and of the surface coverage, can be made. An approximate calculation may be made, however. Interpolating from run 1, the mass of silver ion adsorbed, at 0.001M Ag^+, is 1.52×10^{-4} mole gm^{-1}. From the surface area determination, the number of moles of AgI on the surface of 1 gm. of powder is 1.68×10^{-4}, indicating that the surface was ca. 75% covered, if it is assumed that Ag^+ ions are only adsorbed on I^- ion sites. However, the linearity of the plot at this point is puzzling, since n would be expected to decrease in this region, (this is supported by the fractional order found for the dependence of the rate on the silver ion concentration). A likely explanation is that the powder was breaking up slowly throughout the run, and this is supported by the slope obtained in run 3. This approximate calculation shows that the surface of the silver iodide used in the kinetics runs was fairly fully covered ($>$ 50%) and that the assumption of fairly strong adsorption of silver ions is valid.

One point on the adsorption isotherm of ethyl iodide on silver iodide was also measured. This was done by shaking 100 ml of a 10^{-3} M ethyl iodide solution with 1 gm. of powder, centrifuging and measuring spectrophotometrically the concentration of ethyl iodide remaining. A calibration curve of the absorbances of known ethyl iodide solutions at 250 mμ (extinction coefficient = ca. 260) against their concentrations was constructed and the concentration of the unknown solution interpolated from this. The mass of ethyl iodide adsorbed in equilibrium with a solution containing 5×10^{-4} mole $liter^{-1}$ was $(5.0 \pm 0.5) \times 10^{-5}$ mole gm^{-1}. Thus at this concentration the surface was about 30% covered. It therefore appears that ethyl iodide was also fairly strongly adsorbed on the surface, and that the surface coverage was fairly high.

SUMMARY

In this chapter the kinetics of the reaction between silver nitrate and ethyl iodide on silver iodide powder have been investigated. The reaction at the surface has been shown to occur by means of a Langmuir-Hinshelwood mechanism, and two models, one assuming independent adsorption of the reactants, and the other assuming non-independent adsorption, have been tested. The results favour the latter case but are by no means conclusive. The adsorption isotherm measurements showed that great care must be taken to break the precipitate up completely before the isotherm is measured. They indicated that the assumption of fairly full coverage of the catalyst surface during the kinetic runs was a valid one.

Suggestions for Future Work

The kinetic experiments reported in this chapter should be repeated with a much smaller amount of catalyst and at low temperature (0°C). The measurements should be made over a range of reactant concentration corresponding to a coverage of the catalyst surface ranging from near 0 to near 100%. The adsorption isotherms of the reactants on the catalyst should be determined separately and in the presence of one another.

The effect of substituting silver perchlorate for silver nitrate could be determined.

To quantify the semi-quantitative study (Part I) the effectiveness of a catalyst, its surface area, and the adsorption isotherms of both reactants (preferably in the presence of each other) must be established. This can be done by measuring the above properties for a well defined batch of catalyst, prepared in a manner similar to that used for silver iodide in this chapter. The variation of the catalytic effectiveness of a given material with its method of preparation and the state of its surface could also be investigated.

It would be of interest to determine the effectiveness of a series of insoluble silver salts as catalysts in the Pb^{2+}, Hg_2^{2+}, Hg^{2+} and Tl^+ nitrate systems.

APPENDIX

1) Calculation of liquid junction potentials.

In the measuring system a liquid junction potential was generated at:

i) the junction between the reaction solution and the potassium nitrate bridge solution.

ii) the junction between the potassium nitrate and potassium chloride bridge solutions.

An estimate was made of the magnitude of these potentials by means of the Henderson equation for the case of univalent ions[13]:

$$E_{L.J.} = \frac{RT}{F} \frac{(U_1 - V_1) - (U_2 - V_2)}{(U_1 + V_1) - (U_2 + V_2)} \ln \frac{U_1 + V_1}{U_2 + V_2}$$

where $E_{L.J.}$ is the liquid junction potential and

$U_1 = \sum_i C_i^+ U_i^+$, $V_1 = \sum_i C_i^- U_i^-$ for one side of the boundary under consideration and

$U_2 = \sum_i C_i^{1+} U_i^{1+}$, $V_2 = \sum_i C_i^{1-} U_i^{1-}$ for the other side.

(i) $E_{L.J.}$ was calculated when the solutions on the two sides of the bridge were $AgNO_3 \mid KNO_3$, and when they were $AgNO_3$, $HNO_3 \mid KNO_3$. The values are listed on the next page.

Solution 1	Solution 2		$E_{L.J.}$ (mV)
$AgNO_3$ (0.001M)	KNO_3	0.01M	- 1.39
		0.1 M	- 1.85
		1.0 M	- 2.6
$AgNO_3$ (0.0009M) HNO_3 (0.0001M)	KNO_3	0.01M	- 0.1
		0.1 M	- 1.5
		1.0 M	- 2.5

(ii) $E_{L.J.}$ was calculated for saturated KCl, and for 90% saturated KCl. Slight changes in the strength of the solution appeared to have an insignificant effect on $E_{L.J.}$.

Solution 1	Solution 2		$E_{L.J.}$ (mV)
KCl (satd.)	KNO_3	0.01M	- 2.96
		0.1 M	- 1.92
		1.0 M	- 1.1
KCl (4.19M)	KNO_3	0.01M	- 2.93

2) Calculation of the rate of a transport controlled reaction.

For a transport controlled reaction[5]:

$$-\frac{dc}{dt} = \frac{DA}{V\delta}.c.$$

For the transport of the silver ion to the surface, the following values are assumed: D_{Ag+}[62] $= 1.765 \times 10^{-5}$ cm^2 sec^{-1}, $A = 110$ cm^2., $\delta = 0.01$ cm., $V = 95.75$ cm^3, $c = 10^{-3}$M. These gave a value for $-dc/dt$ of 1.21×10^{-4} mole liter^{-1} min^{-1}.

For the transport of ethyl iodide to the surface, the values assumed were as above, except for D_{EtI}. This was estimated by means of the Stokes-Einstein equation[9d].

$$D = \frac{kT}{6\pi r\eta}$$

where k is Boltzmann's constant

r is the Stokes radius

η is the viscosity of the medium

The value of r, estimated with scale molecular models (from Stuart and Briegleb), was 2.7 Å. This gave a value of $D = 8.0 \times 10^{-6}$ cm^2 sec^{-1}, giving $-dc/dt = 5.5 \times 10^{-5}$ mole liter^{-1}min^{-1}. This value was about 40 times greater than the heterogeneous rate of the reaction measured in the presence of ca. 110 cm^2 of platinum. Thus the diffusion of the reactants to the surface of the catalyst was not the slow step of the reaction.

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