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RESEARCHES INTO THE FUNCTION OF METAL HALIDES IN CATIONIC
POLYMERISATION

by

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A thesis submitted to
the University of Keele in
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of Doctor of Philosophy

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LIST OF PRINCIPAL SYMBOLS

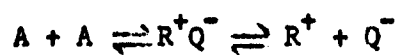
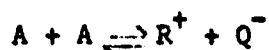
c	- molar concentration.
a_o	- nominal concentration of aluminium halide.
a	- concentration of aluminium halide.
i	- ionic concentration.
κ	- specific conductivity.
κ_e	- specific conductivity at equilibrium.
κ'_e	- estimated specific conductivity at equilibrium.
κ_i	- initial specific conductivity at $t=0$.
κ_{in}	- extrapolated specific conductivity at $a_o=0$.
Λ_T^o	- true equivalent conductivity at infinite dilution.
Λ_T	- true equivalent conductivity.
Λ	- conventional equivalent conductivity.
λ_T^+, λ_T^-	- true ionic conductivities.
K	- ionisation constant of aluminium halides.
K_π	- formation constant of π -complex.
K_n	- dissociation constant of n -complex.
K_p	- ionisation constant of polymer-X + AlX_3 .
K_q	- ionisation constant of t-BuBr + $AlBr_3$.
k_f	- rate-constant of ion formation.
k'_f	- rate-constant of ion formation (dubious significance).
k_b	- rate-constant of ion recombination.
k'_b	- rate-constant of ion recombination (dubious significance).
k_i	- rate-constant of reaction of AlX_2^+ + monomer.
k'_i	- rate-constant of reaction of AlX_2^+ + polymer.

Rb - background count-rate.
Ra - measured count-rate.
Rm - measured count-rate per mg.
R - real count-rate per mg. (estimated from quench-plot).
t - time.
T - temp.

SUMMARY

The work was concerned with the study of the ionisation of aluminium halides in alkyl halides, and the role of these solutions in cationic polymerisations. These are problems of long standing interest which became topical through the proposal of a new theory which ascribed initiation to the ions formed by the self-ionisation of the aluminium halides.

The work described in chapter 3 was concerned with the ionisation of the aluminium halides in alkyl halides. The exploration of this lead us into the interpretation of the kinetics of ionisation, and the analysis of the dependence of conductivity on concentration. At the same time Dr. O. Nuyken was studying in our laboratory the ionisation of $\text{MeCOF} + \text{SbF}_5^{40}$ and both our lines of work pointed to a need to undertake a general theoretical study of the expected dependence of conductivity on concentration for a wide variety of equilibria, such as the following:



Curiously such a general treatment of ionogenic equilibria is lacking from the literature; ours, which has been submitted for publication, is included here as Appendix 1. Hitherto electrochemists have confined their attention almost entirely to equilibria of the kind shown below:



In chapter 4 the effect on the conductivity of altering the concentration and the type of ions in an aluminium halide +

alkyl halide system was examined. This was achieved by titrating the aluminium halides with electron acceptors or electron donors. We were able to confirm the essential features of some very important similar studies by Vesely's group which related the D.P. of polymers to the conductivity of the initiating solutions.

In chapter 5 the electrochemical investigation was extended further to the polymerising systems, and the kinetics of the ionisation during the polymerisation of isobutylene by aluminium bromide were analysed. The work which is described next, perhaps the most curious in the thesis, is concerned with the preparation of non-polymerising solutions of aluminium halide + alkyl halide + isobutylene. The last study described deals with the radio-chemical detection and estimation of the aluminium-carbon bonds in various polymers and thus rounds off and concludes our investigations into the validity of the theory of initiation by self-ionisation.

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CHAPTER ONE

THE INTRODUCTION

1.1 HISTORICAL BACKGROUND

One of the oldest problems in the understanding of cationic polymerisation has been whether a co-initiator is required for the initiation of polymerisations. It has been shown that co-initiators are required for most polymerisations, but there are a few polymerisations in which the presence of a co-initiator has been demonstrated to be quite unnecessary, and it is these which concern us in this thesis.

After showing that aluminium chloride polymerised isobutylene in methylene chloride solution without a co-initiator other than possibly the solvent, and demonstrating that the presence of water had little effect on the initial rate of polymerisation, Beard stated in his Ph.D. thesis in 1963:¹ "The most important problem to be solved before the catalyst can be used to purify the solvent, is whether the solvent reacts with the catalyst. This is a problem which would be worthwhile solving, as it might even help to answer the question whether the solvent could act as a co-catalyst. Various methods could be employed to study the interaction (if any), including measurements of the electroconductivity of the system and its variation with time"; and "Once the electrochemistry of the catalyst-solvent system has been investigated, it would be very worthwhile to extend the electrochemical investigation to the actual polymerisation system. Very few electrochemical

Table 1.1.

Monomer.	Initiator.	Solvent.	Temp. /°C	Remarks.	Ref.
Propylene.	BF ₃	CH ₂ Cl ₂	-35		13,18,19,20.
Isobutylene.	AlBr ₃	n-Heptane	+20 to -60	H ₂ O retarder	3.
"	AlCl ₃	CH ₂ Cl ₂	-60		21,1.
"	"	EtCl	"	Repeated purif. of solvent did not stop polymn.	22.
"	AlBr ₃ /TiCl ₄	n-Heptane	-14		22,23,24.
"	AlI ₃ ,GaCl ₃	"	"		7,8.
"	TiCl ₄	CH ₂ Cl ₂	-74	"Polymn. by Condensation."	16.
"	SnCl ₄	EtCl	-78		23.
"	AlEtCl ₂	n-Heptane	+20 to -55	H ₂ O inhibitor	4.
But-2-ene.	BF ₃	(CH ₂ Cl) ₂	+25	Isomn. Polymn.	16,18,19.
Diphenyl- -ethylene.	TiCl ₄	CH ₂ Cl ₂	-70	"Dimerisation by Condensation"	17.
Isoprene.	AlBr ₃	Benzene. Toluene. n-Heptane.	+21		10,24.
"	AlEtCl ₂	n-Heptane	+21 to -18		11,24.
"	AlCl ₃	n-Heptane Benzene	+21	Initiator in suspension.	12,24.
Indene	TiCl ₄	CH ₂ Cl ₂	-70	Rate increases with H ₂ O or HCl.	13.
"	SnCl ₄	"	-30	"	14.
5-MeO indene	BF ₃	"	> -30		29.
Styrene	TiCl ₄	"	-80		40
α-Me styrene.	"	"	+10 to -72	"	15
"	SnCl ₄	EtCl	+55	Dry?	25
"	AlEt ₂ Cl	MeCl	-50	Isobutylene + styrene need co-initiator under these conditions	26
β-Me styrene	BF ₃	(CH ₂ Cl) ₂	+25	Dimerisation	28.
Cyclopentadiene	TiCl ₃ OBu	CH ₂ Cl ₂	-43 to -70	Rate increases with H ₂ O + HCl	27.
"	AlEt ₂ Cl	MeCl	-50	Isobutylene + styrene need co-initiator under these conditions	26.
1-Me cyclopentene.	BF ₃	n-Hexane	0	Very slow	30.

investigations of actual polymerisation systems have been reported".

These suggestions of Beard summarise some of the lines of thought which stimulated the work described in this thesis. In the period that elapsed since Beard presented his thesis, many more systems have been discovered in which the initiation of cationic polymerisation takes place apparently in the absence of a co-initiator except (in some instances) perhaps an alkyl halide solvent. These observations have stimulated a renewed interest in the problem of the initiation of cationic polymerisation, and many theories have been advanced to account for this phenomenon. Kennedy has recently made a survey of the examples which he could find in the literature of polymerisation systems in which the presence of a co-initiator has been shown to be unnecessary.² The list which Kennedy prepared is shown in Table 1.1; it has been slightly amended, since some examples were omitted, and some new discoveries have been made since the list was first published.

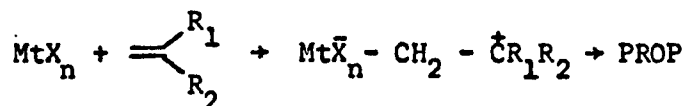
The results in Table 1.1 need little comment, because the range of systems in which the phenomenon is found is self-evident from the Table.

What these observations mean is that in each of these systems a carbenium ion is generated from the mixture of monomer, initiator and solvent. Many theories have been put forward to account for the generation of carbenium ions in such systems, and all those which are known to the author are summarised briefly in Table 1.2 with the appropriate references. Several comparisons of the relative

Table 1.2

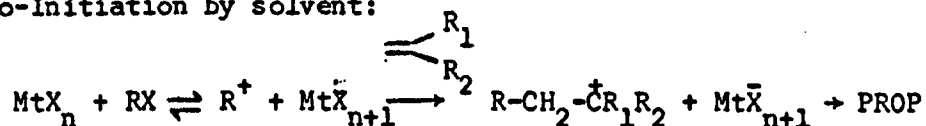
Theories of the initiation of cationic polymerisation in the absence of a co-initiator other than alkyl halide solvent.

1. Direct Initiation by the Hunter Yohé mechanism:

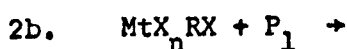


This has been discussed,^{32,33,34} and a slightly modified version has been recently suggested by Sigwalt.³⁵

2. Co-Initiation by solvent:

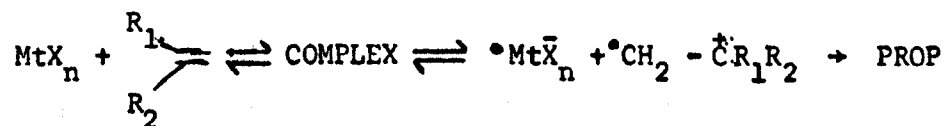


This has been suggested frequently^{32,33,34} but does not apply to systems with alkane solvents.



These have been suggested by Plesch.⁴¹

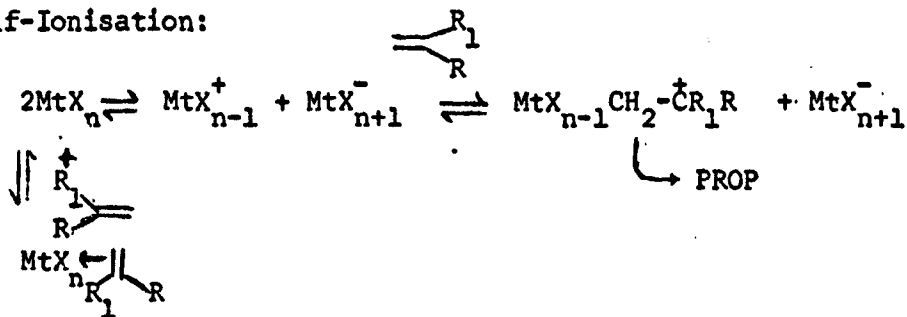
3. Electron Transfer:



This has been discussed by Plesch.³²

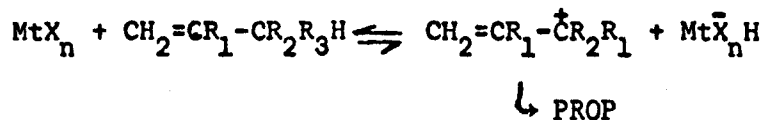
Table 1.2 continued

4. Self-Ionisation:



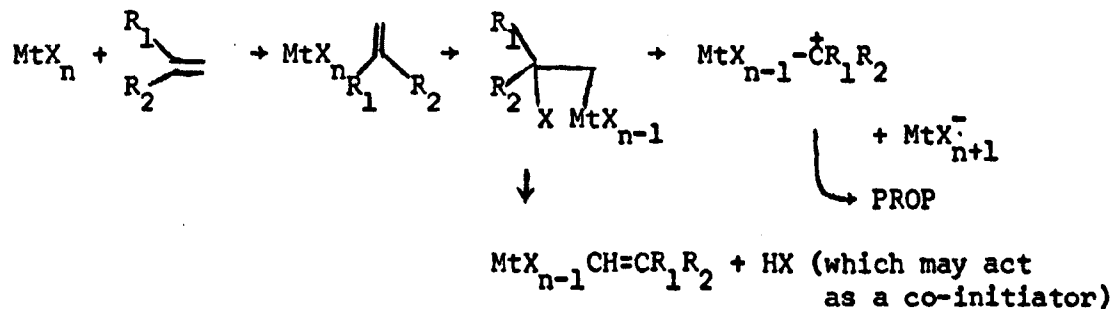
This has been recently advanced by Plesch.^{36 37}

5. Hydride Abstraction, or "Self-Initiation":



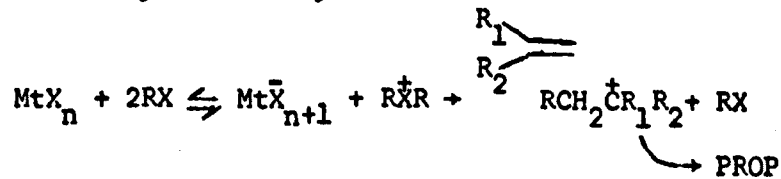
This was recently suggested by Kennedy.²

6. Decomposition of π -donor complex:



This was recently suggested by Olah.³⁸

7. Initiation by the dialkyl halonium ion:



This was recently suggested by Olah.³⁸

merits of some of these theories have been made.^{32,33,34} However, some of the theories presented have been suggested since the dates of these reviews and have therefore not been subjected to comparative analysis.

It would be very time-wasting to discuss each of the theories proposed in detail since the majority can be ruled out easily by a simple discriminating test. In § 5 of this thesis the initiation mechanism has been shown to involve the formation of aluminium-carbon bonds for the following systems: $\text{AlBr}_3 + \text{MeBr} + \text{isobutylene}$ or styrene or norbornadiene, and $\text{AlCl}_3 + \text{EtCl}$ or $\text{CH}_2\text{Cl}_2 + \text{isobutylene}$. Therefore all mechanisms which do not involve the formation of a Mt-C bond in the initiation, may be ruled out for these systems, which leaves only Nos. 1, 4 and 6 to be considered. Nos. 1 and 6 may also be ruled out because of their failure to explain some of the peculiar features of, for example, the polymerisation of isobutylene by aluminium chloride. These can be summarised as follows: (i) If initiator solution is added to monomer solution the polymerisation only proceeds to limited conversion. Addition of more initiator re-starts the polymerisation, but again only incomplete conversion is achieved. (ii) The number of active centres may be as much as a factor of 10^6 lower than the formal concentration of aluminium chloride, which means that the concentration of real initiator is very much smaller than that of aluminium chloride. (ii) If monomer solution is added to a solution of initiator, polymerisation normally proceeds to complete conversion. Therefore any theory which is put forward must explain why only a few of the initiator molecules are effective, and why the order of the mixing of the reagents should

affect the yield of the polymer. If these considerations are applied to schemes 1 and 6, we can see that neither scheme can account for the effect of the order of mixing on conversion nor can it explain why the initiator efficiency is so low. In schemes 1 and 6 there is nothing which would prevent the initiation reactions from continuing until all the initiator is used up, because neither reaction 1 nor 6 is an equilibrium process.

On the other hand, the Self-Ionisation theory (No. 4), can give simple explanations of all the above phenomena for the polymerisation of isobutylene by aluminium chloride along the following lines: If only the ions can initiate polymerisation, if the rate of ionisation is low and if the extent of ionisation is very small, then the low efficiency of ^{the} initiator is easily understood. To explain the effects on the yield, let us examine the consequences of adding initiator solution to monomer solution and vice versa.³⁷

Addition of initiator to monomer solution: When a solution of the initiator is added, only a very small fraction of it is present as ions in that solution, and the ions present will react immediately with the monomer and thus initiate the growth of polymer chains. At the same time, as the initiation reaction is taking place, the monomer reacts with the un-ionised aluminium chloride to form a π -complex, the aluminium chloride is thus inactivated, and hence it cannot form more ions. The polymerisation continues until termination reaction or "smothering" have destroyed or removed all the active centres. As more ions can form at best only very slowly from the initiator complexed with monomer, polymerisation virtually ceases.

If more initiator is added, polymerisation will take place again, until the second batch of active centres is destroyed.

Addition of monomer to initiator solution: Under these circumstances, the aluminium chloride ionises in a large volume and establishes a large concn. of ions before monomer is added, and when the monomer is added, immediate polymerisation to complete conversion takes place. Only if the monomer is very impure is there a possibility of sufficient chains being terminated to stop the polymerisation. In this procedure, it is probable that the rate of polymerisation is greater than the rate at which π -complexes can form, and therefore the aluminium chloride is not prevented from re-ionising.

In the work which follows, all aspects of the Self-Ionisation theory were investigated and confirmed. Values were found for the equilibrium constant of ionisation, the rate of formation and the rate of recombination of the aluminium ions, the rate of attack of the AlBr_2^+ ion on a double bond, and the formation constant of the π -complex. As will become obvious to the reader, the values obtained were completely consistent with the Self-Ionisation theory.

1.2 The Choice of System. Most of the work was undertaken with the methyl bromide + aluminium bromide initiation system. An aluminium halide was chosen because it had been shown that with these halides no co-initiator was required. Aluminium bromide was used at first in preference to aluminium chloride, because it is much more soluble.

Methyl bromide was the solvent of choice for aluminium bromide, because containing only one carbon atom, it cannot rearrange, and the formation of Me^+ is extremely unlikely, and thus the possibility of co-initiation by solvent was remote (c.f. scheme Table 1.2). It is also polar enough to have good solvating properties, and it has a dielectric constant which is low enough to permit cationic polymerisation and at the same time high enough to enable the study of ionisation by conductivity measurements. The methyl bromide was chosen rather than the chloride or the iodide to prevent the possibility of halogen exchange.

All the exploratory work and more detailed investigations were carried out with aluminium bromide. Aluminium chloride was studied to a lesser extent than the bromide, but enough results were obtained with it to show that it behaved in the same manner as the bromide.

Ethyl chloride and methylene dichloride were used as the solvents for aluminium chloride. Methyl chloride would have been the solvent of choice, but its low boiling point makes it difficult

to carry out routine expts. in glass apparatus above ca. -40° . Both ethyl chloride and methylene dichloride have very similar solvating properties to methyl bromide; oddly enough, the dielectric constants of methyl bromide and methylene dichloride are very similar over a very wide range of temperature.

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CHAPTER TWO

EXPERIMENTAL

2.1 MATERIALS

2.1.1 Alkyl halides

2.1.1.1 Methyl bromide. This solvent (B.D.H. Laboratory Gas Service) was obtained in a cylinder 99.5% pure. The following were the likely impurities: Br_2 , CH_2Br_2 , CH_3OH , CH_2O and water. Two purification procedures were tried, the second being the one finally adopted.

The first procedure was to place approximately 500 ml. of methyl bromide in a three necked 1 l. flask cooled in an ice-salt bath and fitted with a mercury-sealed stirrer, an ice-water condenser with a silica-gel drying tube, and a stopper. 5 g. of B.D.H. laboratory reagent AlBr_3 was added, and the flask was stirred for three h. at -10° . Fresh additions of AlBr_3 were made every hour. The methyl bromide was then dist. under high vac. conditions onto freshly activated 4A molecular sieves, and allowed to stand for three hours. The methyl bromide was finally dist. into the storage reservoir, liberal head and tail fractions being discarded. The methyl bromide purified in this way was not satisfactory; the criterion of purity was its behaviour as a medium for studying the ionisation of AlBr_3 , and will be dealt with fully in § 3.

The second, more effective, method was to distil about 500 ml. of methyl bromide directly from the cylinder onto 2 g. of freshly sublimed AlBr_3 . The AlBr_3 solution gradually became yellow on standing

overnight at room temperature. The methyl bromide was dist. from the AlBr_3 onto well-ground calcium hydride which had been kept under high-vac. for several hours, and was allowed to stand for a few days. The methyl bromide was then returned to a flask containing freshly sublimed AlBr_3 , and on this occasion no colour developed. In the first series of experiments the solvent was then dist. onto finely-ground calcium hydride in a storage reservoir, but in later experiments an extra stage was added, and after the solvent had been kept over calcium hydride for a few days it was condensed onto a freshly prepared sodium mirror. A typical purification train is illustrated in Fig. 2.1. G.l.c. showed one peak only. No other impurities were detectable. During the course of the work nine batches of solvent were prepared.

Other properties of methyl bromide, such as electrical conductivity, optical transparency and the procedure used in its dosing will be discussed in the appropriate sections of this thesis.

The method of purification of halogenated solvents by storage over a sodium mirror was recently introduced by Cheradame,¹³ for methylene dichloride; it was adopted with considerable apprehension because of the possibility of a rapid Wurtz reaction leading to an explosion, but our fears proved to be unwarranted. Well purified methyl bromide is perfectly stable over a sodium mirror, indeed g.l.c. analysis of a sample which had been kept in this way for 10 months showed that only a very small amount of ethane had been produced, (ca. 1 : 10,000 vol./vol.); no other impurities were observed. The presence of ethane in the methyl bromide is of little consequence.

Figs. 2.2., and 2.3., illustrate the methods used for dosing of solvent, and, V1 denotes the storage reservoir in both. In Fig. 2.2 the solvent

was condensed into burette, B, by means of the ice-water cooled condenser. In Fig. 2.3., the solvent was condensed into B and the vol. was measured at the intended temp. of the expt. (For instance, if the expt. was to be at -78.5° , then the burette was read at this temp.). The solvent was then condensed into the reaction vessel; the splash head on top of the burette prevented the contents being sprayed over the vac. manifold.

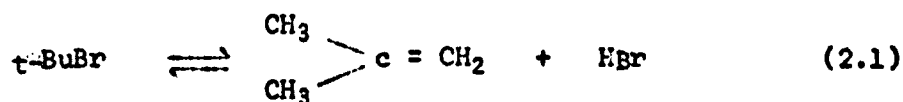
2.1.1.2 Ethyl bromide. The Koch-Light product, of purity not less than 99% was dist. through a Normatron automatic distillation apparatus, at a reflux ratio of 20 : 1. The fraction boiling at 38.4° , 745 mm. was collected, and g.l.c. analysis showed that the purified material contained 1 : 5,000 vol./vol. of ethanol, 3 : 5,000 vol./vol. of water, and no bromine. The ethyl bromide was then dist. onto freshly sublimed AlBr_3 in the vac. apparatus described in § 2.1.1.1, and since no colour developed after a day, the ethyl bromide was presumed to be free from impurities and was dist. into a storage reservoir containing freshly ground calcium hydride. It was dosed in the apparatus illustrated in Fig. 2.3., and described in § 2.1.1.1.

2.1.1.3 Methylene dichloride. This solvent (Honeywill and Stein Ltd.) was purified as described by Weissberger,³¹ and then washed, dried, dist. and stored as described by Jones in his thesis.¹⁹ The methylene dichloride was then dist. on the vac. line from the storage reservoir into a Kon-flask, sealed with a Teflon tap, containing a fresh sodium mirror, and after a day it was dist. into a second vessel containing a sodium mirror over which it was stored. The method is similar to that described by Cheradame.¹³ No impurities were detectable by g.l.c. in the purified material. It was dosed in the apparatus illustrated in Fig. 2.3.

2.1.1.4 Chloroform. This reagent (B.D.H. Ltd.) was used as a medium for determining molecular weight by vapour pressure osmometry, and was used without further purification.

2.1.1.5 Ethyl chloride. This solvent (Hedley & Co. Ltd.) was obtained in a highly pure state (99.9% by g.l.c.). The solvent was dist. directly into a receiver on the vac. line which contained freshly sublimed AlCl_3 (see Fig. 2.1), and after 24 h. no colour developed. The ethyl chloride was subsequently dist. into a storage reservoir which contained freshly ground calcium hydride which had been under high vac. for several h. This solvent was dosed by the apparatus shown in Fig. 2.3.

2.1.1.6 t-Butyl bromide. The commercial product (B.D.H. Ltd.) was fractionally recryst. three times at -20° and subsequently displayed only one peak when subjected to g.l.c. analysis. To preclude the establishment of the following equilibrium, it was necessary to use a neutral drying agent.



The t-butyl bromide was passed down a 10 cm. column of anhyd. calcium bromide, and allowed to remain over more of the desiccant in a flask sealed with a Teflon tap. The material was subjected to further purification by trap-to-trap distillation on the vac. line and was finally stored under its own vapour in the dark. This material was dosed in an apparatus similar to that shown in Fig. 2.7; a 2 ml. burette was used.

Figure 2.1

A typical solvent purification train. V1 to V4 are 2 l. receivers. Tf1 to Tf5 are Teflon taps. X is a magnetic stirrer. V1 is the flask by which the solvent was brought into the vacuum system, V2 contains powdered calcium hydride, V3 re-sublimed aluminium halide and V4 a sodium mirror over which the solvents are stored.

Figure 2.2

A solvent dosing apparatus. B is a burette, Tm1-2 are BiPl taps, and V1 is a 2 l. flask. By warming V1 gently the solvent condenses in the upper part of the apparatus above Tm1.

Figure 2.3

The second type of solvent dosing apparatus, for solvents with a vapour pressure greater than 1 atm. Tf1 is a Teflon tap, V1 a 2 l. flask, S a splash-head and B a burette. The solvent was condensed into B from V1.

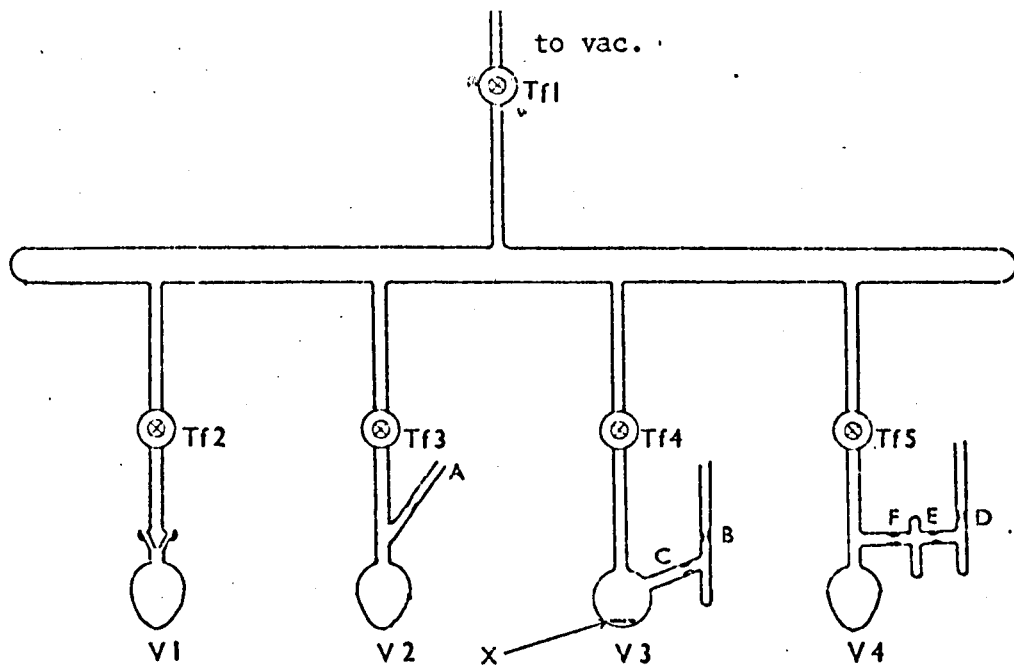


Fig. 2.1

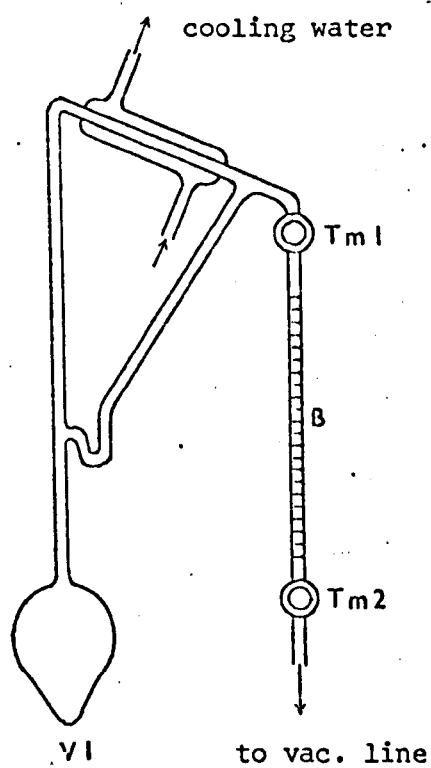


Fig. 2.2

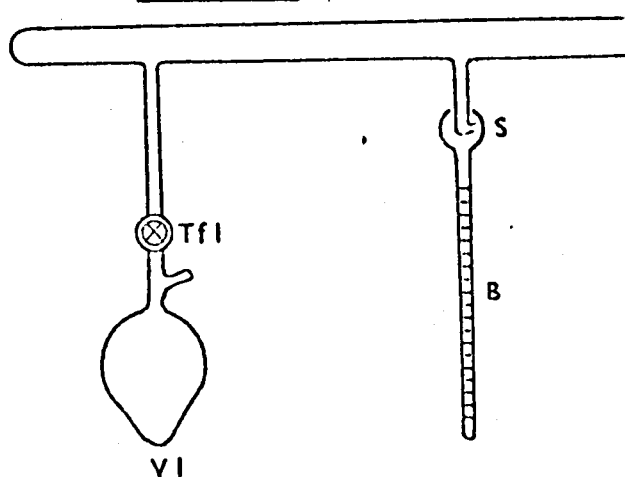


Fig. 2.3

2.1.2 Hydrocarbons

2.1.2.1 Toluene. The toluene was used as a solvent for membrane-osmometry and also as solvent for the radio-chemical assay of polymers. For the first purpose, the purity of the solvent is not of critical importance as long as it contains little dissolved air and is consistent in composition. The air is removed by stirring the solvent at 40° for two h. before use.

For radio-chemical assay the solvent must be dry, and must contain no impurities which contain sulphur, as this causes quenching. The commercial product (B.D.H. AnalaR) was distilled on the vac. line into a flask containing freshly sublimed AlBr_3 , where it was kept overnight; thence it was dist. into a vessel containing a fresh sodium mirror and kept there over night; finally it was stored under its own v.p. in a receiver which was sealed by a Teflon tap.

2.1.2.2 n-Heptane. This material (B.D.H. Ltd.) was purified in the manner described in Perrin, Armarego & Perrin,⁴ after which it was dried over calcium chloride and dist. on the vac. line into a receiver containing freshly sublimed aluminium bromide. It was stored under its own v.p. in a Kon-flask sealed with a Teflon tap over well ground calcium hydride.

This solvent was dosed in an apparatus similar to that shown in Fig. 2.3.

2.1.3 Alcohols

2.1.3.1 Isopropanol. This reagent (B.D.H. AnalaR) was dried by addition of a small amount of sodium (ca. 0.5 g. in 200 ml.), and was then dist. on the vac. line into a flask sealed with a Teflon tap. G.l.c. showed the isopropanol to have a purity greater than 99.9%.

Isopropanol labelled with $250\mu\text{Ci } ^{14}\text{C}$ was obtained from the Radiochemical Centre, Amersham, and this material was diluted with 20 ml. of the purified isopropanol in the apparatus shown in Fig. 2.4. The apparatus was pumped and flamed out and 20 ml. of isopropanol from the storage reservoir V1, was metered into V2 by means of the burette B. The ampoule of ^{14}C isopropanol was cooled in liq. nitrogen, and the break-seal B.S. broken. Several ml. of isopropanol from V2 was allowed to condense into the ampoule, which was then warmed, and the contents dist. into V2. The procedure of washing ampoule A with isopropanol from V2 was repeated several times to ensure that all the activity was transferred to V2.

2.1.3.2 Methanol. The commercial product (B.D.H. Ltd.) technical grade was used without purification for precipitation and re-precipitation of polymers.

2.1.4 Olefins

2.1.4.1 Isobutene. Isobutene (Phillip's Research Grade) 99.56 mol.% pure, was purified as described.^{1,9,10} It was dist. through a trap containing molten sodium at 350°C . which was attached to the high vac. apparatus illustrated in Fig. 2.5. The apparatus was pumped thoroughly and flamed out, then isobutene was condensed directly from the

cylinder through taps T6 and T5 by cooling V2 with liq. nitrogen. The isobutene was degassed, and condensed into V1 via T5, T4, the sodium trap (heated to 350°), T1 and T3; all other taps were shut. The olefin was passed through the trap three times, and on the last occasion it was condensed very rapidly into V1 in order to carry a fine suspension of sodium with it into the flask. The isobutene was finally dist. into the isobutene storage reservoir, which was fitted with a break-seal B.S. and a U-bend A. The U bend was a simple form of safety tap into which isobutene could be frozen with liq. nitrogen in order to create a vac. tight seal. The isobutene reservoir was surrounded by a sheet of metal-gauze. This is an essential safety feature, because, should the flask develop a crack etc. it will explode with considerable force. (I speak from bitter experience).

The monomer was dosed in methyl bromide soln. Fig. 2.6 shows the apparatus in which the soln. was prepared. Isobutene was condensed into burette B, which was cooled with an acetone + solid CO_2 mixture; after measurement of the vol. at room temp. isobutene was condensed into V1 and the contents of the burette were re-determined. Methyl bromide in V2 was condensed into V1 after being metered with the burette B at ambient temp. (23°C). The apparatus was cut at A, and fitted to a burette, from which the soln. was administered; the apparatus is illustrated in Fig. 2.7.

2.1.4.2 Styrene. The commercial product (Hopkin and Williams Ltd.) was purified in a manner similar to that described by Gandini.¹⁷ It was shaken with a conc. sodium hydroxide soln. to remove the inhibitor, washed three times with water, and left standing over calcium chloride

for several h. (No polymer formation was observed on the surface of the calcium chloride). The styrene was then dist. under reduced pressure; the middle fraction, collected over CaH_2 , was approx. 60% of the starting vol. b.p. $40^\circ/15$ mm. (lit.³¹ $40^\circ/15.2$ mm.), after which the styrene was dist. onto freshly ground calcium hydride and remained under its own v.p. for several days. A small amount of hydrogen evolution was obs., which ceased after about one week. After being degassed, the styrene was dist. onto a second amount of calcium hydride in V in the dosing and storage apparatus shown in Fig. 2.8. V was kept at 0° , and in the dark to retard the free-radical polymerisation of styrene. The apparatus functioned as follows: liq. nitrogen was placed in A, whereupon styrene was condensed into the burette. The level in the burette was controlled by Tf2, and Tf1 was used to dose the monomer. When addition of monomer had been completed Tf2 was opened to return all the styrene to V; note that X-Y is slightly inclined so that Tf1 can drain completely.

2.1.4.3 αMethyl styrene. The commercial product was purified in a manner similar to that described for styrene in § 2.1.4.2. It was shaken with several portions of 10% sodium hydroxide soln., followed by several washes with dist. water until the washings were neutral. The monomer was dried over calcium hydride, and was twice fractionally dist. under reduced pressure with a one metre column filled with copper turnings, and on each occasion liberal head and tail fractions were discarded. The collected fraction, at $58.5^\circ/10$ mm. (lit.²⁷ $57^\circ/10$ mm.), showed only one peak when analysed by g.l.c. The αmethyl styrene was dist. from calcium hydride into a flask containing a sodium mirror, whence it was condensed into a storage flask and it was dosed in the manner explained in § 2.1.4.1 and illustrated in Fig. 2.7.

2.1.4.4 2.5-Norbornadiene. This monomer (Koch-Light Ltd.) of purity greater than 99% was purified by distillation through a Normatron automatic distillation apparatus at a reflux ratio of 25 : 1. The fraction boiling at 89.3°/749 mm. was collected (lit.⁸ 89.5°/760 mm.), this was about 60% of the material. This fraction had a refractive index of 1.4682 (lit.²⁴ 1.4682). Analysis by g.l.c. (Pye.Unicam - with OVO-1 columns), showed the presence of one minor peak (1 : 5,000 vol./vol.). The monomer was dried over freshly ground calcium hydride under its own v.p., and then dist. onto a newly prepared sodium-mirror where it was stored over night. A methyl bromide soln. of the monomer was prepared in the manner described in § 2.1.4.1. and it was dosed in an apparatus similar to that shown in Fig. 2.7.

2.1.4.5 Propene. This olefin (I.C.I. Ltd.) was used directly from the cylinder, the only purification being passage of the gas through a sodium mirror which had been condensed onto a 20 cm. long wad of glass wool in an 8 cm. diameter tube.

2.1.4.6 Di-isobutene. A mixture of the isomers 2,4,4-trimethylpentene-1 and 2,4,4 - trimethylpentene-2 was used as a model compound for low molecular weight polyisobutene. It was dist. before use.

Figure 2.4

This apparatus was used for diluting ^{14}C labelled isopropanol. Ampoule A contained the labelled isopropanol. BS is a break seal. The unlabelled alcohol was kept in the 200 ml. flask V1, and dosed by the burette B. The diluted labelled alcohol was condensed into the 50 ml. flask V2. Tfl-2 are Teflon taps.

Figure 2.5

Isobutylene purification apparatus. T1 to T7 are greased high vacuum taps. V1 and V2 are 500 ml. flasks. N is a trap containing sodium. E is a tube furnace. V3 is the isobutylene storage reservoir. BS is a break seal and Tfl is a Teflon tap.

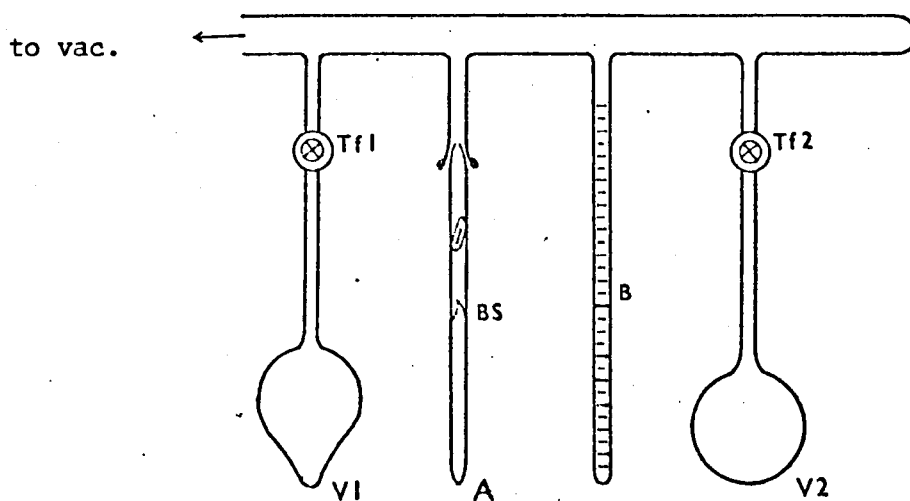


Fig. 2.4

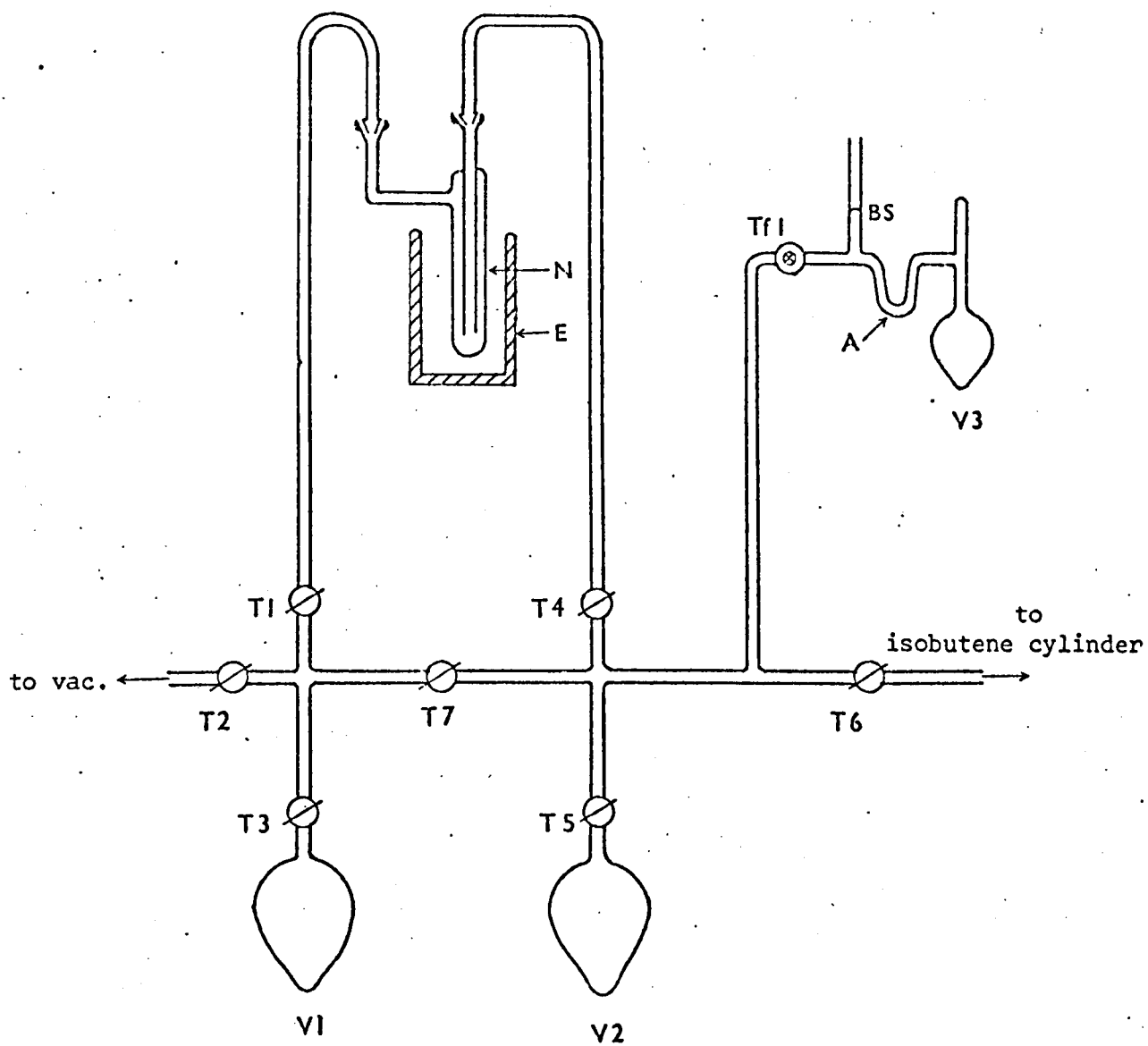


Fig. 2.5

Figure 2.6

Apparatus for the preparation of solutions of isobutylene in methyl bromide. V3 is the isobutylene reservoir. V2 is the solvent reservoir, B is a burette and V1 is a 100 ml. flask in which the monomer solution was stored. Tf1 to Tf4 are Teflon taps.

Figure 2.7

Apparatus for dosing the solution of monomer. V1 is as in Fig. 2.6, B is a 2 ml. burette.

Figure 2.8

Apparatus for storage and dosing of styrene. A is a cold finger, B a 1 ml. burette, V is a 2 l. flask. Tf1 and Tf2 are Teflon taps.

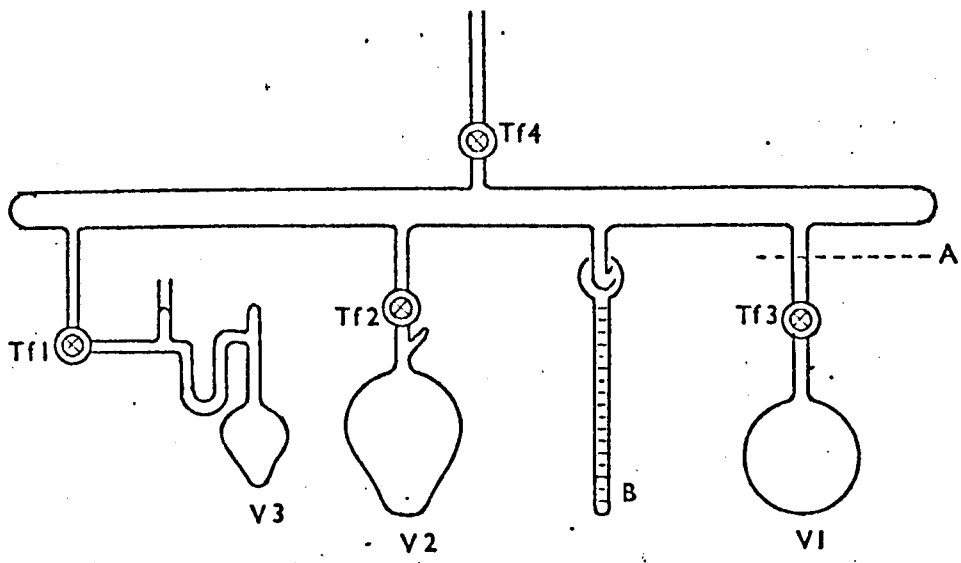


Fig. 2.6

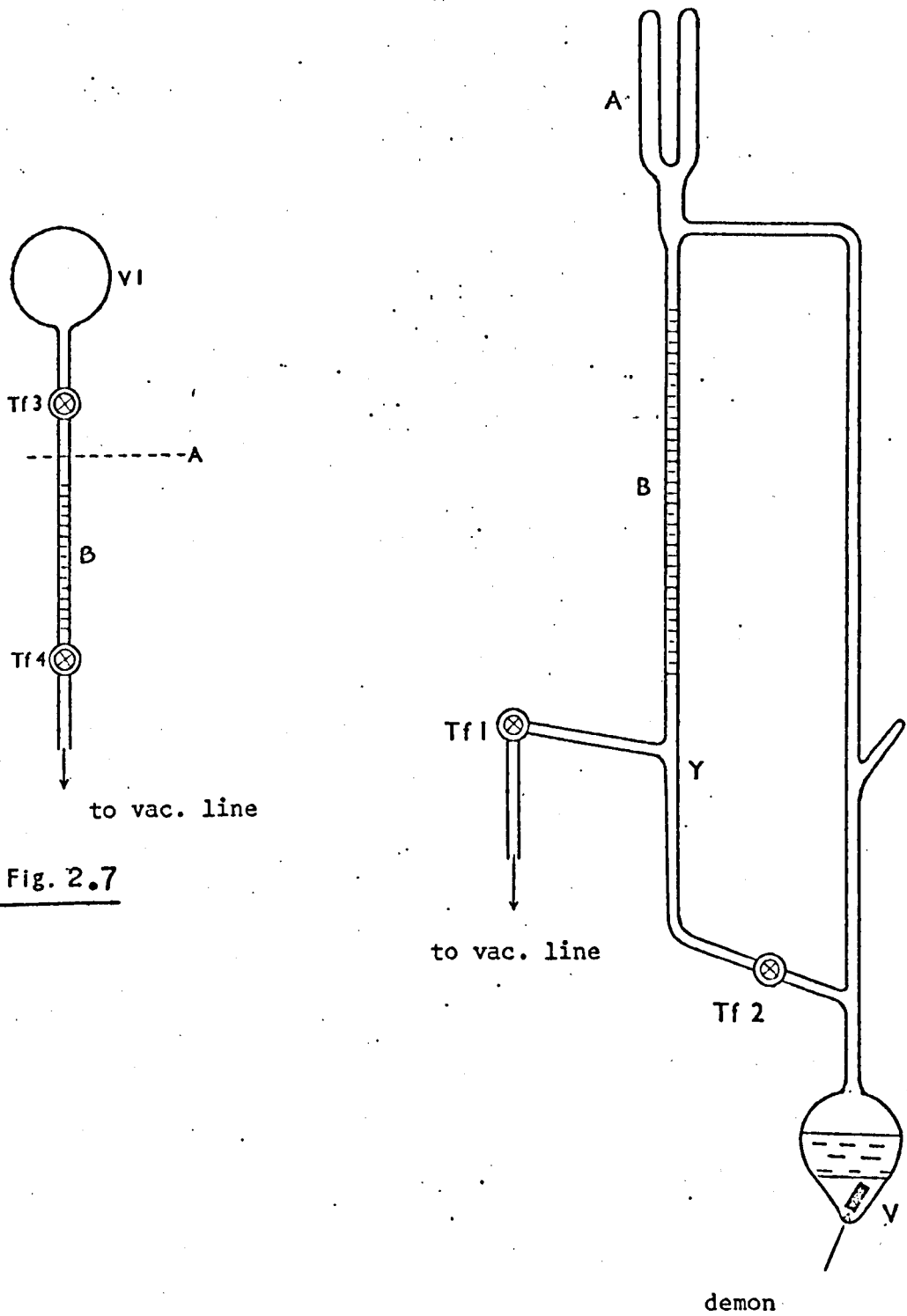


Fig. 2.7

2.1.5 Initiators

2.1.5.1. Aluminium bromide. Aluminium bromide was prepared directly from the elements in the apparatus shown in Fig. 2.9. The prep. was performed under a stream of dry nitrogen, which passed slowly through taps T2, T3 and through the exit tube T. None of the taps or joints was greased. 80 g. of bromine (B.D.H. AnalaR) was placed in B, and 12 g. of aluminium wire, A, (B.D.H. AnalaR or Koch-Light - high purity) was coiled up in V1, above a thick wad of well cleaned glass-wool, G. A few ml. of bromine was added, and the flask A was warmed with the isomantle I until aluminium bromide began to reflux. Bromine was run in slowly; and the temp. of the reaction mixture was controlled very carefully so that the aluminium bromide refluxed, but did not distil over. When all the bromine had been added, the contents of the flask were allowed to reflux until the bromine colour had disappeared. The temp. was increased in order to distil the aluminium bromide into V2. When the first 20% had been collected, V2 was replaced swiftly with a second flask and the middle fraction was collected; the final 20% of the material was discarded. The apparatus was rapidly dismantled before the joints set, and the content of V2 was redistilled under nitrogen into a flask containing aluminium wire, W, and having a break-seal BS, as shown in Fig. 2.10. When the distillation was complete, the exit-tube was sealed at X, and a lightly greased stopper placed in A. V2 was sealed to a vac. manifold, and the AlBr_3 was re-sublimed several times in an apparatus which is illustrated in Fig. 2.11. When all the apparatus had been well pumped and flamed out (the

phials were flamed with a very small and cool flame), the seal BS1 was broken, and the apparatus was sealed off at S4. The contents of V1 were sublimed into V2 by warming V1 gently with a large cool flame, and V1 was removed by sealing off at S1. The seal BS2 was then broken and the process of re-sublimation was repeated, so that the aluminium bromide was transferred into V3. The phials were filled by subliming the contents of V3 into section P, and then removing V3 by sealing it off at S3. The phials were filled by "chasing" the aluminium bromide in with a small "soft" flame, and subsequently sealing them off. The contents of the phials were measured by the "mid-point" method.²⁸ When the phials had been filled, the excess of aluminium bromide was sublimed into V4, which was then sealed off at S4. V4 was provided with two break-seals BS4 and 5. The aluminium bromide was always re-sublimed in the presence of aluminium wire, to remove any free bromine.

The purified product consisted of white crystals.

2.1.5.2 Aluminium chloride. This compound (B.D.H. Ltd.) was re-sublimed five times under nitrogen, and then another five times in a vac. apparatus by the techniques and with the apparatus described in § 2.1.5.1. The purified compound was a white powder.

2.1.5.3 Titanium tetrachloride. Phials were obtained which had been prepared by Longworth, in the manner described in his Thesis.²²

Figure 2.9

Apparatus for preparation of aluminium bromide. T1, T2 and T3 are un-greased taps. B contains bromine. V1 and V2 are 250 ml. flasks. G is a mat of glass-wool. A is a wad of aluminium wire. I is an isomantle. T is nitrogen exit tube.

Figure 2.10

Apparatus for re-distillation of aluminium bromide. V1 and V2 are 250 ml. and 100 ml. flasks respectively. W is aluminium wire. BS is a break seal.

Figure 2.11

Apparatus for filling phials with aluminium bromide or chloride. V1 to V4 are 100 ml. flasks. BS1 to BS5 are break seals. S1 to S6 are sealing-off points. Tm1 is a BiPl tap. P is the manifold containing the phials.

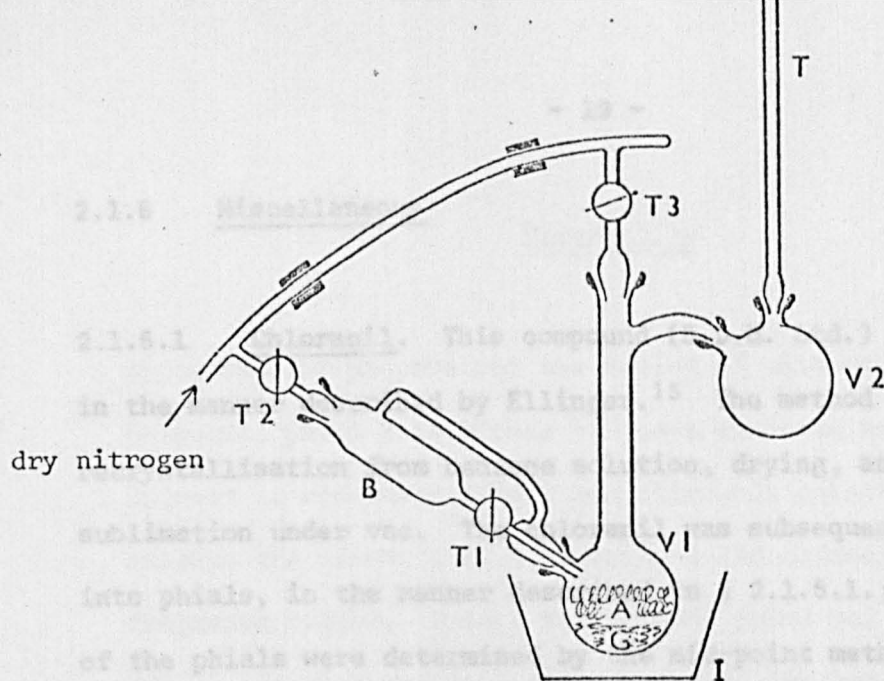


Fig. 2.9

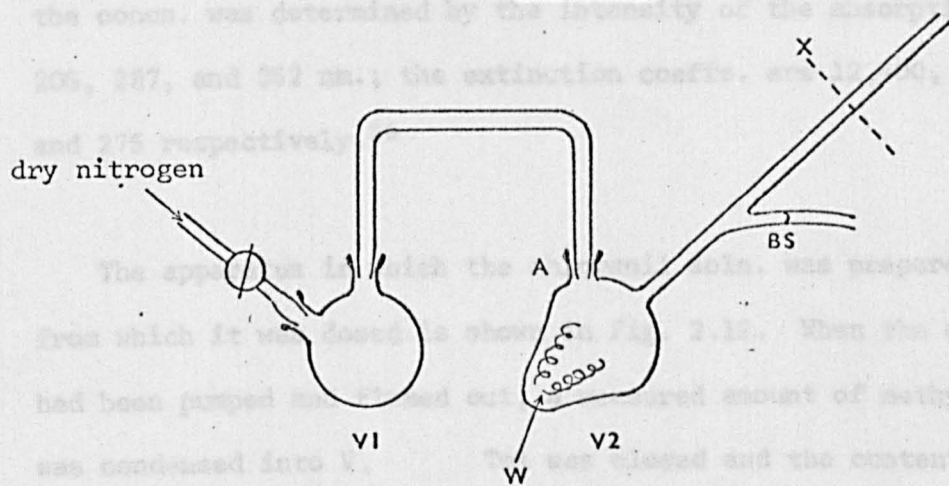


Fig. 2.10

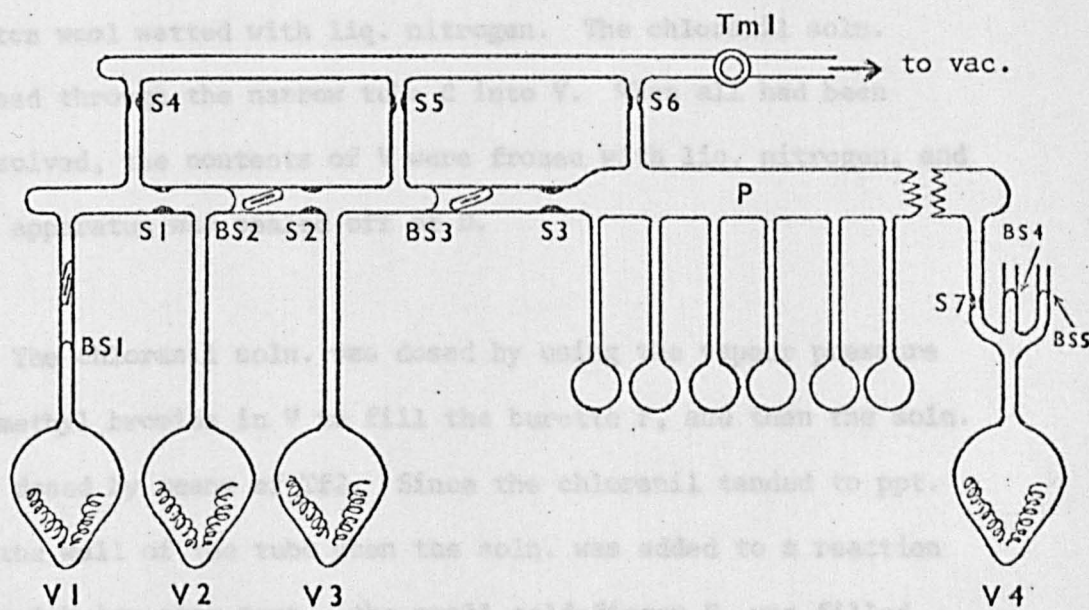


Fig. 2.11

2.1.6 Miscellaneous

2.1.6.1 Chloranil. This compound (B.D.H. Ltd.) was purified in the manner described by Ellinger.¹⁵ The method consisted of recrystallisation from benzene solution, drying, and then sublimation under vac. The chloranil was subsequently sublimed into phials, in the manner described in § 2.1.5.1.; the contents of the phials were determined by the mid-point method.²⁸ A methyl bromide soln. of chloranil was prepared under vac. conditions; the concn. was determined by the intensity of the absorptions at 206, 287, and 362 nm.; the extinction coeffs. are 12,400, 14,000 and 275 respectively.²⁶

The apparatus in which the chloranil soln. was prepared and from which it was dosed is shown in Fig. 2.12. When the apparatus had been pumped and flamed out, a measured amount of methyl bromide was condensed into V. Tm1 was closed and the contents of V allowed to warm. The phial B containing chloranil, was broken and methyl bromide was condensed into the tube T by means of cotton wool wetted with liq. nitrogen. The chloranil soln. passed through the narrow tube C into V. When all had been dissolved, the contents of V were frozen with liq. nitrogen, and the apparatus was sealed off at D.

The chloranil soln. was dosed by using the vapour pressure of methyl bromide in V to fill the burette F, and then the soln. was dosed by means of Tf2. Since the chloranil tended to ppt. on the wall of the tube when the soln. was added to a reaction vessel below room temp., the small cold-finger E, was filled

Figure 2.12

Apparatus for preparation and dosing of chloranil solutions. Chloranil phial B is broken by glass enclosed magnet A. Solvent is condensed into T and chloranil solution passes through the narrow tube C, leaving solid chloranil and glass fragments behind. D is a sealing-off point and V is a 200 ml. flask. Tml is a BiPl valve and Tfl and 2 are Teflon taps. E is a cold finger.

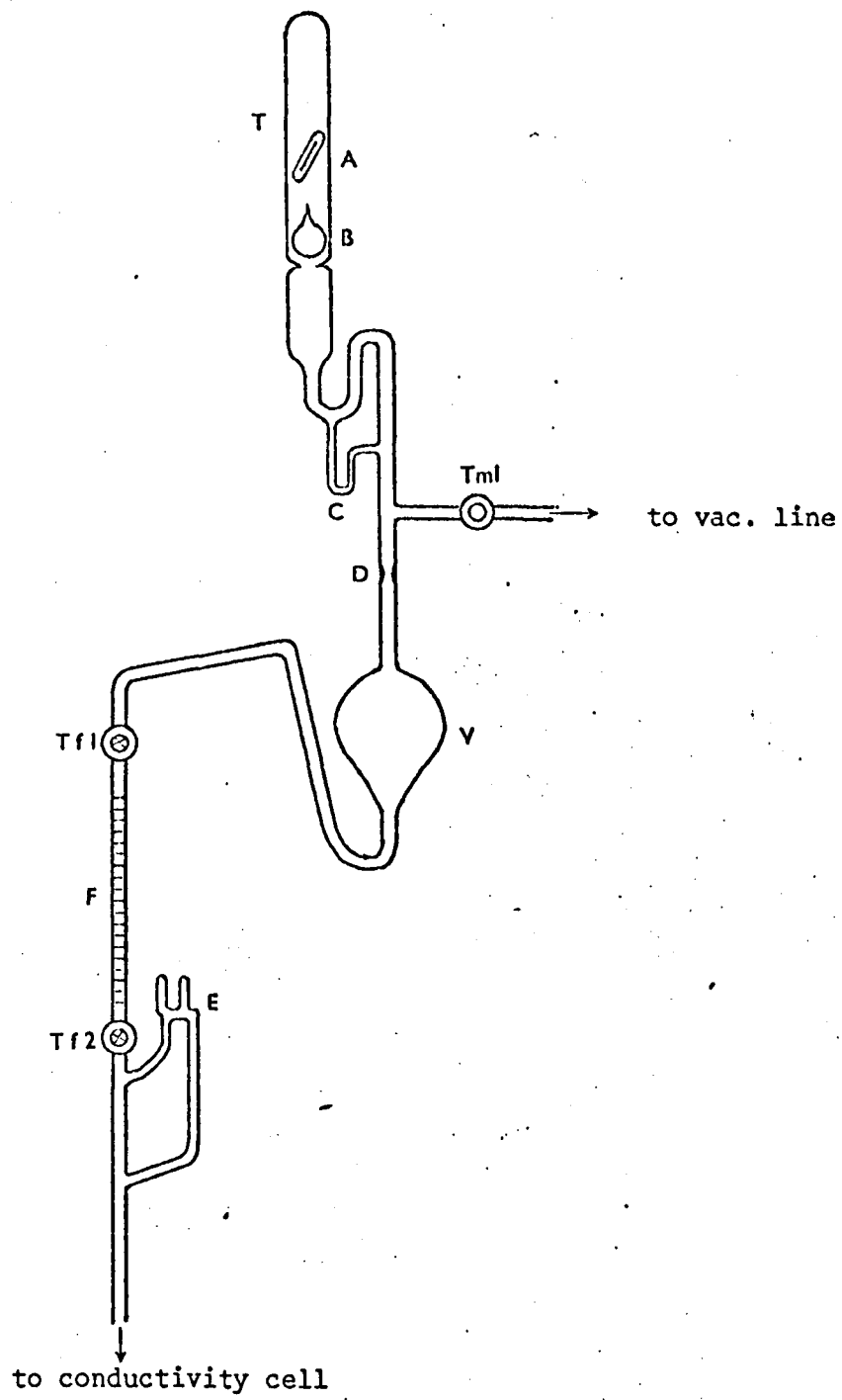


Fig. 2.12

with liq. nitrogen so that it condensed solvent, and after a few min. created a small stream which washed the solid chloranil into the reaction vessel.

2.1.6.2 Tetranitromethane. This compound (Koch-Light, AnalaR) was of purity greater than 99%, and was reputed to be highly explosive in the presence of impurities.²⁴ The material was purified in the manner described in Organic Syntheses,²⁵ and then distilled into a receiver on a vac. line, into which methyl bromide was subsequently added. 2.1 M and 2.2×10^{-3} M, solns. were prepared in this way.

It was dosed in the manner described for isobutene in § 2.1.4.1.

2.1.6.3 Diethyl ether. This material (B.D.H. AnalaR) was freed from peroxides by wetting it with a small amount of water and then drying it with calcium hydride. The production of hydrogen by this means reduced any peroxides which were present. The ether was kept over calcium hydride for about a week before it was dist. on the vac. line on to a second amount of calcium hydride over which it was stored.

It was dosed in methyl bromide soln., and also in bulk, in the manner described for isobutene in § 2.1.4.1.

2.1.6.4 Nonadecane and polyisobutene. These compounds were used in check and blank experiments. Nonadecane (B.D.H. Ltd.) and polyisobutene (obtained from experiment No. D6, and from a previous member of this group, Dr. Beard) were dissolved in ethyl bromide and were then dried over well-ground calcium hydride.

2.2 APPARATUS AND TECHNIQUES

2.2.1 Apparatus

2.2.1.1 Conductivity measurements. Several designs of conductivity-cell were used, and these can be classed as follows: Type (a) had a small vol. ca. 200 ml. and efficient mixing, and was used for kinetic studies and in polymerisation experiments. Type (b) was large in vol., ca. 1000 ml. and was used to study conductivity vs. concn. behaviour. Type (c) was evolved from type (b), but had provision for withdrawing samples of the contents.

The considerations which were taken into account when building the cells are listed below:

The cell must hold vac., and stand pressure to 3 atm., contain no glass taps or cone-socket joints which are sealed with grease; De Khotinsky cement ¹⁸ may be used sparingly to seal ground glass (or preferably Clearfit) joints. The cell should have a phial-breaker, a thermocouple pocket, a stirrer, and platinum electrodes which should be firmly mounted as near as possible to the base of the cell so that the minimum volume which can be used should be as small as possible. The leads to the electrodes should consist of screened-cable, or they should be mounted as far apart as possible to minimise the lead-capacitance, and they must be covered by (a) glass sleeve(s) to a point immediately above the electrodes. The cell should withstand temps. as low as -135° and be able to survive frequent handling.

Type (a)

Several variations of a design due to Bertoli,^{3 4} were used.

Fig. 2.13 shows a version that contained no ground-glass joints and was intended for working under very clean conditions. Tf 1,2,3 represent Teflon washers which hold the stirrer shaft in place; two are used at the top so that their interface acts as a bearing surface. G is a glass tube which holds the lower Teflon ring in place. It was found convenient to cut notches out of the washers Tf 1,2,3, to aid cleaning of the cell. T is a thermocouple pocket, and E denotes the electrodes which are 1 cm² plates of platinum held 1.5 mm. apart by lead-glass beads at each corner.

To ensure that platinum metal only was exposed to the cell contents, and that the minimum amount of expensive 0.5 mm. platinum wire was used, the rather complicated scheme of connections illustrated in Fig. 2.13 was adopted. Note that the copper wire inside the soda-glass tubes was crimped to avoid strain due to thermal contraction or expansion at the soda-glass/platinum wire seals.

In Fig. 2.14 a design is illustrated which proved to be very useful because of the rapidity with which it could be set up, the ease of installation and repair of the electrodes and because it was easy to extricate polymer from it. The electrodes had a conventional arrangement, and were sealed through the base of a 10 mm. soda-glass tube, which was connected by means of a graded seal to a B24 tail-cone. Co-axial cable was used to connect the electrodes to the leads from the conductivity bridge.

Figure 2.13

Type (a) conductivity-cell containing no ground glass joints.

Tf1, 2 and 3 are Teflon bearings. G is a glass "spacer"

tube which holds Tf3 in place. S is the stirrer shaft.

Th is a thermocouple pocket. B is a glass enclosed magnet,

to break the phial P. E denotes the electrodes.

In the diagram showing the arrangement of the leads;

Cu. is copper wire, Sd is a soldered joint, W is tungsten wire,

SW is a spot-weld, Pt is platinum wire, SS is a silver soldered joint.

ROTATING MAGNET.

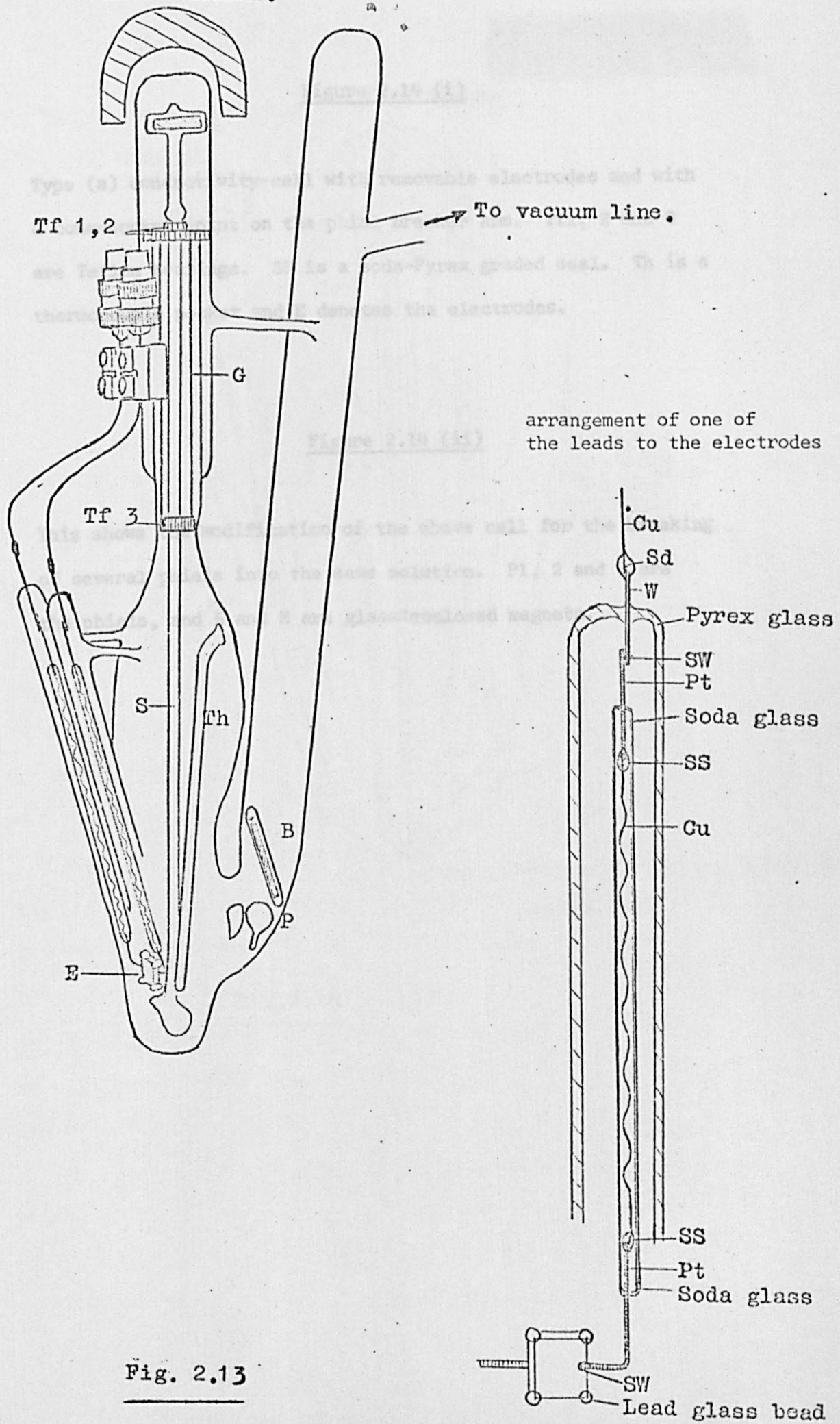


Fig. 2.13

Figure 2.14 (i)

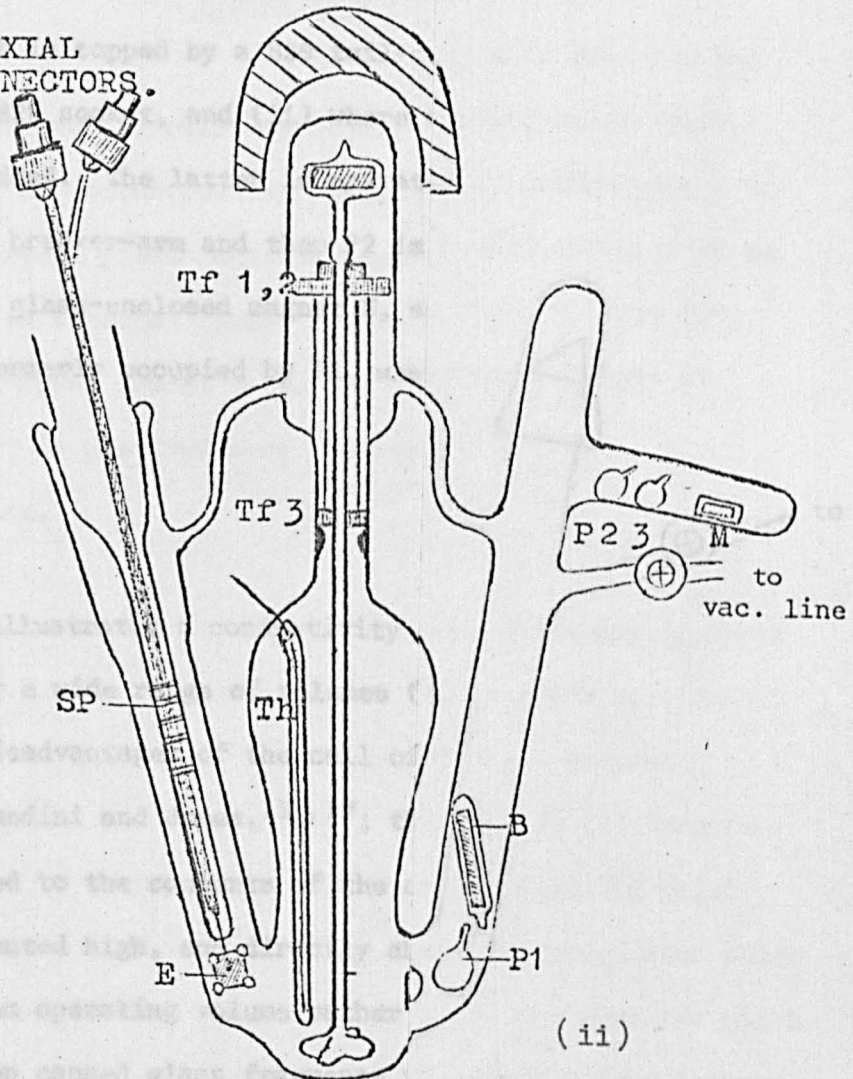
Type (a) conductivity-cell with removable electrodes and with a cone-socket joint on the phial breaker arm. Tfl, 2 and 3 are Teflon bearings. SP is a soda-Pyrex graded seal. Th is a thermocouple pocket and E denotes the electrodes.

Figure 2.14 (ii)

This shows the modification of the above cell for the breaking of several phials into the same solution. Pl, 2 and 3 are the phials, and B and M are glass-enclosed magnets.

ROTATING MAGNET.

COAXIAL
CONNECTORS.



(ii)

please lift

Fig.2.14 (i)

Two arrangements of the breaker-arm tube are shown:

(i) in which it is topped by a B29 tail-cone with drip-end and capped with a B29 socket, and (ii) where a multi-phial-breaker arm has been added. The latter is operated by withdrawing B to the top of the breaker-arm and then P2 is pushed up the reverse slope with the glass-enclosed magnet M, so that P2 falls into the position formerly occupied by P1, whereupon B breaks it.

Type (b)

Fig. 2.15 illustrates a conductivity cell which was designed to operate over a wide range of volumes (30 to 1,000 ml). and to overcome the disadvantages of the cell of similar purpose described by Gandini and Jones,^{19, 17}; these were: (i) Tungsten wire was exposed to the contents of the cell. (ii) The phial breaker was mounted high, and directly above the electrodes which made the minimum operating volume rather high, and when the phial was broken often caused glass fragments to become lodged between the plates. (iii) It contained no thermocouple pocket. (iv) The electrodes were mounted too rigidly, which caused the bottom of the cell to become highly strained when it was cooled to ca. $< -30^{\circ}$. The result was that the glass beads on the electrodes often broke off, or that the body of the cell cracked.

In the cell shown in Fig. 2.15 the electrodes, E were spot-welded to 0.5 mm. platinum wire, Pt and were held 1.5 mm. apart with leads of lead glass. The leads to the electrodes were contained in parallel 5 mm. tubes which were made of Pyrex glass

Figure 2.15

Type (b) conductivity-cell for studies of the dependence of conductivity on concentration. M is a magnet, the shaded areas N represent glass-enclosed magnets, Tf is a Teflon washer. SC is screened cable. Th is a thermocouple pocket. SP is a soda-Pyrex graded seal. SS is a silver soldered joint, and Pt is platinum wire leading to the electrodes E. P is the phial.

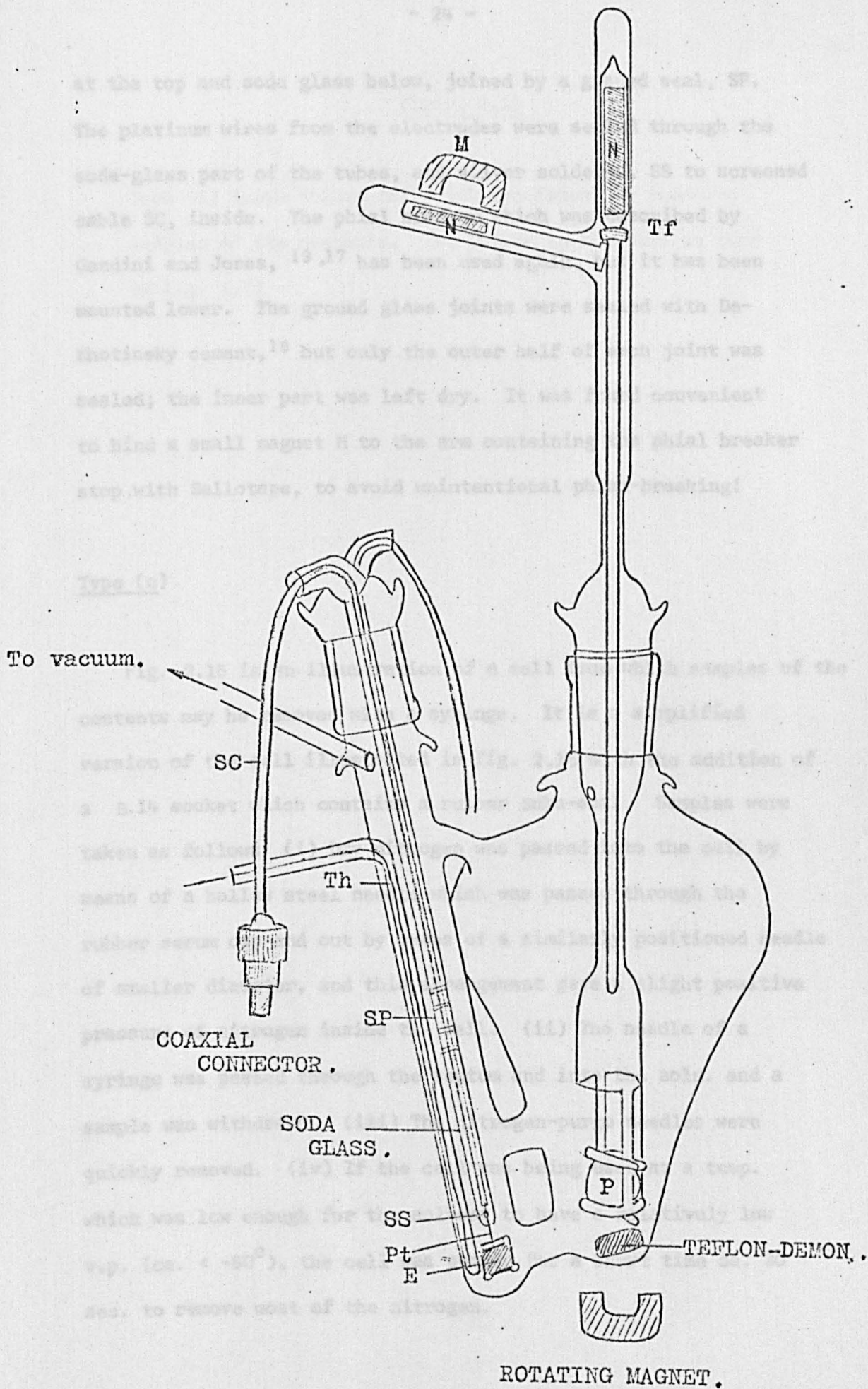


Fig.2.15

at the top and soda glass below, joined by a graded seal, SP. The platinum wires from the electrodes were sealed through the soda-glass part of the tubes, and silver soldered, SS to screened cable SC, inside. The phial breaker which was described by Gandini and Jones, ^{19,17} has been used again, but it has been mounted lower. The ground glass joints were sealed with De-Khotinsky cement,¹⁸ but only the outer half of each joint was sealed; the inner part was left dry. It was found convenient to bind a small magnet M to the arm containing the phial breaker stop, with Sellotape, to avoid unintentional phial-breaking!

Type (c)

Fig. 2.16 is an illustration of a cell from which samples of the contents may be removed with a syringe. It is a simplified version of the cell illustrated in Fig. 2.15 with the addition of a B.14 socket which contains a rubber Suba-seal. Samples were taken as follows: (i) Dry nitrogen was passed into the cell by means of a hollow steel needle which was passed through the rubber serum cap and out by means of a similarly positioned needle of smaller diameter, and this arrangement gave a slight positive pressure of nitrogen inside the cell. (ii) The needle of a syringe was passed through the septum and into the soln. and a sample was withdrawn. (iii) The nitrogen-purge needles were quickly removed. (iv) If the cell was being used at a temp. which was low enough for the solvent to have a relatively low v.p. (ca. $< -60^{\circ}$), the cell was pumped for a short time ca. 30 sec. to remove most of the nitrogen.

Figure 2.16

Type (c) large volume cell with provision for removing samples of the contents. The legend is the same as that of Fig. 2.15

Conductivity Bridge

The conductivity was monitored with a Wayne-Kerr B.221 bridge with an AA-221 Autobalance adapter, which had an output of 0 - 100 mV, and was monitored by one channel of a Rikadenki B - 24 chart recorder. The bridge operates on the transformer ratio-arm principle,¹² has a source of 1592 c./sec., and is capable of reading in the range from 1 to 10^{-11} mho, with an accuracy better than 0.1% in the range from 1 to 10^{-8} mho. The bridge functions at its best when the leads to the electrodes are short and coaxial.

Cell-Constant

The cell-constants were measured at 25° with 0.01 M B.D.H. Volucon potassium chloride soln. made up to 2 l. with de-ionised and dist. water with a very low conductivity. The volume of the flask was calibrated with dist. water at 25°. The Lind-Zwolenik-Fuoss equation was used to calculate the cell constants.²¹ The cell-constant was not corrected for temp. because it is only affected by slight changes in the dimensions of the electrodes, which counterbalance one another to some extent. The cell-constant of electrodes of the conventional arrangement has been calc. as changing by 0.1% over 100°.

2.2.1.2 Radiochemical assay. Scintillation counting. Both ^{14}C and ^3H are weak β^- emitters. ^{14}C has a half-life of 5730 years and a particle energy of 0.156 MeV., but it is stopped completely by the glass wall of its container. Because the radiation of these sources is weak, it is difficult to detect with counters which have ionisation chambers which the radiation must penetrate in order to be observed, i.e. Geiger or proportional counters. It is necessary to use a scintillation method where the source is either in soln. with/or adjacent to a phosphor which emits photons when irradiated with β^- particles; the emitted photons are easily counted with a photomultiplier. There are many good accounts of the scintillation process.^{23,20} When the source is in soln. with the phosphor, this is termed liq. scintillation counting and it was the technique that was used in this work; the efficiency of this process of observing emitted photons rather than the actual disintegrations is normally about 75% for ^{14}C and 25% for ^3H . It is well known that the number of counts p.s. is accurately proportional to the disintegrations p.s.^{23,20,16}

The concn. of a species which has been labelled with a radioactive source can thus be determined easily by measuring the c.p.s. of a known amount of soln.

Koch Light KL 356 liquid phosphor was the scintillator which was chosen. It is especially suitable because it is based on xylene, has a high efficiency for ^{14}C and ^3H , and it has an emission max. at 425nm which matches the photomultipliers of the I.D.L. counter used in this work.

Toluene was chosen as the solvent for radiochemical assay, since it is ideal for scintillation work, ^{16,23,20} and all of the polymers studied were soluble in it.

Determination of count rate. The procedure was based on that used by Bevington's group,⁸ with whom I was fortunately able to spend a few days studying it.

(i) The background count R_b c.p.s., was measured by placing 3.5 ml. of phosphor soln. in a size A glass counting vial, and measuring the number of counts in a series of 1,000 sec. periods for ca. 30 min. The time required for counting varied in a manner which depended on the activity of the sample to be measured and the degree of fluctuation of the count rate.

(ii) 0.25 ml. of a toluene soln. of a sample of unknown activity was added to the phosphor solution, and the count rate, R_a c.p.s. was determined as in (i).

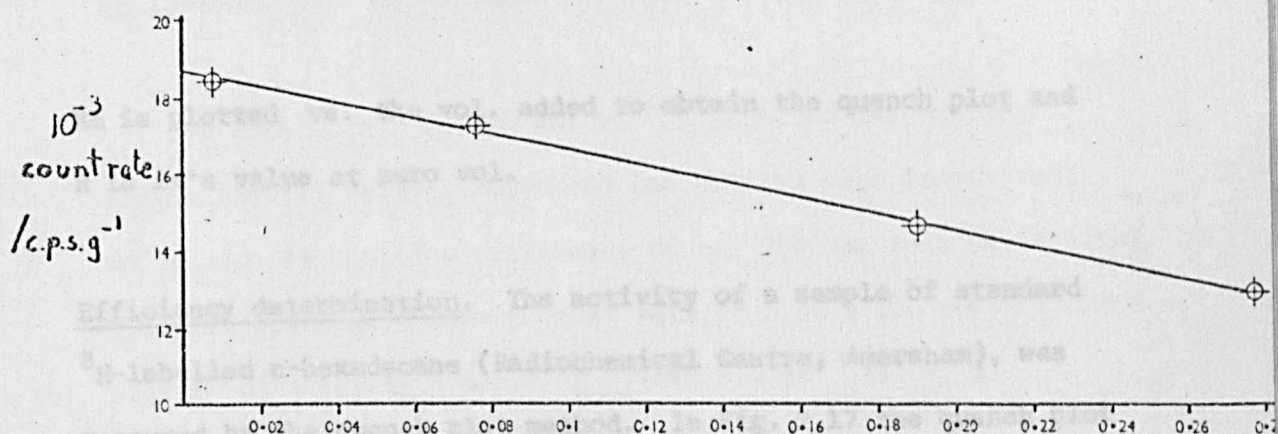
(iii) The procedure (ii) was repeated three times until the total vol. in the vial was 4.5 ml.

Figure 2.17

Quench plot for a standard solution of ^3H labelled n-hexadecane in toluene. The intercept at zero g. of n-hexadecane gives the count-rate uninfluenced by quenching. This is considered to be a good quench plot.

(iv) The count rate per mg. of the sample, R_a , was plotted vs. the vol. of added solvent, and the activity of the sample X was taken from the intercept of the plot at zero added vol. This is referred to as a 'quench plot', and overcomes any reduction of counting efficiency due to impurities such as water or air in the polymer soln.^{5,7,8} The background count R_b must be subtracted from R_a to obtain the actual count rate for each addition of solvent vol. If each addition contains X g. of active material, the count rate per mg. R_a is given by:-

$$R_a = (R_a - R_b) / 10^{-3} \times \text{c.p.s. mg.}^{-1}$$



no. of g. of n-hexadecane.

Fig. 2.17

(iv) The count rate per mg. of the sample, R_m , was plotted vs. the vol. of added toluene soln., and the activity of the sample R was taken from the intercept of the plot at zero added soln. This is referred to as a, 'quench plot', and overcomes any reduction of counting efficiency due to impurities such as water or air in the polymer soln.^{5,7,8} The background count R_b must be subtracted from R_a to obtain the actual count rate for each addition of toluene soln. If each addition contains x g. of active material, the count rate per mg. R_m is given by:-

$$R_m = (R_a - R_b)/10^3 x \quad \text{c.p.s. mg.}^{-1}$$

R_m is plotted vs. the vol. added to obtain the quench plot and R is it's value at zero vol.

Efficiency determination. The activity of a sample of standard ^3H -labelled n-hexadecane (Radiochemical Centre, Amersham), was measured by the quench plot method. In Fig. 2.17 the quench plot gives a sample activity, R , of 18.6 c.p.s. mg.⁻¹. The sample was certified by the Radiochemical Centre, Amersham as having an activity of 78.330 d.p.s. mg.⁻¹ on 1st March 1973, when the counter efficiency was checked. (Because ^3H has a short half-life the activity drops a small, but significant, amount each month, and allowance must be made). The efficiency for ^3H was $100 \times 18.6/78.330 = 23.8\%$. The ^{14}C efficiency was similarly determined by means of a ^{14}C -labelled benzoyl peroxide of known activity, kindly given by Professor J.C. Bevington,⁸ and was found to be 73%.

Calculations. The procedure for calculating the number of g. equivalents of labelled atoms per mole of material:

The amount of incorporated ^3H -labelled hydrogen was calculated as follows: 5 mCi of tritiated water (Radiochemical Centre, Amersham) was diluted to 100 ml. One g. equivalent of hydrogen, (or $\frac{1}{2}$ mole of the water) has $9 \times 5 \times 3.7 \times 10^5$ d.p.s. Since the efficiency is ca. 24% this means that for each g. equivalent of hydrogen 4.00×10^6 c.p.s. will be observed, and if a polymer has a count rate of R c.p.s. g^{-1} it contains $R \times 10^{-6} \times 0.25$ equivalents g^{-1} of labelled hydrogen.

For work with ^{14}C , 250 μCi of ^{14}C -labelled isopropanol (Radiochemical Centre, Amersham) was diluted with isopropanol to 20 ml. At counting efficiency of ca. 73% one mole of labelled material gives an observed count rate of 2.58×10^7 c.p.s., and a polymer of activity R c.p.s. g^{-1} , has $R \times 10^{-7} / 2.58$ g. equivalents of ^{14}C incorporated.

Instrumentation. An I.D.L. tritium scintillation counter type 6012 was used. This comprises a lead-shielded coincidence counting head, and a coincidence control unit. Inside the counting head are two photomultiplier tubes mounted on opposite sides of the counting chamber. When in the coincidence mode of operation the control unit recognises only those events which occur simultaneously in both tubes, and thus nearly all the tube noise is eliminated, which means that the background count, R_b , is very low, ca. 0.5 c.p.s. This makes it possible to count accurately weak emitters such as ^3H and ^{14}C , down to low levels with great ease.

The pulse output from the control unit was fed into a Panax series P 7100 scaler, which was regulated by a Panax series P 7200 timer. The timer and scaler were controlled by a Panax PXPCU-1 unit, which enabled the counter to run automatically with a fixed time interval and the number of counts and the time interval were recorded on a Kienzle printer. For ^3H the high voltage settings used were HV1, 1580V. and HV2, 1740V., and for ^{14}C , HV1, 1300V. and 1380V., in each case the upper gate was 40V. (These values were recommended by the I.D.L. manual).

With this counter it is possible to count separately the ^{14}C and ^3H content of a doubly labelled sample. The high voltage settings are reduced until H^3 does not register, and the efficiency for ^{14}C is determined; this is channel 1. The efficiencies for both ^{14}C and ^3H are determined at the normal high voltage settings for ^3H ; this is channel 2. A doubly labelled sample of unknown composition is analysed by counting it on channel 1 and finding the ^{14}C content, and then on channel 2 and subtracting the calculated count rate for the ^{14}C from the total and hence obtaining the count rate for ^3H .

2.2.1.3 Distillation. Fractional distillations were performed with a Normatron automatic laboratory distillation apparatus, which consisted of a two m. vac.-jacketed, silvered column packed with Fenske-helices, surmounted by a still-head in which the take-off was controlled by a magnetically operated valve. The column was equivalent to ca. 100 theoretical plates, and would

operate up to a reflux ratio of 100 : 1. Very accurate control of the collected fractions was possible by means of contact thermometers which activated an audible warning when the temp. of the distillate rose by $> 0.05^{\circ}$.

2.2.1.4 Gas-chromatography. Most of the measurements were made on a Hewlett-Packard Series 5700A instrument, with 8' x 1/16" columns of 80-100 mesh Porapak-Q. This instrument was acquired during the latter part of the work, and is much superior to the Perkin-Elmer F11 which was used at first and is described in previous theses (for instance see Jones).¹⁹ The chromatograph has a 0.1% repeatability of oven temp., and an arrangement for programming the oven temp; dual-column analysis by flame-ionisation-detection, f.i.d. and thermal-conductivity, t.c. are both available, though not simultaneously. The f.i.d. is a new design which is capable of registering to the p.p.b. level, and the t.c. is one of the most sensitive of this type available which makes possible detection down to p.p.m. quantities. The advantage of the t.c. system is the uniformity of response to all manner of materials (especially water). The f.i.d. system does not respond to water or air. T.c. detection is particularly useful in monitoring impurities in solvents, and provides a useful method for checking various drying procedures.

Certain cmpds. such as α -methylstyrene and styrene were not suitable for analysis with Porapak Q columns, and were analysed with the Perkin Elmer F 11 instrument¹⁹ with Chromosorb S.E.20 columns.

2.2.1.5. Molecular weight determination. M.w. below ca. 15,000 was determined with a Mechrolab Vapour Pressure Osmometer, Model 301A which had a non-aqueous probe. The instrument operated at 37°, and the determinations were made in chloroform soln. Polymers of greater m.w. were measured in toluene soln. with a Hewlett Packard High Speed Membrane Osmeter 1852A which operated at 30°. The membrane osmometer was calibrated with a polystyrene of known m.w.

2.2.1.6 G.l.c. - mass spectrometry. Measurements were made with a Pye-Unicam g.l.c. machine containing the appropriate columns, attached directly to a Perkin-Elmer-Hitachi mass-spectrometer.³²

2.2.1.7 Greaseless vacuum taps. Teflon and metal Bi Pl.¹¹ taps were both used. Several makes of Teflon taps were tried, the most useful proved to be the Rotaflo.³³ The Teflon tap made by J. Young Ltd.,³⁴ does not have an adjustable seal between the body of the valve and the key as do the Rotaflo and Torion taps but relies on the provision of an extra rubber O ring. The Torion tap³⁵ makes use of an O ring made of a Teflon-silicone rubber sandwich to make a vac. tight seal between the key and the body of the valve.

This O ring can be adjusted by means of a compression screw, but is very easily torn.

The Rotaflo tap has the advantage that the seal between the key and the glass barrel of the tap is visible, and when the Teflon is in good contact with the glass it appears to "wet" the glass surface. As opposed to the Bi Pl tap, the Rotaflo tap does not hold vac. as well. A good Rotaflo tap will not hold black vac. ($< 10^{-4}$ mm.) for more than ca. four days, and can therefore only be used in applications where this is of little consequence. (i.e. under positive pressure, against liq. or for use shortly after pumping).

The technique for using Rotaflo taps

- (i) The tap must be free from grit and dust, have an even barrel and an unscored Teflon key.
- (ii) The tap must be gently flamed out before use, and then adjusted to give an evenly shaped area of contact between the glass barrel and Teflon key.
- (iii) When in use the tap must be kept as near room temp. as possible, because Teflon has a higher coefficient of expansion than glass, and the spark from a Tesla coil must never be allowed to come near the Teflon, which is easily punctured by the spark.

2.2.1.8 Temp. measurement. The temp. of the contents of the cells was measured by a three-point-copper-constantan thermocouple, with the reference junctions in a dist. water-ice bath. The output was monitored by feeding the difference between the potential of the thermocouple and a smaller accurately known potential, supplied by a Doran-mini-thermocouple potentiometer, into a Rikadenki A-10 Microvoltmeter having a range between 1 μ V and 2 mV and an internal resistance of several M Ω . The scale reading of the microvoltmeter was in turn monitored by one channel of a Rikadenki B-24 chart recorder. This system enabled me to measure 0.01 $^{\circ}$ changes in temp. with ease. The thermocouple was calibrated at the f.p. of methylene chloride, -96.7 $^{\circ}$, chloroform at -63.5 $^{\circ}$, carbon tetrachloride at -22.8 $^{\circ}$ and water, and the calibration curve agreed well with that in the literature.^{18(b)}

2.2.2 Spectroscopy

2.2.2.1 Infra red spectroscopy. All i.r. spectra were run on a Perkin-Elmer 257 Grating Infrared Spectrometer. The instrument was calibrated by means of a polystyrene film. With high m.w. polymers, transparent films were prepared directly on the rock salt plates by evaporating to dryness a conc. soln. in methylene dichloride. Low m.w. polymers were scanned on sodium chloride plates or as 1% solns. in carbon tetrachloride.

2.2.2.2 Ultraviolet and visible spectroscopy. The spectra reported in this work were run on either a Beckman D.B. recording

spectrophotometer or a Unicam SP.800 instrument. To measure the absorption of species which were sensitive to the atmosphere, or were in methyl bromide soln., an apparatus was used which has been described by Bertoli in his thesis on page 29,³ and has been described in the literature.⁴

2.2.2.3 Nuclear magnetic resonance spectroscopy. A Perkin-Elmer M-R10 n.m.r. Spectrometer, provided with an integrating circuit, was used throughout this work. This instrument has a ^1H resonance at 60 Mc. sec.^{-1} and is thermostated at 35° . For compounds dissolved in carbon tetrachloride the position of the n.m.r. bands was determined by reference to TMS at 10τ as an internal standard.

2.2.3 Experimental Methods

2.2.3.1 Conductivity expts. The expts. were carried out in the cells described and illustrated in § 2.2.1.1. The temp. and conductance were simultaneously and continuously recorded throughout each expt. with the Rikadenki chart recorder in the manner described in § 2.2.1.1. and 2.2.1.8. Expts. were performed at -126° , with a slush bath of methyl-cyclohexane, at -78.5° with a mixture of acetone and solid carbon dioxide, at -63.5° with a chloroform freezing mixture, at -23° with a mush of carbon tetrachloride and at 0° with a bath of ice and dist. water. With careful attention it was possible to maintain the temp. to within a degree, and since in many cases the temp. dependence of the studied properties was slight, this proved to be quite adequate.

A typical procedure for a conductivity expt. was as follows. The cell was washed (i) for ca. 30 sec. with 20% vol./vol. hydrogen fluoride soln. (ii) water (iii) with dilute sodium hydroxide soln. (iv) with ca. ten amounts of dist. water until the pH of the washings was seven (monitored by B.D.H. universal indicator). The cell was sealed to the vac. line, pumped down to ca. 10^{-4} torr (black vac.) and heated with a hot-air-blower for ca. 4 h.; if possible the cell was kept under high vac. for 24 h. before use. Solvent was dist. into the cell in the way described in § 2.1.1.1., and its conductivity was noted. When the temp. and conductivity were stable the phial of aluminium halide was broken and the change of conductivity was observed. Normally at the end of the expt. the solvent was dist. out and the aluminium halide was hydrolysed and analysed as described in § 2.2.3.4.

2.2.3.2 Polymerisations. The initiator soln. was prepared in the manner described in § 2.2.3.1. A polymerisation was conducted by adding the monomer with the appropriate dosing apparatus directly into this soln. The burettes which contained monomer were either sealed directly to the top of the cell, or to a side arm. The latter arrangement is illustrated in Fig. 2.18, and vessel C contains the monomer soln. The monomer was run in when the conductivity was relatively stable, so that when it was added in several amounts, between ca. 15 min. and 1 h. was allowed to elapse in between additions, to allow the conductivity to re-equilibrate..

Figure 2.18

Apparatus for carrying out polymerisations which were followed by the hydrolysis of polymers with labelled water. On the left is the conductivity cell shown in Fig. 2.14 (i). E denotes the electrodes, P the phial and B the phial breaker. Tf1 to TF10 are Teflon taps, B1 is a 1 ml. burette, B2 is a 2 ml. burette and B3 is a 20 ml. burette. A is a 50 ml. portable flask containing tritiated water. C contains monomer solution and D contains toluene.

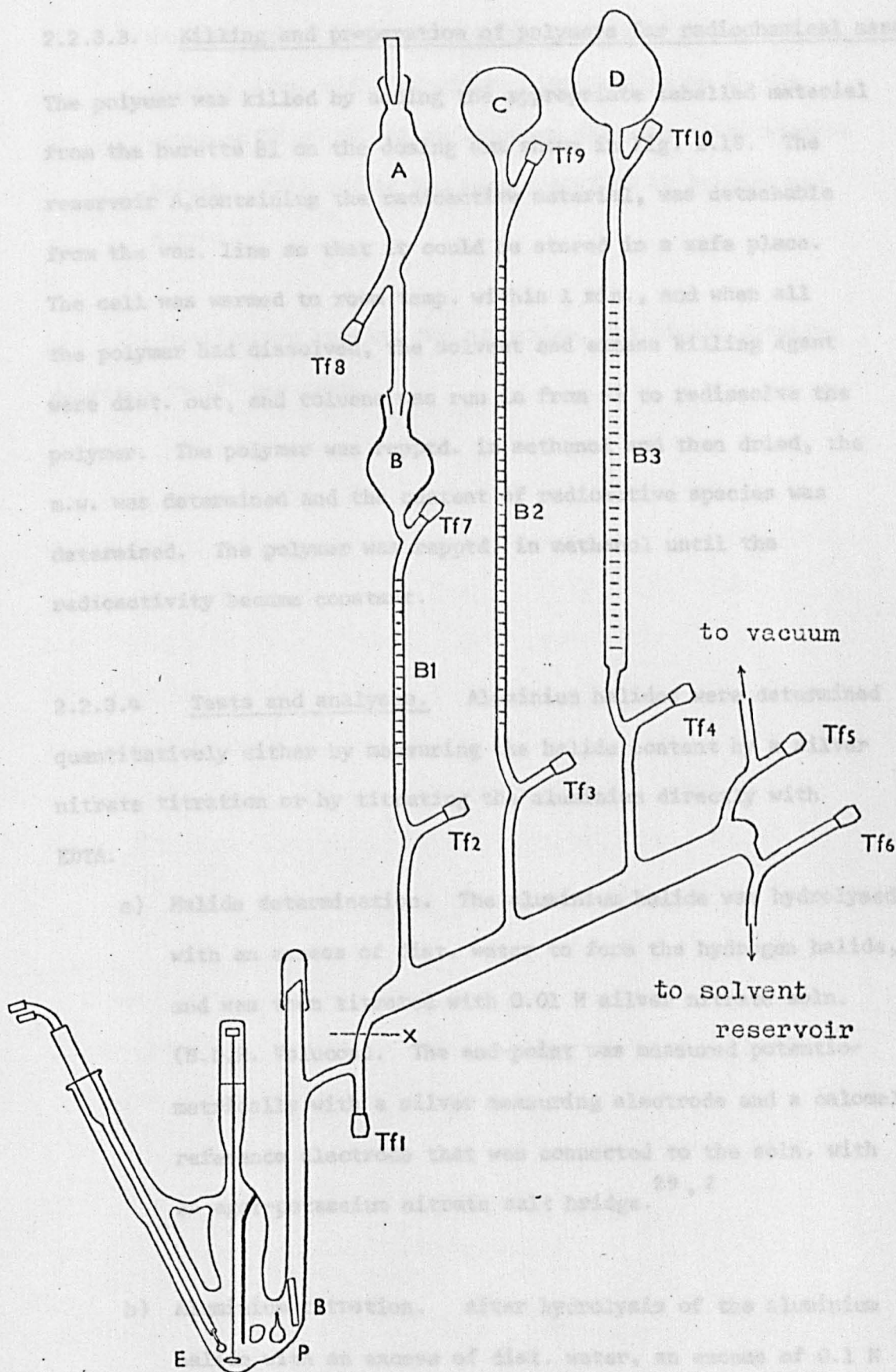


Fig.2.18

2.2.3.3. Killing and preparation of polymers for radiochemical assay

The polymer was killed by adding the appropriate labelled material from the burette B1 on the dosing arm shown in Fig. 2.18. The reservoir A, containing the radioactive material, was detachable from the vac. line so that it could be stored in a safe place. The cell was warmed to room temp. within 1 min., and when all the polymer had dissolved, the solvent and excess killing agent were dist. out, and toluene was run in from B3 to redissolve the polymer. The polymer was repptd. in methanol and then dried, the m.w. was determined and the content of radioactive species was determined. The polymer was repptd. in methanol until the radioactivity became constant.

2.2.3.4 Tests and analyses. Aluminium halides were determined quantitatively either by measuring the halide content by a silver nitrate titration or by titrating the aluminium directly with EDTA.

- a) Halide determination. The aluminium halide was hydrolysed with an excess of dist. water to form the hydrogen halide, and was then titrated with 0.01 M silver nitrate soln. (B.D.H. Volucon). The end-point was measured potentiometrically with a silver measuring electrode and a calomel reference electrode that was connected to the soln. with an agar-potassium nitrate salt bridge.^{29, 2}
- b) Aluminium titration. After hydrolysis of the aluminium halide with an excess of dist. water, an excess of 0.1 M disodium EDTA soln. was added, and then the aluminium

was determined by back-titrating with 0.06 M magnesium nitrate soln. with Eriochrome black indicator in the presence of 10 ml. of an ammonium chloride + 880-ammonia buffer. This method has been described by Belcher and Nutten.²

For qualitative testing for aluminium, the highly sensitive Aluminon test³⁰ was used.

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CHAPTER THREE

THE INVESTIGATION OF THE CHEMISTRY OF ALKYL HALIDE SOLUTIONS OF ALUMINIUM HALIDES

3.1 INTRODUCTION

The interaction between an aluminium halide and an alkyl halide has been the subject of much speculation and experimental work. The elimination of hydrogen halide, the isomerisation of the alkyl group, the conductivity, the vapour pressure, the exchange of halogen atoms between the halides represent but a few of the studies. To summarise the work has obviously been a problem, and this undoubtedly accounts for the comprehensive rather than critical nature of most of the recent literature surveys. In order to place the experimental work presented here in its correct context, a short review of the relevant papers has been included at the beginning of this chapter.

For an understanding of the role of the aluminium halides as initiators of cationic polymerisation we must know what is their state in solution, especially with reference to formation of ions and the effects of impurities. While the experiments to be described were being carried out, a general theoretical interpretation of the behaviour of various types of ionogenic equilibria was also being made, and this is included in Appendix 1. As will become clear from the literature survey, the ionisation of these systems had not been properly interpreted hitherto, and many interpretations have been expressed without theoretical or experimental backing.

Figure 3.1

The results of previous conductivity studies for aluminium bromide and methyl bromide by Wertyporoch³⁴ in 1931 at -78° , Fairbrother and Scott²⁰ in 1955 at 25° , and Jacober and Kraus¹⁹ in 1949 at 0° and -78° and the results obtained in this work at -63° and 0° .

3.2 A short literature survey of aluminum halide chemistry

3.2.1 Physical properties. The halides of aluminum differ

markedly from the fluoride to the iodide. The fluoride and chloride have the coordination number six, but for the bromide and iodide it is four. Aluminum fluoride is a polymer (see later).

Aluminum chloride is a dimer (see later) with a melting + boiling + decomposition point of 192°C + 180°C + 180°C respectively.

Aluminum bromide is a dimer with a melting point of 95°C and a boiling point of 255°C. It is a weak Lewis acid.

Aluminum iodide is a dimer with a melting point of 119°C and a boiling point of 346°C. It is a weak Lewis acid.

The halides of aluminum are all Lewis acids. The fluoride is the strongest, followed by the chloride, bromide, and iodide.

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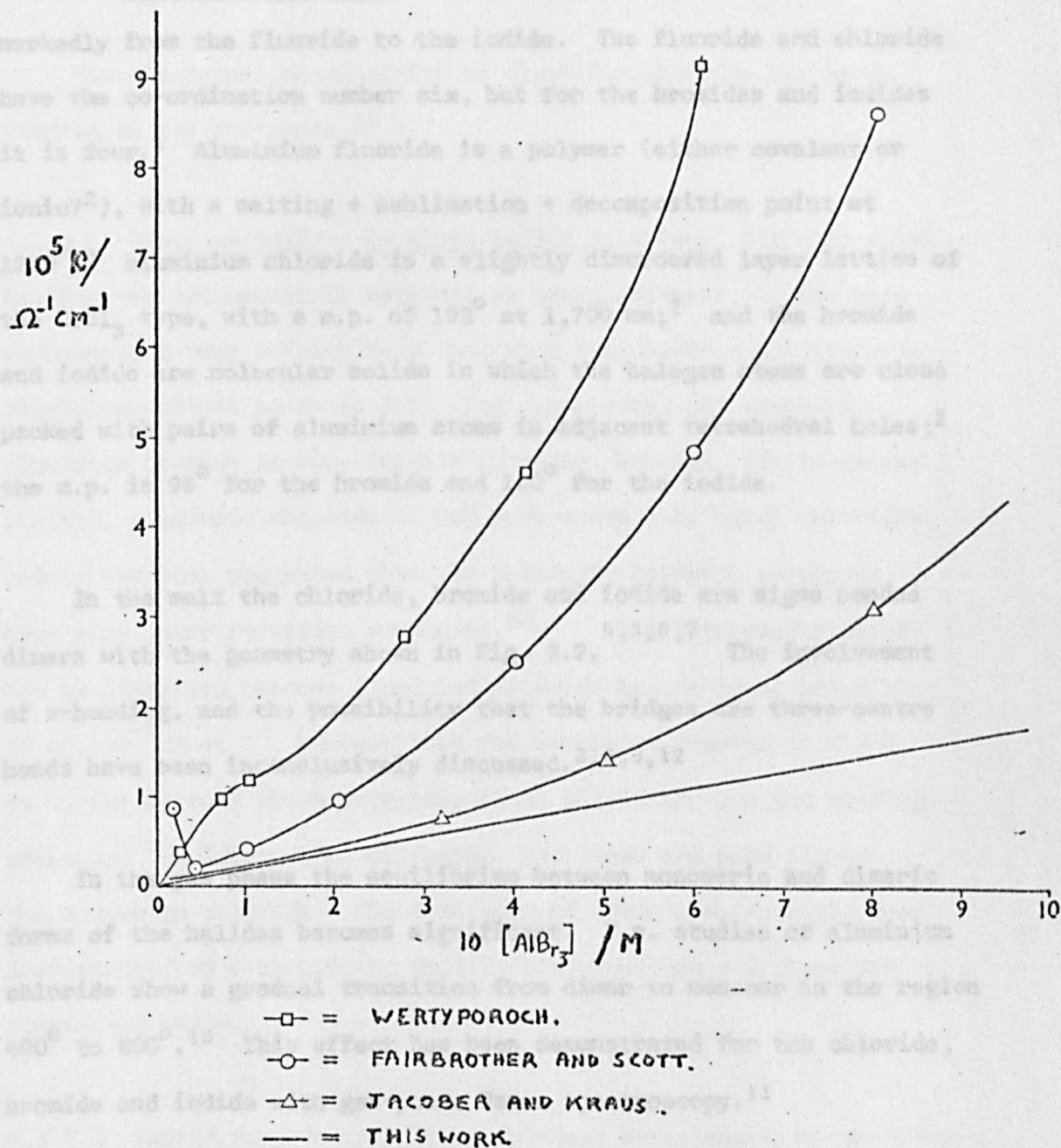


Fig.3.1

3.2 A short literature survey of aluminium halide chemistry

3.2.1 Physical properties. The halides of aluminium differ markedly from the fluoride to the iodide. The fluoride and chloride have the co-ordination number six, but for the bromides and iodides it is four.¹ Aluminium fluoride is a polymer (either covalent or ionic?²), with a melting + sublimation + decomposition point at 1290°;³ aluminium chloride is a slightly disordered layer lattice of the CrCl_3 type, with a m.p. of 193° at 1,700 mm;² and the bromide and iodide are molecular solids in which the halogen atoms are close packed with pairs of aluminium atoms in adjacent tetrahedral holes;² the m.p. is 98° for the bromide and 180° for the iodide.

In the melt the chloride, bromide and iodide are sigma bonded dimers with the geometry shown in Fig. 3.2.^{4,5,6,7} The involvement of π -bonding, and the possibility that the bridges are three-centre bonds have been inconclusively discussed.^{3,8,9,12}

In the gas phase the equilibrium between monomeric and dimeric forms of the halides becomes significant. V.p. studies of aluminium chloride show a gradual transition from dimer to monomer in the region 400° to 800°.¹⁰ This effect has been demonstrated for the chloride, bromide and iodide with gas-phase Raman spectroscopy.¹¹

An interesting feature of aluminium chloride is that the solid shows an electrical conductivity which increases with temp. until the m.p. whereupon it falls to zero, and as the temp. increases beyond the m.p. the conductivity rises steadily.^{13,14} Aluminium iodide and bromide are conducting in the melt only. (The conductivity of

aluminium chloride has been used to argue that it is an ionic solid, but it may be that the conductivity is a feature of a layer lattice structure. e.g. graphite; (see Olah Vol. 1. page 239).⁵²

The electrical conductivity of aluminium chloride has been studied in the gas-phase.¹⁵

3.2.2 Aluminum halides in alkyl halide solution. Although alkyl halides are not generally regarded as basic solvents, it has been demonstrated very conclusively that they can donate n electrons to aluminium halides so as to form 1:1 complexes, and therefore aluminium bromide is very soluble in methyl bromide, for instance. However, aluminium chloride is not very soluble in alkyl chlorides, and it has been suggested that the analogous chloride complexes have much lower formation constants.^{80,17} This interpretation may not be justified because aluminium chloride has an ideal solubility of ca. 10^{-5} M at 0° , whereas that for aluminium bromide is 1.3 M at 0° . The factors which determine ideal solubility are the melting point and the latent heat of fusion, and these are both higher for aluminium chloride. The existence of these complexes has been demonstrated by a surprising variety of techniques and these are summarised below.

3.2.2.1 Vapour pressure studies. In these experiments the dependence of the vapour pressure of a solution of an aluminium halide in an alkyl halide as a function of the mole fraction was measured. Compound formation was shown when the vapour pressure became constant as the molar ratio of alkyl halide to aluminium was decreased, and the stoichiometry was given by the composition at which this occurred.

Table 3.1

Walker's⁴⁸ results for the equilibrium constant of dimerisation of aluminium bromide in methyl bromide.

Temp./°	$K_n / (\text{mole.l}^{-1})^{\frac{1}{2}}$
5.3	0.256
0	0.216
-8.1	0.137
-23.9	0.076

$$K_n = \frac{(\text{MeBr}) (\text{Al}_2\text{Br}_6)^{\frac{1}{2}}}{(\text{MeBr} : \text{AlBr}_3)}$$

Aluminium bromide and methyl bromide have been shown to form a 1:1 complex.^{28,48,80,17} Walker⁴⁸ measured the value of the equilibrium constant of dimerisation by this method for the above system, and in addition deduced that the strength of the n-donor bond was 19 k.cal.mole.⁻¹. The variation of the equilibrium constant of dimerisation with temperature is shown in Table 3.1.

3.2.2.2 The elevation of boiling point. Dumarevska⁵¹ measured the molecular weight of aluminium bromide in ethyl bromide solution as ca. 270 (calculated value = 266.7), by the elevation of the boiling point. (Ethyl bromide boils at 38° at 1 atm). This shows clearly that the solute is largely monomeric, and that the bridged dimer is at best a scarce species in these solutions.

3.2.2.3 Dielectric polarisation. The existence of the weak complex between aluminium bromide and ethyl bromide was elegantly demonstrated by Sheka and Sheka,⁵⁰ who had noted the ebullioscopic study by Dumarevska (§ 3.2.2.2) and had construed the results to be indirect evidence of a complex with solvent. By measuring the divergence of the experimentally determined dielectric constant and dielectric polarisation from the values predicted by simple addition of the components, and assuming that a maximum in this divergence occurs at the ratio of the components which corresponds to the composition of the complex, its existence and stoichiometry were confirmed. (This "divergence", is more commonly called "dielectric loss"). They obtained curves with maxima at a 1:1 ratio of aluminium bromide to ethyl bromide.

3.2.2.4 Freezing point phase diagram. Burbage and Garrett⁵⁶ found that whereas the aluminium bromide + bromine, aluminium bromide + bromoform and aluminium bromide + bromobenzene systems gave simple eutectics, aluminium bromide + ethyl bromide showed compound formation at a 1:1 ratio of components. Brown and Wallace^{65,66} determined the freezing point phase diagram of aluminium bromide + methyl bromide, and showed the presence of a 2:1 complex which crystallised out at -31° to -45.8° , in addition to the 1:1 complex.

3.2.2.5 U.v. spectroscopy. Korshak and Lebedev^{57,64} noted that the threshold of absorption of ethyl bromide was altered from below 250nm to 256 nm in the presence of aluminium bromide, and that the intensity of absorption was increased. (At 250nm the absorption was doubled). Although the concn. was varied from 2 to 20%, little or no alteration in the phenomenon occurred. Their explanation was that a large number of solvent molecules must be associated with each molecule of aluminium bromide, and quoted their value of the heat of solution, $0.95 \text{ k.cal.mole.}^{-1}$ in support of this. H.C. Brown⁶⁶ suggested that the effect was due to the strong dipole set up in the complex. Why the effect is independent of solute concentration has not been explained satisfactorily.

3.2.2.6 I.r. and Raman spectroscopy. Several studies^{53,55,62} of the methyl bromide solution of aluminium bromide have been carried out. The two most extensive are the measurements in the i.r. by Rice and Bald⁵³ and in the Raman by Kinsella and Coward.⁵⁵ Despite some minor differences of opinion as to the assignment of certain bands, confirmation was obtained of the aluminium bromide complexes in methyl and ethyl bromide solution. Kinsella and Coward noted that the bands due to Al_2Br_6 decreased with increasing dilution.

Sixma and Hendriks^{72,73} used a spectrophotometric titration method to demonstrate the 1:1 complex between aluminium bromide and β -phenylethyl bromide.

3.2.2.7 Conclusions. It may be concluded that from 0° to -90° the aluminium bromide molecules are present in methyl bromide solution mainly as a 1:1 n donor complex with the solvent, with a very small amount of the dimer. A small concentration of the 1:2 and 2:1 complexes may also be present.

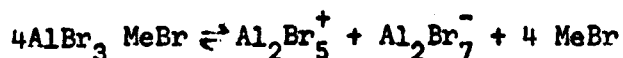
3.2.3 The ionisation of aluminium halides in alkyl halide solution

3.2.3.1 Conductivity studies. In 1904 J.W. Walker¹⁸ observed that whereas aluminium chloride solutions in methyl, ethyl and n-propyl iodide and in ethyl bromide conducted electricity, ferric chloride solutions did not. In the inter-war period several groups of Russian workers investigated alkyl halide + aluminium halide + alkali-metal halide systems and reported the effect of the alkali metal halide on the overall conductivity.^{16,27,60} Katsnelson²⁷ investigated the conductivity of highly concentrated solutions of aluminium bromide in ethyl bromide and found a maximum in the conductivity at a mole fraction of solute of ca. 0.39, which compares interestingly with the result found by Longworth and Plesch²² who found a similar maximum at a mole fraction of 0.031 for titanium chloride in methylene chloride. In 1931 Wertyporoch^{26,34} attempted a serious study of the concentration dependence of the conductivity of aluminium bromide in ethyl bromide, but he found that the conductivity was unstable and that the solutions were yellow, which indicates that a high concentration of impurities was present.

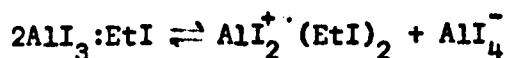
Further studies were made in 1949 by Jacober and Kraus,¹⁹ with methyl bromide solvent and in 1955 by Fairbrother and Scott²⁰ who used ethyl bromide. Jacober and Kraus found that the equivalent conductance changed little with concentration or temperature, but measurements were made at six concentrations only. Fairbrother found that the solns. were unstable; the conductivity increased with time, and he assumed that this was caused by the slow dissociation of the ethyl bromide solvent to form ethane and hydrogen bromide. He therefore made conductivity measurements at 25°, by keeping the solutions at -78°, and then following the change in conductivity after the conductivity cell had been rapidly warmed to 25°. He obtained a reading by extrapolating the conductivity to zero time. In Fig. 3.1 the results of the above conductivity determinations are compared. It is reasonable to suppose that the overall conductivity depends on the amount of impurities present. Jacober and Kraus worked with methyl bromide which can be obtained purer than ethyl bromide, because the dissociation equilibrium shown below does not exist.



(It has also been observed that aluminium bromide in ethyl bromide solution undergoes photodecomposition.⁵⁴) All three curves show an upward curvature, and the conductivity is roughly proportional to the square of the concentration which suggests that the dissociation is as follows (see Appendix 1).



In 1963 Halpern and Polaczek²¹ reported studies of the conductivities of aluminium, gallium and indium iodides in alkyl iodide solvents. They found that the conductivity increased with time, and they therefore used Fairbrother's method of obtaining the "real" conductivity. For aluminium iodide in ethyl iodide the conductivity depended linearly on concentration, which suggests an ionisation of the following type: (see Appendix 1).



Halpern and Polaczek disagreed with Fairbrother's idea that the steady increase in conductivity was due to de-hydrohalogenation of solvent, because after making mass-spectrometric investigations no relative change in the ratio of the peak heights of hydrogen iodide and ethyl iodide was observed after 70 h.

Švestka²⁴ studied the conductivity of aluminium bromide in heptane and in benzene solution. This work provides an interesting comparison with the experiments with alkyl halides as solvents. The dissociation was interpreted according to the scheme shown below, and dissociation constants of 7×10^{-23} and 7.5×10^{-17} M at 21° for heptane and benzene solution respectively, were obtained.



This interpretation is an oversimplification because the dielectric constant of these solvents is so low that the major conducting species are probably agglomerates of ions, (i.e. Al_2Br_5^+ , Al_2Br_7^- , and $\text{Al}_2\text{Br}_5^+\text{Al}_2\text{Br}_7^-\text{Al}_2\text{Br}_5^+$ etc.) rather than simple monomeric and/or singly

Table 3.2

Results of the transport experiments of Sheka and Sheka and of Van Dyke, for aluminium bromide in alkyl bromide solvent.

No	Ref	Solvent	Vol. /ml.	Original Concn./M	Final concn./M		No of Faradays	g. of Al. plated out at cathode	Temp/°C
					Anode	Cathode			
A	28	MeBr	127	0.915	0.913	0.869	6.24×10^{-3}	1.15	-78°
B	28	MeBr	132	0.602	0.602	0.561	7.9×10^{-3}	1.55	-78°
					Decrease in conc. in cathode section.				
C	39 40	EtBr	-	0.625	-	8.74×10^{-4}	1.335×10^{-3}	?	ca. 20°?
D	39 40	EtBr	-	0.623	-	9.78×10^{-4}	1.466×10^{-3}	?	ca. 20°?

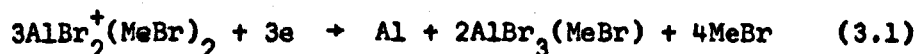
Note: Van Dyke stated that the Aluminium deposit was very fine and hard to recover. He managed to obtain about 50%

Van Dyke suggested has also been found to be wrong, the data which they produced have been re-interpreted by the writer.

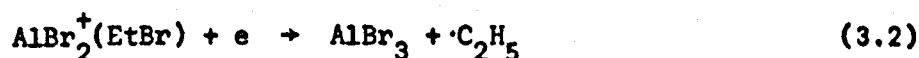
The ionisation of an aluminium halide in alkyl halide has been shown to proceed thus:



In methyl bromide solution the cathode process is probably:



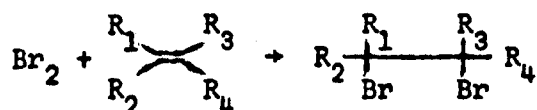
In ethyl bromide this is accompanied by:



The anode process is almost certainly:



And in ethyl bromide this is ^{probably} followed by the reaction:



In methyl bromide the change in the number of moles of aluminium bromide per Faraday is $(t_- - t_+)$ in the anode section and $(t_+ - t_- - \frac{1}{3})$ in the cathode compartment.

In ethyl bromide, if reaction (3.2) replaces (3.1) then in the cathode part $(t_+ - t_- - \frac{1}{3})$ becomes $(t_+ - t_-)$.

Some of the results of Sheka and Sheka and of Van Dyke are shown in Table 3.2.

Van Dyke's results yield a value of t_+ of 0.5 ± 0.01 , and $t_- 0.5 \pm 0.01$.

The results of Sheka and Sheka, (assuming that (3.2) predominates over (3.1)) give $t_+ = 0.17 \pm .04$ and $t_- = 0.83 \pm .04$. (If (3.1) predominates, then $t_+ = 0.33$ and $t_- = 0.67$).

The results of Van Dyke make sense, because it is logical that the AlBr_4^- and $\text{AlBr}_2^+(\text{MeBr})_2$ ions should have similar mobilities, whereas those of Sheka and Sheka are much harder to explain; it would seem that in ethyl bromide, according to Stokes Law,⁹⁶ the cation should have a radius that is between 2 and 5 times greater than that of the anion!

The transport results are so important because they do show decisively that the great majority of cations, at least in methyl bromide solution, are neither carbenium ions nor Me_2Br^+ ions which Olah has found under some conditions.

3.2.3.3 Spectroscopic identification of the ions. Kinsella and Coward⁵⁵ who studied the aluminium bromide solution in methyl bromide and the aluminium iodide solution in methyl iodide were able to identify and characterise the AlX_4^- ion by its Raman absorption, by addition of tetraethyl ammonium bromide and tetra-n-butyl ammonium iodide respectively.

Kidd and Truax⁸⁶ achieved a similar result by means of ^{27}Al n.m.r.

3.2.3.4 Kinetics of ionisation. Most investigators of the conductivity of aluminium halide + alkyl halide systems have commented on the instability of these solutions with respect to time: Fairbrother²⁰ thought that this was caused by the decomposition of ethyl bromide, but Halpern and Polaczek²¹ demonstrated that this was unlikely, and in addition published plots of conductivity vs. time. Hartmut Wendt²⁵ made a kinetic investigation of the ionisation of aluminium chloride and bromide in nitrobenzene. The work was based on extensive conductivity determinations which had been made by Kraus and Van Dyke.^{19,67,68} Wendt divided the curves of equivalent conductivity vs. concentration into three regions and he assumed that different self-ionisation schemes predominated in each. This approach is not completely justified. In the region from 10^{-3} to 10^{-1} M, Λ was roughly constant, which suggests that there is a 2:2 ionisation (see Appendix 1), which is the conclusion that Wendt came to

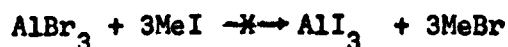
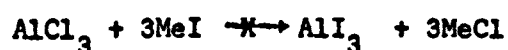


At high concentration Λ became smaller, possibly because of ionic strength effects or, as Wendt suggested, by formation of dimeric ions. At low concentrations Λ increased, and though Wendt assumed that this was because the ionisation had changed to that shown in reaction 3.6, it was much more likely to have been caused by the presence of impurities in the solvent (see Appendix 1).

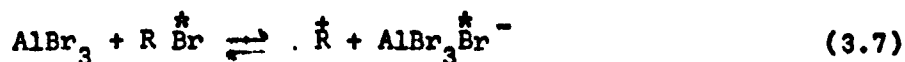


Wendt measured the effect of pressure "jumps" on reaction 3.5. He obtained values for k_{12} and k_{21} , and hence K , by measuring the relaxation times of the conductivity.

Brown and Wallace⁶⁶ showed that in mixed systems:



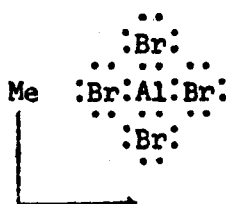
Thermochemical calculations showed that the reverse processes are unfavourable; the entropy changes are small, thus the enthalpy change is a good guide. At first it was supposed that the exchange went through an ionic mechanism³⁷ as shown in reaction 3.7, but later it became apparent that a molecular mechanism was more likely.



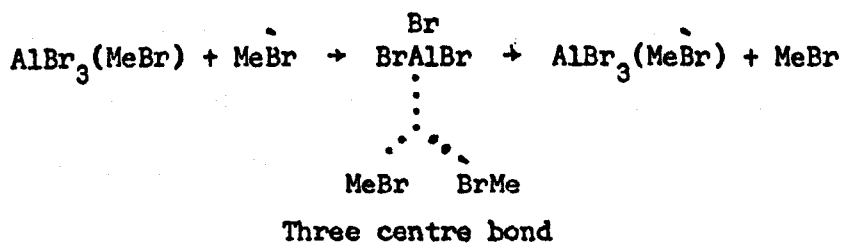
Sixma and Hendriks discovered that the kinetics of bromine exchange between aluminium bromide and ethyl bromide were of third order overall (second order in AlBr_3 , first order in EtBr) and the reaction had an activation energy of $11.7 \pm 0.8 \text{ k.cal.mole.}^{-1}$. Since the expts. were carried out in carbon disulphide solvent, it was not clear whether aluminium bromide was present as dimer or monomer. If Walker's value of K for the equilibrium between dimeric and monomeric aluminium bromide in methyl bromide,⁴⁸ can be taken as an indication of that in ethyl bromide if the solvent CS_2 is assumed to be inert, then at 0° the monomeric form would have predominated completely under the conditions of this experiment.

The rate determining step therefore appears to involve at least two molecules of aluminium bromide! The mechanism would therefore appear to be a more complicated form of an SN2 process.

H.C. Brown^{79,80} suggested that the halogen exchange process occurred by the movement of the alkyl group around the outside of a tetrahedron of halogen atoms, without any cleavage of bonds.



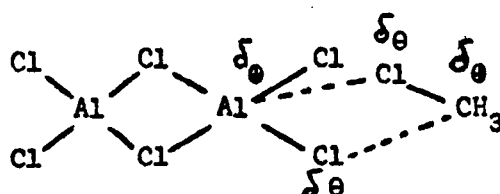
The rate determining process however would undoubtedly be something like the following scheme:



Sixma and Hendriks^{47,70,71} and Halpern and Polaczek^{74,75,76,77,78} discovered that the rate of halogen exchange is decreased in the presence of any electron donor. This has been termed "the exchange-blocking effect". The latter authors made extensive studies with gallium, aluminium and indium iodide in ethyl iodide solution and with aluminium bromide in ethyl bromide solution, where diethyl ether was added as the electron donor.⁷⁷ It was found that when an electron donor was added, the energy of activation increased, and that the rate of exchange fell to a low value. They argued, that if the exchange proceeded by the often suggested reaction³⁷ (347), that in

the presence of an electron donor, R^+ would be better solvated and that the equilibrium should be pushed to the right. The rate of exchange might therefore be expected to increase.

Kennedy and Baldwin⁸³ studied the exchange of chlorine between aluminium chloride and methyl chloride. The exchange rate was higher when the aluminium chloride was not all dissolved than when it was in solution. Kennedy attributed this to the high polarising power of the surface of crystalline aluminium chloride, and suggested that for the heterogeneous system the exchange proceeded rapidly with a "concerted ionic" mechanism, but that when the aluminium chloride had dissolved the exchange continued slowly by an SN_2 process. It is interesting that Polaczek⁷⁸ independently came to a similar conclusion for the exchange of bromine between aluminium bromide and alkyl bromide, but for this system the dissolution of the solid is much more rapid than for the chloride. The concerted ionic mechanism:



3.2.5 The properties of aluminium halides in alkyl halides, relevant to this work.

Aluminium bromide dissolves in methyl bromide to form colourless stable solutions, by forming a 1:1 complex which has an n-donor methyl bromide to aluminium bond with an estimated⁴⁸ strength of 19 k.cal.mole.⁻¹. Ethyl bromide solutions are less stable. For the latter system halogen exchange proceeds by a third order process which suggested that the mechanism is concerted.

The activation energy for Br exchange in this system is about 11.7 k.cal.mole⁻¹. The size of the latter activation energy is very interesting because it means that the rate determining step of the exchange is not an ionisation, which would require an activation energy of at least 200 k.cal.mole⁻¹, the heterolytic dissociation energy of Al-Br, nor a unimolecular decomposition of the 1:1 complex between aluminium bromide and alkyl bromide, which would require an activation energy of at least 19 k.cal.mole⁻¹, and this is strong evidence for the concerted mechanism which has been suggested.

The solutions probably ionise slowly to a small extent to yield AlBr_4^- ions and cations which contain aluminium and have a mobility similar to that of the anion. In methyl bromide solution they are most probably $\text{AlBr}_2^+(\text{MeBr})_2$.

Aluminium iodide, gallium iodide and indium iodide solutions in alkyl iodides have properties which are very similar to those of the corresponding bromide systems. Solutions of aluminium chloride in alkyl chloride behave somewhat differently with regard to complexes, exchange reactions, solubility. No conductivity study of aluminium chloride in alkyl chloride had been made hitherto, though there were several in other solvents.^{31,30,41,42,43,44,46,25,19} It has been shown by ²⁷Al n.m.r. to ionise as follows in acetonitrile:⁴⁵

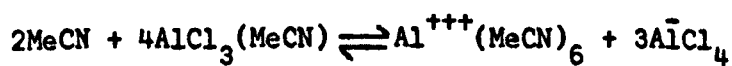


Figure 3.2

The stereochemistry of the dimeric aluminium bromide molecule.

Figure 3.3

The change in conductivity when a phial of aluminium bromide is broken into methyl bromide at 0° . The final concentration of aluminium bromide was 2×10^{-3} M.

Figure 3.4

As above, but at -23° ; the final aluminium bromide concentration was 2×10^{-2} M.

Fig.3.2

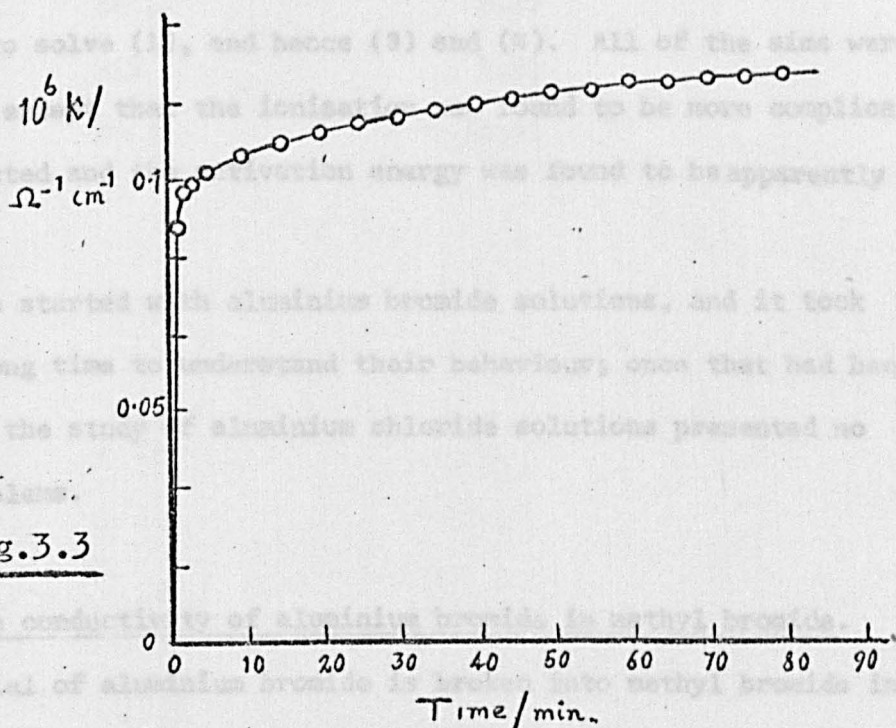
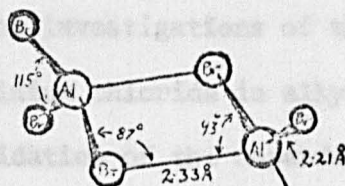


Fig.3.3

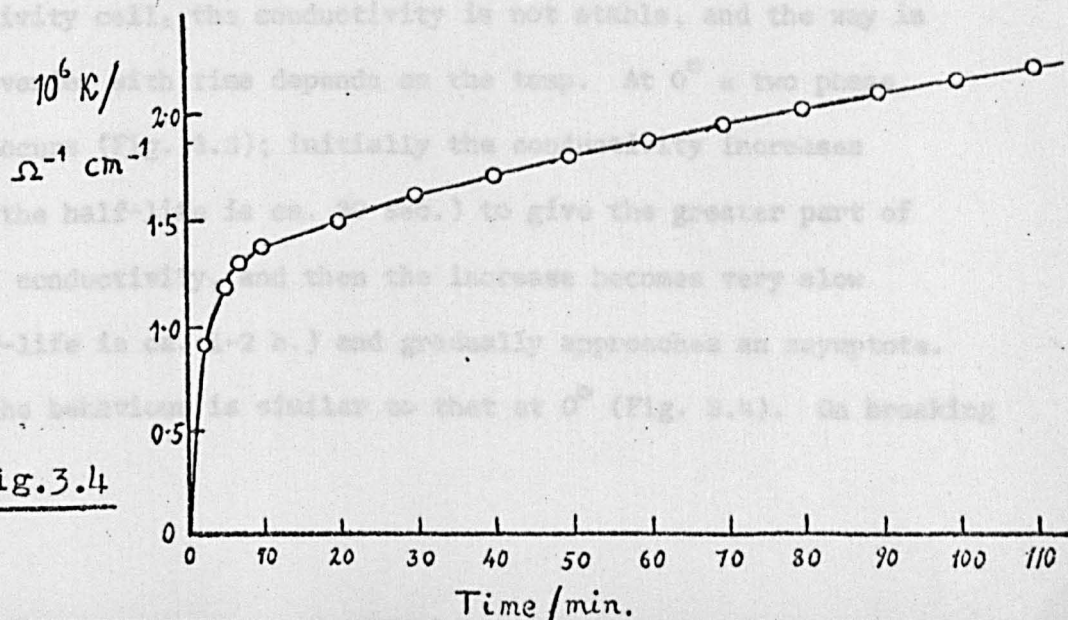


Fig.3.4

3.3 Results. The aims of the investigations of the conductivity of aluminium bromide and aluminium chloride in alkyl halide solutions were as follows: (1) The elucidation of the dependence of the conductivity on concentration to find out how the ionisation occurred. (2) The interpretation of the kinetics of ionisation. (3) The temperature dependence of the conductivity and hence the variation of the equilibrium constant with temperature. (4) The variation of the rate of ionisation with temperature to find out the activation energy of the ionisation.

We soon found out that elucidation of (2) was necessary in order to solve (1), and hence (3) and (4). All of the aims were achieved, except that the ionisation was found to be more complicated than expected and the activation energy was found to be apparently negative.

We started with aluminium bromide solutions, and it took quite a long time to understand their behaviour; once that had been achieved, the study of aluminium chloride solutions presented no extra problems.

3.3.1 The conductivity of aluminium bromide in methyl bromide.

When a phial of aluminium bromide is broken into methyl bromide in a conductivity cell, the conductivity is not stable, and the way in which it varies with time depends on the temp. At 0° a two phase process occurs (Fig. 3.3); initially the conductivity increases rapidly (the half-life is ca. 30 sec.) to give the greater part of the total conductivity, and then the increase becomes very slow (the half-life is ca. 1-2 h.) and gradually approaches an asymptote. At -23° the behaviour is similar to that at 0° (Fig. 3.4). On breaking

Figure 3.5

The vagaries of the conductivity when phials of aluminium bromide are broken into methyl bromide at -63° . All of the solutions had about the same concentration.

<u>No</u>	$10^3 [\text{AlBr}_3] / \text{M}$
K5 I	1.59
R16	1.52
K3	3.03
K4 II	3.29
R12	7.21
K4 I	2.21

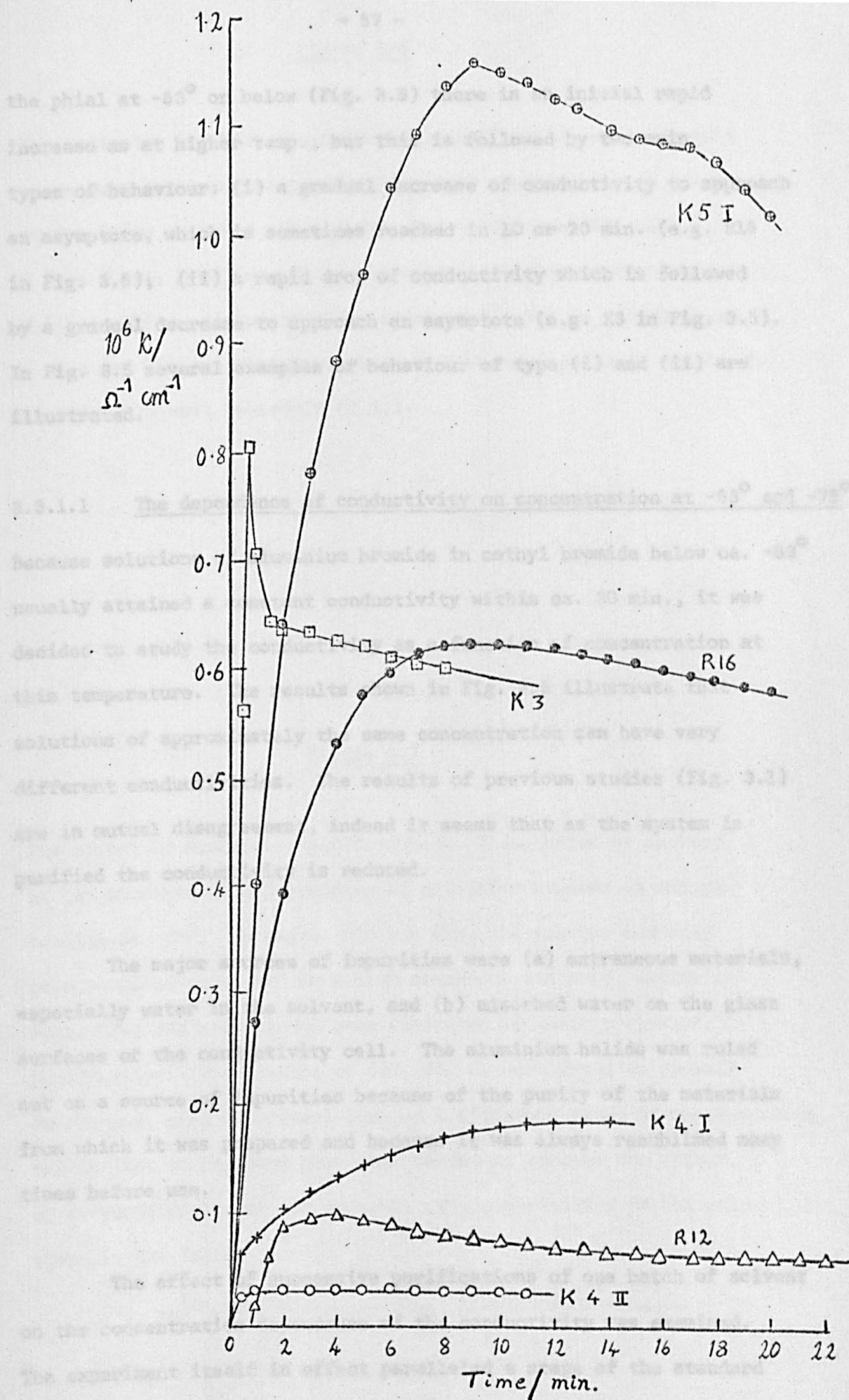


Fig.3.5

the phial at -63° or below (Fig. 3.5) there is an initial rapid increase as at higher temp., but this is followed by two main types of behaviour: (i) a gradual decrease of conductivity to approach an asymptote, which is sometimes reached in 10 or 20 min. (e.g. R16 in Fig. 3.5); (ii) a rapid drop of conductivity which is followed by a gradual decrease to approach an asymptote (e.g. K3 in Fig. 3.5). In Fig. 3.5 several examples of behaviour of type (i) and (ii) are illustrated.

3.3.1.1 The dependence of conductivity on concentration at -63° and -78°

Because solutions of aluminium bromide in methyl bromide below ca. -63° usually attained a constant conductivity within ca. 30 min., it was decided to study the conductivity as a function of concentration at this temperature. The results shown in Fig. 3.5 illustrate that solutions of approximately the same concentration can have very different conductivities. The results of previous studies (Fig. 3.1) are in mutual disagreement, indeed it seems that as the system is purified the conductivity is reduced.

The major sources of impurities were (a) extraneous materials, especially water in the solvent, and (b) adsorbed water on the glass surfaces of the conductivity cell. The aluminium halide was ruled out as a source of impurities because of the purity of the materials from which it was prepared and because it was always resublimed many times before use.

The effect of successive purifications of one batch of solvent on the concentration dependence of the conductivity was examined. The experiment itself in effect paralleled a stage of the standard

Figure 3.6

The apparatus in which one batch of methyl bromide solvent could be re-used and hence re-purified for many experiments. C is the conductivity cell (cf. Fig. 2.15). Tm1 to Tm5 are BiPl taps. B is a 20 ml. burette. V1 is the solvent storage reservoir (2 l.), which contains calcium hydride, added at 0°. Tfl is a Teflon tap. A is a wad of glass wool onto which sodium was distilled. V2 is the secondary solvent reservoir (2 l.).

Figure 3.7

The effect of successive purifications of one batch of solvent on the concentration dependence of aluminium bromide in methyl bromide at -63° . In expts. C18 and C19, the solvent had only been purified once, and no sodium treatment was used, whilst in expt. C24, the solvent had been subjected to seven cycles of purification. The results of C23, 22, 21 were found to closely correspond, each experiment covered a different range of concentration, and it just so happened that this tended to conceal the effect of re-purification of the solvent. The conductivity of the solvent is shown in the Table:

No. of Expt.	$10^8 \kappa (\text{solvent})/\Omega^{-1} \text{cm.}^{-1}$
C19, C18	ca. 9
C20	4.9
C21	2.6
C22	2
C23	1.6
C24	0.34

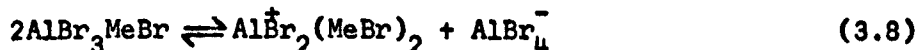
purification procedure (c.f. § 2.1.1.1.). In Fig. 3.6 the apparatus in which these experiments were carried out is shown. It consisted of a solvent reservoir V1, which contained powdered calcium hydride, a trap A, which contained a wad of glass-wool coated with sodium, a vessel, V2 from which the solvent was dosed by means of a burette B, and the conductivity cell C.

An experiment was carried out as follows. The methyl bromide was distilled from the calcium hydride, over a fresh sodium surface into the dosing reservoir, V2 which had been well pumped and flamed out. From there it was dosed into the conductivity cell and the dependence of the specific conductivity on the concentration of aluminium bromide was measured at -63° and -23° . At the end of the expt. the solvent was distilled into V1, and the conductivity was measured during this process to see whether it changed in the same way during concentration as it had during dilution of the aluminium bromide. In all experiments the two κ -c curves were coincident within exptl. error.

At the end of each experiment all the methyl bromide was returned to V1, and the aluminium bromide which remained in the conductivity cell was hydrolysed and titrated.

The results of this series of experiments are shown in Fig. 3.7. It can be seen that as the purity of the solvent improved, (i) its conductivity decreased; (ii) the conductivity of the aluminium bromide solutions decreased; (iii) the intercept on the conductivity axis diminished; (iv) the temp. dependence of the conductivity became smaller.

The conclusion was drawn that in a really pure solvent the conductivity of aluminium bromide depends linearly on its concentration, and that when the intercept on the conductivity axis was zero the conductivity was unaffected by impurities. The linear dependence of κ on concentration indicates the existence of a 2:2 equilibrium (see Appendix 1), hence the ionisation probably occurs thus:



These conclusions are not of course justified merely on the basis of these experiments and the further experiments described in § 3.3.1.2. to § 3.3.1.3. were carried out to confirm and extend them.

3.3.1.2 The dependence of conductivity of solvent on the concentration of impurities.

In the preceding expt. the conductivity of the solvent appeared to be a measure of the purity. This criterion has been used before by Morgan and Lowry.⁸⁸ An experiment was performed with ethyl bromide in which deionised water was added to the pure, dry solvent at 25° by means of a micro-syringe. The water concentration was measured by g.l.c. with t.c. detection. The conductivity of the solvent, which was ca. $5 \times 10^{-9} \Omega^{-1} \text{cm}^{-1}$ hardly changed when water was added, not even when a saturated solution had been obtained. However when a tiny amount of hydrochloric acid (2-3 $\mu\text{l.}$ of conc. HCl) was added, there was a hundredfold increase of conductivity. It is therefore clear that the conductivity of a solvent yields no direct information about the concentration of water, but it does reveal the presence of traces of acid, and is therefore dependent on the acidity of the glass surface of the conductivity cell (and hence it is an indication of the cleanliness of the apparatus!).

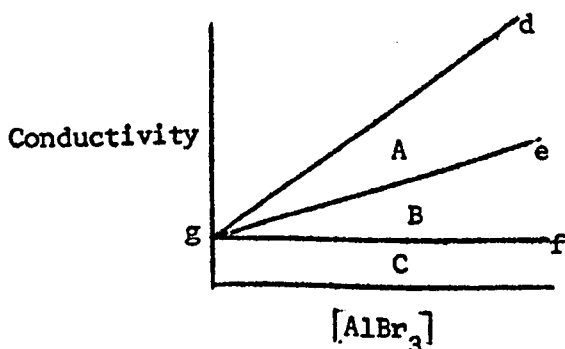
Experiments were tried in which a direct voltage of 400V(4kV.cm.⁻¹) was applied to the electrodes of the conductivity cell in an attempt to reduce the conductivity of the solvent by electrolysis; this was partly successful. The conductivity was reduced from 6×10^{-8} to $5.2 \times 10^{-8} \Omega^{-1}\text{cm.}^{-1}$ in 90 min., in a typical experiment when rather an impure solvent was used. (90% of the change occurred in the first 20 min.)

In later experiments the solvents were purified by storage over sodium mirrors, and extremely low conductivities were achieved. As a result of the above expt. care was always taken that the conductivity cells, (a) were clean; (b) had neutral glass surfaces; (c) were as dry as possible.

3.3.1.3 The effect of impurities on the ionisation of aluminium bromide in methyl bromide.

The acid concentration in a solvent with a rather high conductivity say, ca. $5 \times 10^{-9} \Omega^{-1}\text{cm.}^{-1}$ is around 10^{-7}M , and this is far too low to explain the magnitude of the high conductivity of impure aluminium bromide solutions, (c.f. Fig. 3.7) and in addition it does not explain the difficulty experienced if one tries to correlate exactly the conductivity of the aluminium bromide solution with the acid concentration. The presence of acid in a solvent undoubtedly signifies the presence of water. It is known that calcium hydride reduces the water concentration of a solvent to ca. 10^{-5}M , and the conductivities of solvents after calcium hydride drying suggest an acid concentration of around 10^{-7}M .

In the diagram below, a conductivity curve has been split into its components.



The line g-f represents the conductivity which arises from the reaction of the water in the solvent, the line g-e shows the extra conductivity from the reaction of the water in the cell, and the line g-d represents the total conductivity including that from self ionisation.

This slightly oversimplified picture, which ignores the effect of the common tetrabromoaluminate ion is summarised in equ. (1).

$$\kappa = \Lambda_T(x/2 \cdot 10^3 + y/2 \cdot V) + \Lambda_T K^{\frac{1}{2}} a_0 / 10^3 (1 + 2K^{\frac{1}{2}}) \quad (1)$$

Where V is the volume, Λ_T is the true equivalent conductance which has been assumed to be roughly the same for both pairs of ions, and a_0 is the concentration of aluminium bromide. For simplicity and with justification K' has been assumed to be very large.

If the results shown in Fig. 3.7 are re-examined, it is obvious that the simple picture described above is a good description of the real situation. As the cell became drier, the slope of the plots decreased, and as the solvent became more pure the intercept on the conductivity axis became smaller. However, from this experiment alone it is impossible to know whether all the water from the cell has been removed. This is even true for expt. C24, the most "pure" experiment.

Figure 3.8

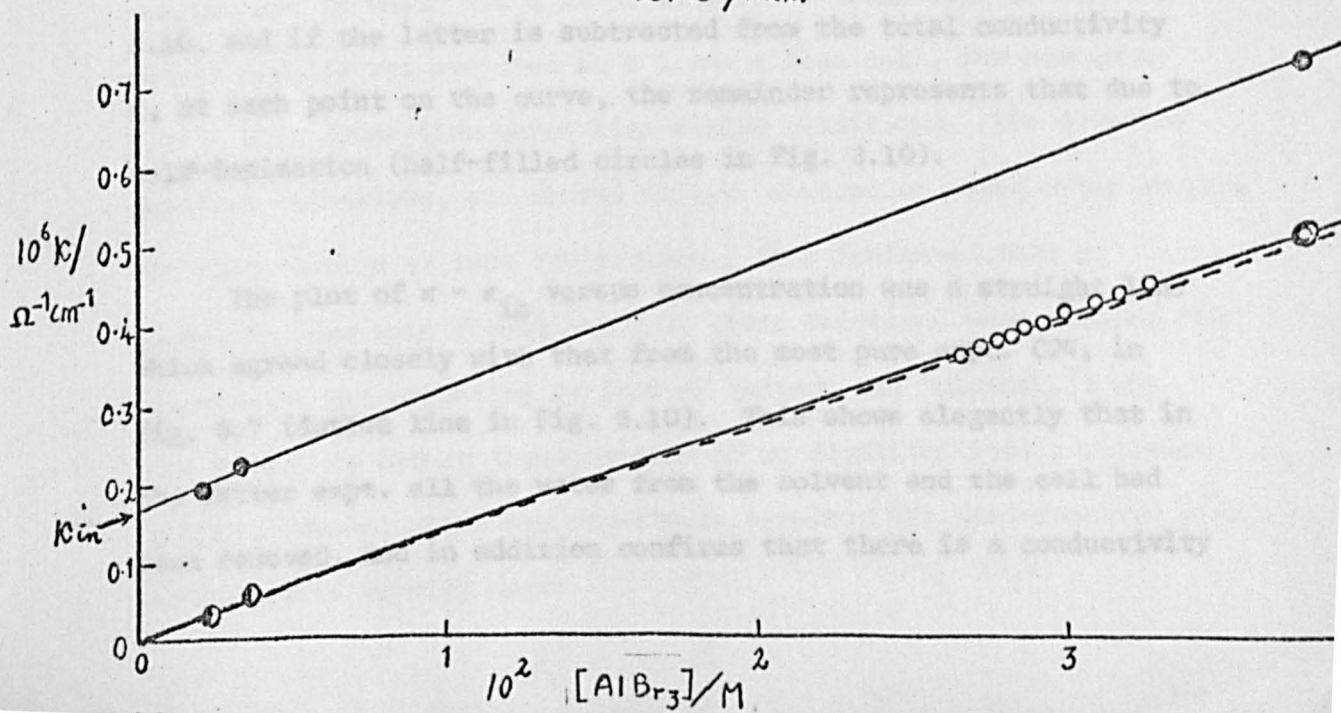
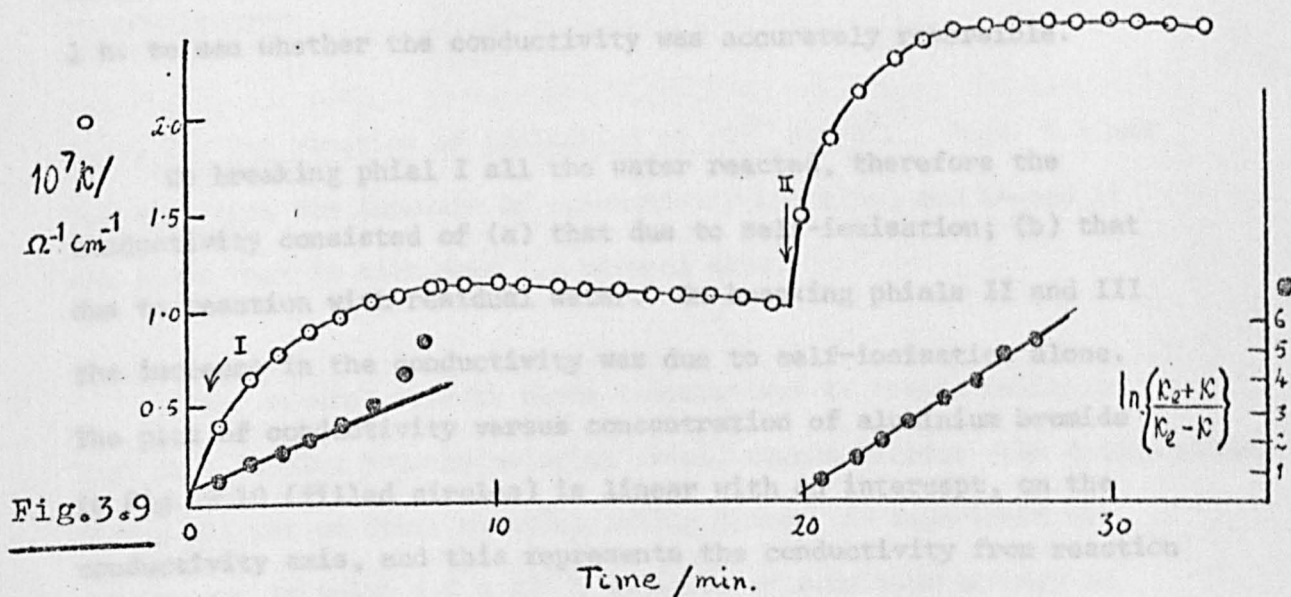
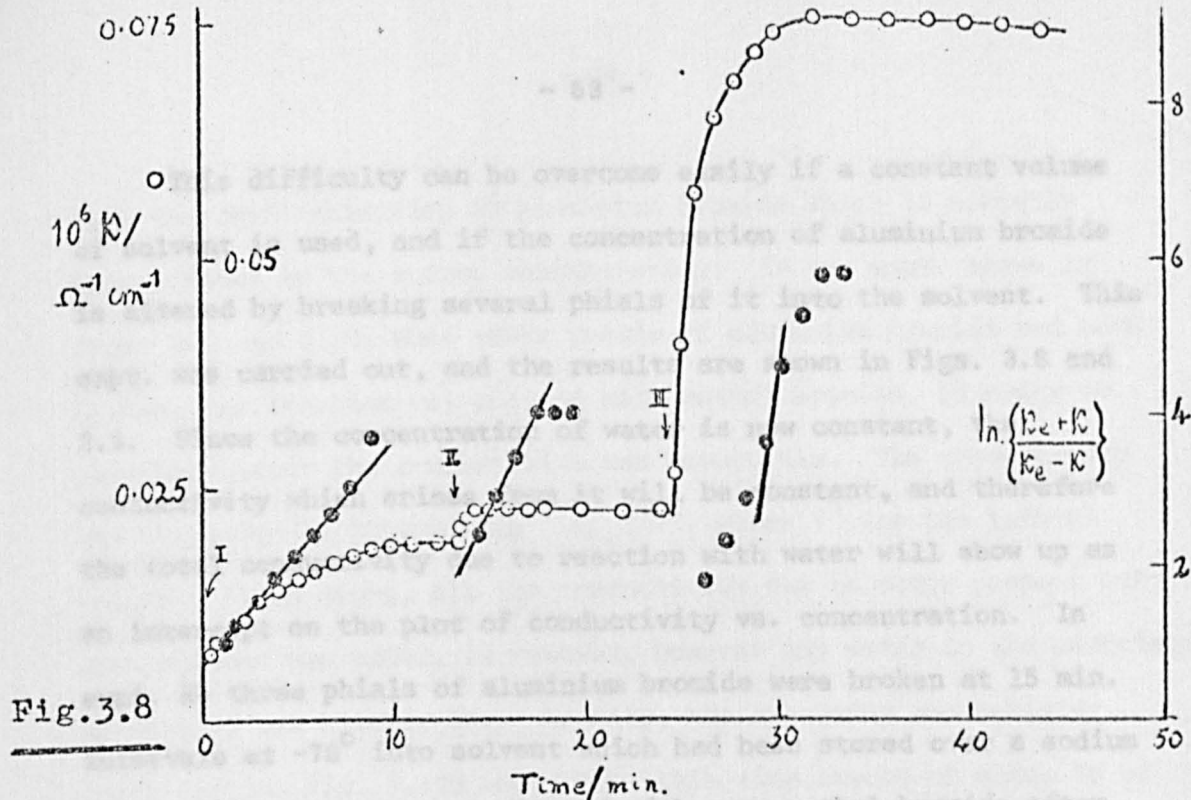
Expt. K4: The change of conductivity, and the plots of the kinetics when three phials of aluminium bromide were broken into methyl bromide at -78° . The individual concentrations were as follows: I 2.2×10^{-3} M. II 3.3×10^{-3} M and III 3.8×10^{-2} M.

Figure 3.9

Expt. K5: The change of conductivity, and the plots of the kinetics when two phials of aluminium bromide were broken into methyl bromide at -78° . The individual concentrations were as follows: I 1.6×10^{-3} M II 2.6×10^{-2} M.

Figure 3.10

Plot of specific conductivity versus concentration for the results shown in Fig. 3.8. The filled circles show the total conductivity when 3 phials of aluminium bromide are broken into methyl bromide at -78° ; when the intercept, κ_{in} is subtracted this gives the half-filled points. When a dilution expt. was carried out after the three phials had been broken the conductivity was corrected by subtracting $\kappa_{in} V/V^{\circ}$ where V° was the original volume of the solution and V was the increased volume (open circles). The dotted line represents the results from expt. C24 shown in Fig. 3.7.



This difficulty can be overcome easily if a constant volume of solvent is used, and if the concentration of aluminium bromide is altered by breaking several phials of it into the solvent. This expt. was carried out, and the results are shown in Figs. 3.8 and 3.9. Since the concentration of water is now constant, the conductivity which arises from it will be constant, and therefore the total conductivity due to reaction with water will show up as an intercept on the plot of conductivity vs. concentration. In expt. K4 three phials of aluminium bromide were broken at 15 min. intervals at -78° into solvent which had been stored over a sodium mirror. The solution was diluted with more methyl bromide after 1 h. to see whether the conductivity was accurately reversible.

On breaking phial I all the water reacted, therefore the conductivity consisted of (a) that due to self-ionisation; (b) that due to reaction with residual water. On breaking phials II and III the increase in the conductivity was due to self-ionisation alone. The plot of conductivity versus concentration of aluminium bromide in Fig. 3.10 (filled circles) is linear with an intercept, on the conductivity axis, and this represents the conductivity from reaction 3.10, and if the latter is subtracted from the total conductivity κ , at each point on the curve, the remainder represents that due to self-ionisation (half-filled circles in Fig. 3.10).

The plot of $\kappa - \kappa_{in}$ versus concentration was a straight line which agreed closely with that from the most pure expt. C24, in Fig. 3.7 (dotted line in Fig. 3.10). This shows elegantly that in the latter expt. all the water from the solvent and the cell had been removed, and in addition confirms that there is a conductivity

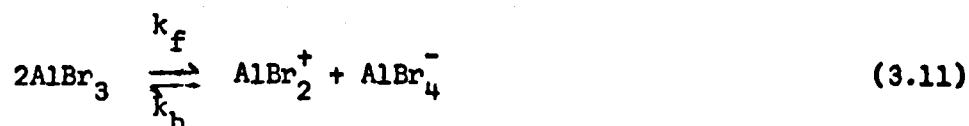
from the self-ionisation of aluminium bromide which is directly proportional to the solute concentration. In the expt. shown in Figs. 3.8 and 3.10, when three phials of aluminium bromide had been broken, the solution was diluted with methyl bromide, in order to examine whether the conductivity was reversible. The conductivity was corrected by subtracting $\kappa_{in} V/V^0$, where V^0 was the initial volume. By so doing, all the conductivity due to water present before more solvent was added, is removed, however any water in the additional solvent is not allowed for. Luckily, the resulting conductivity, (open circles Fig. 3.10) shows that this tiny amount of water is of no consequence.

3.3.1.4 The kinetics of ionisation at -23° and 0° . Figs. 3.4 and 3.5 show that the increase of conductivity was slow, and indeed it was noted that it continued for several days.

After several days at these temperatures it seemed unlikely that an aluminium bromide solution would remain without some decomposition of the solvent or other reaction taking place. An experiment was carried out in which a $2 \times 10^{-3} M$ solution of aluminium bromide in methyl bromide was prepared in a 1 cm. silica cell, for measuring u.v. - vis. absorption under high vacuum conditions. The solution remained colourless, and showed no u.v. absorption, even after storage for three months at room temperature. This indicated that no carbenium ions were formed and that these solutions were stable; this observation was supported by that of Halpern and Polaczek,²¹ who were unable to detect decomposition of an aluminium iodide solution in ethyl iodide, when they repeatedly examined its mass-spectrum over the course of several days.

It therefore seemed possible that the slow increase of conductivity was due rather to a very slow ionisation than to a decomposition reaction, and therefore an analysis of the kinetics was undertaken.

3.3.1.5 Analysis of the kinetics. Initially the results defied interpretation; the relationship of conductivity to concentration varied wildly from one solution to the next; the kinetics did not yield to simple 1st, 2nd or 3rd order analysis. The magnitude of the conductivity indicated that the fraction of the aluminium bromide which ionised was below 0.001 and therefore as the ionisation proceeds, the concentration of aluminium bromide molecules can be treated as constant. If the mechanism of ionisation is considered to be simply



then the net rate of ionisation is given by:

$$\frac{di}{dt} = k_f [a_0 - 2i]^2 - k_b i^2 \quad (ii)$$

Here a_0 is the total concentration of aluminium bromide, and i is the concentration of each ion.

But $a_0 \gg i$, and therefore equation (ii) can be simplified to give (iii).

$$\frac{di}{dt} = k_f a_0^2 - k_b i^2 \quad (iii)$$

But at equilibrium

$$k_f a_0^2 = k_b i_e^2$$

where i_e is the concentration of each ion at equilibrium.

$$\frac{di}{dt} = k_b (i_e^2 - i^2) \quad (iv)$$

On integration and substitution of $10^3 \kappa / \Lambda_T$ for i , equ. (iv) yields:

$$\frac{1}{2\kappa_e} \ln \frac{\kappa_e + \kappa}{\kappa_e - \kappa} = \frac{k_b \cdot 10^3 \cdot t}{\Lambda_T} + d \quad (v)$$

κ_e is the specific conductivity at equilibrium, t the time and d the constant of integration. If at zero time the conductivity has a value κ_i , the constant of integration can be substituted for as follows:

$$\ln \frac{\kappa_e + \kappa}{\kappa_e - \kappa} - \ln \frac{\kappa_e + \kappa_i}{\kappa_e - \kappa_i} = \frac{2\kappa_e k_b \cdot 10^3 t}{\Lambda_T} \quad (vi)$$

But,

$$10^3 \kappa_e / \Lambda_T = i_e = a_0 K^{\frac{1}{2}}$$

where K is the equilibrium constant of reaction 3.11 and equation (vi) can be re-written as:

$$\ln \frac{\kappa_e + \kappa}{\kappa_e - \kappa} - \ln \frac{\kappa_e + \kappa_i}{\kappa_e - \kappa_i} = 2a_0 k_b K^{\frac{1}{2}} t \quad (vii)$$

A plot of $\ln \frac{\kappa_e + \kappa}{\kappa_e - \kappa}$ against t should be a straight line, and the slope should yield a value for k_b , and from the intercept κ_i may be obtained. At 0° and -23° , the ionisation has a rapid phase which is followed by a slow process. (Figs. 3.4 and 3.5, § 3.3.1.4). Since κ_i can be associated with the rapid part of the ionisation the two phases may be separated accurately. By this means it is possible to study separately the dependence of conductivity on concentration and the dependence on temperature of the rapid and slow phases of ionisation.

An inherent difficulty is that the scheme requires a knowledge of the value of κ_e , which is difficult to estimate when the ionisation is very slow.

Figure 3.11

A kinetic plot of one set of results, which shows the effect of varying κ_e , the estimated value of the conductivity at equilibrium.

No.	A	B	C	D	E
$10^6 \kappa_e$ $/\Omega^{-1} \text{cm.}^{-1}$	1.0	1.1	1.2	1.4	2.0

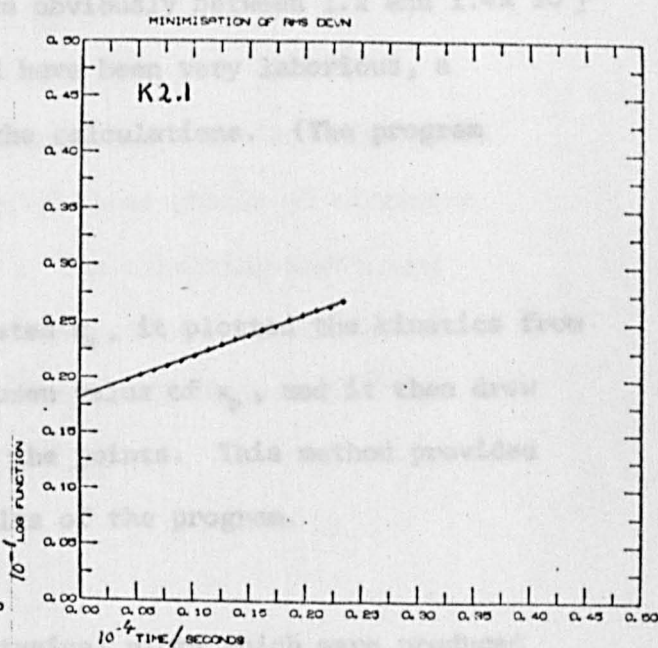
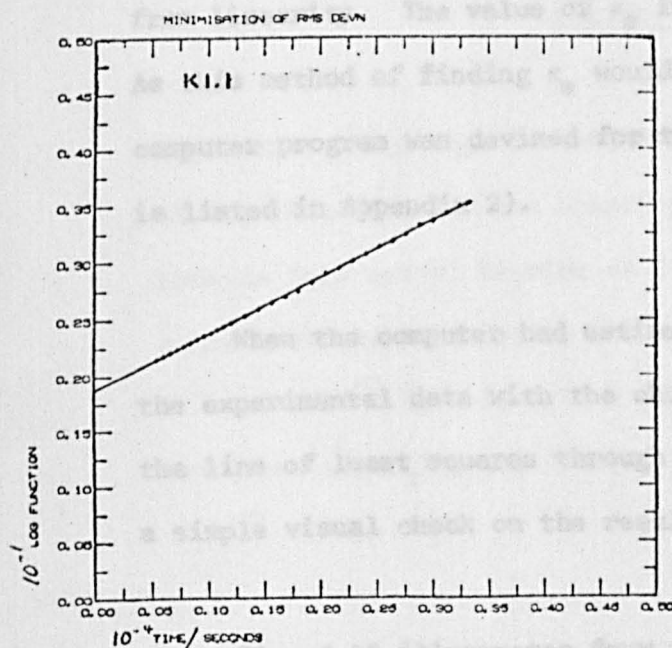
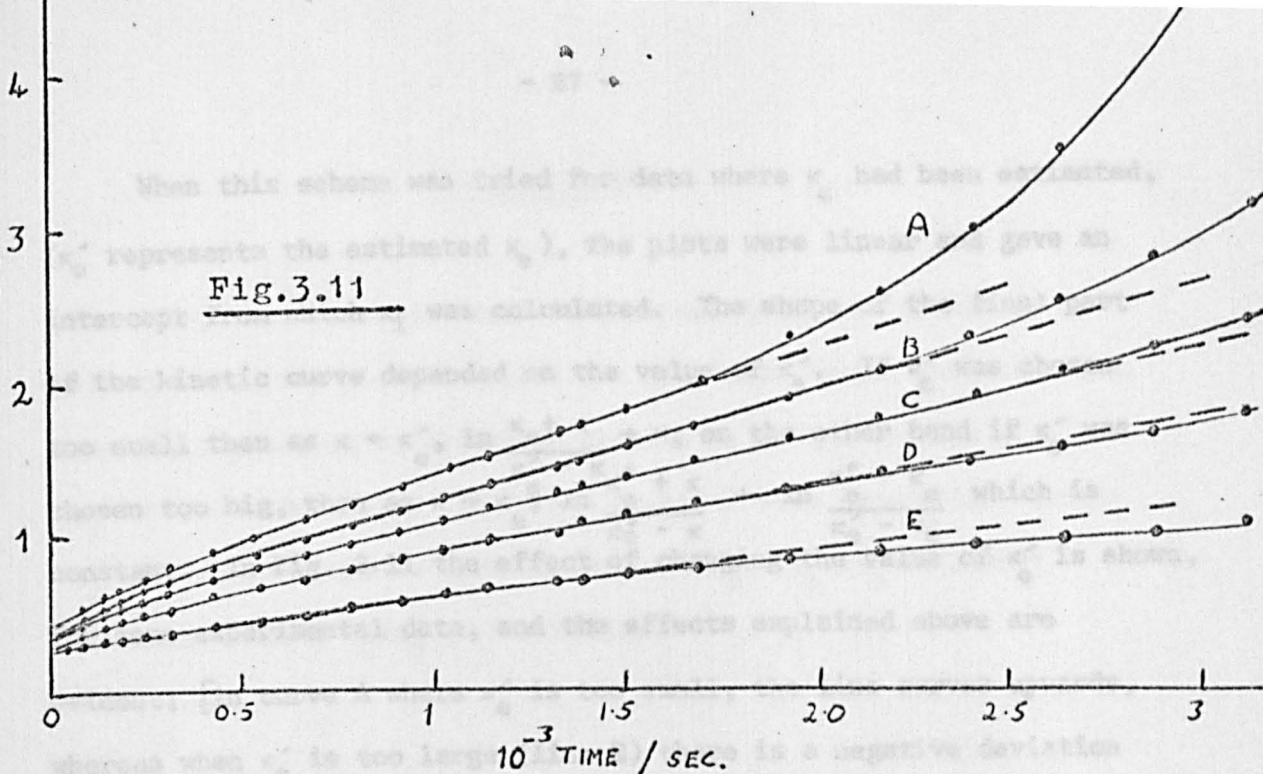
Clearly $10^6 \kappa_e$ lies between 1.4 and 1.2

Figure 3.12

This figure is included merely to show what the computer plots of the kinetics of the ionisation of aluminium bromide in methyl bromide at 0° looked like, and to emphasise that the data yielded very good straight lines. The + points are taken from the data, and the line is calculated by the method of least squares.

$$\ln \left(\frac{k_e + k}{k_e - k} \right)$$

Fig.3.11



KINETIC PLOT C26

C 15

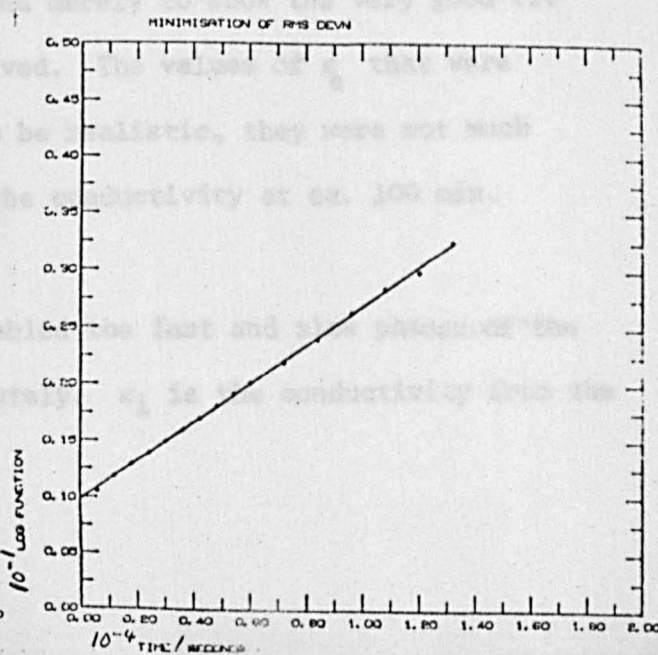
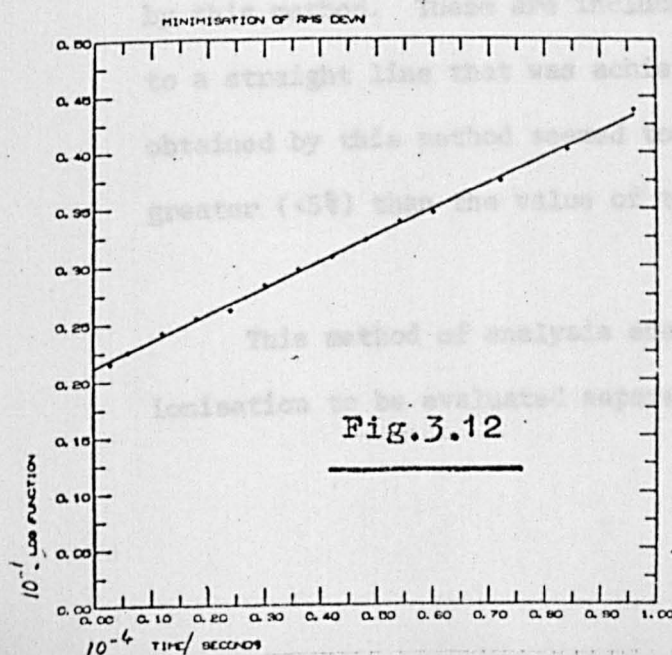


Fig.3.12

When this scheme was tried for data where κ_e had been estimated, (κ_e' represents the estimated κ_e), the plots were linear and gave an intercept from which κ_i was calculated. The shape of the final part of the kinetic curve depended on the value of κ_e' . If κ_e' was chosen too small then as $\kappa \rightarrow \kappa_e'$, $\ln \frac{\kappa_e' + \kappa}{\kappa_e' - \kappa} \rightarrow \infty$; on the other hand if κ_e' was chosen too big, then as $\kappa \rightarrow \kappa_e'$, $\ln \frac{\kappa_e' + \kappa}{\kappa_e' - \kappa} \rightarrow \ln \frac{\kappa_e' - \kappa_e}{\kappa_e' - \kappa_e}$ which is constant. In Fig. 3.11 the effect of changing the value of κ_e' is shown, for some experimental data, and the effects explained above are evident; [in curve A where κ_e' is too small, the line curves upwards, whereas when κ_e' is too large (line E) there is a negative deviation from linearity. The value of κ_e is obviously between 1.2 and 1.4×10^6]. As this method of finding κ_e would have been very laborious, a computer program was devised for the calculations. (The program is listed in Appendix 2).

When the computer had estimated κ_e , it plotted the kinetics from the experimental data with the chosen value of κ_e , and it then drew the line of least squares through the points. This method provided a simple visual check on the results of the program.

Fig. 3.12 illustrates four typical plots which were produced by this method. These are included merely to show the very good fit to a straight line that was achieved. The values of κ_e that were obtained by this method seemed to be realistic, they were not much greater (<5%) than the value of the conductivity at ca. 100 min.

This method of analysis enabled the fast and slow phases of the ionisation to be evaluated separately. κ_i is the conductivity from the

Figure 3.13

The two parts of the conductivity, separated by the method of kinetic analysis plotted versus the aluminium halide concentration, for the ionisation of aluminium bromide in methyl bromide at 0° . κ_i is the conductivity due to the reaction with impurities, whilst $\kappa_e - \kappa_i$ is that due to self-ionisation. $(\kappa_e - \kappa_i)/a_0$ is almost constant whereas κ_i/a_0 varies wildly.

Figure 3.14

Expt. K2: The change in conductivity, and the associated plots of the kinetics, for the breaking of three phials of aluminium bromide into methyl bromide at 0° . The resulting individual concentrations produced by the contents of each phial were:
I 4.27×10^{-3} M, II 8.55×10^{-3} M, III 10.13×10^{-3} M,
therefore (AlBr_3) total = 2.3×10^{-2} M.

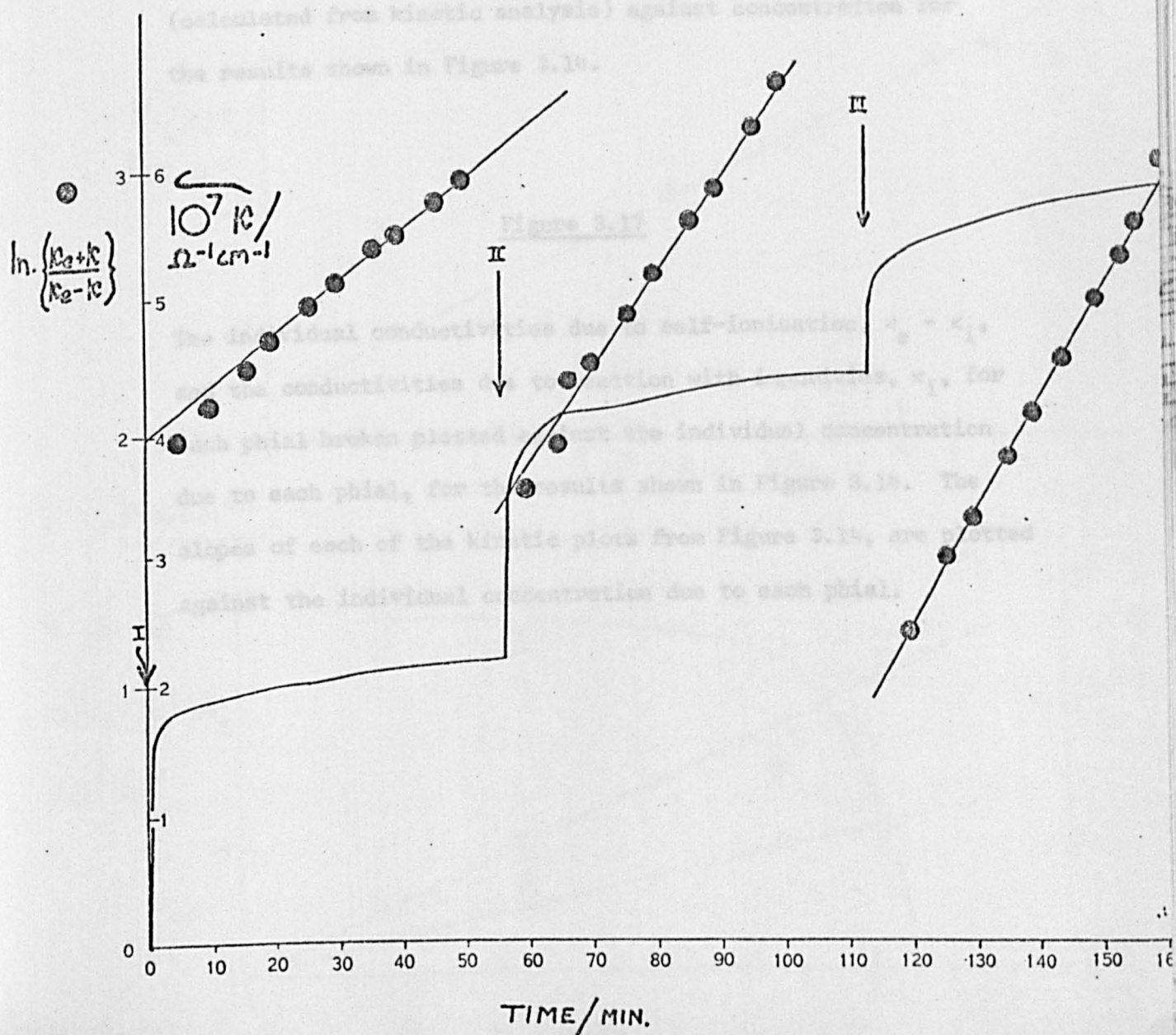
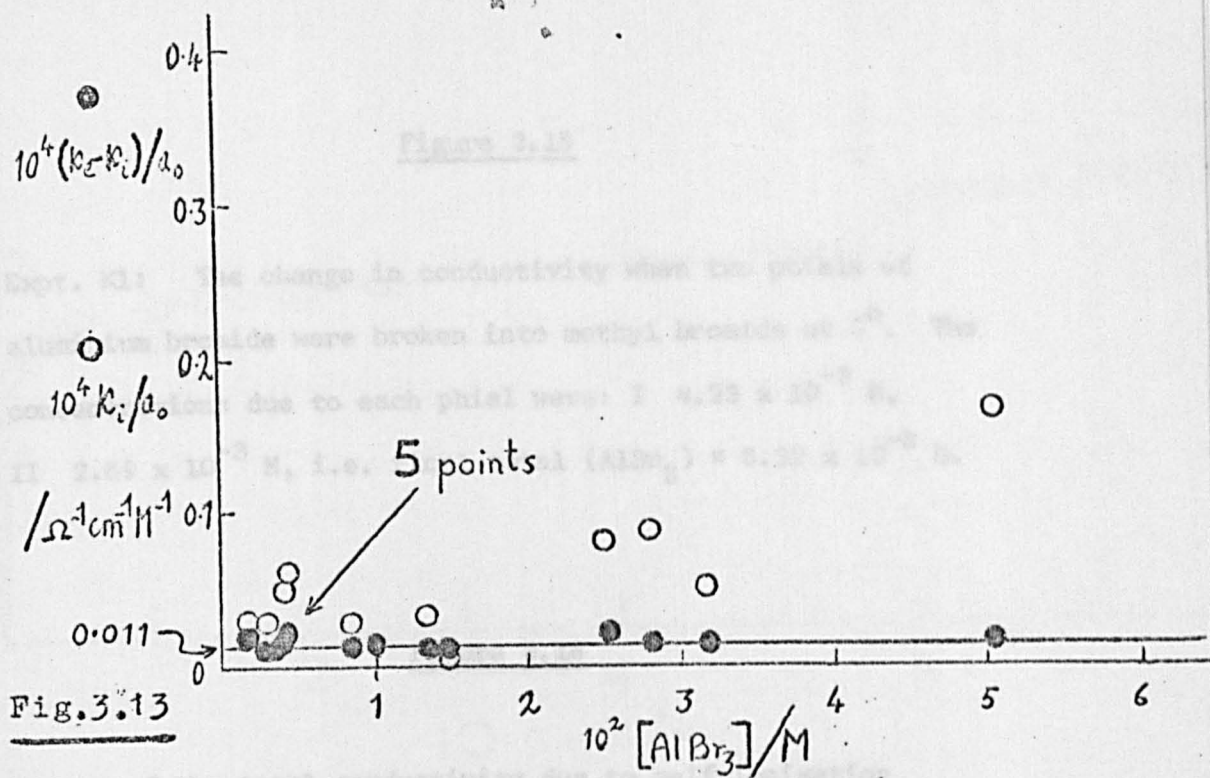


Figure 3.15

Expt. K1: The change in conductivity when two phials of aluminium bromide were broken into methyl bromide at 0° . The concentrations due to each phial were: I 4.23×10^{-3} M, II 2.69×10^{-3} M, i.e. final total (AlBr_3) = 6.32×10^{-3} M.

Figure 3.16

A plot of the total conductivity due to self ionisation (calculated from kinetic analysis) against concentration for the results shown in Figure 3.14.

Figure 3.17

The individual conductivities due to self-ionisation, $\kappa_e - \kappa_i$, and the conductivities due to reaction with impurities, κ_i , for each phial broken plotted against the individual concentration due to each phial, for the results shown in Figure 3.14. The slopes of each of the kinetic plots from Figure 3.14, are plotted against the individual concentration due to each phial.

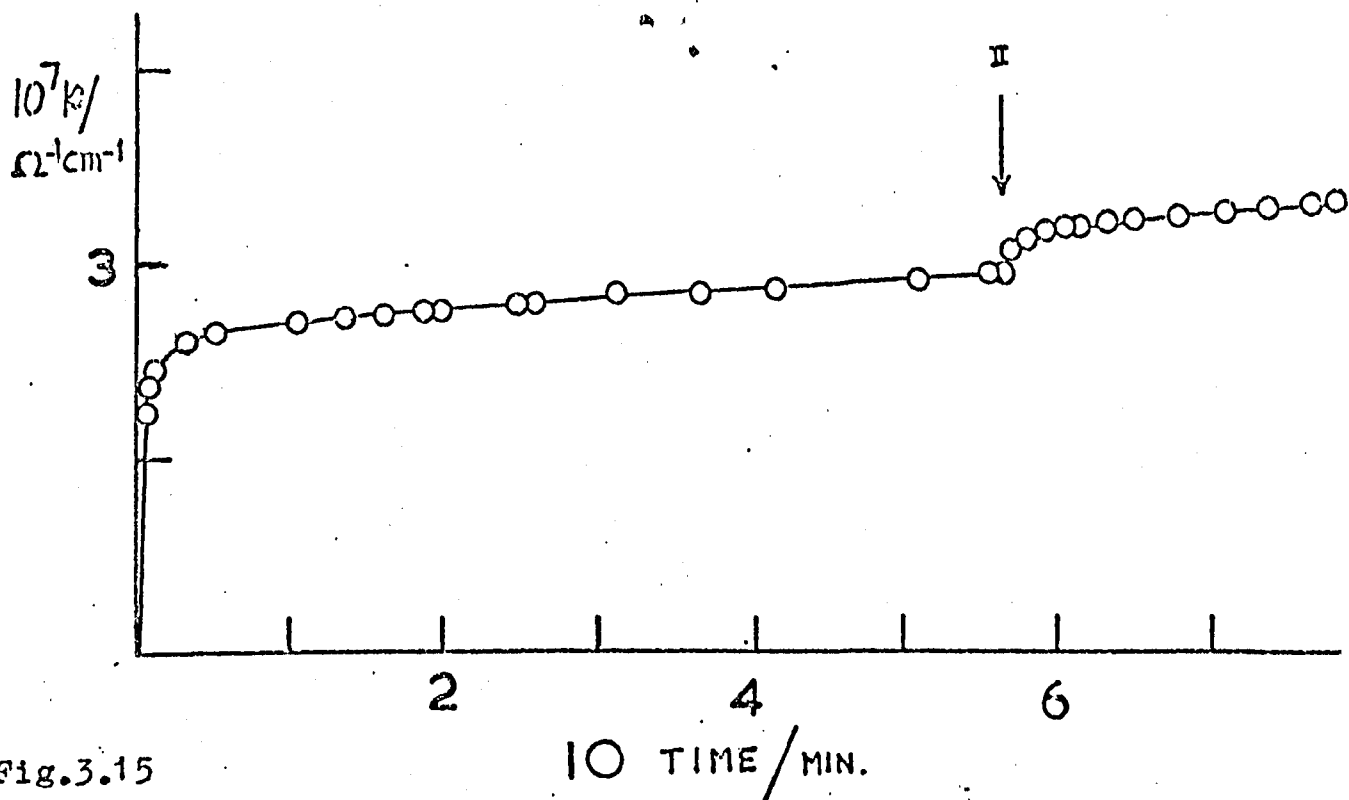


Fig. 3.15

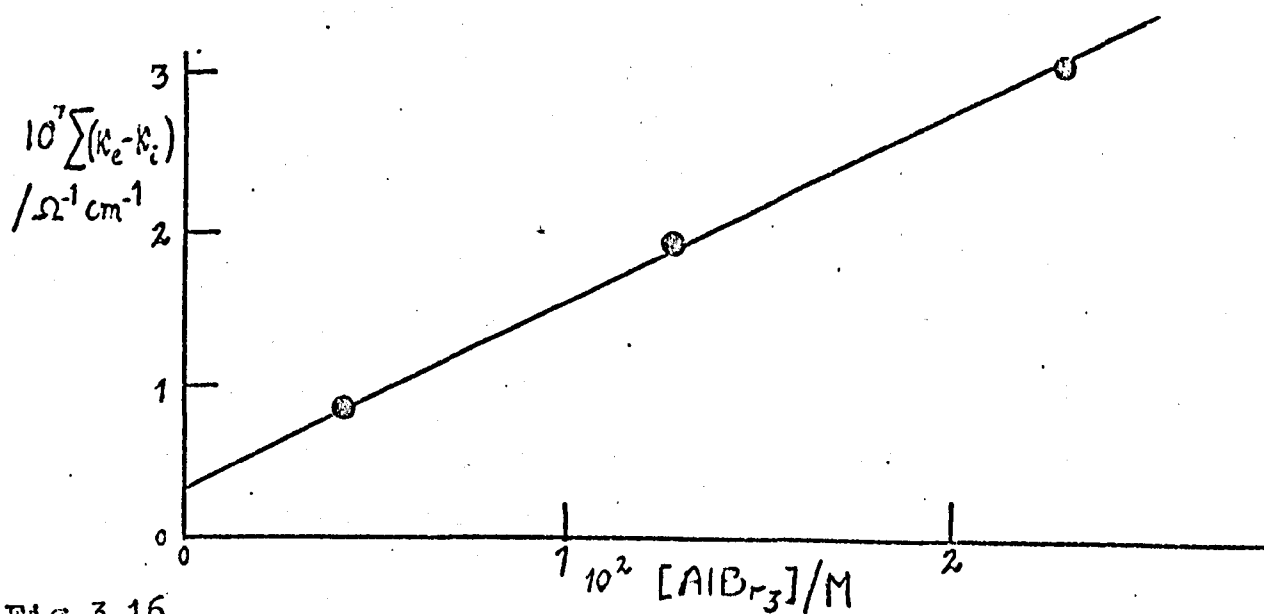


Fig. 3.16

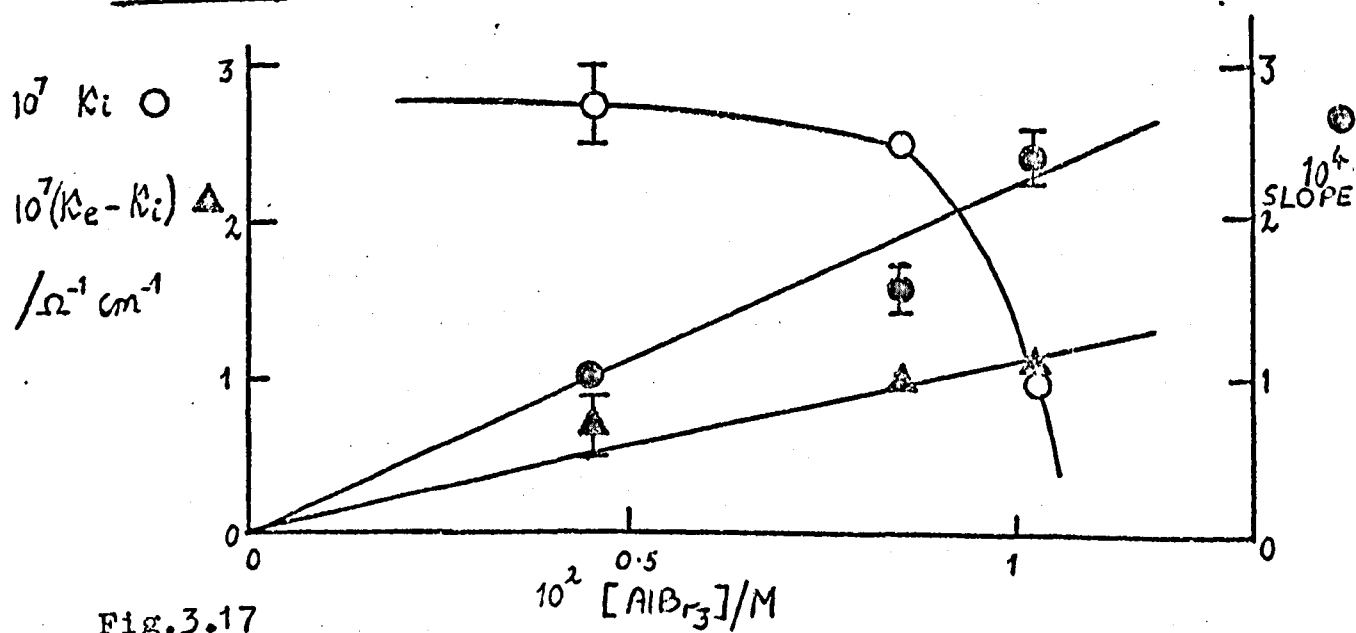


Fig. 3.17

initial phase of the ionisation and the magnitude of the subsequent slow phase is given by $\kappa_e - \kappa_i$. For a 2:2 equilibrium (see Appendix 1) κ is proportional to the concentration, a_o .

If the conductivity due to self-ionisation divided by the concentration of aluminium bromide, a_o , is plotted against a_o the expected result would be a straight line parallel to the concentration axis. When the two phases of the conductivity were separately divided by a_o , and plotted against a_o for the data at 0° , the result shown in Fig. 3.13 was obtained. Whereas κ_i/a_o varies in a random fashion, $(\kappa_e - \kappa_i)/a_o$ is almost constant as expected. From this it can be concluded that the slow phase comes from the self-ionisation and the fast phase is due to a rapid reaction with impurities, probably mainly water.

If the results for expt. C24 shown in Fig. 3.7 are re-examined, it is found that the change of conductivity with temperature for a pure solution is almost negligible. The results of C24 in Fig. 3.7, Fig. 3.10 and Fig. 3.13 are re-plotted in Fig. 3.18, and it can be seen that they lie fairly close together.

To confirm and expand this interpretation of the ionisation, experiments were carried out at 0° where several phials of aluminium bromide were broken in succession into the same solution. (Fig. 3.14 and 3.15). For the results in Fig. 3.14, a plot of $\Sigma(\kappa_e - \kappa_i)$ against Σa_o was linear, (Fig. 3.17). This differs from the result of the same type of experiment when performed at low temperature (§ 3.3.1.3 and Figs. 3.8, 3.9, 3.10). It seems that whereas at -63° and -78° the reaction with water is rapid and complete, at 0° it is still rapid but

Figure 3.18

This figure summarises all the conductivity versus concentration data for aluminium bromide in methyl bromide.

Figure 3.19

The plot of the van't Hoff isochore for the ionisation of aluminium bromide in methyl bromide. The point at very low temperature -126° should not be taken seriously.

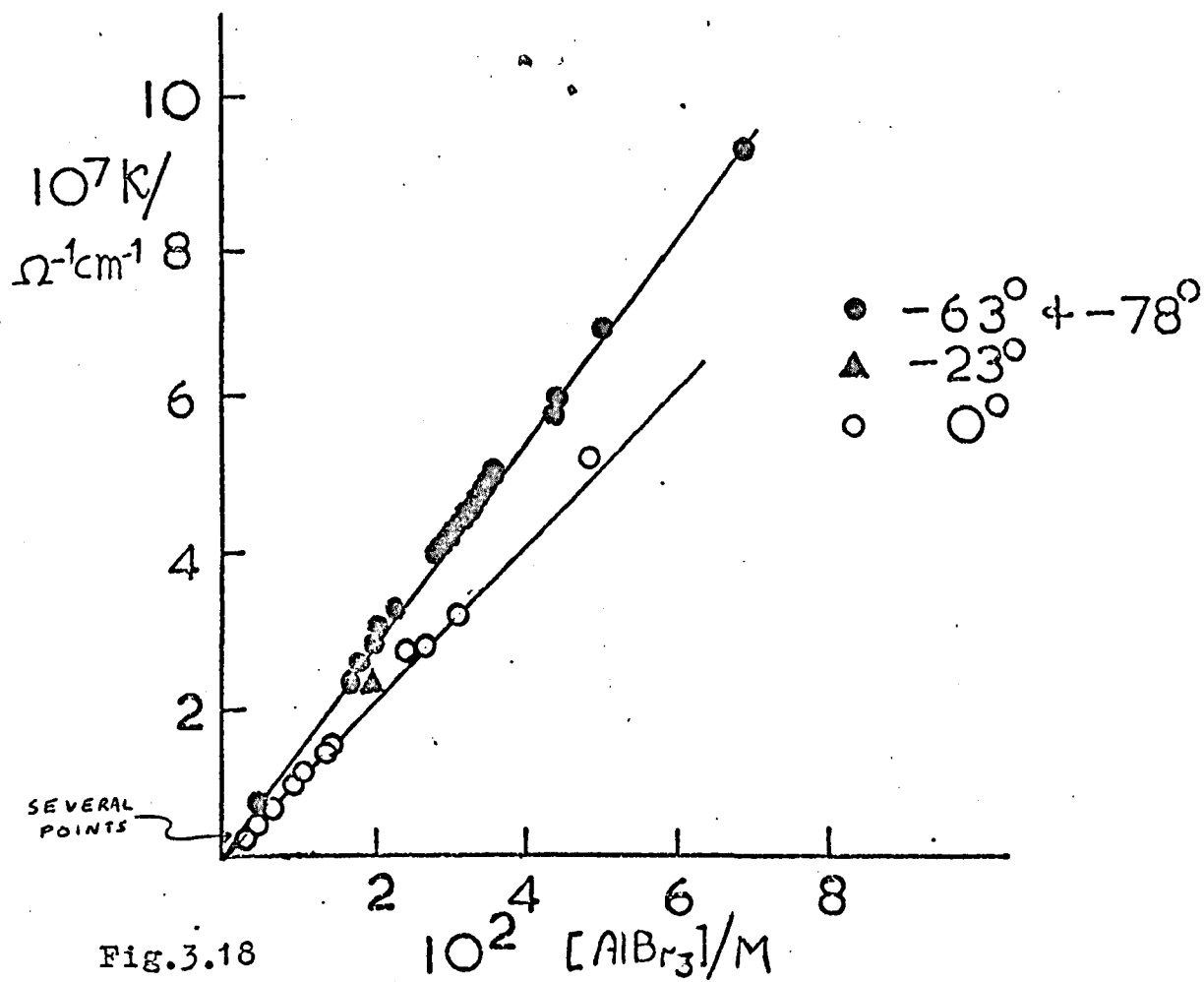


Fig.3.18

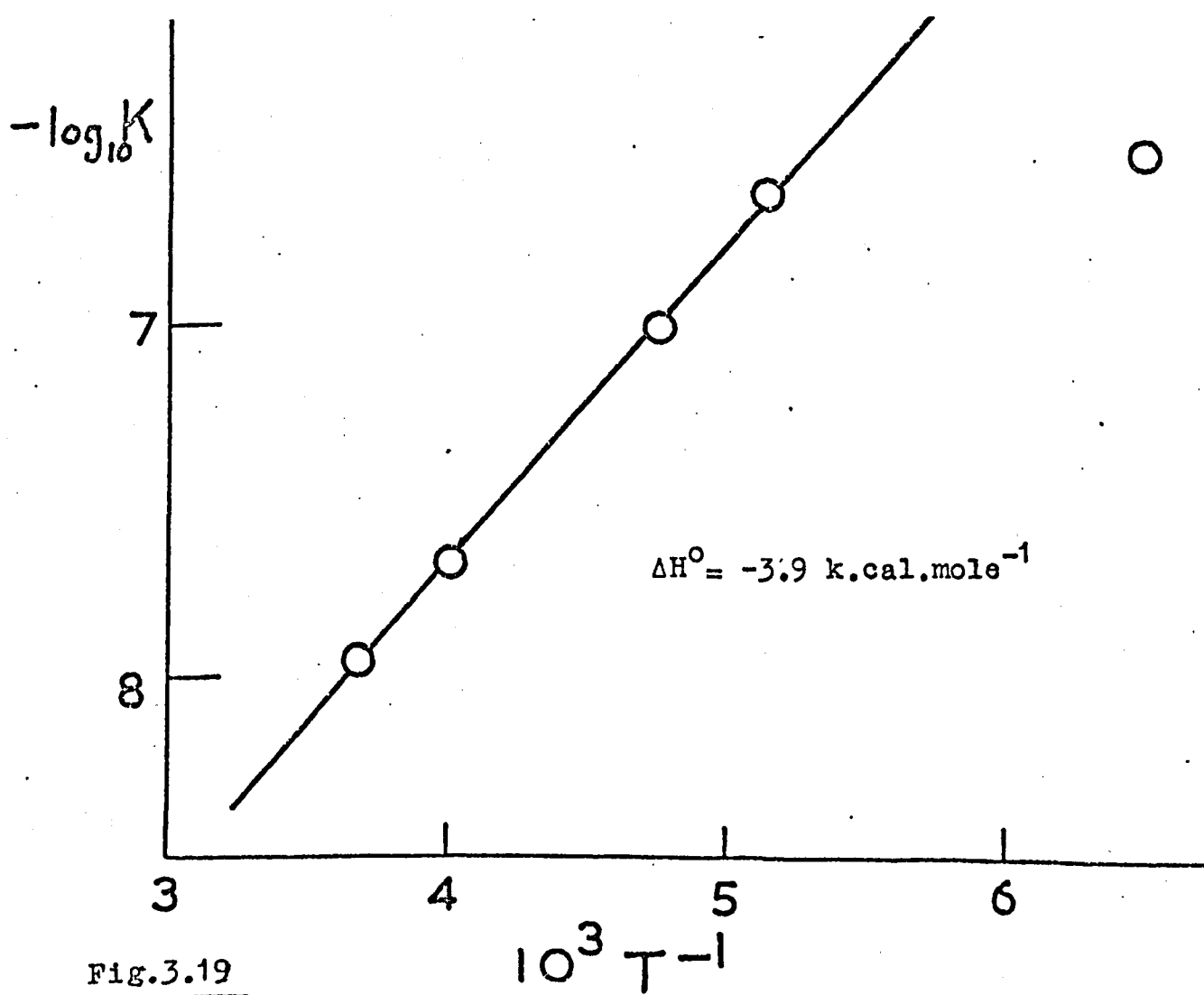


Fig.3.19

not complete and a genuine equilibrium between the water and the aluminium bromide seems to be set up. The plot of $\kappa_e - \kappa_i$ against a_o , (for each phial separately), is shown in Fig. 3.17, together with a plot of the slope of the kinetic plots ($\ln \frac{\kappa_e + \kappa}{\kappa_e - \kappa}$ vs. time) for each phial versus a_o . The slope of the kinetic plot is given by $2a_o k_b K^{\frac{1}{2}}$ and therefore the slopes should be proportional to the a_o , and Fig. 3.17 demonstrates this to be so, approximately.

Fig. 3.18 summarises the dependence of conductivity on concentration for the self-ionisation of aluminium bromide in methyl bromide at various temperatures.

An interesting observation was that if a pure solution of aluminium bromide is diluted or concentrated by addition or removal of solvent at 0° , the conductivity re-equilibrates immediately, and there is no slow change of κ . This phenomenon is important because it means that any change in the concentration does not affect the equilibrium i.e. the ratio of molecules to ions remains constant. This is only true if the equilibrium involved has equal numbers of species on each side of the equation, and this is one of the characteristic properties of a 2:2 ionogenic equilibrium. (reaction 3.11).

The best value of the conductivity at 0° was obtained from expt. C24. As was explained in § 3, this was the final dilution expt. of a series in which the same solvent was repeatedly purified, and the true $\kappa - c$ dependence for a pure aluminium bromide solution was revealed. This result was checked by expt. K4 in which the concentration was varied by adding aluminium bromide to methyl bromide.

At the end of the dilution in expt. C24, at -63° , the solution was warmed to 0° ; the conductivity decreased by a very small amount. (Fig. 3.7). The solution was re-cooled to -63° and the conductivity returned to the original value. This was a key expt., because (i) the solution was the purest that has been obtained; (ii) the reversibility and stability of this solution was a further indication of its high purity; (iii) it revealed that for a pure solution the conductivity decreased very slightly with increase of temp; (iv) the value of the conductivity at 0° fitted in well with the plot of $(\kappa_e - \kappa_i)a_0^{-1}$ versus a_0 (Fig. 3.13); and this gave us confidence in the computer method of finding $\kappa_e - \kappa_i$, and in the assertion that the part of the conductivity given by $\kappa_e - \kappa_i$ does in fact represent the conductivity due to self-ionisation.

3.3.1.6 The application of the kinetic scheme to the results at -63° and -78°

The kinetic scheme was applied to the ionisation at -63° and -78° with little success. As is shown in Figs. 3.5, 3.8, and 3.9, the conductivity usually passes through a maximum, and this makes the estimation of κ_e rather uncertain. If however, only the initial part of the curve is examined, and κ_e is assumed to be a little higher than the maximum, straight line plots could be obtained, from which formal values of κ_i , k_b and k_f could be calculated. However, it was found that at these temps. the values of $\kappa_e - \kappa_i$ obtained in this way could not be interpreted as the conductivity due to self-ionisation, as had been done at 0° and -23° . The ratio $(\kappa_e - \kappa_i)/\kappa_i$ bore no relationship to the purity of the solution, which was assessed by the number of cycles of purification of solvent, and the ratio κ/c . This means that the rate-constants calculated for the two low temps. do not have the same significance as those obtained at the higher temps.,

and to distinguish them the rate-constants of dubious significance obtained at the lower temps. are denoted by k'_f and k'_b .

I wanted to analyse the $\kappa - t$ curves at low temps. because it would have been very useful to examine the variation of the rate-constants with temp., since it appeared from the $\kappa - t$ curves in Fig. 3.5 that the ionisation was faster than at 0° or -23° , which suggested a negative "activation energy". The studies of conductivity as a function of concentration reported in § 3.3.1.1. to § 3.3.1.3. showed that at least two types of ionisation were present, and these are summarised by reactions 3.9 and 3.10.

It is an obvious guess that the same thing happens at the lower temperatures, but that both reactions have roughly the same rate, so that the conductivity-time curves at -63° and -78° are probably composed of two inseparable parts arising from two concurrent reactions.

For this reason it is not clear what k'_f and k'_b represent, but if our guess is right, they represent the maximum possible values of k'_f and k'_b . It is interesting to note that solutions which were purer than average gave smaller values of k'_f and k'_b . (see Table 3.4).

3.3.1.7 The dissociation and rate constants. As is explained in Appendix 1, the information that can be obtained from studies of the dependence of κ on concentration for 2:2 ionogenic equilibria is rather limited. It is not possible to evaluate Λ_T^0 and K separately from the slope of the $\kappa - c_0$ plots, which is given by $10^3 \Lambda_T K^{\frac{1}{2}} / (1 + 2K^{\frac{1}{2}})$. If Λ_T could be found by some independent method, then K could be calculated.

In this work Λ_T^0 was calculated by means of the Stokes equation:⁸⁹

$$\Lambda_T^0 = 8.20 \times 10^{-2} \eta^{-1} (r_+^{-1} + r_-^{-1}), \quad (\text{viii})$$

where η is the viscosity in poise and r_+ and r_- are the radii of the cation and anion, in 10^{-1} nm.

The radius of the tetrabromoaluminate ion has been calculated to be 0.346 nm from the Al-Br bond distances in Al_2Br_6 (Fig. 3.2), and the atomic radius of bromine, 0.119 nm. From the measurements of transport numbers by previous workers it is known that $\lambda_{T+} = \lambda_{T-}$ for aluminium bromide in methyl bromide (c.f. § 3.2.3.2) and therefore probably $r_+ = r_-$.

As the viscosity of methyl bromide has been measured at one temp. only,⁶¹ the viscosity at other temps. was estimated by comparison with other similar compounds of known viscosity. From this, the constants in the De Guzman equation, below, were estimated to be, $A = 4.39 \times 10^{-5}$ poise, $B = 2.46$ k.cals., the viscosity calculated in this way is probably within 5% of the correct value from -80° to 0°

$$\eta = A e^{B/RT}$$

where η is the viscosity in poise,

Table 3.3(a)

The variation with temp., of the equilibrium constant for the self-ionisation of aluminium bromide in methyl bromide.

Temp. /°C	Viscosity (De Guzman) /centipoise	Λ_T^0 (Stokes) / $\Omega^{-1}\text{cm}^2\text{mole}^{-1}$	$10^8 K$
0°	0.397	119	1.12
-23°	0.54	88	2.15
-63°	1.15	41	11.1
-78°	1.7	28	24.3
-120°	ca. 5	ca. 9	40

The values of the ionisation constant K in Table 3.3(a) were calculated from the conductivity results in Figs. 3.13 and 3.18. To obtain K , the slope of the κ versus $[AlBr_3]$ plots was substituted into the following relation (see Appendix 1).

$$K^{\frac{1}{2}} = 10^3 \Lambda_T^{0-1} \kappa / [AlBr_3] \quad (ix)$$

The way in which the $\kappa - c$ plots in Fig. 3.18 were obtained was not simple and it is summarised below.

The conductivity results at -63° were taken from the dilution expt. C24 in which the solvent was especially pure (§ 3.3.1.1), and from expt. K4, which was used to check the result of expt C24. In both these expts. there was no significant change of conductivity when the temp. was changed by $\pm 20^\circ$.

No dilution experiments were performed at 0° , because of the low rate of equilibration of the conductivity at this temp., but for each such experiment the analysis of the kinetics of ionisation gave a value of $\kappa_e - \kappa_i$, which could be plotted against the appropriate $[AlBr_3]$ and thus the $\kappa - c$ curve for the self-ionisation at 0° was obtained. When these values were plotted, several fell on the same line as given by expt. C24, and these are the results shown in Fig. 3.18.

Each expt. at 0° and -23° , which yielded to kinetic analysis, gave a value of the ratio $(\kappa_e - \kappa_i)/a_0$, which was substituted into equ. (ix) to obtain K . These rather scattered values of K are shown in Table 3.3(b). The average \bar{K} , of all K was taken, the values of

Table 3.3(b)

The values of the equilibrium constants calculated directly from experiment, for the ionisation of aluminium bromide in methyl bromide at 0°

Expt. No.	$10^8 K$	$10^7 (\kappa_e - \kappa_i)$ $/\Omega^{-1} \text{cm.}^{-1}$	$10^2 [\text{AlBr}_3]$ $/M.$
C3	3.7	0.456	0.23
C4	2.6	0.216	0.13
C5	1.6	0.221	0.17
C10	1.0	2.32	2.25
C15	ca.8	0.437	0.15
C25	1.8	6.91	5.0
C26	1.5	4.04	3.2
C27A	1.0	0.371	0.36
C27B	1.0	0.340	0.33
C28	0.8	1.29	1.4
K1.1	3	0.749	0.42
K1.2	4	0.433	0.21
K2.1	4	0.886	0.43
K2.2	1.3	1.01	0.86
K2.3	1.3	1.17	1.0
R1	1.5	4.67	3.7

First average of $K = 1.98 \pm 0.8 \times 10^{-8}$

Second average of $K = 1.4 \pm 0.2 \times 10^{-8}$

K falling within $\bar{K} \pm 50\%$ were re-averaged, and a second average \bar{K} was thus obtained; the error in \bar{K} was taken as the mean deviation. The \bar{K} was 1.4×10^{-8} whereas from the $\kappa - c$ plot in Fig. 3.18 a value of $K = 1.1 \times 10^{-8}$ was obtained, and the difference between these values is probably a reasonable measure of the uncertainty.

The scatter in K in Table 3.3(b) is caused by the fact that small errors in concentration and conductivity are magnified by equ. (ix). For instance, 10% errors in conductivity and concentration lead to a 50% error in K. Conductivity results at 0° , which have been obtained from the computer method are also subject to error, because $\kappa_e - \kappa_i$ is very often much smaller than either κ_i or κ_e . In some circumstances a small error in κ_e , say 1%, could cause a 50% error in $\kappa_e - \kappa_i$.

Fig. 3.19 shows a van't Hoff plot of K (from K taken from Table 3.3a) from which a value of $\Delta H^\circ = -3.9 \text{ k.cal.mole}^{-1}$ was calculated. The value of K at -120° was out of line, probably because the solvent was an equimolar mixture of ethyl and methyl bromides. Not only does this mean that the value of K might have increased because of the presence of ethyl bromide, but the viscosity of this solvent was hard to gauge, and hence the value of Λ_T° used to obtain K was very dubious. This result has therefore little significance.

Table 3.4 contains values of k_b and k_b^* and k_f and k_f^* . The values of k_b and k_b^* were found from the slopes of the kinetic plots which are given by $2[\text{AlBr}_3] k_b k^{1/2}$ (c.f. equ. (vii)); k_f and k_f^* were calculated from $k_f = k_b K$, $k_f^* = k_b^* K$. The error in k_b and k_b^* was

Table 3.4

The values of k_b and k_f for the ionisation of aluminium bromide in methyl bromide at various temp.

Temp/°C	Expt No.	$10^{-2}k_b$ /l.mole. ⁻¹ sec. ⁻¹	10^6k_f /l.mole. ⁻¹ sec. ⁻¹	Average $10^{-2}k_b$ /l.mole. ⁻¹ sec. ⁻¹	Average 10^6k_f /l.mole. ⁻¹ sec. ⁻¹
0	C3	3.5	3.9	4.0 ± 1	4.5 ± 1
0	C4	3.5	3.9		
0	C5	3.9	4.4		
0	C10	6.1	6.8		
0	C15	5.3	5.9		
0	C25	.5	0.6		
0	C26	.4	0.4		
0	C27A	4.1	4.6		
0	C27B	2.9	3.2		
0	C28	1.8	2.0		
0	K11	5.9	6.6		
0	K12	2.3	2.6		
0	K21	3.7	4.1		
0	K22	2.5	2.8		
0	K23*	2.8	3.1		
0	R1	0.4	0.4		
-23	R2	0.82	1.8		
		k'_b	k'_f	k'_b	k'_f
-63	C12	69	766	44 ± 30	490 ± 380
-63	C13	100	1110		
-63	C16	66	732		
-63	C20	22	244		
-63	C21	94	1043		
-63	C24*	5.0	56		
-63	R3	0.6	7		
-63	R4	16	178		
-63	R8	29	321		
-78	C9	24	576	25 ± 11	600 ± 260
-78	C29	50	1200		
-78	K41	22	528		
-78	K42	34	816		
-78	K43*	17	408		
-78	R11	3	72		

* is a particularly pure experiment.

Figure 3.20

The variation of the conductivity with temperature of an impure solution of aluminium bromide in methyl bromide. This solution had a concentration of 1.2×10^{-3} M.

Expt. C19, $(\kappa_e - \kappa_i)/\kappa_i = 0.095$.

Figure 3.21

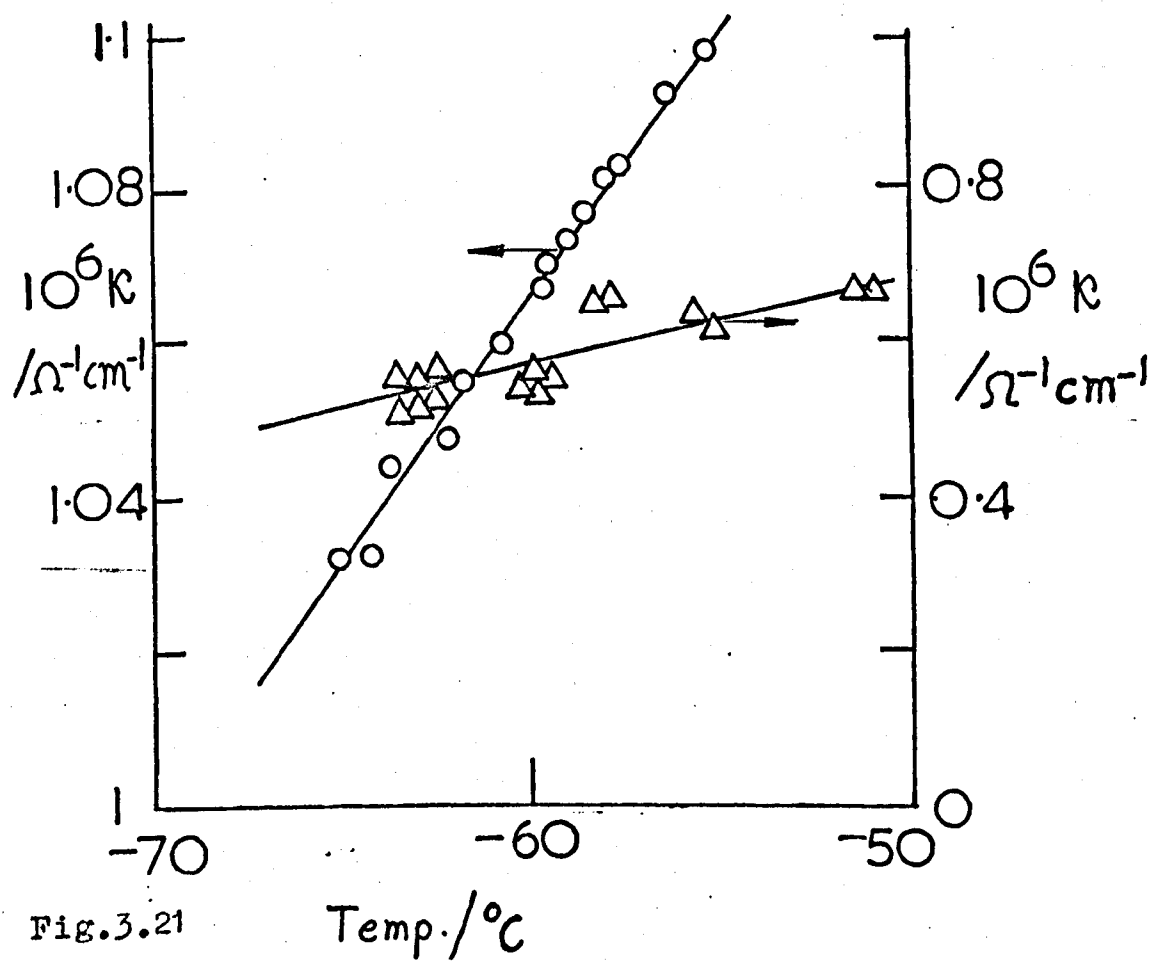
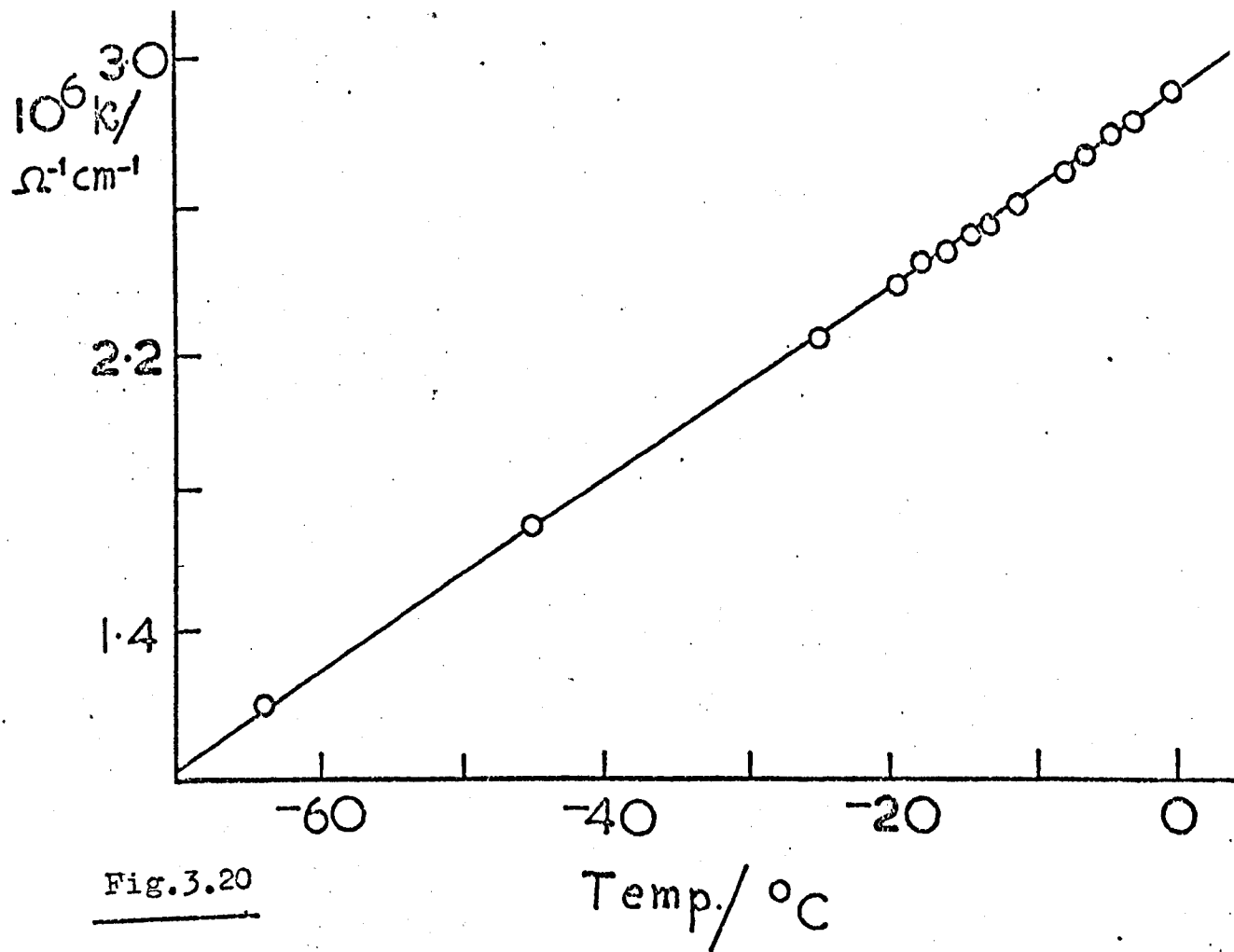
The variation of conductivity with temp. for impure solutions of aluminium bromide. See page 75 for a detailed explanation.

Circular points, Expt. C11, $[\text{AlBr}_3] = 4.25 \times 10^{-3}$ M.

$(\kappa_e - \kappa_i)/\kappa_i = 0.63$,

Triangular points, Expt. C13, $[\text{AlBr}_3] = 2.3 \times 10^{-3}$ M.

$(\kappa_e - \kappa_i)/\kappa_i = 0.68$.



calculated from the mean deviation of the results, and is therefore a measure of the scatter of the results. The scatter of the rate constants at low temp. is much greater than at 0° , and this is probably an indication of the composite nature of k'_b and k'_f as opposed to k_f and k_b which refer only to the self-ionisation process (c.f. § 3.3.1.6.).

Whether the fact that $k'_f > k_f$ and $k'_b > k_b$ is significant is debatable.

3.3.1.8 The variation of conductivity with temperature. The theoretical relation between the conductivity of an aluminium halide solution and temp. is dealt with in the discussion. § 3.4.3. It was observed that the conductivity of an impure solution of aluminium bromide increases linearly and quite strongly with increasing temperature whereas that of a pure solution decreases, but only slightly. (see Figs. 3.7 and 3.18). As has been explained the criterion of purity is the ratio $(k_e - k_i)/k_i$. For a solution in which this ratio was 0.095, the conductivity increases linearly with increase of temp. (Fig. 3.20.) This simple behaviour was observed for several solutions, and this is shown in Fig. 3.21.

3.3.2 The conductivity of aluminium chloride in methylene dichloride and ethyl chloride at 0° and -78° . The behaviour of the conductivity of solutions of aluminium chloride resembled closely that of aluminium bromide. Aluminium chloride is very insoluble in comparison with the bromide, so that the usable concentration range was much smaller, and also the chloride dissolves more slowly than the bromide.

Figures 3.22 to 3.25

The ionisation and the plots of its kinetics for aluminium chloride in ethyl chloride and methylene dichloride at 0° and -78°.

Fig.	3.22	3.23	3.24	3.25
Expt.	D2	R9	D4	D1
Solvent	EtCl	EtCl	CH ₂ Cl ₂	CH ₂ Cl ₂
Temp.	0°	-78°	0°	-78°
$\frac{[AlCl_3]}{M}$	1.1×10^{-3}	2.0×10^{-3}	1.25×10^{-3}	1.1×10^{-4}

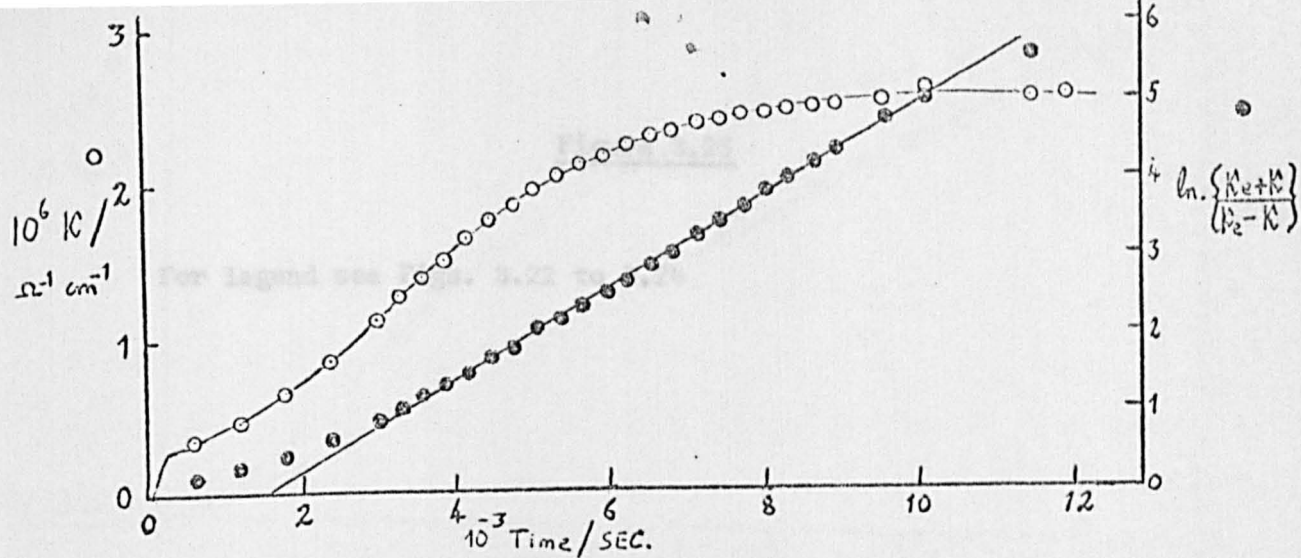


Fig.3.22

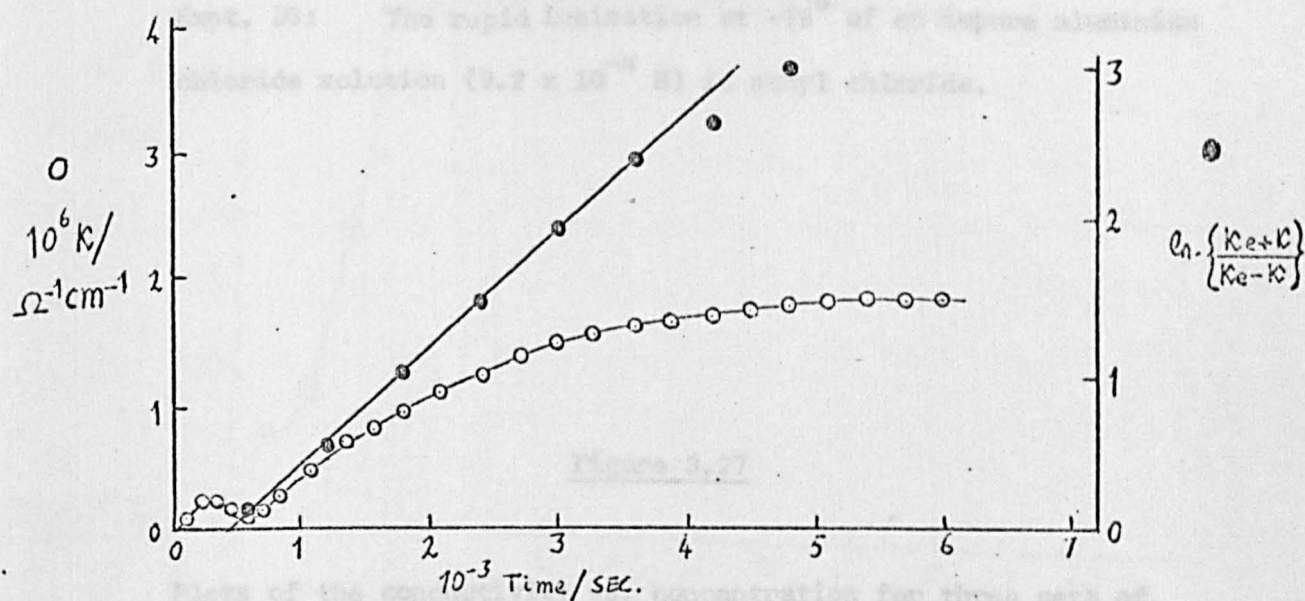


Fig.3.23

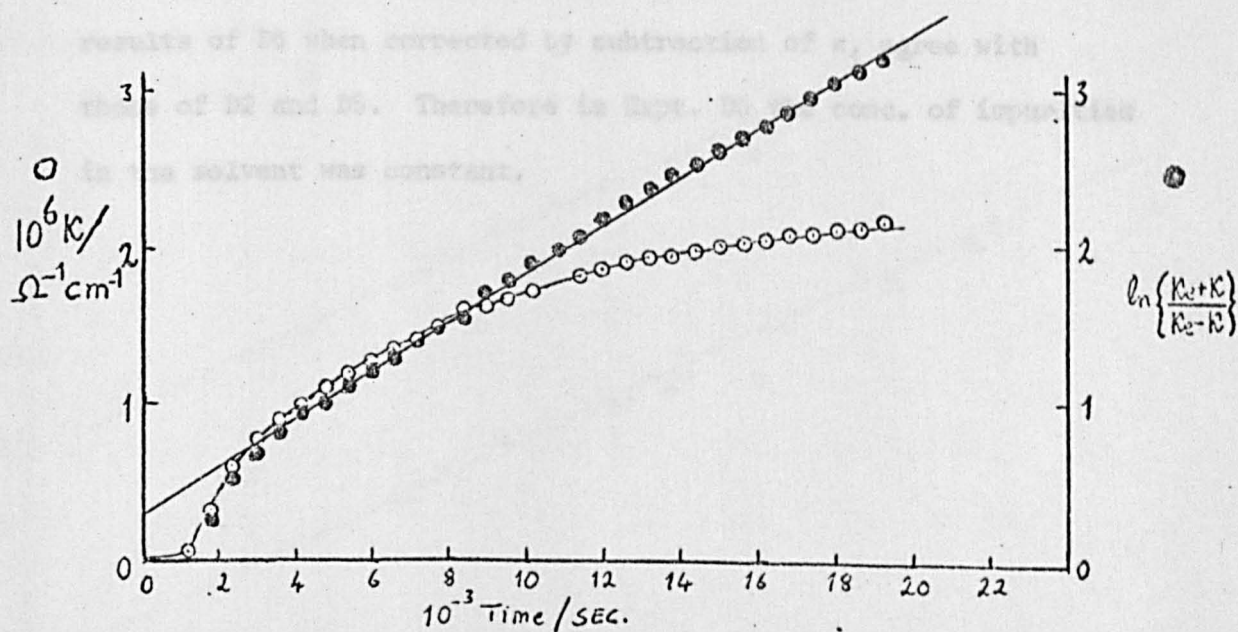


Fig.3.24

Figure 3.25

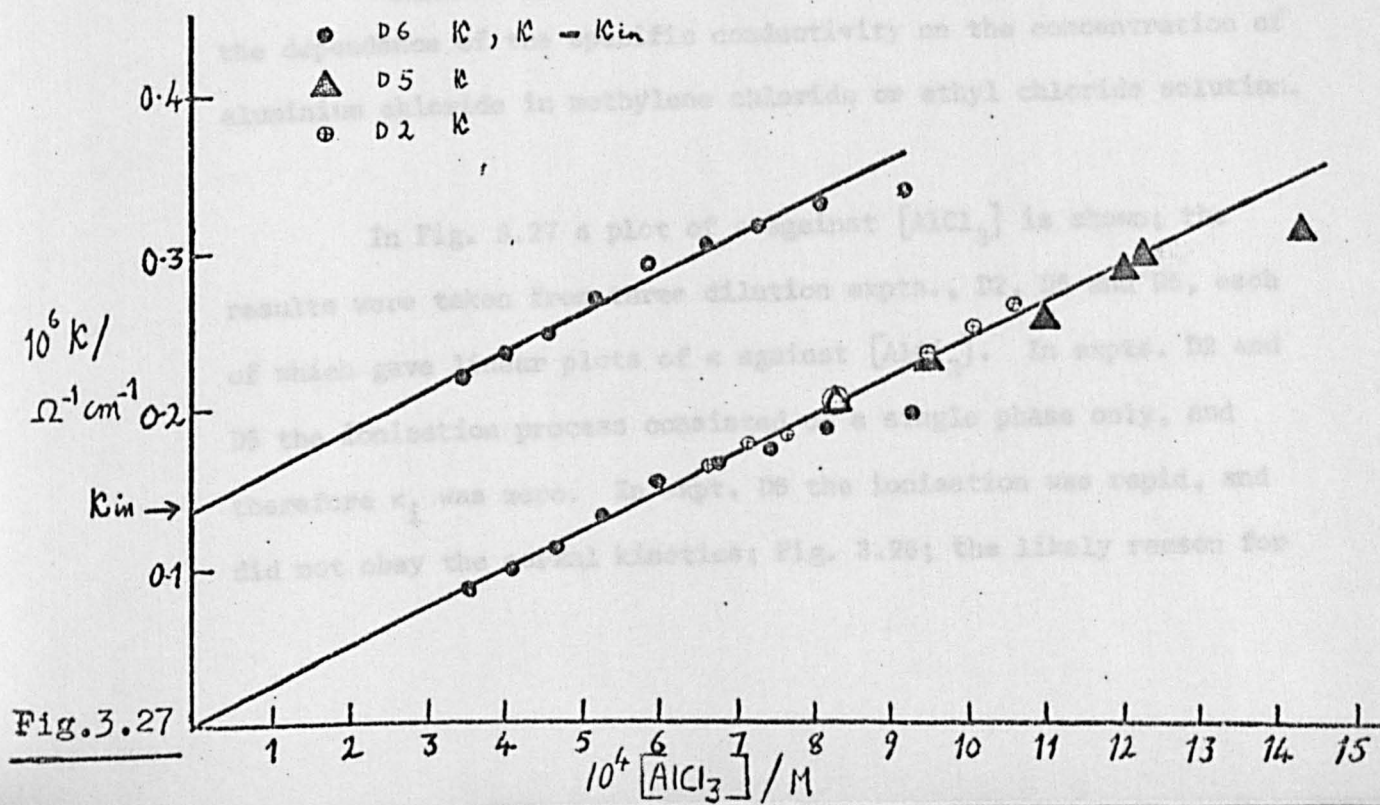
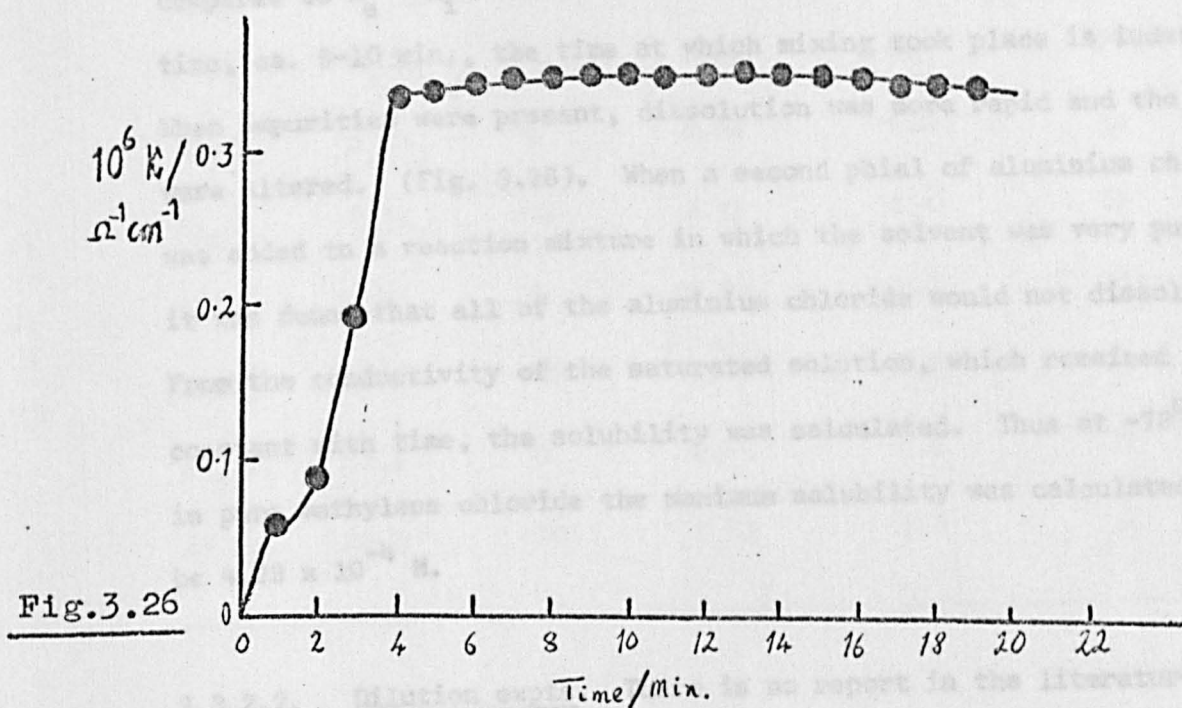
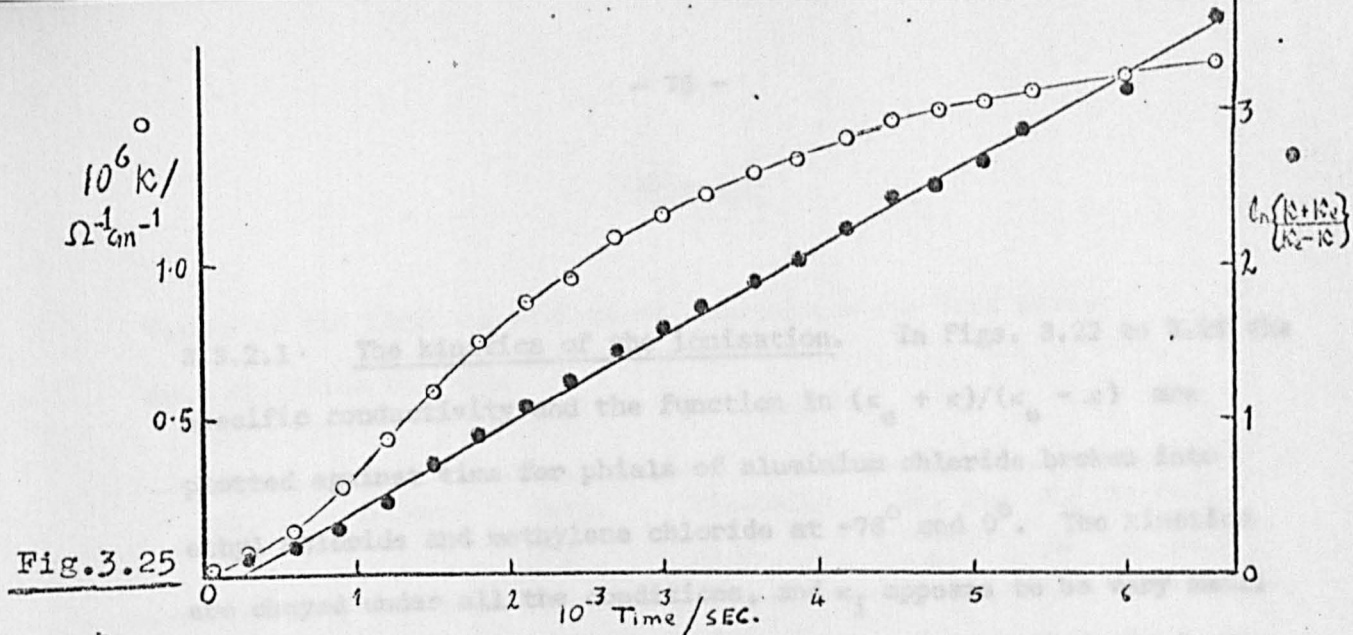
For legend see Figs. 3.22 to 3.24

Figure 3.26

Expt. D6: The rapid ionisation at -78° of an impure aluminium chloride solution (9.2×10^{-4} M) in ethyl chloride.

Figure 3.27

Plots of the conductivity vs. concentration for three sets of results, for aluminium chloride in ethyl chloride at -78° . The results of D6 when corrected by subtraction of κ_i agree with those of D2 and D5. Therefore in Expt. D6 the conc. of impurities in the solvent was constant.



3.3.2.1. The kinetics of the ionisation. In Figs. 3.22 to 3.25 the specific conductivity and the function $\ln (\kappa_e + \kappa)/(\kappa_e - \kappa)$ are plotted against time for phials of aluminium chloride broken into ethyl chloride and methylene chloride at -78° and 0° . The kinetics are obeyed under all the conditions, and κ_i appears to be very small compared to $\kappa_e - \kappa_i$. Since the dissolution took a relatively long time, ca. 5-10 min., the time at which mixing took place is indeterminate. When impurities were present, dissolution was more rapid and the kinetics were altered. (Fig. 3.26). When a second phial of aluminium chloride was added to a reaction mixture in which the solvent was very pure, it was found that all of the aluminium chloride would not dissolve. From the conductivity of the saturated solution, which remained constant with time, the solubility was calculated. Thus at -78° in pure methylene chloride the maximum solubility was calculated to be 4.23×10^{-4} M.

3.3.2.2. Dilution expts. There is no report in the literature of the dependence of the specific conductivity on the concentration of aluminium chloride in methylene chloride or ethyl chloride solution.

In Fig. 3.27 a plot of κ against $[\text{AlCl}_3]$ is shown; the results were taken from three dilution expts., D2, D5 and D6, each of which gave linear plots of κ against $[\text{AlCl}_3]$. In expts. D2 and D5 the ionisation process consisted of a single phase only, and therefore κ_i was zero. In expt. D6 the ionisation was rapid, and did not obey the normal kinetics; Fig. 3.26; the likely reason for

Table 3.5

Values of the limiting equivalent conductance for ions derived from aluminium chloride.

Ion	Solvent	Temp. /°C	Viscosity /c.p.	10. Ion radius / nm	Λ_T^0 (Stokes) $/\Omega^{-1}\text{cm}^2\text{mole}^{-1}$
AlCl_4^-	CH_2Cl_2	0	0.54	6.4	95
AlCl_4^-	CH_2Cl_2	-78	2.15	6.4	24
Al_2Cl_7^-	CH_2Cl_2	0	0.54	6.4	48
Al_2Cl_7^-	CH_2Cl_2	-78	2.15	6.4	12
AlCl_4^-	EtCl	0	0.34	3.2	151
AlCl_4^-	EtCl	-78	1.85	3.2	28
Al_2Cl_7^-	EtCl	0	0.34	3.2	75
Al_2Cl_7^-	EtCl	-78	1.85	3.2	14

Table 3.6

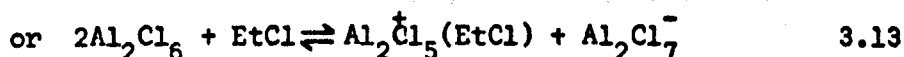
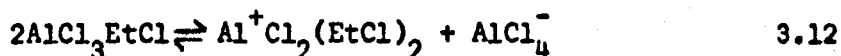
The dissociation constant K , and the forward and backward velocity constants k_f and k_b , for the ionisation of aluminium chloride, (Assuming double ions).

Temp /°C	Solvent	K	k_f /1.mole. ⁻¹ sec. ⁻¹	k_b /1.mole. ⁻¹ sec. ⁻¹	Expt. No.
0	EtCl	9.7×10^{-6}	8.4×10^{-4}	87	O2
-78	EtCl	$1.23 \times 10^{-5*}$	5.7×10^{-4}	47	R9
0	CH ₂ Cl ₂	9×10^{-4}	1.9×10^{-3}	2.1	D4
-78	CH ₂ Cl ₂	1.3×10^{-2}	3.2×10^{-1}	25	D1

*Taken from the result of Fig. 3.27, expts. D2, D5, D6.

this is that the ethyl chloride probably contained traces of water. When a dilution expt. was performed for this expt., the plot of κ against $[\text{AlCl}_3]$ was linear, but gave a large intercept, κ_{in} on the conductivity axis. (Note, κ_{in} must be carefully distinguished from κ_i , since the latter is the calculated conductivity at zero time from the kinetic analysis of ionisation). When $\kappa - \kappa_{\text{in}}$ was plotted, the curve matched that for D2 and D5 in Fig. 3.27.

The linear plot of κ against $[\text{AlCl}_3]$ in Fig. 3.27 can be accounted for by either reaction 3.12 or 3.13 (see Appendix 1).



Since we do not know whether aluminium chloride is predominantly monomeric or dimeric under our conditions, we calculated Λ_T^0 by the Stokes equation (c.f. § 3.3.1.7. (viii)), for both the single and the double ions. The radii of the ions were calculated from the interatomic distances in the Al_2Cl_6 dimer,^{4, 5, 6, 7} and the atomic radius of chlorine, and they are shown in Table 3.5. The viscosity of methylene chloride over the required temp. range has been determined,⁵⁹ but that of ethyl chloride has not. It was estimated from the viscosities of the following closely related compounds which are taken from the literature:^{58, 61, 87} EtBr, i-PrBr, t-BuBr, EtI, i-BuI, t-BuI, MeCl, i-PrCl, t-BuCl. The results are shown in Table 3.5.

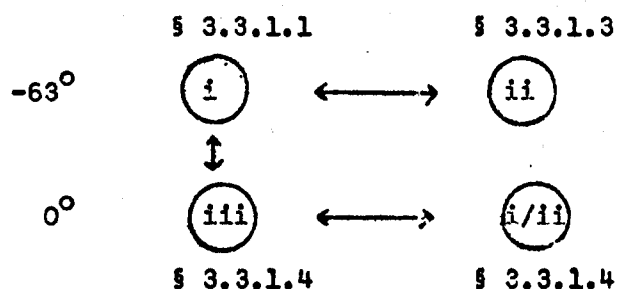
3.3.2.3 The extent and rate of ionisation. Table 3.6 shows the values of K , the equilibrium constant for reaction 3.13, k_f and k_b , the values of forward and reverse rate constants. The value of K for aluminium chloride in ethyl chloride at -78° was obtained

by substituting the slope of the plot in Fig. 3.27 into equ. vii. The remaining values of k_b , k_f and K were calculated from individual experiments in the following manner. The ionisation was slow under the conditions of each expt., and in addition when kinetically analysed gave very low values of κ_{in} . For each expt. a value of $\kappa_e - \kappa_i$ was determined, and the ratio, $(\kappa_e - \kappa_i)/[AlCl_3]$ was substituted into equ. (ix) to give a value of K . (These values of K rest on the assumption that a 2:2 ionogenic equilibrium such as reaction 3.12 or 3.13 is present under the conditions of each experiment, and that κ is therefore proportional to $[AlCl_3]$. (see Appendix 1). A $\kappa - c$ plot was obtained for aluminium chloride in ethyl chloride at -78° only, c.f. § 3.3.2.2). The values of k_b and k_f were determined from the slope of the kinetic plots in the manner described for aluminium bromide in § 3.3.1.7.

3.4 Discussion, and comparison with results of other workers

3.4.1. Comparison of the conductivity results of aluminium bromide with those of previous workers. It should now be clear to the reader that there is much difficulty in obtaining the real conductivity of aluminium bromide solutions. What I consider to be the important feature of the results presented here, in comparison with those of previous workers,^{19,20,21,26,34} is that we have succeeded in detecting and measuring the conductivity from self-ionisation by a combination of three methods: (i) by examining the influence of solvent purity on dilution expts.; (ii) by studying the concentration behaviour by increasing the amount of solute with a constant volume of solvent; (iii) by analysing the kinetics of ionisation, and finding that at 0° and -23° the ionisation due to

impurities is much faster than the self-ionisation. The determinations all support the existence of reaction 3.9, each method was used to obtain a $\kappa - c$ plot, and they each support the other in the following way:



The work of all earlier experimenters was influenced considerably by impurities and it was all carried out with relatively high solute concentrations.

3.4.2 Other similar systems. Giusti and his co-workers⁹¹ have recently been studying the ionisation of aluminium diethyl chloride in methyl chloride solution by conductivity measurements. I spent a week in Pisa examining the results, and found that they were very similar to those of aluminium bromide and aluminium chloride solutions. For instance, when an experiment was performed at -40°, in which three phials containing equal amounts of aluminium diethyl chloride were broken at ten minute intervals, there was a large and fairly rapid rise of conductivity (ca. 5 min.) for the first phial, which was followed by a slow and persistent increase. The remaining phials gave small increases of conductivity, and again the slow increase of conductivity was observed. The major part of the conductivity from the first phial was clearly due to the reaction with impurity (probably water), whereas only a slow self-ionisation was seen when the next two phials were broken. The slow ionisation was amenable to the normal

kinetic analysis, and values of K , k_b and k_f were determined, and these are shown in Table 3.7. When a phial was broken at -78° , the behaviour was similar to that of expt. K3 shown in Fig. 3.5., except that the conductivity decreased quickly to half the maximum value. When a dilution expt. was performed on this system, the conductivity was found to increase when solvent was added, which showed that the solvent was very impure.

In 1963, Halpern and Polaczek²¹ published curves of conductivity as a function of time and concentration, for gallium, aluminium and indium halides in alkyl halide solvents. As I wanted to examine the original conductivity data, I wrote to both authors, but they could not provide the required information. Thus I had to be content with a kinetic analysis of the published curves, and by this rather imprecise method values of k_b , k_f and K were obtained. (see Table 3.8)

The kinetic plots were reasonably linear, and gave values of $(\kappa_e - \kappa_i)/\kappa_i \approx 1$, for indium and aluminium iodide, and ≈ 0.3 for gallium iodide. The conductivity of gallium iodide is therefore mainly due to impurities, and this probably explains why the values of k_b , k_f and K are rather different from the values for indium and aluminium iodide.

Table 3.9 summarises all the results which have been produced by the kinetic method of analysis, and by the interpretation of the curves of conductivity versus concentration for a group of related systems. These will now be discussed.

Table 3.7

The dissociation constant K , and the forward and reverse rate constants k_f and k_b for the self-ionisation of diethyl aluminium chloride in methyl chloride. (Unpublished results of P. Giusti et al.).

Temp/ $^{\circ}\text{C}$	Λ_T° (Stokes) Assuming double ions $/\Omega^{-1}\text{cm}^2\text{mole}^{-1}$	K	k_f $/\text{l.mole}^{-1}\text{sec}^{-1}$	k_b $/\text{l.mole}^{-1}\text{sec}^{-1}$	No. of Expts.
-40	43	3×10^{-8}	4×10^{-5}	1.4×10^{-3}	5
-78	16	1×10^{-9}	-	-	1

Table 3.8

The dissociation constant K , and the forward and reverse rate constants k_f , k_b at 22° , calculated from the data published by Halpern and Polaczek.²¹

Metal Halide	Solvent	Λ_T^0 (Stokes) Assuming single ions $/\Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$	K	k_b $/1.\text{mole}^{-1} \text{ sec}^{-1}$	k_f $/1.\text{mole}^{-1} \text{ sec}^{-1}$
AlI_3	CH_3I	87	7×10^{-9}	60	4×10^{-7}
AlI_3	$\text{C}_2\text{H}_5\text{I}$	ca.70	4×10^{-9}	190	7×10^{-7}
GaI_3	$\text{C}_2\text{H}_5\text{I}$	ca.70	7×10^{-13}	7×10^5	5×10^{-9}
InI_3	$\text{C}_2\text{H}_5\text{I}$	ca.70	4×10^{-9}	240	1×10^{-6}

Table 3.9

Metal Halide	Solvent	Ion	10 Radius of ion / nm	Temp / °C	Viscosity / cp	$2\lambda_T^0$ - Stokes ($=\lambda_T^0$) / $\Omega^{-1} \text{cm}^2 \text{mole}^{-1}$	K	k_b / $\text{l.mole}^{-1} \text{sec}^{-1}$	k_f / $\text{l.mole}^{-1} \text{sec}^{-1}$	Source of Data	No of measurements
AlCl_3	ϕNO_2	AlCl_4^-	3.2	25	1.87	27.4	$(4.5 \pm 1) \times 10^{-3}$	2.85×10^4	ca. 130	25	?
AlBr_3	ϕNO_2	AlBr_4^-	3.5	25	1.87	25.2	$(2.2 \pm 0.5) \times 10^{-2}$	380 ± 60	ca. 8	25	?
AlI_3	CH_3I	AlI_4^-	3.93	22	0.48	86.9	7×10^{-9}	58.5	4×10^{-7}	74	1
AlI_3	$\text{C}_2\text{H}_5\text{I}$	AlI_4^-	3.93	22	0.67	62.3	3.6×10^{-9}	189	6.8×10^{-7}	74	1
GaI_3	$\text{C}_2\text{H}_5\text{I}$	GaI_4^-	ca. 4	22	0.67	ca. 65	7×10^{-13}	7,000	4.8×10^{-9}	74	1
InI_3	$\text{C}_2\text{H}_5\text{I}$	GaI_4^-	ca. 4	22	0.67	ca. 65	4×10^{-9}	240	1×10^{-8}	74	1
AlBr_3	CH_3Br	AlBr_4^-	3.5	0	0.397	119	1.1×10^{-8}	400 ± 100	$(4.5 \pm 1) \times 10^{-6}$	This work	20
AlBr_3	CH_3Br	AlBr_4^-	3.5	-23	0.54	88	2.2×10^{-8}	82	1.8×10^{-6}	This work	2
AlBr_3	CH_3Br	AlBr_4^-	3.5	-63	1.15	41	1.1×10^{-7}	$(44 \pm 30) \times 10^2 \dagger$	$(4.9 \pm 3.3) \times 10^{-4} \dagger$	This work	7
AlBr_3	CH_3Br	AlBr_4^-	3.5	-78	1.7	28	2.4×10^{-7}	$(25 \pm 11) \times 10^2 \dagger$	$(6.0 \pm 26) \times 10^{-4} \dagger$	This work	5
AlBr_3	CH_3Br	AlBr_4^-	3.5	-120	ca. 5	ca. 9	$\text{ca. } 4 \times 10^{-7}$	(Very fast)		This work	1
* AlCl_3	CH_2Cl_2	AlCl_4^-	3.2	0	0.54	95	2.25×10^{-4}			This work	2
* AlCl_3	CH_2Cl_2	AlCl_4^-	3.2	-78	2.15	24	3.25×10^{-3}			This work	2
* Al_2Cl_6	CH_2Cl_2	Al_2Cl_7^-	6.4	0	0.54	48	9×10^{-4}	2.1	1.9×10^{-3}	This work	2
* Al_2Cl_6	CH_2Cl_2	Al_2Cl_7^-	6.4	-78	2.15	12	1.3×10^{-2}	25	0.32	This work	2
* AlCl_3	$\text{C}_2\text{H}_5\text{Cl}$	AlCl_4^-	3.2	0	0.34	151	2.43×10^{-6}			This work	2
* AlCl_3	$\text{C}_2\text{H}_5\text{Cl}$	AlCl_4^-	3.2	-78	1.85	28	3.0×10^{-4}			This work	2
* Al_2Cl_6	$\text{C}_2\text{H}_5\text{Cl}$	Al_2Cl_7^-	6.4	0	0.34	75	9.7×10^{-6}	87	8.4×10^{-4}	This work	2
* Al_2Cl_6	$\text{C}_2\text{H}_5\text{Cl}$	Al_2Cl_7^-	6.4	-78	1.85	14	1.2×10^{-5}	47	5.7×10^{-4}	This work	2
* AlEt_2Cl	CH_3Cl	$\text{AlEt}_2\text{Cl}_2^-$	ca. 3.2	-40	ca. .35	90	8×10^{-9}			94	1
* AlEt_2Cl	CH_3Cl	$\text{AlEt}_2\text{Cl}_2^-$	ca. 3.2	-78	ca. 1	60	3×10^{-10}			94	1
* AlEt_2Cl	CH_3Cl	$\text{AlEt}_4\text{Cl}_3^-$	ca. 6.4	-40	ca. 35	45	3×10^{-8}	1.4×10^3	4×10^{-5}	94	1
* AlEt_2Cl	CH_3Cl	$\text{AlEt}_4\text{Cl}_3^-$	ca. 6.4	-78	ca. 1	30	10^{-9}			94	1

*For these metal halides there is uncertainty as to whether they give monomeric or dimeric ions.

†These are values of k_b' and k_f' .

3.4.3. The innisation constants. All the values of K in Table 3.9 are very small.

a) Change of solvent. In the polar solvent nitrobenzene, the values of K are higher than in alkyl halides. This is to be expected since the ion solvation energy will be much greater in the former solvent, and will cause K to increase.

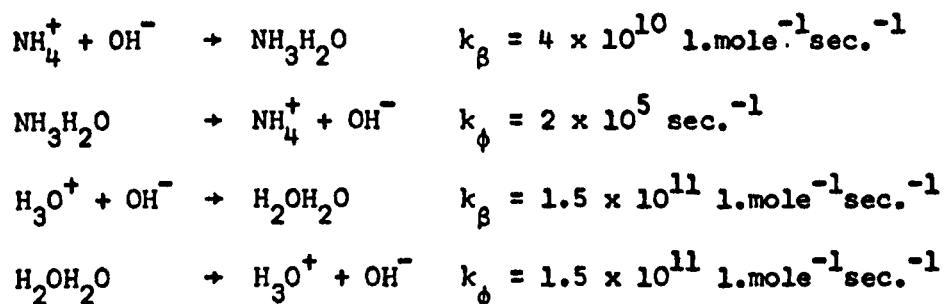
b) Change of halide. For aluminium halides in alkyl halide solution, K increases from the iodide to the bromide to the chloride, but this order is reversed in nitrobenzene solution. The value of K in a particular solvent depends on the relative solvation energy of the molecules and the ions. If the former is increased while the latter remains constant when the solvent is changed, K decreases, (and vice versa). If there is a specific solvent effect, as is more likely to be the case with alkyl halides than with nitrobenzene it could easily alter the relationships between the values of K in different solvents. It is therefore hard to decide exactly what is the significance of this reversal of the ordering of K.

c) Change of temperature. K increases by a factor of ca. ten for an 80° decrease in temp. in all the systems so far studied. This behaviour is expected because the dielectric constant of the solvent increases with decreasing temp. (Methyl bromide has a dielectric constant of 9 at 25° and 16 at -80°). The solvation energy of the ions therefore increases with decreasing temp. and the equilibrium constant shifts in favour of ions.

3.4.4 The rate-constants. The most notable features of the rate-constants are shown in Table 3.9.

The three main points of interest are (i) the small size of k_f ; (ii) the wide variation of k_f in comparison with k_b ;

(iii) the apparent increase of rate with decreases in temp. Point (ii) seems to be a fairly general phenomenon for ionisation, as is illustrated by the following results.³⁶



The relatively moderate variation of k_β may be due to the fact that it represents the rate of re-combination of ions, and is therefore to some extent independent of their nature.

The apparent increase of k_β and k_ϕ with decrease in temp. is regarded as a dubious result for the reasons expressed in § 3.3.1.6, and it is therefore rather pointless to discuss it. It would however be very interesting if this was caused by a dielectric acceleration effect.

3.4.5 The variation of conductivity with temperature. The conductivity of aluminium bromide solutions in methyl bromide was discovered to be practically independent of temperature. This behaviour seemed surprising because of the very considerable increase of the viscosity of methyl bromide with decrease in temp., and therefore a theoretical examination of the parameters involved was carried out to see if this behaviour could be simply rationalised.

Viscosity has been treated by the theory of absolute reaction rates, and the following relation derived. It describes the viscosity

behaviour of many simple liquids quite well. (within 6%).

$$\ln \eta_1 - \ln \eta_2 = \frac{\Delta H_v}{3.5R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (x)$$

Where ΔH_v is the latent heat of evaporation of methyl bromide (5.7 k.cal.mole.⁻¹₉₀)

The van't Hoff isochore below gives the variation of dissociation constant with temp.

$$\ln K_1 - \ln K_2 = \frac{\Delta H^0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (xi)$$

The dissociation constant is given by xii (c.f. (ix))

$$K = 10^6 \kappa^2 / \Lambda_T^2 [AlBr_3]_o^2 \quad (xii)$$

Substituting equ. (xii) into equ. (xi) yields

$$2 \ln \kappa_1 / \kappa_2 + 2 \ln \Lambda_{T2} / \Lambda_{T1} + 2 \ln [AlBr_3]_{o2} / [AlBr_3]_{o1} = \frac{\Delta H^0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (xiii)$$

Walden's rule ⁵² relates Λ_T to the viscosity as follows:

$$\Lambda_{T1} \eta_1 = \Lambda_{T2} \eta_2 \quad (xiv)$$

Eqs. (xi), (xiv) and (xiii) may be solved to yield,

$$\ln \kappa_1 / \kappa_2 + \ln [AlBr_3]_{o2} / [AlBr_3]_{o1} = R^{-1} (\Delta H_v / 3.5 + \Delta H^0 / 2) \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (xv)$$

Thus if $\Delta H_v / 3.5 - \Delta H^0 / 2$ is very small, $\ln \kappa_1 / \kappa_2 \approx 0$. ΔH^0 was measured as -3.9 k.cal.mole.⁻¹, and $\Delta H_v = 5.7$ k.cal.mole.⁻¹

$\Delta H_v / 3.5 - \Delta H^0 / 2 = 0.3$. The fact that ΔH_v and ΔH^0 nearly cancel each other explains why the conductivity is relatively unaffected by changes of temp.

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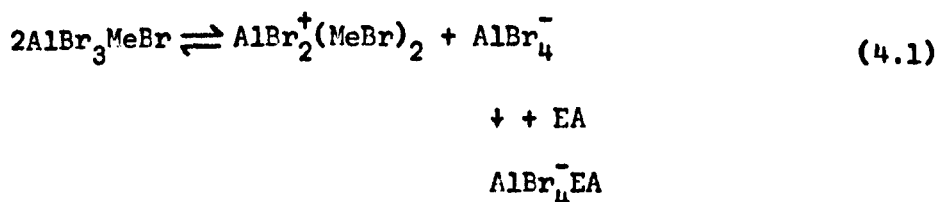
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CHAPTER FOUR

THE TITRATION OF ALUMINIUM HALIDE SOLUTIONS BY ELECTRON ACCEPTORS AND ELECTRON DONORS

4.1 INTRODUCTION

Investigations were made into the effect of electron donors and electron acceptors on alkyl halide solutions of aluminium halides. The object of this work was two-fold. One aim was to attempt a repetition of the work of Zlámal, Kazda, Vesely and Ambroz^{1,2,3,4,5,6} who had studied the effect of ether on the conductivity of aluminium chloride, and had demonstrated an antibatic relationship between the conductivity of a solution containing AlCl_3 and ether and the molecular weight of a polymer initiated by it. (ZAV effect). The second aim was to increase the extent of ionisation of aluminium halide by adding an electron acceptor to complex the anion, in the way shown in scheme 4.1. If the anion could be complexed thus, the cation would be unaffected, but its concentration would be increased. We had hoped to increase the concentration of cations in Al halide solutions to facilitate the study of their interaction with olefins, because with sufficiently high concentrations of ions, u.v. and n.m.r. methods might have been used.



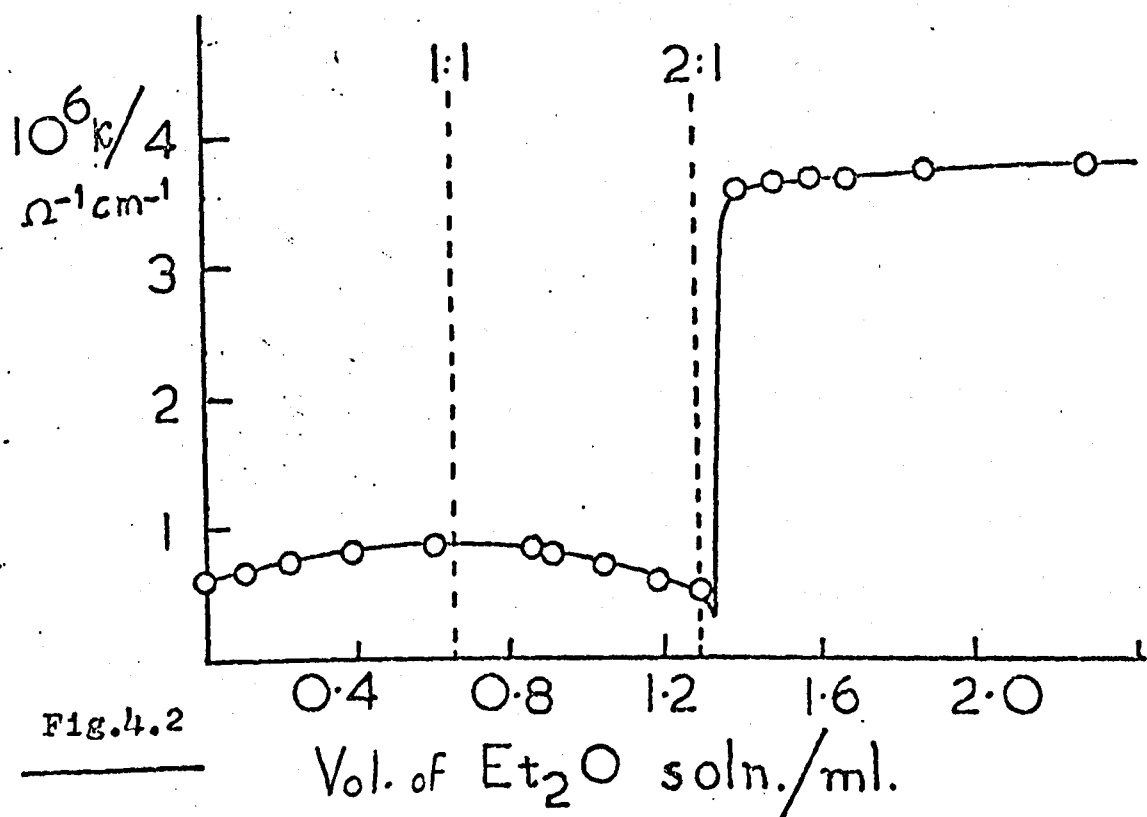
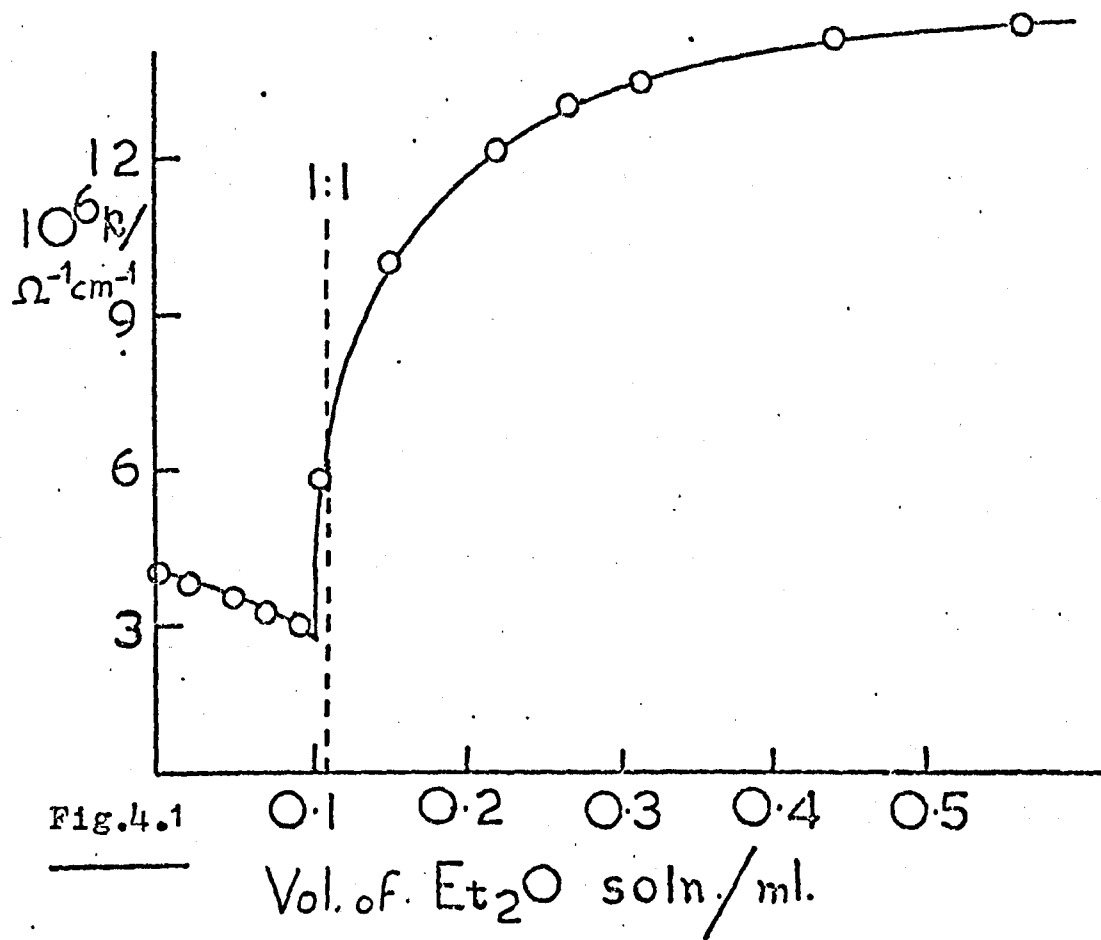
The latter object was not achieved for several reasons which will become evident later. However, simpler methods of increasing the $[\text{AlX}_2^+]$ were discovered as will be explained in § 5.

Figure 4.1

Expt. C31. The change of conductivity of a 1.07×10^{-3} M. solution of AlCl_3 in ethyl chloride when a 1.46 M solution of diethyl ether in methyl bromide was titrated in at -78° .

Figure 4.2

Expt. C29. The change of conductivity of a 1.66×10^{-2} M. solution of AlBr_3 in methyl bromide when a 1.46 M solution of diethyl ether in methyl bromide was titrated in at -78° .



4.1.1 The ZAV Effect. When diethyl ether (or any suitable n-electron donor, such as ethyl alcohol etc.) is titrated into an alkyl halide solution of aluminium halide, the conductivity rises steadily by ca. 5% to a maximum which occurs at a molar ratio of ether to aluminium chloride of ca. 0.5:1; as more electron donor is added, the conductivity drops, to nearly zero, until a molar ratio of 1:1 is achieved, after which a startling increase occurs which gives a steady value about ten times greater than the first maximum. Curves of this shape are shown in Figs. 4.1 and 4.2. The composition where the minimum in the conductivity occurs I have termed the transition point. This behaviour has been observed independently by two groups of workers for aluminium chloride in ethyl chloride,^{1,2,3,4,5,6} and for aluminium bromide in nitrobenzene,^{16,17,18} but no satisfactory theoretical explanation has been given.

The Czech workers^{1,2,3,4,5,6} were primarily concerned with the role of aluminium chloride as an initiator of cationic polymerisation. They studied the effect of varying the ratio of aluminium chloride to diethyl ether in solutions which were used to initiate the polymerisation of isobutylene. They discovered that the molecular weight depended inversely upon the number of ions in the initiator solution. Two explanations of this behaviour are conceivable. The first explanation, which has hitherto held sway,^{19, 23,24} is that the anions take part in chain-breaking reactions, and therefore as the concentration of ions increases, the concentration of chain-breaking agents grows larger and hence the molecular weight of the polymer decreases. The second is that the ions are responsible for the initiation, and hence, as the concentration of ions increases, the concentration of initiating species grows larger, and thus the molecular weight of the polymer falls.

Direct evidence which would favour either of these alternatives has not been available hitherto, but in § 5 evidence is presented that the AlX_2^+ species is responsible for initiation, and this favours strongly the first explanation.

Heublein and Römer²⁵ studied the copolymerisation of isobutyl vinyl ether and isobutylene initiated by aluminium bromide in toluene or hexane, in the presence of small amounts of electron donors such as dimethylsulphoxide and dimethylformamide. It was found that the nature of the additive and its concentration can change the copolymer composition and the molecular weight over a wide range.

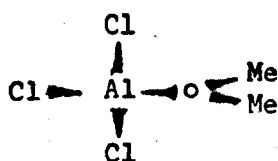
4.1.2. The reaction of ethers with aluminium halides. There have been many investigations of the n-donor complexes which exist between ethers and aluminium halides.²² A few of the more interesting properties of the complexes are mentioned below.

The ionisation of aluminium bromide in THF has been described in § 3, and the existence of the $AlBr_4^-$ anion has been demonstrated. It has also been found that aluminium is deposited at the cathode during the electrolysis of solutions of aluminium chloride in diethyl ether.²¹ Self ionisation of the complexes of ether and aluminium chloride to yield ions containing aluminium is thus clearly shown.

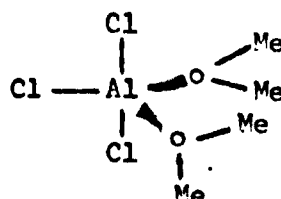
Halpern and Polaczek demonstrated that when the AlX_3 is complexed by ether, the halogen exchange with alkyl halides is retarded.^{9,10,11,12} (c.f. § 3.2.4). They called this the "exchange blocking" effect.

The existence of 1:1 and 1:2 complexes between aluminium chloride and ether was confirmed^{15,20} by means of the freezing-point phase diagram. Richards and Thompson¹⁵ estimated a strength of 18.6 k.cal.mole⁻¹ for the ether-aluminium chloride bond, and 23.2 k.cal.mole⁻¹ for the ether-aluminium bromide bond.

Jones and Wood¹⁴ isolated the 1:1 and 1:2 complexes of aluminium chloride and dimethyl ether as white, air-sensitive, crystalline solids, and investigated their i.r. spectra. They concluded that they have the structures shown below:



I



II

Haraguchi and Fujiwara⁸ showed by ²⁷Al n.m.r. that the 1:2 complexes with aluminium bromide and aluminium chloride are intermediate between tetrahedral and octahedral, which supports the trigonal bipyramidal structure II of Jones and Wood.

4.1.3 The interaction between electron acceptors and aluminium halides.
There is no report in the literature of any study of interaction between electron acceptors and aluminium halides. There are however, reports of the behaviour of nitromethane, to the effect that it forms an ionic(?) gel with aluminium bromide.^{7,13}

Although no direct studies of the influence of electron acceptors has been made, it has been discovered that they can increase the rate of cationic polymerisation considerably.²⁶

Table 4.1
Results of the Z. A. V. experiments

No	Aluminium Halide	Solvent	10^3 [AlX ₃]/M	Temp/C°	Whether Polymn. expt.	[AlCl ₃]/[Et ₂ O] Molar ratio at which trans. occurred.*	Vol. Initiator Soln./ml.	[IB]/M.	Vol. IB Soln./ml.	Cell Type.†
C28	AlBr ₃	MeBr	13.0	0°	x	No transition				(a)
C29	AlBr ₃	MeBr	17.3	-78°	x	2.05:1				(a)
C30	AlBr ₃	MeBr	61.0	-78°	✓	1.33:1	1	2.05	4	(c)
C31	AlCl ₃	EtCl	1.04	-78°	x	1.2:1				(c)
C32	AlCl ₃	EtCl	4.05	-78°	✓	ca. 1:1	2	3.32	2	(c)

IB = isobutylene

* = The transition point is the point during a titration when a large and very rapid increase of conductivity occurs. (c.f. Figs. 4.1 and 4.2).

† See § 2.2.1.1 and Figs 2.13, 2.14, 2.16.

4.2 Experiments with electron donors

4.2.1 Titration with diethyl ether. The expts. were carried out in a cell of type (a) (§ 2.2.1.1, Figs. 2.13, 2.14) and the ether was dosed as described in § 2.1.6.3. The results of titrating aluminium chloride, and aluminium bromide solutions with diethyl ether at -78° are shown in Figs. 4.1 and 4.2, and are summarised in Table 4.1.

A preliminary expt. was carried out at 0° in which a 1.37×10^{-2} M solution of aluminium bromide in methyl bromide was titrated with a 0.232 M methyl bromide solution of diethyl ether to a molar ratio of aluminium bromide to ethyl ether of 1:2. With each addition of ether the conductivity dropped sharply but took a long time to become constant.

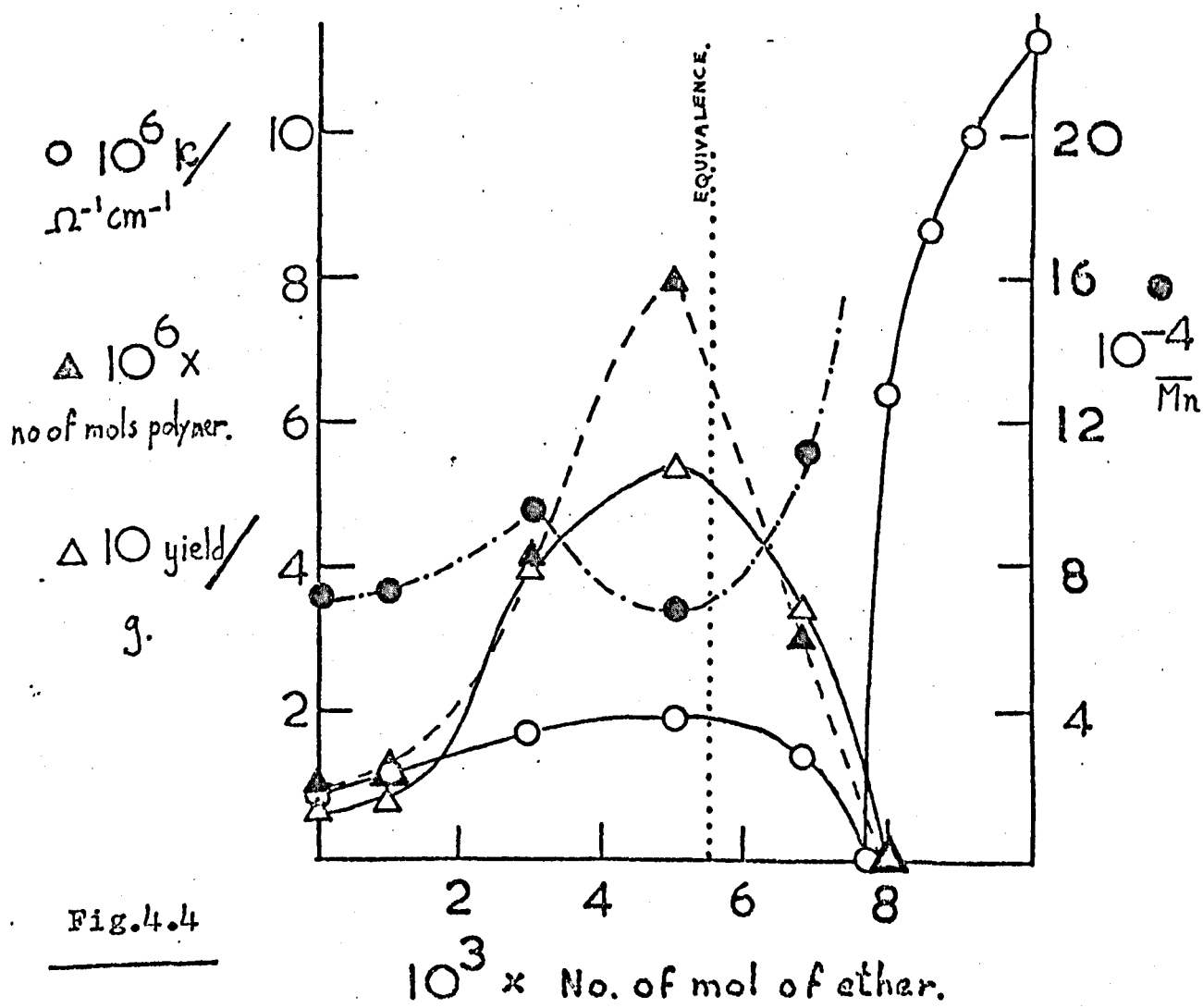
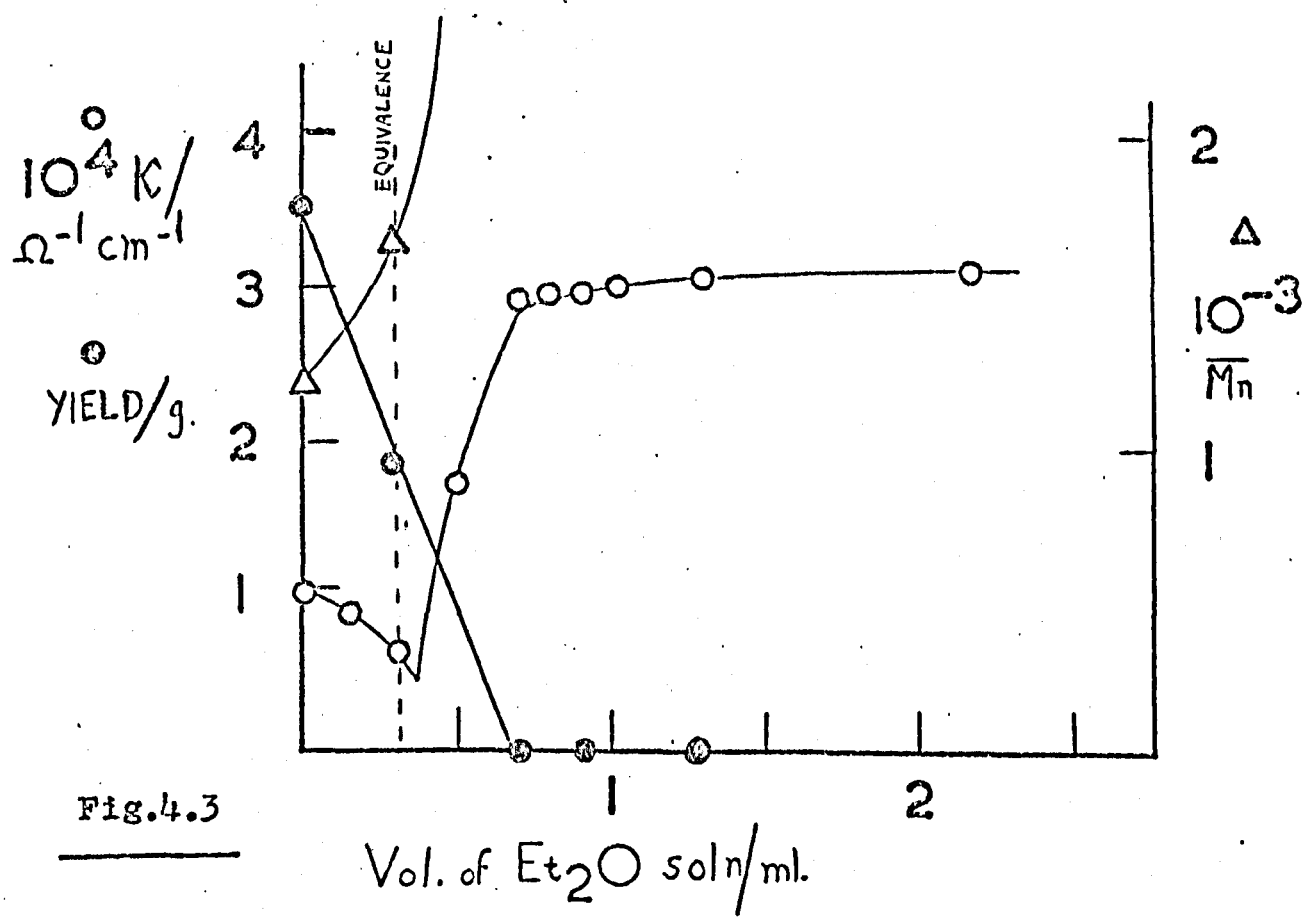
When 1.66×10^{-2} M. aluminium bromide in methyl bromide solution was titrated with a 1.47 M. solution of diethyl ether at -78° , (Fig. 4.2 and expt. C29 in Table 4.1), the re-equilibration of the conductivity was very much faster than at 0° . (The half-life was ca. 5 min.). The shape of the conductivity titration curve (Fig. 4.2) was very similar to that obtained by Zlámal et al.^{1,2,3,4,5,6} who used aluminium chloride in ethyl chloride solution, but, the transition point occurs at a molar ratio of $\text{Et}_2\text{O}:\text{AlBr}_3$ of 2:1 whereas in their expts. it was at a 1:1 ratio. In view of the obvious disagreement between my result and those of previous workers who found that the transition point always occurred at a molar ratio of 1:1 (c.f. § 4.1.1.) the concentrations were checked very carefully. The aluminium bromide concentration was calculated from the weight in the phial and was checked by halide titration of the aluminium bromide remaining after solvent had been removed, and the results agreed to within 1%. The solution of ether in MeBr used in this expt. was also

Figure 4.3

Expt. C32. The open circles show the change of conductivity of a 4.1×10^{-3} M solution of aluminium chloride in ethyl chloride when a 1.46 M. solution of diethyl ether was titrated in at -78° . The filled circular, and the triangular points show the yields and molecular weights of polyisobutylenes which were produced when 2 ml. samples of the initiation solution was added to 2 ml. of 0.33 M. isobutylene solution in methyl bromide at -78° .

Figure 4.4

Expt. C30. The result of an experiment similar to that shown in Fig. 4.3, in which a 6.1×10^{-2} M. aluminium bromide solution in methyl bromide was titrated with pure ether (9.6 M.) at -78° . 1 ml. samples of the aluminium halide solution at -78° were added to 4 ml. portions of a 2.05 M. isobutylene solution in methyl bromide.



used in later experiments with aluminium chloride, in which transition points at a ratio of 1:1 were observed, and therefore its concentration is not in any doubt. When an experiment was carried out later in which samples of solution were removed, (expt. C30 in Table 4.1 and Fig. 4.4, see § 4.2.2.) the transition point occurred at a ratio 1.33:1. However, this experiment was probably more affected by impurities than expt. C29, described above, because of the syringe method of sampling and the nitrogen atmosphere in the conductivity cell, and in addition, the shape of the conductivity titration curve was affected by the removal of some of the cell contents, (during the expt. the total amount of aluminium bromide was reduced by 10%). The effect of impurities e.g. water, would probably be either to act in a manner very similar to ether or the effect of this would be to reduce the molar ratio of ether to aluminium bromide at which the transition point occurred. This ratio of 1.33:1 in expt. C30, is therefore sufficiently large not to be in serious conflict with the observation of expt. C29, (Fig. 4.2) that the transition point does not occur at 1:1 for a pure solution of aluminium bromide in methyl bromide, but at $[\text{Et}_2\text{O}]:[\text{AlBr}_3] = 2:1$.

When 1.07×10^{-3} M aluminium chloride in ethyl chloride solution was titrated with a 1.47 M solution of diethyl ether in methyl bromide at -78° , (Fig. 4.1 and No. C31 in Table 4.1), the shape of the conductivity titration curve was very similar to those obtained by Kraus, Jacober, Van Dyke and Crawford^{16, 17, 18} for the titration of aluminium bromide in nitrobenzene solution with diethyl ether at 25° . In the latter expts. the transition point occurred at $[\text{AlBr}_3]:[\text{Et}_2\text{O}] = 1:1$.

4.2.2 The initiation of the polymerisation of isobutylene with the aluminium halide + diethyl ether + alkyl halide system.

The method of polymerisation and the apparatus have been described in § 2.2.1.1. Each experiment was carried out by titrating ether into an aluminium halide solution in a cell of type (c), (§ 2.2.1.1., Fig. 2.16) at -78° , to give increasing ratios of $[\text{Et}_2\text{O}]/[\text{AlX}_3]$; samples of the solutions thus obtained were removed with a syringe and added directly to ampoules which contained isobutylene in methyl bromide solution at -78° . If polymer formed, it was removed from the solution by evaporation of the solvent and the yield and molecular weight were measured.

In Table 4.1 and Fig. 4.3 are shown the results of expt. C32 in which aluminium chloride was used as the initiator. The conductivity behaved in a manner which was very similar to expt. C31 (Table 4.1 and Fig. 4.3). The first interesting thing about these results is the behaviour of the yield, which dropped steadily as ether was added, until at, and after the transition point there was no polymerisation. Where polymerisation did occur, it can be seen from the two points obtained, that the molecular weight increased as the conductivity decreased.

Expt. C30 (Table 4.1 and Fig. 4.4) was a similar, but more detailed experiment with aluminium bromide. As was mentioned before, the conductivity titration curve bears a resemblance to that shown in Fig. 4.2 (C29 in Table 4.1), and the transition point occurred well beyond a molar ratio of 1:1. In agreement with expt. C32, the yield and the total number of polymer molecules produced, varied in a manner

Figure 4.5

The dependence of the conductivity on concentration at -78° of various mixtures of aluminium chloride and diethyl ether. (Expts. C31, C32). The open circles represent the conductivity with no added ether, the filled circles show the conductivities at the transition point (min. κ), and the triangular points represent the conductivities at the final maximum conductivity in the presence of excess of ether.

Figure 4.6

Plots for the interpretation of the conductivity behaviour of an $A + B \xrightleftharpoons{K} R^{+} + Q^{-}$ equilibrium for the addition of ether, aluminium halide and ether complex. (see Appendix 1). The open circles are taken from the results shown in Fig. 4.2, the filled circles are taken from the results shown in Fig. 4.1.

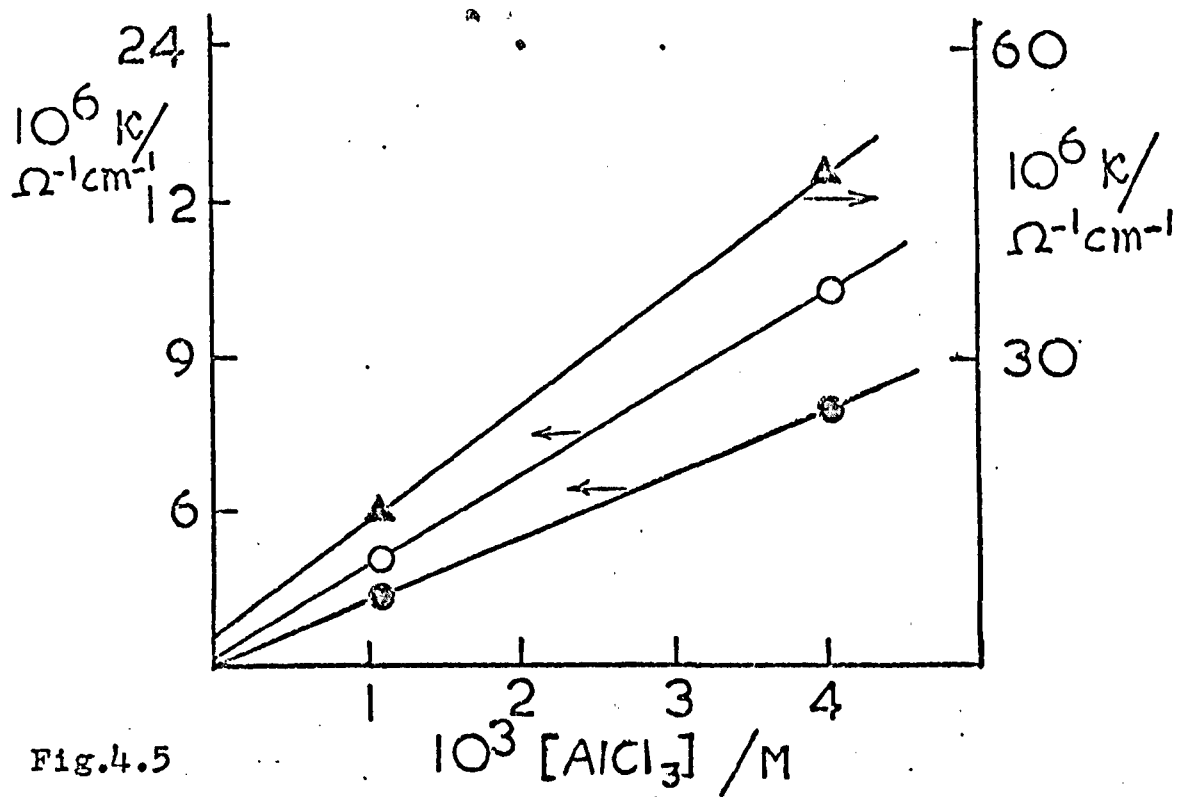


Fig.4.5

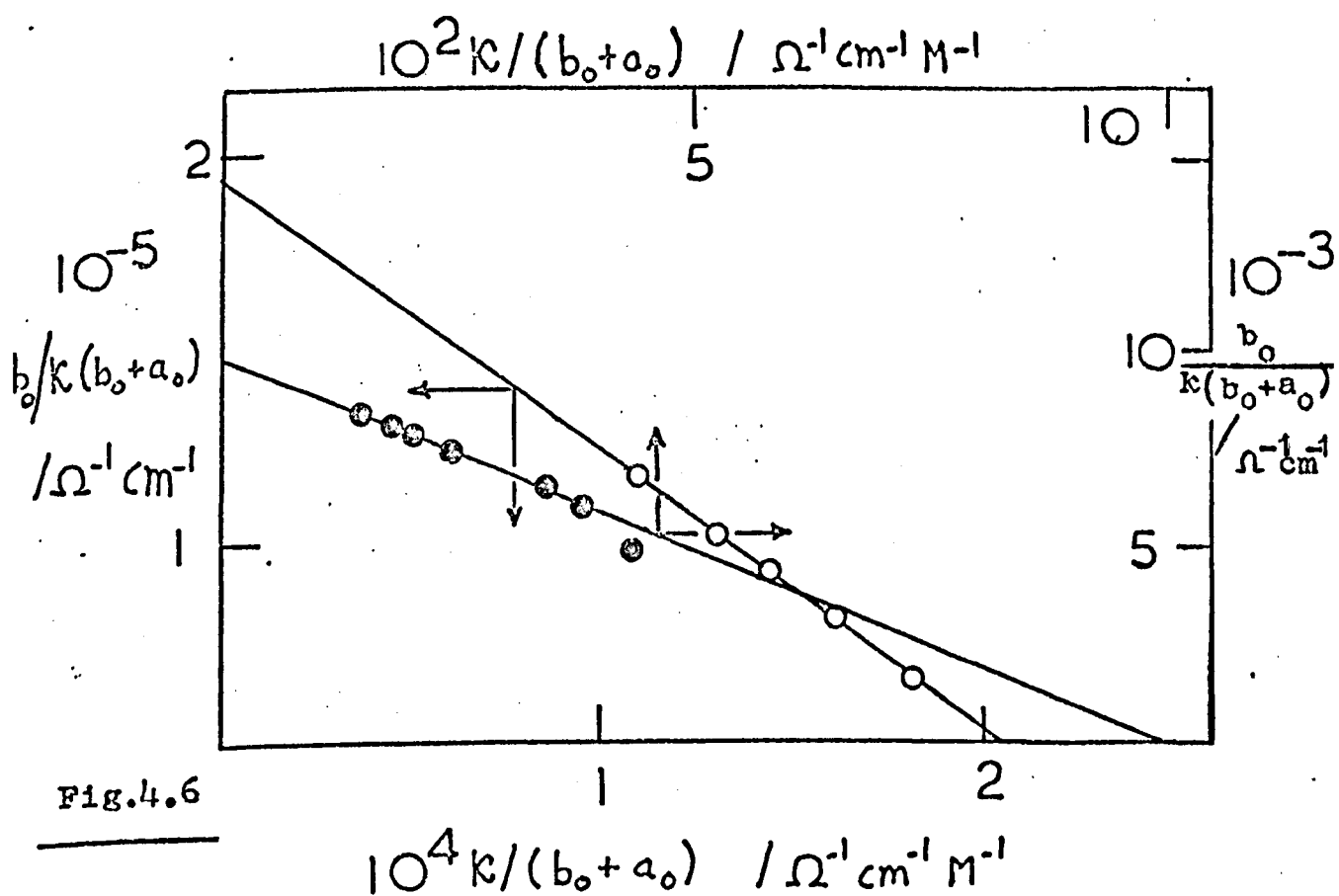


Fig.4.6

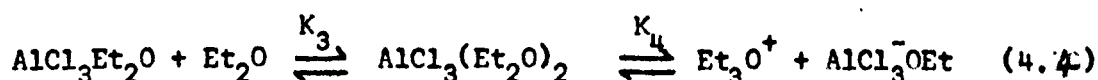
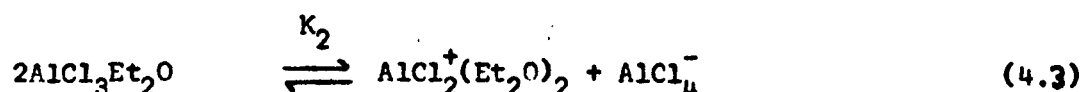
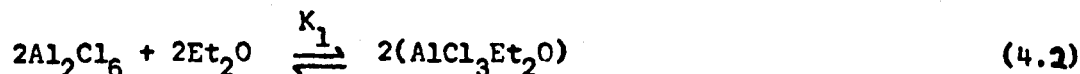
that followed the shape of the conductivity curve, exaggeratedly, up to the transition point, after which both fell to zero. The molecular weight varied antipathetically with the conductivity.

The two polymerisation experiments gave results which resembled one another closely, but differed in some respects from those of Vesely et.al.,^{1,2,3,4,5,6} chiefly in that we got no polymerisation after the transition point.

Ambroz and Kazda⁶ examined the relation of the conductivity to conc. for various complexes of aluminium chloride with diethyl ether in ethyl chloride solution. They found that the conductivity was directly proportional to the concentration. We were able to check this observation with the conductivity results for expts. C31 and C32. the conductivity at three points on each titration curve, namely the initial value, the value at the transition point and the maximum value, were each plotted against the aluminium chloride concn. The results are shown in Fig. 4.5, and they were found to be consistent with those of Ambroz and Kazda. This behaviour suggests that 2:2 equilibria, of the kind shown in reaction 3.9, are operative. (see Appendix 1).

4.2.3 Discussion. As was mentioned in the introduction, no convincing scheme has ever been advanced to account for the interestingly shaped conductivity titration curves. However, they can be explained in terms of a succession of equilibria as the ratio $[\text{Et}_2\text{O}]/[\text{AlX}_3]$ increases. My results show a clear distinction between the behaviour of aluminium chloride and that of aluminium bromide. A scheme has been devised to account for the behaviour of aluminium chloride, but a similar

explanation for aluminium bromide has not yet been developed and the reasons for this are explained below. The ideas involved are expressed by the following equations.



After the formation of the 1:1 complex has gone to completion (reaction 4.2), the addition of more ether establishes equilibrium 4.4. There are good reasons for believing that $K_1 > K_3$, $K_4 > K_2$, but $K_1 \gg K_2$. Reaction 4.3 is an $A + A \rightleftharpoons R^+ + Q^-$ equilibrium (see Appendix 1) because two molecules of the 1:1 complex are in equilibrium with two ions, but reaction 4.4 may be considered to be an $A + B \rightleftharpoons R^+ + Q^-$ equilibrium (see Appendix 1, section A3), because 1 molecule of the 1:1 complex plus one molecule of ether are in equilibrium with two ions. If equilibrium 4.4 is considered to be responsible for the dramatic rise in conductivity after the transition point, it should obey the equation given in Appendix 1, section A3. This equation can be re-written as follows,

$$\left[10^3(1-K_3^{-1}K_4^{-1})/\Lambda_T^2 \right] \kappa(a_o+b_o)^{-1} = 1/\Lambda_T - 10^{-3}a_o b_o (a_o+b_o)^{-1} \kappa^{-1}$$

where K_3 and K_4 are the equilibrium constants for reaction 4.4, a_o is the concentration of the 1:1 complex, b_o is the concentration of uncomplexed ether, and $\kappa = \kappa_{\text{total}} - \kappa_{\text{tp}}$ ($\text{tp} \equiv$ transition point). In the example under consideration the change of conductivity has been observed when b_o is increased, and a_o is held constant. A plot of

$\kappa(a_o + b_o)^{-1}$ against $b_o(a_o + b_o)^{-1} \kappa^{-1}$ should give a straight line of slope $-10^6 a_o^{-1} (1 - K_3^{-1} K_4^{-1}) / \Lambda_T^2$, and the intercept $= 10^3 a_o^{-1} \Lambda_T^{-1}$ when $\kappa(a_o + b_o)^{-1} = 0$.

The results of expt. C31 (Fig. 4.1, Table 4.1), when treated by the above method gave the plot shown in Fig. 4.6 (filled circles) and $\Lambda_T = 94 \text{ cm}^2 \Omega^{-1} \text{ mole}^{-1}$, $K_3 K_4 = 15$. These values are not unreasonable, and probably of the right order of magnitude.

Two assumptions have been made, one is that κ_{tp} , the conductivity arising from reaction 4.3, stays constant. This is not quite correct since the concentration of the 1:1 complex will be reduced as reaction 4.4 becomes more important. It has also been assumed that an $A + B \rightleftharpoons D \rightleftharpoons R^+ + Q^-$ equilibrium (c.f. reaction 4.4) can be treated like an $A + B \rightleftharpoons R^+ + Q^-$ equilibrium. This assumption is justified (see Appendix 1), providing the concentration of D does not become greater than ca. one tenth of A, B, R^+ or Q^- .

Different equilibria must be devised to account for the behaviour of aluminium bromide. If, however, the above treatment is applied to the results of C29, (Fig. 4.6, open circles), a straight line plot is obtained, which gives the plainly ridiculous value $\Lambda_T = 0.2 \text{ cm}^2 \Omega^{-1} \text{ mole}^{-1}$ and $K_3 K_4 = 28$. Before the behaviour of aluminium bromide can be interpreted in detail, it is necessary to determine the dependence of the conductivity on the concentration for each one of the $AlBr_3 + Et_2O$ complexes, in the way that Ambroz and Kazda⁶ did for aluminium chloride. By this means information would be obtained about the type of equilibria present, about which we can only speculate at the moment.

In the polymerisation experiments, all the results in the region before the transition point show the antibatic relation between conductivity and molecular weight observed by Vesely et al.^{1, 2, 3, 4, 5, 6} and in addition show a variation of yield that follows the conductivity, which the latter authors either omitted to mention or did not observe. The absence of polymerisation beyond the transition point in my experiments is in conflict with the observations of Vesely et al., who found that polymerisation continued. There could be several reasons for this. The solutions which they used to initiate the polymerisations were probably more affected by impurities than were my initiator solutions. The evidence for this is that the conductivities they record in their polymerisation papers,^{1, 2, 3, 4, 5} are higher than those which I found by a factor of 2 to 5, and as was shown in § 3, this is normally a clear indication of the presence of impurities.

The Czech workers used a technique in their polymerisation expts. which was quite different from the method that I used, and this perhaps may account for some of the differences in results. Whereas I withdrew samples of initiator directly from conductivity titration experiments, the Czech group prepared separate mixtures of aluminium chloride and diethyl ether, which were then syringed into monomer solution.

If these solutions were not used in a fresh condition they might have contained ions produced from slow reactions with impurities, and these ions could have been responsible for the initiation of polymerisation, beyond the transition point.

For all these reasons I have considered only the results of my expts. in the discussion which follows. I believe that the absence of polymerisation after the transition point is due either to the

formation of oxonium ions, as shown in reaction 4.4(ii), which cannot initiate the polymerisation of isobutylene, or to the presence of highly solvated $AlX_2^+(Et_2O)_n$ ions ($n>3$), which cannot react with isobutylene, since the latter, (a weak π donor) is unable to displace the powerful n-electron donating molecules of ether which surround the cation.

At this interesting, though inconclusive point, a more promising line displaced the pursuit of this topic.

4.3 The titration of aluminium bromide solutions with electron acceptors.

4.3.1 Results. The first experiments were carried out with chloranil at -23° . A solution of chloranil in methyl bromide was added slowly to a 1.6×10^{-2} M solution of aluminium bromide in methyl bromide, until the equivalence point was reached. No significant change in the conductivity occurred, but the solution became yellow, then blue/purple and finally intense bronze over ca. 2 h. When the cell was opened to the atmosphere, the colour vanished. Since there was little effect on the conductivity, the effect of the more powerful electron acceptor, tetranitromethane, (TNM), was investigated.

Two kinds of behaviour occurred when aluminium bromide solutions were titrated with TNM solutions.

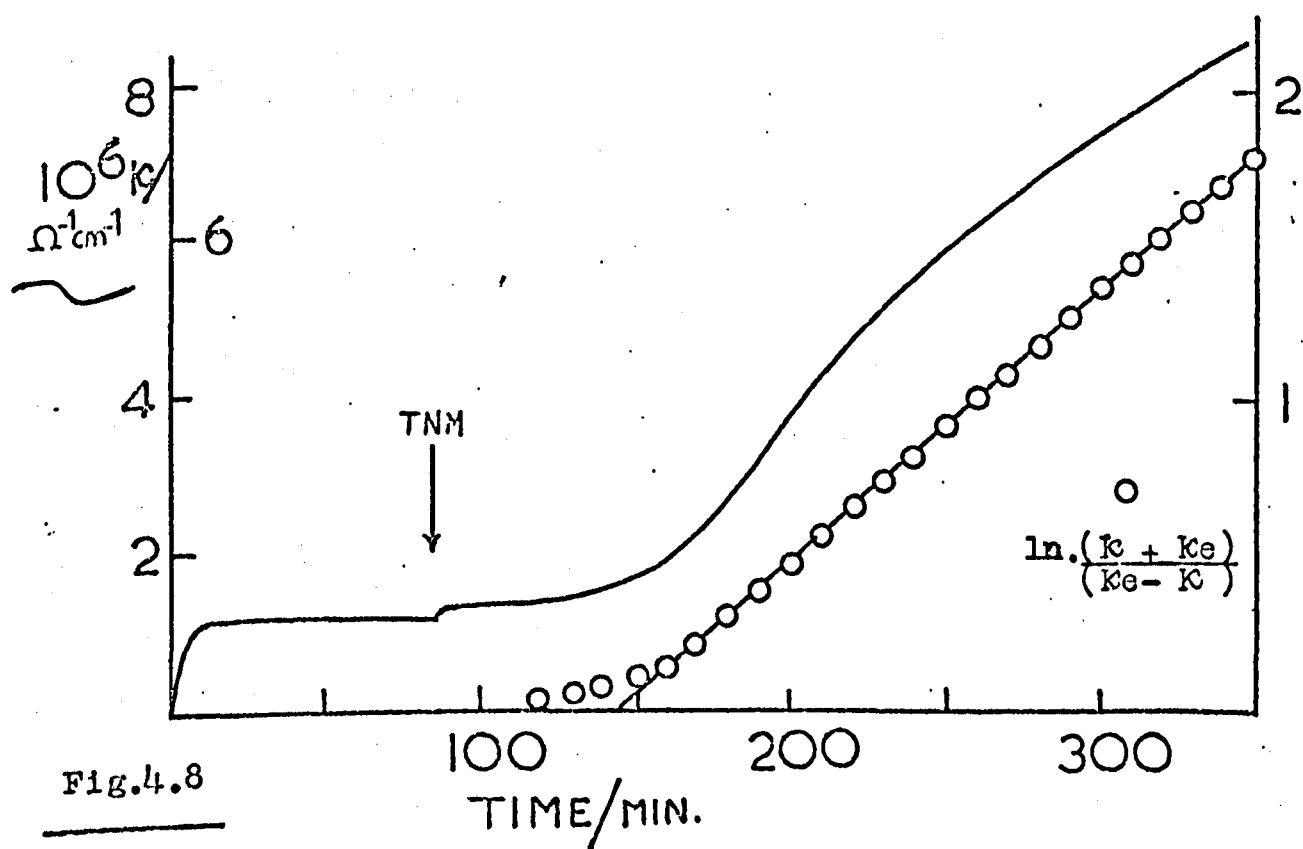
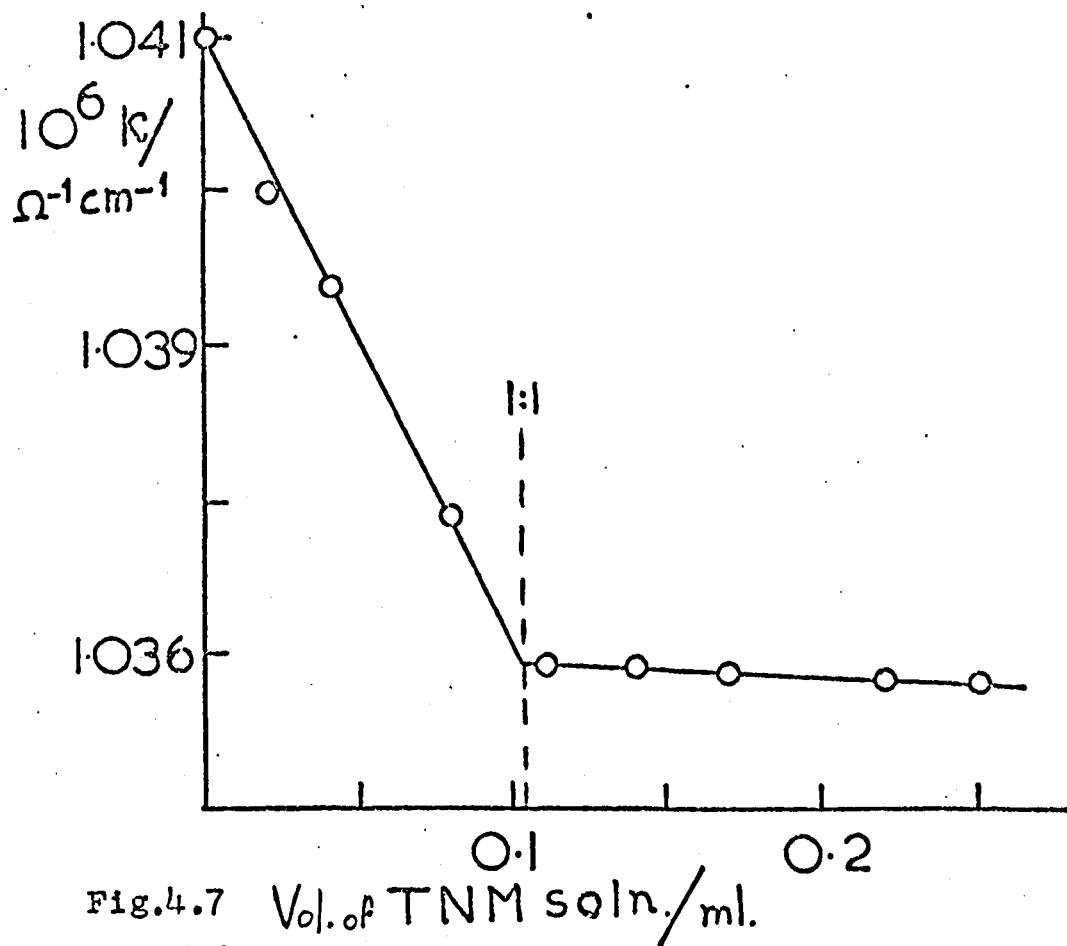
In Fig. 4.7, the effect is shown of adding 2.1 M tetranitromethane in methyl bromide to 4.6×10^{-2} M aluminium bromide at 0° . A simple conductivity titration curve was obtained, although the change in

Figure 4.7

The titration of a 4.6×10^{-2} M solution of aluminium bromide in methyl bromide at 0° with a 2.07 M solution of tetranitromethane solution in methyl bromide.

Figure 4.8

The kinetics of the re-equilibration of the conductivity of a 3.6×10^{-3} M. aluminium bromide solution in methyl bromide at 0° , when a tenfold excess of tetranitromethane was added.



conductivity was very small. This suggests that there is a strong interaction between aluminium bromide and TNM, to form a 1:1 complex. The small change in κ simply means that $\Sigma c_i \lambda_i$ changes only very slightly. The formation of bigger ions is probably compensated by the simultaneous formation of more ions.

Fig. 4.8 shows a later experiment in which a 10 fold excess of TNM (over aluminium bromide) was added to a 3.6×10^{-3} M. solution of aluminium bromide at 0° . This did not cause the conductivity to decrease, but made it increase slowly to give a conductivity vs. time curve which yielded to analysis by the kinetic interpretation developed in § 3 for the ionisation of an aluminium halide. The open circles in Fig. 4.8 are the plot of $\ln(\kappa + \kappa_e) - \ln(\kappa_e - \kappa)$ versus time. The "induction" period of the re-equilibration is due to the fact that the TNM was added as vapour and therefore went into solution fairly shlowly.

Further experiments in which very dilute solutions of TNM were added to AlBr_3 solutions with the object of complexing preferentially with the anions were not successful.

4.3.2. Discussion of the effect of electron acceptors. These few experiments show conclusively that electron acceptors do interact with at least one of the constituents of aluminium bromide solutions. The result of the experiment with chloranil, in which the absorption was shifted to longer wavelength, is a classical indication of complex formation, probably by the formation of a very weak π -donor bond.

The results with TNM indicate that there is a 1:1 interaction, and that the presence of a large amount completely alters the dissociation equilibrium of aluminium bromide. A curious parallel exists here between these results and those obtained with isobutylene, to be discussed in § 5; when isobutene is added very slowly to an aluminium bromide or aluminium chloride solution the conductivity decreases, but when it is added rapidly in excess, a big increase in conductivity occurs, coupled with polymerisation.

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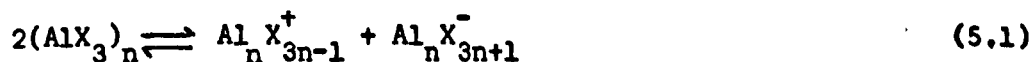
CHAPTER FIVE

THE INTERACTION OF OLEFINS AND ALUMINIUM HALIDES IN ALKYL HALIDE SOLUTIONS

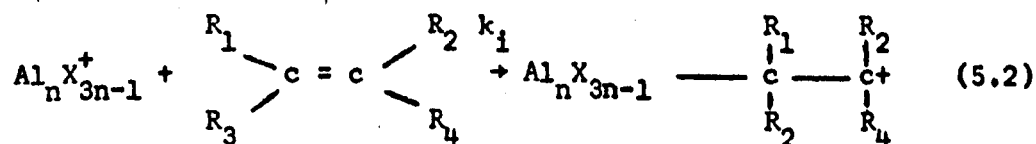
5.1 INTRODUCTION

The work described in this chapter was carried out mainly with the intention of finding some direct confirmation of the Self-Ionisation theory,^{7,8} of the initiation of cationic polymerisation. The latter theory was mentioned briefly in § 1, and the essentials of it are contained in the following three statements.

1. Aluminium halides dissolve in alkyl halides and ionise slowly, in the way shown in reaction 5.1:

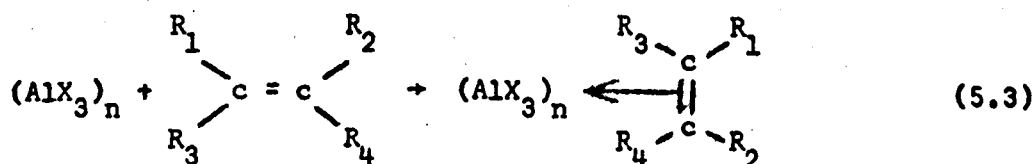


2. The $\text{Al}_n^+ \text{X}_{3n-1}^-$ cation reacts with an olefin to form a carbenium ion in the way shown in reaction 5.2:



The carbenium ion so formed can react with more olefin so that a polymerisation is initiated.

3. The un-ionised aluminium halide reacts with an olefin to form a π -donor complex, as shown in reaction 5.3:



The formation of this complex lowers the concentration of $(AlX_3)_n$, and thus interferes considerably with reaction 5.1, to the extent that under some circumstances the formation of ions may be almost stopped.

The importance of reactions (5.1) to (5.3) depends on circumstances. If the monomer solution into which the AlX_3 solution is introduced, or, indeed the catalyst solution itself, contains an appreciable concentration of ionogenic impurities, the dominant initiating mechanism will involve the ions generated from impurities rather than those formed by reaction (5.2).

The Self-Ionisation theory is therefore mainly relevant to highly pure, anaerobic, and anhydrous systems.

5.1.1. The evidence supporting statements (1), (2) and (3).

Statement (1). The evidence for the self-ionisation of aluminium halides in alkyl halide solutions was discussed at length in § 3, and no more need be said here.

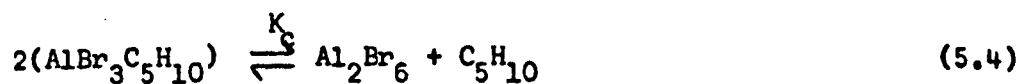
Statement (2). Hitherto there has been no direct evidence for this reaction, but there are phenomena which may be taken as indications of it.

It has been shown in § 4, that the molecular weight of polyisobutylene initiated by mixtures of aluminium chloride (or aluminium bromide) and ether, depends on the ionic concentration in

the initiator solution. As was explained in § 4, this behaviour would be expected if ions are responsible for the initiation of polymerisation.

Statement (3). The formation of π -donor complexes between aluminium and olefins has been established for many years.

Electronic considerations of π -complex formation: Aluminium bromide has sp^3 hybridisation, and therefore it has a vacant orbital, which is filled by n -donor electrons from the bridge bromines in the dimer. When a π -complex is formed, the π -orbital of the olefin overlaps with the vacant sp^3 orbital of the aluminium. For aluminium chloride, it is not known whether π -complexes are formed. Although aluminium chloride normally has sp^3 hybridisation, it apparently adopts a co-ordination number of six in the crystalline state, which suggests that either the $4s$ orbitals or the T_{2g} orbitals can receive electrons. Fairbrother and Field³ in 1956 studied the interaction between aluminium bromide and pent-1-ene in the binary mixture, by measuring the vapour pressure. At low concentrations the aluminium bromide was found to be monomeric, whereas at high concentration it was dimeric. The presence of monomeric aluminium bromide was taken as an indication of 1:1 complex formation between the olefin and the aluminium bromide. From these observations Walker⁴ calculated $K_c = 3$ for reaction 5.4

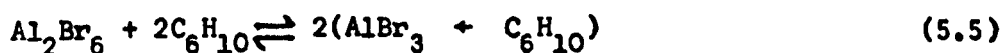


From this value of K_c , and the change in entropy calculated by the Sackur-Tetrode equation, Walker estimated the strength of the π -donor bond to be $17.4 \text{ k.cal.mole}^{-1}$.

When the π -donor bond is formed, the electron density in the double bond decreases, and this has two important effects: (i) The carbon-carbon bond distance in the double bond increases, and thus the wavelength of the double bond absorption in the i.r. increases, i.e. the wavelength decreases; for a strong platinum-ethylene complex the shift in the absorption is -140 cm^{-1} ; (ii) The electron density of the hydrogens in the 1 position with respect to the double bond will be decreased slightly, and this will result in a downfield shift of the n.m.r. absorption of these hydrogens.

Perkampus and Weiss¹ studied the interaction between aluminium bromide and olefins by i.r. spectroscopy and found that for most olefins the double bond absorption decreased by 50 cm^{-1} , which clearly indicates weak complex formation. Amongst the olefins examined were ethylene, various isomers of pentane, but-1-ene, hex-1-ene etc.

Perkampus and Orth² observed that when aluminium bromide was added to cyclohexane, the absorption of the 1 hydrogens shifted downfield. This observation lead Perkampus to postulate equilibrium 5.5. The formation constant of the complex was not estimated.



Matyska, Svestka and Mach⁵ studied the u.v. spectrum of aluminium bromide + isoprene in toluene, benzene and heptane solvents. They claimed that the absorptions at 440 nm. in aromatic solvents, and 360 nm. in aliphatic solvents were caused by the formation of a charge-transfer complex.

5.2. The Change of Conductivity during Polymerisation

5.2.1 Introduction. If reaction 5.2 in § 5.1 is valid, then it has some interesting consequences. Every time it occurs, an aluminium-carbon bond is formed, and a new pair of ions is produced. The change of conductivity during a polymerisation is therefore a measure of the change in the number of ions and therefore, under certain circumstances, of the change in the number of growing chains, and of the number of aluminium-carbon bonds.

The results which follow show the change in conductivity during polymerisation in several different systems. In this work the increase of conductivity during a polymerisation was attributed to the formation of pairs of propagating carbenium ions and $\text{Al}_n \text{X}_{3n+1}^-$ anions.

It is possible that other ions were produced by side reactions, but since no direct evidence of this was found, this possibility has not been considered.

In addition to the problem of relating the observed conductivity to the type of ions which are present, there are also theoretical and experimental difficulties which make the calculation of the ionic concentration from the conductivity rather uncertain. These difficulties are explained below.

The conductivity κ of a pair of ions, is related to their concentration, i , by the following equation,

$$10^3 \kappa = i \Lambda_{\pm}$$

Λ_T is the true equivalent conductivity which is made up of the individual ionic conductivities.

$$\Lambda_T = \lambda_{T+} + \lambda_{T-}$$

If λ_{T+} is that of a polymeric carbenium ion, then $r_+ \gg r_-$, and thus it follows from the Stokes relation (§ 3.3.1.7) that $\lambda_{T+} \ll \lambda_{T-}$.

Λ_T was taken as equal to λ_{T-} of the $Al_n X_{3n+1}^-$ anion. (The values of Λ_T for various aluminium halides are given in Table 3.9, § 3. λ_{T-} can be obtained from these values by simply dividing them by two).

The viscosity of a solution in which polymerisation is occurring increases considerably as polymer is formed, provided that the polymer is soluble. Such an increase of viscosity would reduce Λ_T considerably.

A further experimental problem with the solutions studied was that in many experiments especially at low temp., a large part of the polymers came out of solution and this caused two detrimental effects. (i) Since the measured conductivity was due only to ions in solution, it underestimated the total concn. of ions by the number which were occluded in the precipitated polymer; (ii) When polymer was precipitated, it sometimes collected around the electrodes which increased the resistance of the measuring system and thus simulated a decrease in the conductivity of the solution.

In Table 5.1 an attempt has been made to show the varying degrees of solubility of polymers under various conditions of polymerisation. It is a very approximate guide, because the observations on which it was based were made visually. The combined effect of the experimental

Figure 5.1

The change in conductivity during the polymerisation of isobutylene by a solution of aluminium bromide in methyl bromide. In each expt. the isobutylene was added in several similar doses, as a 3.3 M. solution in methyl bromide. The polymerisations were finally stopped with a large excess of tritiated water.

Fig.No.	Expt. No.	Temp /°C	$10^2 [\text{AlBr}_3]$ /M	Vol. of AlBr_3 sol./ml.	$10^3 \times$ No. of moles of isobutylene added				
					I	II	III	IV	V
5.1	R1	0	3.6	56	2.39	2.05	2.21	3.1	2.65
5.1	R2	-23	2.0	56	2.39	2.39	2.39	2.39	4.78
5.1	R3	-63	4.8	56	3.32	3.32	3.32	3.32	3.32
5.2	C10	0	2.0	37	2.0	2.0	2.0	2.0	

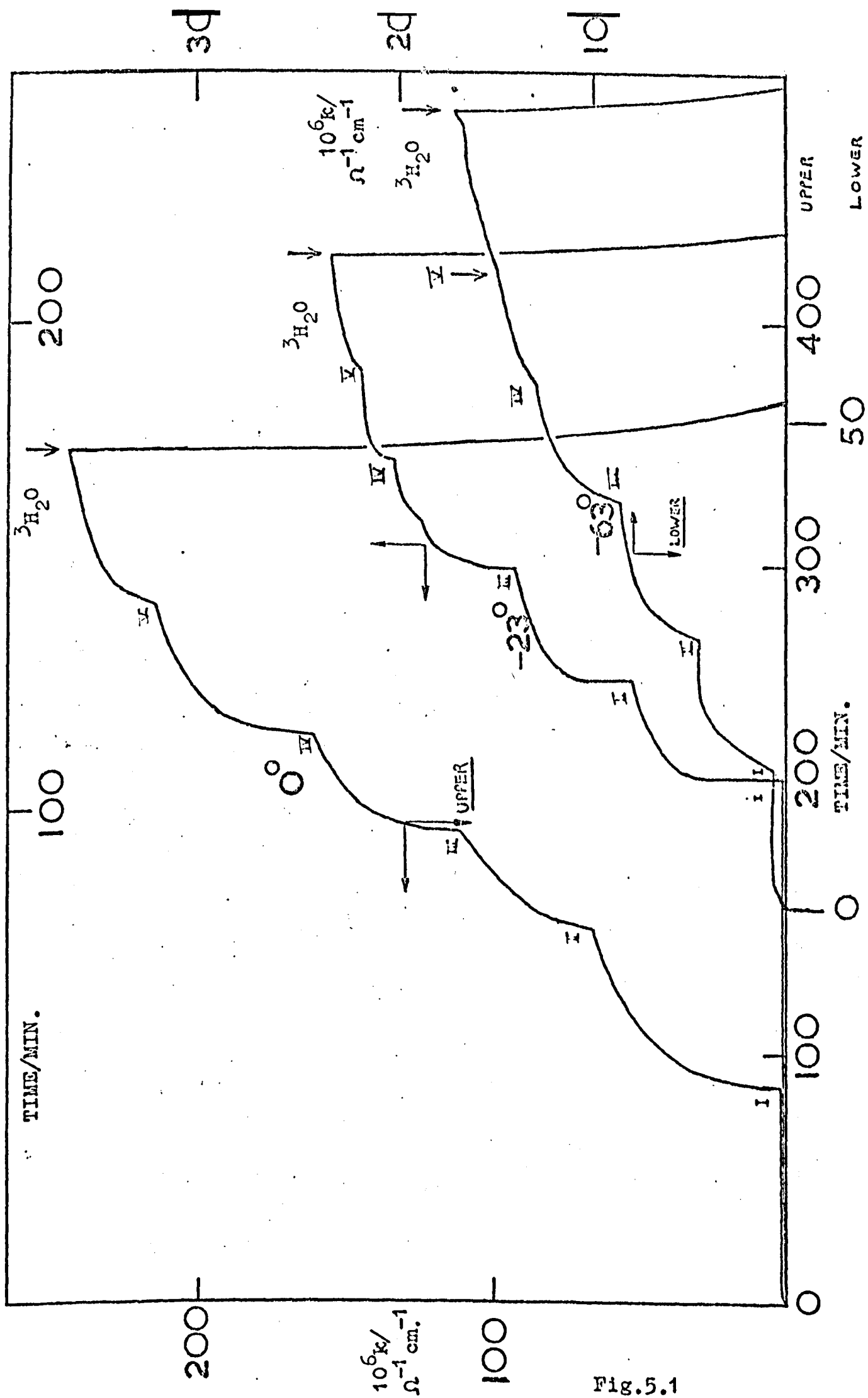


Fig.5.1

Table 5.1

The solubility of polymers during polymerisation

Expt. No.	Initiator	Solvent	Monomer	Temp. /°C	Monomer added in soln.	Monomer added in bulk	Polymer in solution				
							All	Most	Half	Some	None
R1. C10	AlBr ₃	MeBr	IB	0	✓		✓				
R2	AlBr ₃	MeBr	IB	-23	✓		✓				
R3 R8	AlBr ₃	MeBr	IB	-63	✓			✓			
R11	AlBr ₃	MeBr	IB	-78	✓			✓			
R15 C8	AlBr ₃	MeBr	IB	-78		✓				✓	
D4	AlCl ₃	EtCl/CH ₂ Cl ₂	IB	0	✓		✓				
R9 D3 D6	AlCl ₃	EtCl/CH ₂ Cl ₂	IB	-78	✓				✓		✓ R9
R12	AlBr ₃	MeBr	St	-63		✓				✓	
R14	AlBr ₃	MeBr	St	-78	✓				✓		
R4	AlBr ₃	MeBr	NBD	-63	✓					✓	
R10	AlBr ₃	MeBr	NBD	-125	✓						✓

difficulties is that the conductivity of a polymerising solution is of dubious significance and the ionic concentration calculated from it must be a minimum.

Despite the many problems associated with the interpretation of the conductivity of a polymerising system, the results obtained were surprisingly consistent. Not only were conductivities found to be reproducible, but we were able to analyse the kinetics of the ionisation during polymerisation, and to find the dependence of the conductivity on concentration for active polymer solutions. We also found that the conductivities of active polymer solutions were remarkably stable.

5.2.2 Results

5.2.2.1. The polymerisation of isobutylene with solutions of aluminium bromide in methyl bromide. The polymerisations were carried out in a cell of type (a), (§ 2.2.1.1., Figs. 2.13 and 2.14) at 0° , -23° , -63° and -78° . In each expt. ca. six similarly sized doses of a methyl bromide solution of isobutylene were added at ca. 15 min. intervals.

On each occasion when the monomer was added a large and rapid increase of conductivity was observed. This is illustrated in Fig. 5.1, for polymerisations at 0° , -23° and -63° . (The details of each expt. are shown in the legend to Fig. 5.1). Several general observations were made. (i) The conductivity during polymerisation was ca. 100 times greater than the conductivity of the initiator solution. (ii) The shapes of the conductivity-time curves of the polymerisations were similar at all temps. (iii) The total final conductivity after each addition of isobutylene was proportional to the total nominal isobutylene concentration. (see Fig. 5.3).

Figure 5.2

Expt. C10. For explanation and experimental details see legend to Fig. 5.1.

Figure 5.3

The conductivity^{*} of polymerising mixtures of isobutylene and AlBr_3 in methyl bromide plotted against the isobutylene concentration.

Expt. No.	R1	C10	R2	R3	R8	R11
$10^2 [\text{AlBr}_3] / \text{M.}$	3.5	2.0	2.0	4.8	1.3	0.6
Temp/ $^{\circ}\text{C}$	0	0	-23	-63	-63	-78

* The conductivity used is the estimated value at equilibrium for each addition of isobutylene, κ_x .

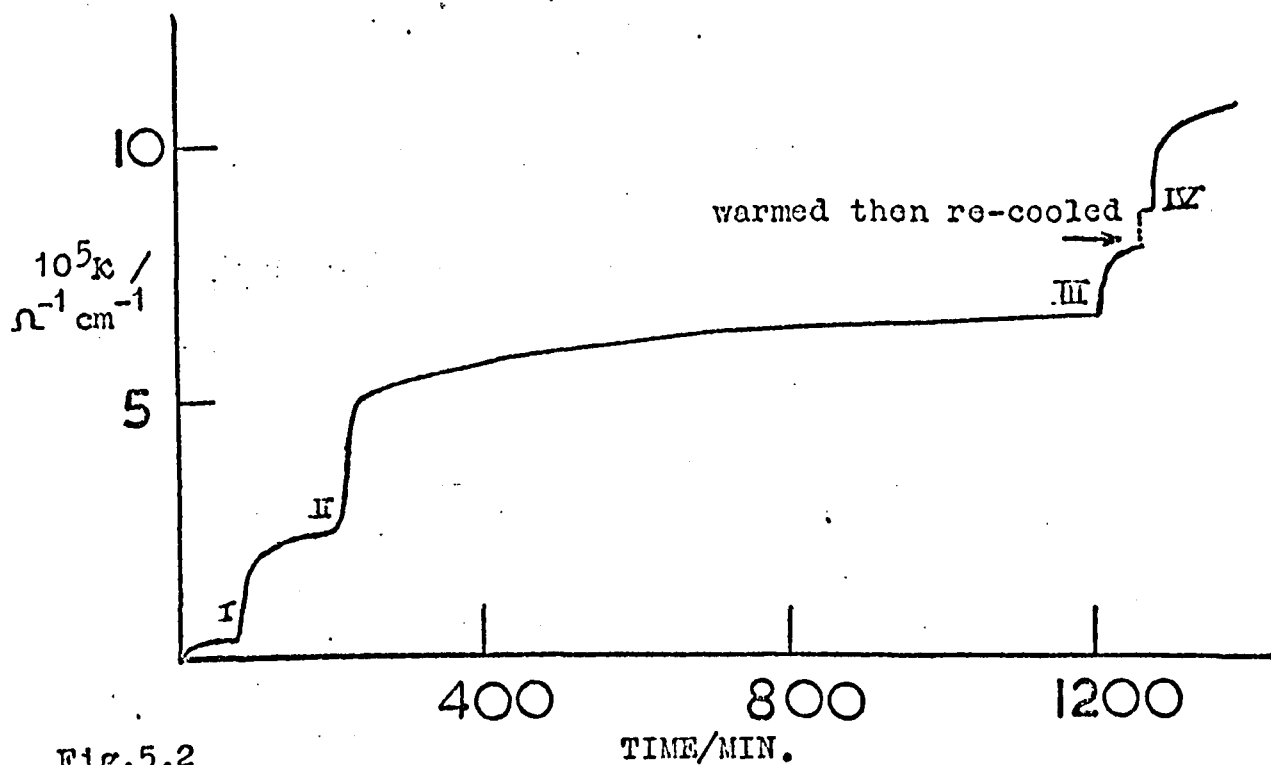


Fig. 5.2

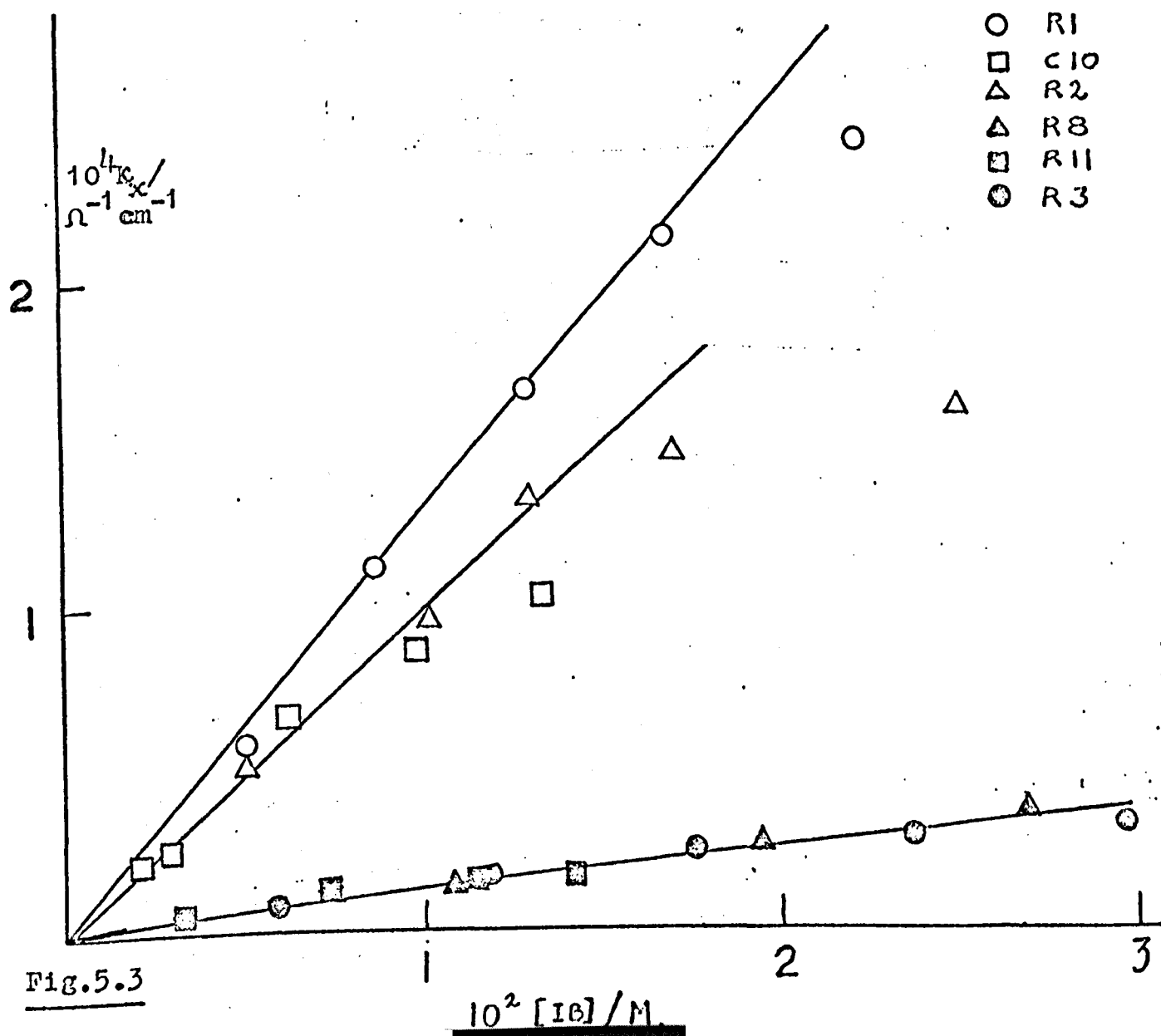


Fig. 5.3

A polymerisation was carried out at 0° , in which an interval of ca. 2 h. was allowed to elapse between the second and third isobutylene doses. (Fig. 5.2). This showed that the conductivity became completely stable within ca. 1 h. The effect of warming and re-cooling this solution was to bring the conductivity to equilibrium rapidly. (see Fig. 5.2).

In Fig. 5.3 the dependence of conductivity on the concentration of added isobutylene is shown for six experiments. This shows that the conductivity during polymerisation was repeatable from expt. to expt. The results obtained at -63° and -78° were very similar. The conductivities of the initiator solutions before addition of the isobutylene were so low, in comparison with those of the solutions containing growing polymer, that the plots in Fig. 5.3 appear to pass through the origin.

After four or five additions of monomer, the increment of conductivity for a given dose of added isobutylene, decreased. This could have been caused by the increasing viscosity of the solution, or the decreasing concentration of initiator or several other effects which cause a reduction of the observed conductivity such as those discussed in § 5.2.1.

5.2.2.2. The polymerisation of isobutylene with solutions of aluminium chloride in ethyl chloride. The polymerisations were carried out in the manner described in § 5.2.2.1., and expts. were made at -78° and 0° .

The concn. of aluminium chloride was ca. ten times lower than that of aluminium bromide in the polymerisations described in § 5.2.2.1.

At -78° much more of the polymer came out of solution during polymerisation than in the polymerisations by aluminium bromide.

The behaviour of the conductivity was in many respects similar to that described in § 5.2.2.1. (Compare Figs. 5.4 and 5.5 with Figs. 5.2 and 5.1). At -78° there was a big increase of conductivity for the first dose of isobutylene, but with further additions, the changes in conductivity became less pronounced, and the overall tendency was a decrease in conductivity. The latter effect could have been caused by any of the difficulties described in § 5.2.1.

The results are interpreted as being a further, though rather qualitative, illustration of the behaviour which was exhibited during the polymerisation with aluminium bromide. § 5.2.2.1.

Note: Several expts. were carried out at -63° and -78° with aluminium chloride and bromide as initiator, in which isobutylene was rapidly added in one large batch. As polymerisation occurred most of the polymer precipitated, and high molecular weight polymer ($\bar{M}_n \approx 250,000$) was obtained. The conductivity showed little change under these circumstances and on one occasion it actually decreased.

5.2.2.3. The polymerisation of Styrene, St and, Norbornadiene, NBD, with solutions of aluminium bromide in methyl bromide.

The polymerisations were carried out by the method described in § 5.2.2.1. St was dosed with the apparatus described in § 2.1.4.2., and also in methyl bromide solution. NBD was dosed in methyl bromide solution as described in § 2.1.4.4.

Figure 5.4

Expt. D4. The change of conductivity in 62 ml. of a 1.25×10^{-3} M. solution of aluminium chloride in methylene chloride at 0° , when 3.4×10^{-3} mole of isobutylene was added quickly. Oligomerisation occurred.

Figure 5.5

Expt. D6. The change in conductivity during the polymerisation of isobutylene by 53 ml. of a 1.0×10^{-3} M solution of aluminium chloride in ethyl chloride at -78° . The isobutylene was added as a 3.3 M. solution in methyl bromide, in six doses of 2×10^{-3} moles each.

Figure 5.6

Expt. R14. The change in conductivity during the polymerisation of styrene, by 70 ml. of a 3.6×10^{-2} M solution of aluminium bromide in methyl bromide at -78° . The styrene was added as a 5 M. solution in methyl bromide, in six doses of 1.7×10^{-3} moles each.

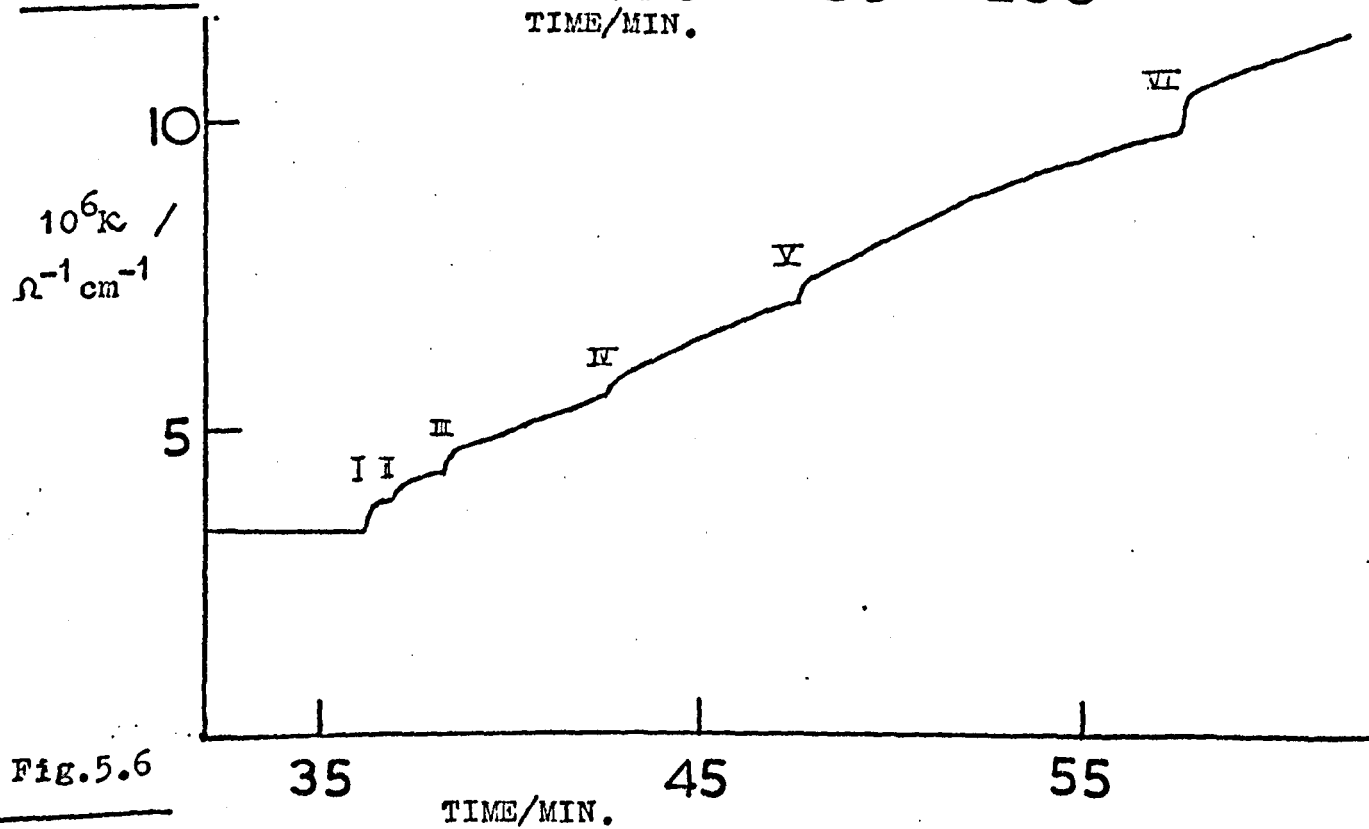
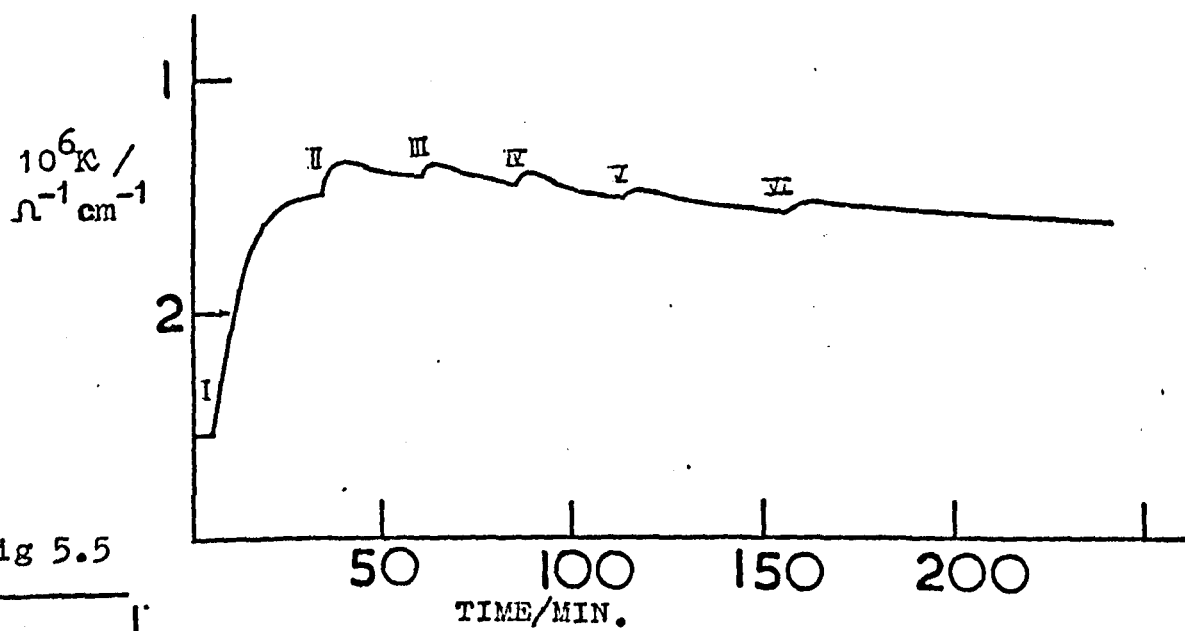
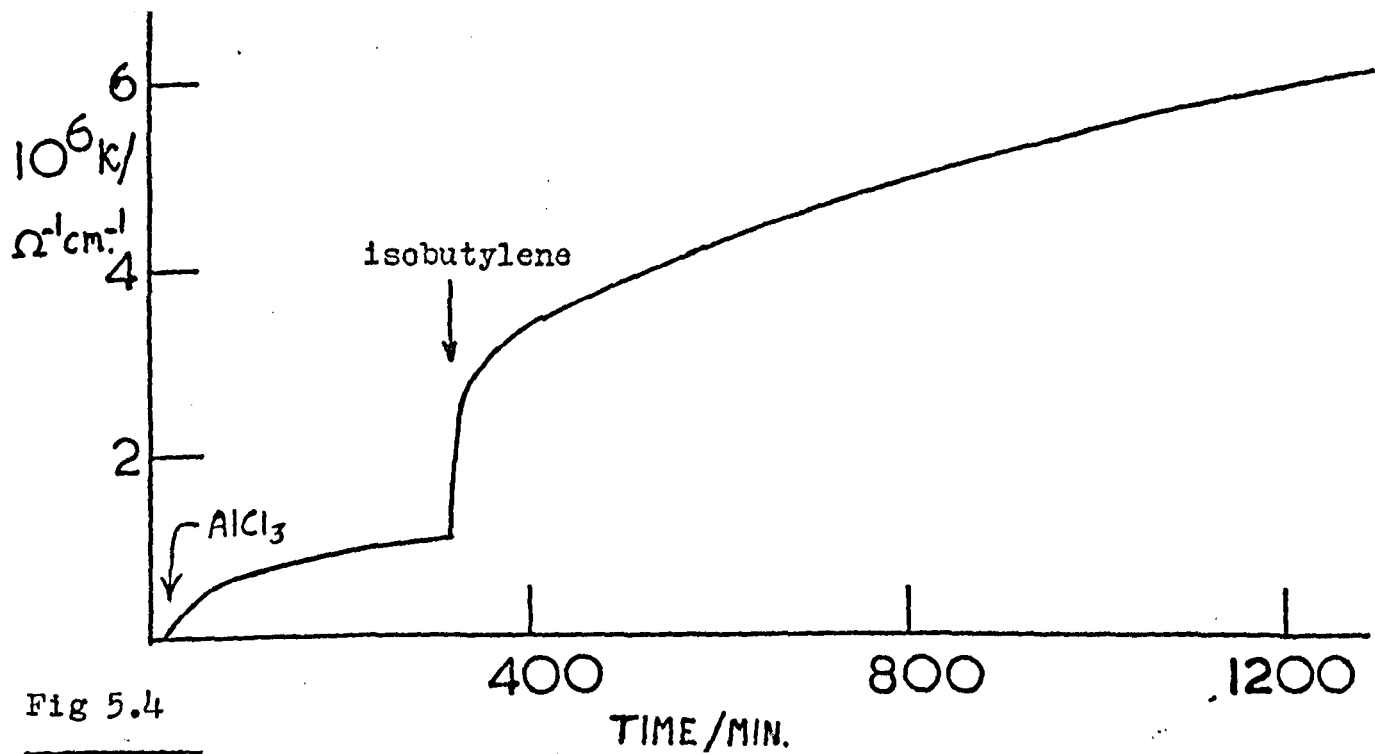


Figure 5.7

Expt. R4. The change of conductivity for the polymerisation of five doses of 5.5×10^{-3} mole each of norbornadiene with 56 ml. of a 1.8×10^{-2} M solution of aluminium bromide in methyl bromide at -63° . The NBD was added as a 2.5 M. solution in methyl bromide.

Figure 5.8

Expt. D4. The dependence of the conductivity on concentration and on temperature, for a solution of polyisobutylene in methylene dichloride. The polymerisation was carried out at 0° , with 3.4×10^{-3} mole of isobutylene and 62 ml. of 1.25×10^{-3} M aluminium chloride. The solution was not "killed" for several days after conductivity studies which followed the polymerisation. The conductivity was stable, and the solution remained colourless throughout.

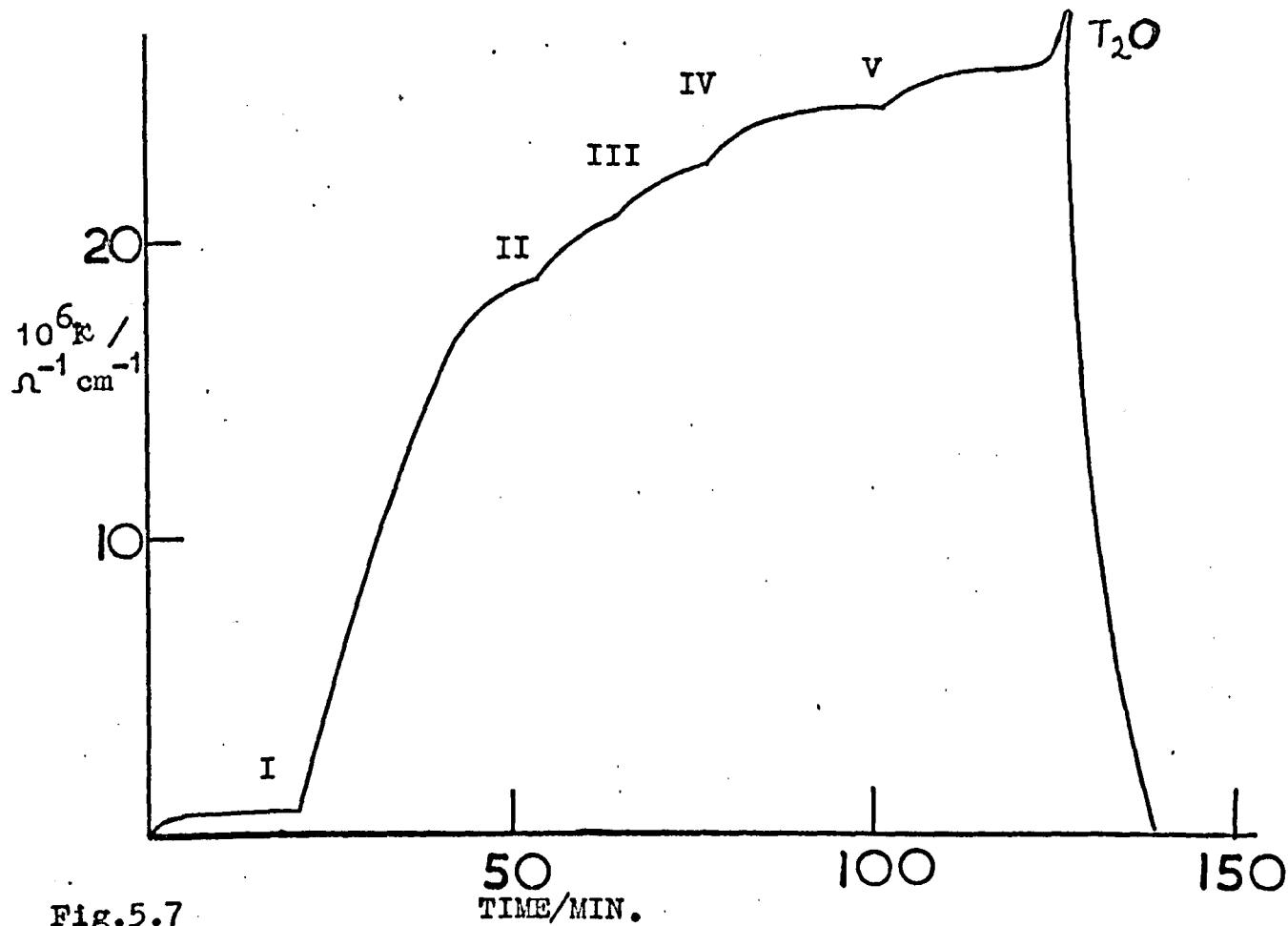


Fig. 5.7

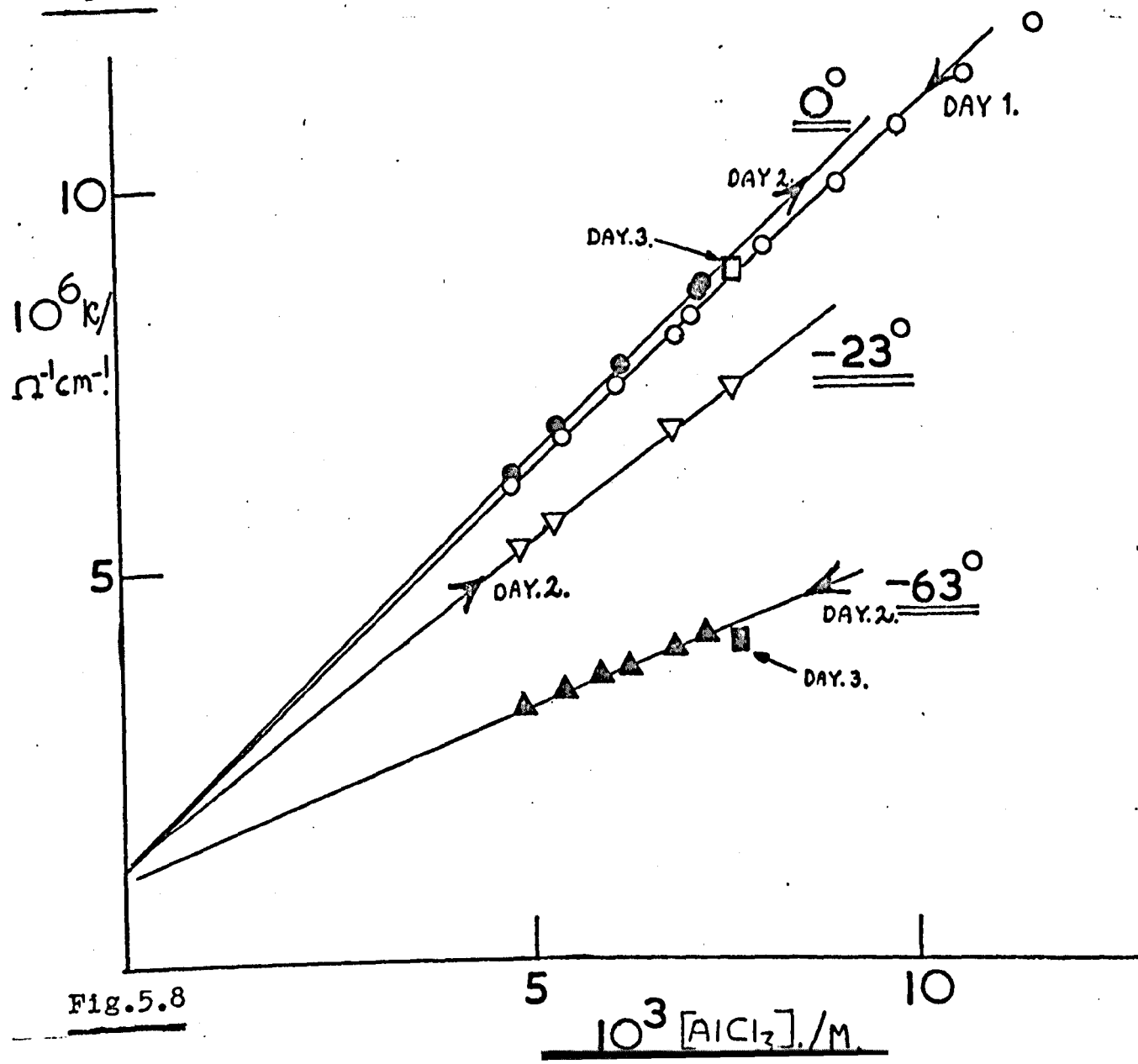


Fig. 5.8

Two polymerisations of St were performed, and the one at -78° in which the St was added in a methyl bromide solution gave the conductivity changes shown in Fig. 5.6; the other polymerisation, at -63° , in which St was added in bulk, showed only a very small increase of conductivity during polymerisation.

Fig. 5.7 illustrates the conductivity change during the polymerisation of NBD at -63° . Although a cross-linked polymer was obtained, enough remained in solution during the polymerisation for the conductivity increase to be seen. NBD was also polymerised at -125° , but though the polymer obtained was not cross-linked none remained in solution during polymerisation, and only small changes in conductivity were observed.

5.2.2.4. The dependence of the conductivity on the concentration of an active solution of polymer. An expt. was performed in which 3.4×10^{-3} moles of isobutylene was polymerised by 62 ml. of a 3.4×10^{-3} M. solution of aluminium chloride in methylene chloride at 0° . The conductivity of the solution increased from 2×10^{-6} to $12.5 \times 10^{-6} \Omega^{-1} \text{cm.}^{-1}$ on polymerisation; all the polymer remained in solution. The dependence of the conductivity of this solution on the concentration and the temp. was studied over the course of three days. The concentration of polymer was varied by distilling solvent into and out of the solution.

The plots shown in Fig. 5.8 are linear, with a small intercept κ_{in} on the conductivity axis. κ_{in} probably arose from the presence of impurities in the solvent. (c.f. § 3.3.1.3).

Figure 5.9

Expt. K5. The dependence of conductivity on concentration for an equimolar mixture of aluminium bromide and t-butyl bromide in methyl bromide solution at -78° .

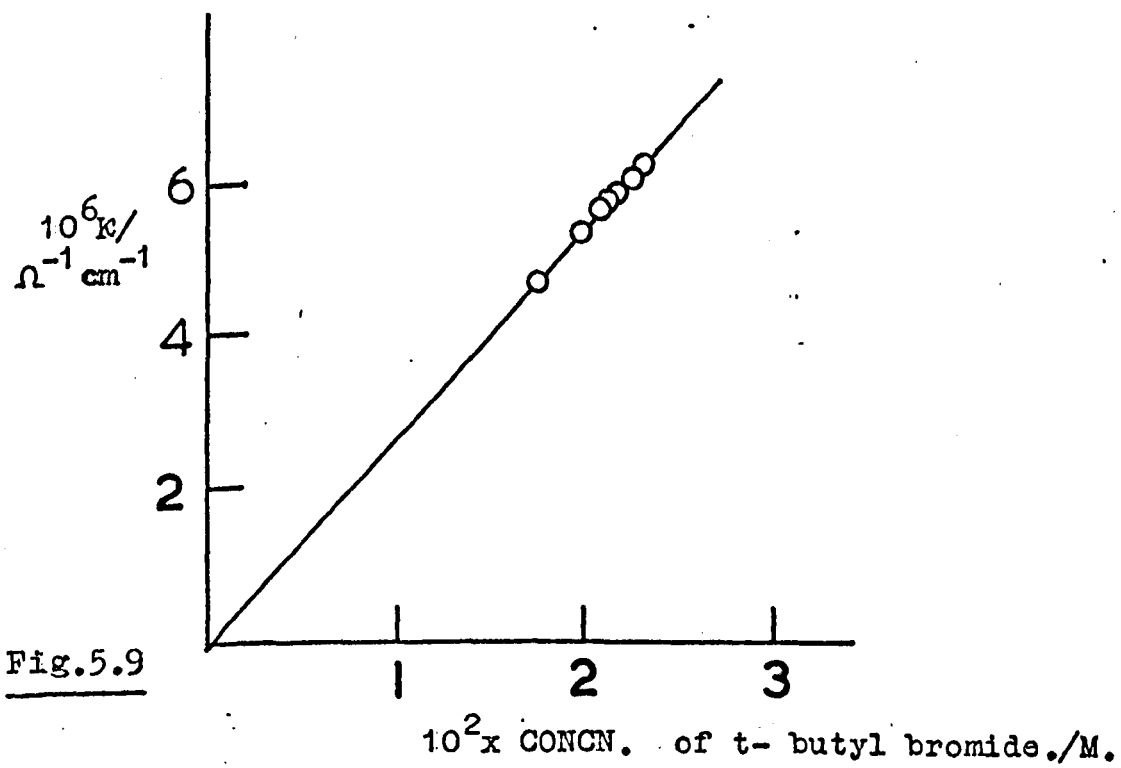
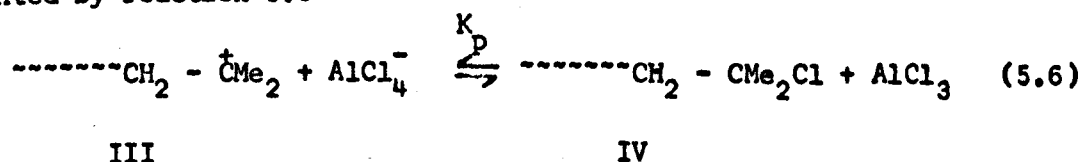


Fig.5.9

The arrows on the lines indicate whether the κ -c curves were obtained by concentration (distillation of solvent out) or dilution (distillation of solvent in). The dependence of conductivity on concentration and on temperature remained the same, within experimental error, for the three days of the experiment.

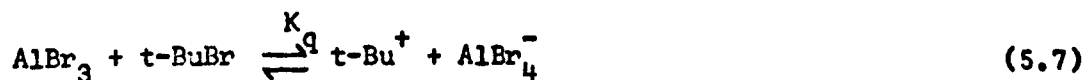
The stability of the ions is shown by the absolute reversibility of the system with respect to time, temp. and concentration.

The linear κ -c dependence indicates the presence of a 2:2 ionogenic equilibrium (see Appendix 1), which is probably best represented by reaction 5.6



By assuming that the total number of moles of polymer = 1×10^{-4} (D.P. = 17), the ionisation constant K_p was calculated as 3×10^{-3} at 0° and 9×10^{-3} at -63° .

To substantiate the existence of the equilibrium 5.6, an experiment was carried out in which t-butyl bromide was used as a model for species IV. This system should be a model for equilibrium 5.6, as is illustrated by reaction 5.7.



The κ -c dependence of an equimolar mixture of aluminium bromide and t-butyl bromide, was investigated at -78° and is shown in Fig. 5.9.

In this experiment a small portion of the κ -c curve was determined and then the mixture was hydrolysed and examined by g.l.c. - mass spectrometry. Only two major peaks in the g.l.c. were observed, and the mass-spectrum revealed them to be t-butanol and t-butyl bromide. The recovery of these two materials shows that the carbenium ions formed are stable; there appear to be no side reactions producing other species, such as oligomer or polymer, which normally happens in impure systems. The κ -c plot, although rather short, is clearly linear and passes through the origin which indicates the existence of a 2:2 ionogenic equilibrium. The value of K_q calculated from these results is 2×10^{-4} at -78° . The fact that this is about a power of ten smaller than that for equilibrium 5.6 cannot be given much significance until both constants have been confirmed by further measurements. (The value of λ_T was taken as that of λ_T^- of $AlBr_4^-$ in Table 3.9, see § 5.2.1).

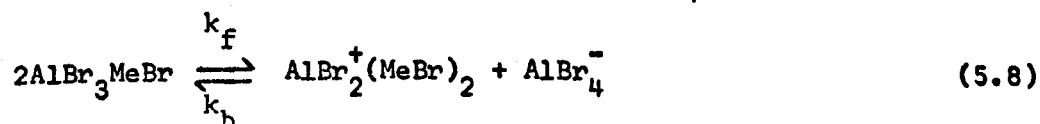
It should be noted that the observation of equilibrium 5.6 provides factual support for Plesch's surmise that it exists and is important.¹⁰ Further our results provide the first instance, as far as we know, of the preparation of a stable solution of t-alkyl ions in a normal solvent, rather than in a super-acid.

5.2.2.5. The analysis of the kinetics during polymerisation. Only the system isobutylene + methyl bromide + aluminium bromide gave reasonable and reproducible κ -t curves, and therefore this system only has been considered.

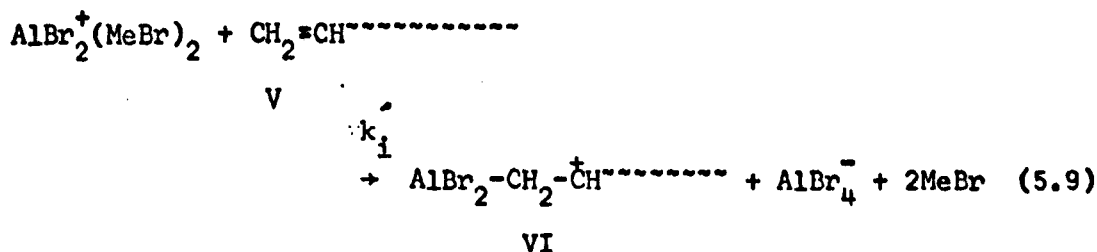
Normally the polymerisation appeared to be complete within a few seconds, but the conductivity rose slowly over a period of ca. 30 min. Thus the change in conductivity is clearly not associated with the polymerisation reaction, and therefore must result from a slow reaction of the polymer and the initiator. This is understandable because after the polymerisation has taken place, most of the polymer molecules contain a terminal double bond for the reasons explained below.

Consider the polymerisation of isobutylene; every polymer molecule is started either by initiation or by transfer. If by initiation, it is started by the reaction of monomer with $\text{AlBr}_2^+(\text{MeBr})_2$ or if it is started by transfer, it is started by a proton. The growth of every molecule is broken off either by termination or by transfer. If by termination, this could be by reaction with an impurity Y, giving a terminal $-\text{CMe}_2\text{Y}$ group.

If chain growth is stopped by transfer an unsaturated end-group is formed. If we neglect initiation and termination by impurities, it follows that almost every molecule has, at the moment when it stops growing, a terminal double bond. If a system contains at a certain instant n polymer molecules, and x propagating carbenium ions, (and therefore x Al-C bonds), then there are $n-x$ terminal double bonds present. There is no inherent reason why these double bonds should not be attacked by AlX_2^+ ions in a manner analogous to reaction 5.3 (evidence for this is presented in § 5.4.2). We therefore conclude that the slow change of conductivity is due to this aluminatation reaction 5.9, which creates the ions VI and AlBr_4^- :



Where $K = k_f/k_b$



The symbol k_i was chosen for the rate-constant of reaction 5.9 because it is of the same nature as the initiation reaction but it can be expected that for steric reasons k_i will be somewhat smaller than k_i , the rate-constant of reaction 5.2.

There are two ways of treating the kinetics of the formation of the new ions. One can assume that the self-ionisation is very slow so that the formation of $\text{AlBr}_2^+(\text{MeBr})_2$ is the rate controlling process, or one can assume that the formation of $\text{AlBr}_2^+(\text{MeBr})_2$ is relatively fast so that the ionogenic equilibrium is maintained, but drained by the relatively slow reaction of $\text{AlBr}_2^+(\text{MeBr})_2$ reaction with terminal double bonds.

Thus the formation of ions should be a simple second order process, if the formation of the dibromoaluminate cation is rate-controlling.

$$\frac{di}{dt} = k_f(a_o - 2i)^2, \quad (5.i)$$

where i is the concentration of ions.

On integration of (5.i), and substitution of $10^3 \kappa \Lambda_T^{-1}$ for i , (5.i) yields the integrated rate equation (5.ii):

$$\Lambda_T(2 \times 10^3 \kappa)^{-1} = a_o^{-1} + k_f^{-1} t^{-1} a_o^{-2} y^{-2} \quad (5.ii)$$

If the kinetics are obeyed, a plot of κ^{-1} against t^{-1} should be a straight line. This equation was tested for the increase of conductivity

for the first polymerisation of isobutylene in expt. R1, and the plot is shown in Fig. 5.10, open circles; it is clearly unsatisfactory; therefore the second approach was tried.

The rate equation for the "drained equilibrium" treatment is again of second order and is shown below.

$$\frac{di}{dt} = k_i [AlBr_2^+] [P_n^-] \quad (5.iii)$$

Where $AlBr_2^+ \equiv AlBr_2^+(MeBr)_2$, $[P_n^-]$ = conc. of terminal C=C groups.

From the charge balance,

$$[AlBr_4^-] = [P_n^+] + [AlBr_2^+] \quad (5.iv)$$

From the mass balance of aluminium bromide,

$$a_o = [AlBr_2^+] + [P_n^+] + [AlBr_4^-] + [AlBr_3] \quad (5.v)$$

Where a_o is the formal concentration of uncomplexed aluminium bromide.

From the mass balance of the polymer,

$$[P_n]_o = [P_n^-] + [P_n^+], \quad (5.vi)$$

where $[P_n]_o$ is the total concentration of terminal olefin groups.

The equilibrium constant for the self-ionisation is

$$K = [AlBr_2^+] [AlBr_4^-] [AlBr_3]^{-2} \quad (5.vii)$$

Substitution of (5.viii) and (5.vi) into (5.vii) gives,

$$\frac{di}{dt} = k_i K [AlBr_4^-]^{-1} [AlBr_3]^2 ([P_n]_o - [P_n^+]) \quad (5.viii)$$

But, in the initial stages of the ionisation, the ionic concentration is much less than that of the polymer, or of the aluminium bromide, and in addition, the concentration of the ions from the

Figure 5.10

Expt. R1. The treatment of the increase of conductivity during the polymerisation of isobutylene, by two rate equations. For details of expt. R1 see Fig. 5.1. The filled circles are from the "drained equilibrium" treatment, and the open circles are from the second order plot.

Figure 5.11

An example of the plot of the kinetics of the increase in κ for several polymerisations of isobutylene, in expt. R3. Other details of expt. R3 can be found in the legend to Fig. 5.1.

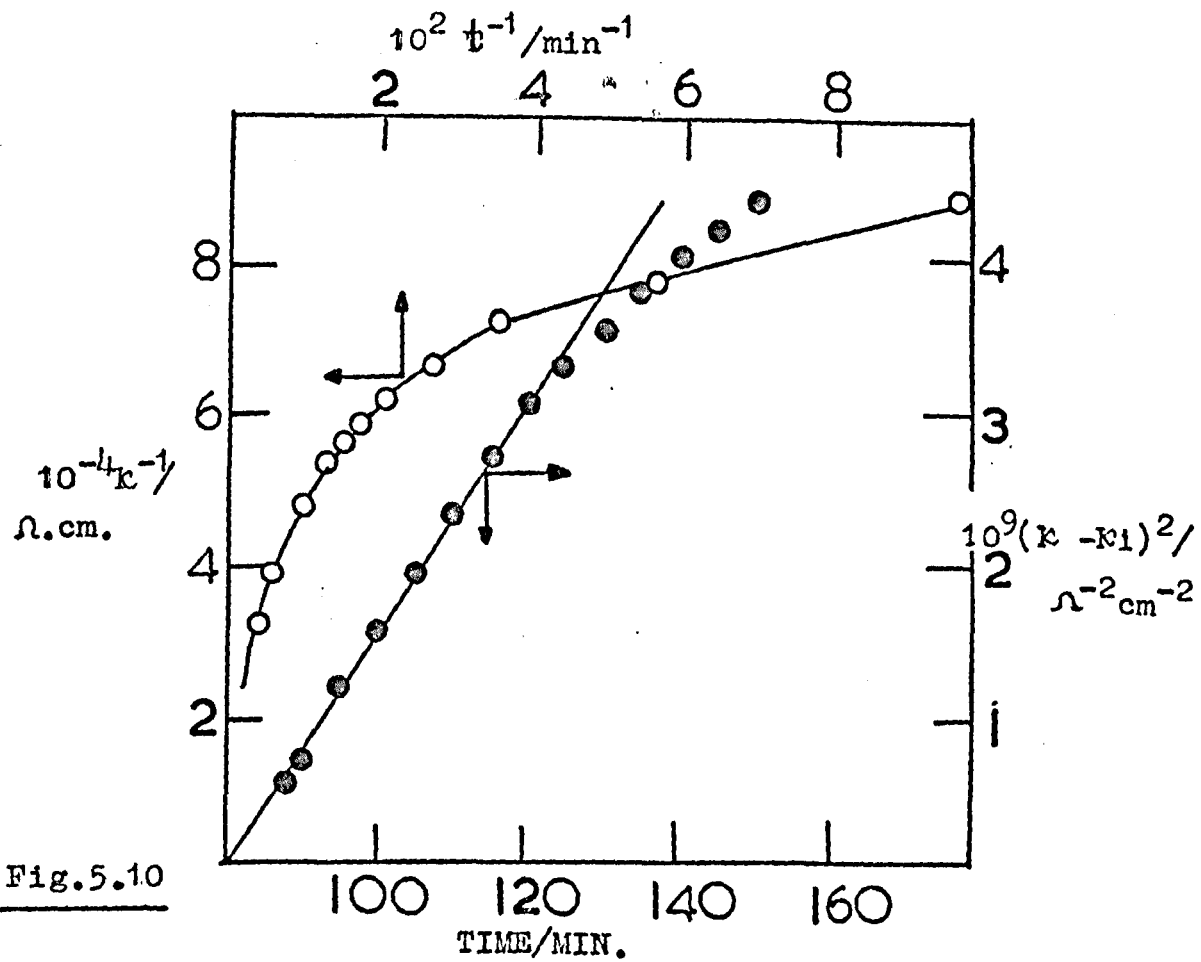


Fig.5.10

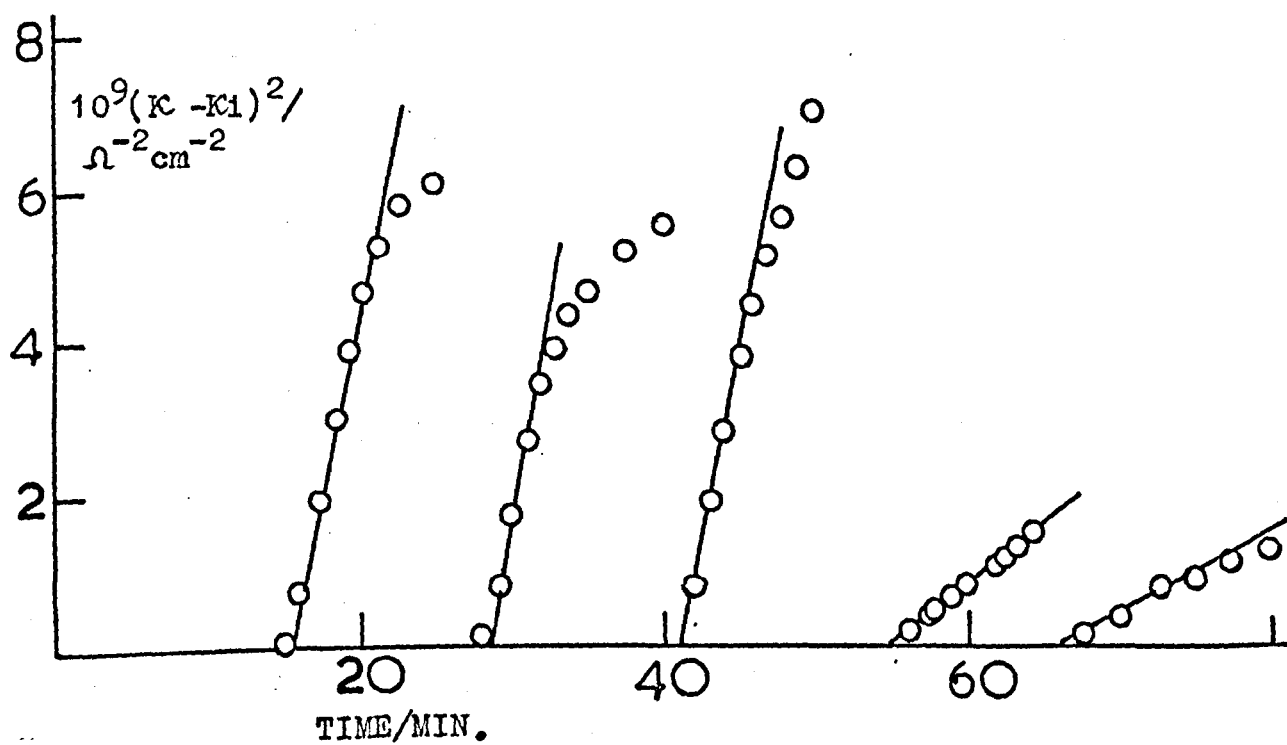


Fig.5.11

self-ionisation will be very much smaller than that of the ions from the reaction of aluminium bromide with olefin (reaction 5.8),



and $[AlBr_3] > [AlBr_4^-]$

$$i = [AlBr_4^-]$$

Therefore equation (5.viii) becomes

$$\frac{di}{dt} = k_i K i^{-1} a_o^2 [P_n]_0 \quad (5.ix)$$

On integration and substitution of $10^3 \kappa \Lambda_T^{-1}$ for i , one obtains the integrated rate equation (5.x):

$$10^6 \kappa^2 \Lambda_T^{-2} = 2k_i K a_o^2 [P_n]_0 t \quad (5.x)$$

A plot of κ^2 against t should give a straight line for the initial part of the ionisation.

When the results of expt. R3 were treated by this scheme, a linear plot was obtained for the first forty minutes of the ionisation following the addition of monomer. This is shown in Fig. 5.10. Considering the number of assumptions involved in obtaining this scheme, it seemed a remarkable result.

Since the kinetic scheme was apparently successful, it was applied to the results of expts. at 0° , -23° and -63° . The remarkable result was that on all occasions linear κ^2 - t plots were obtained. In each expt. the κ^2 - t plots for the first ca. 3 additions of isobutylene had almost the same slope, but the slope decreased by about a half for later polymerisations. An example of a series of plots is shown in Fig. 5.11.

Table 5.2

No.	Temp /°C	$10^2 [\text{AlBr}_3]$ /M.	10^8 Slope / $[\text{IB}]_0$ / $\Omega^{-2} \text{cm}^{-2} \text{sec}^{-1} \text{M}^{-1}$	10^8 Slope / $[\text{P}]_0$ / $\Omega^{-1} \text{cm}^{-2} \text{sec}^{-1} \text{M}^{-1}$	DP	10^8 K	Λ_T^{-1} / $\Omega^{-1} \text{cm}^{-2} \text{mole}^{-1}$	k'_i /1 mole sec ⁻¹
R3	-63	4.8	0.91±0.5	91±5	~100	11	20	9
R8	-63	1.3	1.3±4	585	450	11	20	790
R2	-23	2.0	11±2	230	~30	2.2	44	190
R1	0	3.7	16±3	160	~10	1.1	60	30
C10	0	2.0	~3.7	37	~10	1.1	60	23

The calculation of k'_i the rate constant of reaction (5.9) from the plots of κ^2 against t , for the polymerisation of isobutylene by aluminium bromide in methyl bromide solution. In each expt. several polymerisations were made, and each gave a value for k'_i . The value of k'_i shown is obtained from the average of the slope / $[\text{IB}]_0$ for the first three polymerisations in each expt. The scatter in k'_i is probably an indication of the uncertainty in it. The DP in expts. R2, R1 and C10 was not known very accurately. It was estimated roughly by comparing the height of the absorption of the double bond in the i.r. spectrum, with that of di-isobutene.

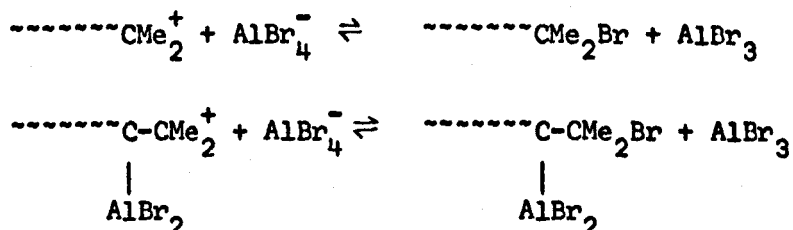
Estimation of k_1' . The slope of the plot of κ^2 against t was 5×10^{-7}
 $\frac{a_o^2 [P_n]_o K \Lambda_T^2 k_1'}{[P_n]_o}$. $[P_n]_o$ was estimated from the yield and the D.P. of
the polymer, Λ_T was taken as that for Λ_T for $AlBr_4^-$, a_o was the formal
concentration of aluminium bromide. The values of k_1' calculated in
this way are shown in Table 5.2. Notice that although expts. R3 and R8
had a very similar value of the ratio $\text{Slope}/[P]_o$, the values of k_1'
differed enormously because of the difference in aluminium bromide
concentration. The scatter in the values of k_1' , probably represents
the margin of error in their determination.

Considering the large number of parameters in the slope, an
error in any could seriously affect the value of k_1' obtained.

5.2.3 Discussion. Because of the difficulties which are
involved in analysing the conductivity it is probably better that
the results presented in this section be considered as qualitative
descriptions of behaviour. It is interesting to note that Svestka
et. al. have reported very similar changes of conductivity for the
polymerisation of isoprene by aluminium bromide in heptane and
toluene solution.⁵

The linear dependence of κ on $[IB]$ during a series of polymerisations
of isobutylene by aluminium bromide, may be taken as a further
indication of equilibrium 5.6. At a particular temp., it is reasonable
to assume that a given amount of monomer always gives rise to the same
number of moles of polymer, because the molecular weight is entirely
controlled by chain-transfer processes. The polymer produced will
consist of molecules containing either terminal carbenium ions, or
terminal double bonds which have been attacked by AlX_2^+ ions as

described in § 5.2.2.5., so that they also contain terminal carbenium ions. Therefore the following two equilibria may be envisaged.



Thus a certain amount of monomer always gives the same number of polymeric carbenium ions and polymer molecules. Since the two above equilibria both have two molecules producing two ions, the ratio of ions to molecules remains constant, (see Appendix 1), and therefore a fixed amount of monomer should give the specified conductivity.

5.3 The Preparation of non-polymerising solutions of aluminium halides and isobutylene at -63° and -78°

5.3.1 Introduction. The expts. described in this section originated from observations which were quite accidental. In each of the three expts. to be described we had hoped to obtain polymerisation, by adding isobutylene vapour very slowly to a solution of an aluminium halide, and the reason why we could not achieve it was not understood. Later on it became clear to us that the non-occurrence of polymerisation was probably due to the formation of the π -complex between the AlX_3 and the isobutylene, as will be explained below.

To the best of our knowledge, these expts. are the first in which polymerisation in the isobutylene + aluminium chloride/bromide + alkyl bromide/chloride systems has been totally absent.

Figure 5.12

The change of conductivity when isobutylene is added very slowly to solutions of aluminium bromide in methyl bromide at ca. -78° . No polymerisation occurred.

Expt. No.	$10^2 [\text{AlBr}_3]/\text{M.}$	Final $[\text{IB}]/\text{M.}$	Time of addition/min
C7	0.37	1.38	160
C9	1.0	5	105

Figure 5.13

The g.l.c. of the recovered solvent from expt. C7, (see Fig. 5.12) where no polymerisation occurred. This showed that isobutylene and diisobutylene and an unknown product, were recovered.

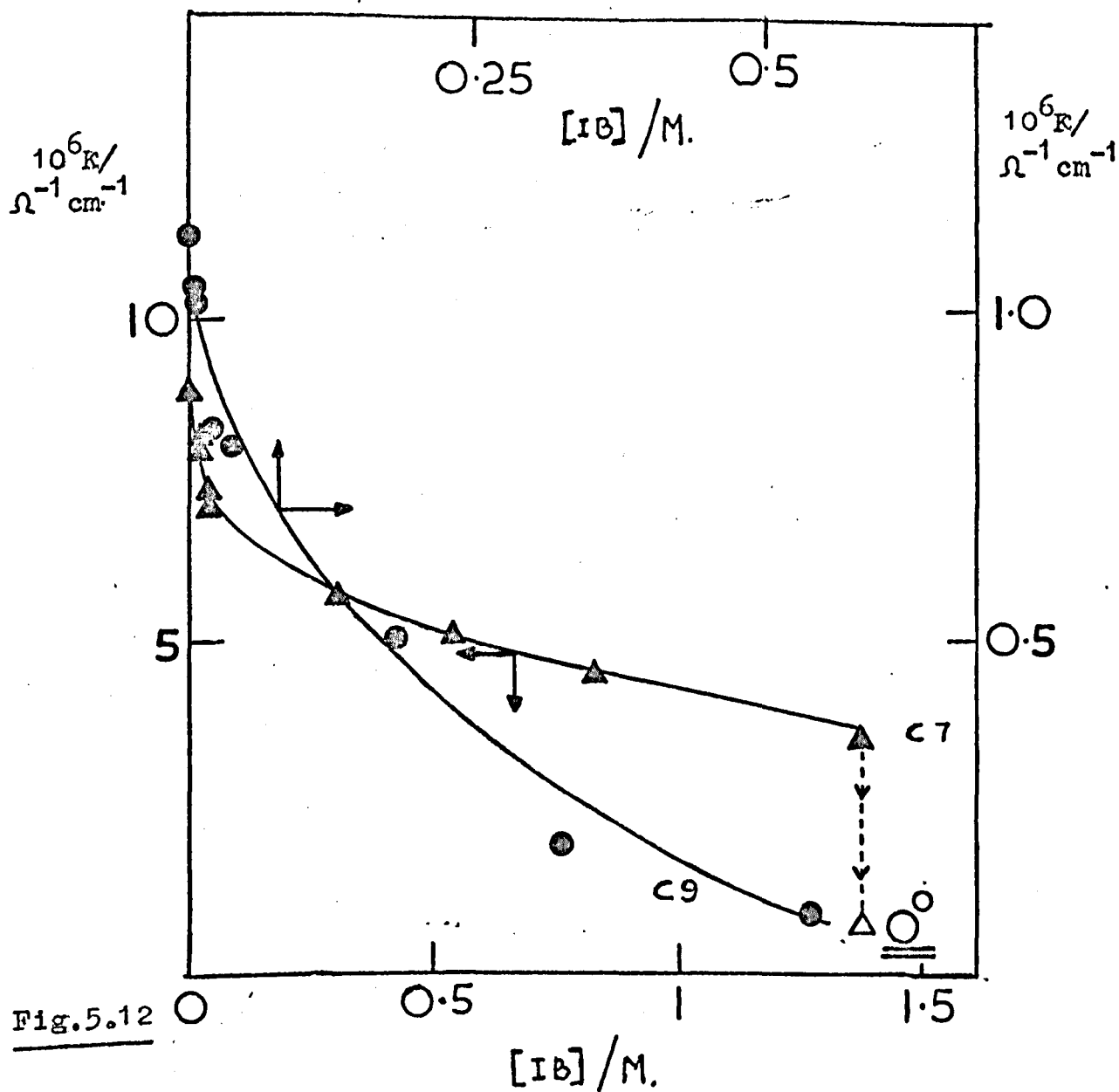


Fig.5.12

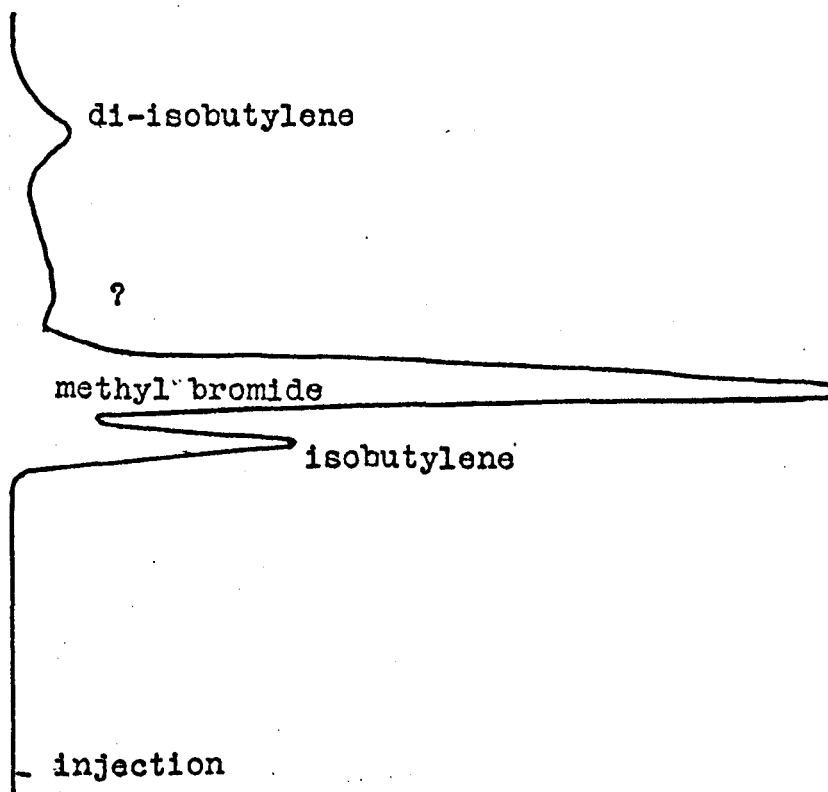


Fig.5.13

5.3.2 . Results. If isobutylene is distilled very slowly into a solution of either aluminium chloride or aluminium bromide, no polymerisation occurs. If the isobutylene is added rapidly, polymerisation takes place immediately.

In Fig. 5.12 the change of conductivity during the addition of isobutylene to aluminium bromide solutions has been shown for two expts. in which polymerisation did not occur.

In expt. C7, (triangular points, Fig. 5.12) 5×10^{-2} moles of isobutylene was added at -70° over ca. 2 h. to 1.4×10^{-4} moles of aluminium bromide in 40 ml. of methyl bromide. According to the ratio $(\kappa_e - \kappa_i)/\kappa_i$, which was 0.25, the initiator solution was rather impure. No polymer formed and the isobutylene was found to be nearly all present as monomer. In Fig. 5.13 is shown the g.l.c. of the solution after addition of isobutylene. This shows that some dimerisation had occurred, but most of the isobutylene was unchanged. On warming this solution to 0° , the conductivity decreased to nearly zero.

In expt. C9, (circular points, Fig. 5.13) 0.75 moles of isobutylene was added at -80° to 3.3×10^{-3} moles of aluminium bromide in 40 ml. of methyl bromide over ca. $1\frac{1}{2}$ h. According to the ratio $(\kappa_e - \kappa_i)/\kappa_i$, which was ca. 10^3 , the initiator solution was very pure. No polymerisation took place; the isobutylene was shown to be unchanged by g.l.c. analysis.

In each expt. the conductivity decreased to nearly zero as the isobutylene was added; this behaviour contrasts strongly with the large

increases of conductivity that occur during polymerisation.

In expt. C8, in which conditions were similar to expts. C7 and C9, the isobutylene was added rapidly in ca. 1 min., and polymer of high molecular weight was formed immediately.

In expts. C7 and C9, the initiator solutions remained clear and colourless throughout the addition of isobutylene. At the end of the experiments the solutions were hydrolysed, and immediately the cloudy precipitate of $\text{Al}(\text{OH})_3$ was observed. This showed that under the conditions of the expt. the initiator solution had not been hydrolysed.

The same behaviour was later discovered for the addition of isobutylene to solutions of aluminium chloride in ethyl chloride. In expt. D2, 2.9×10^{-2} moles of isobutylene were added slowly to 8.3×10^{-5} moles of aluminium chloride in 78 ml. of ethyl chloride at -78° ; the addition took 40 min. The ratio $(\kappa_e - \kappa_i)/\kappa_i$ was very high $>10^4$. During the isobutylene addition the conductivity dropped steadily to about half the initial value, and no polymerisation took place.

Even though subsequently large quantities of isobutylene ($[\text{IB}]/[\text{AlBr}_3]=10^2$) were added rapidly no polymerisation took place; it seems therefore that once the non-polymerisation of isobutylene had been established, it mattered not whether further isobutylene was added slowly or rapidly; no polymerisation took place.

5.3.3. Discussion. The lack of polymerisation and the associated decrease of conductivity in the systems described, means that (i) the concentration of the molecular species in equilibrium with the ions must have been reduced, because if only the ions had been removed, the system would have re-equilibrated fairly quickly to replace them; (ii) the concentration of non-complexed monomer or that of the initiating species (i.e. $\text{Al}_n\text{X}_{3n-1}^+$ cations) or both was never high enough for a polymerisation to take place; (iii) no ionogenic reactions took place because these would have caused an increase in conductivity.

The most probable explanation of these expts. is as follows: When monomer is added sufficiently slowly, it will most likely interact with an aluminium halide molecule rather than with an ion, because the former are in ca. 10,000 fold excess over the ions in a normal aluminium bromide solution. Such reactions between electron-deficient metal halides and olefins to give π -complexes are well known. As the $[\text{AlX}_3]$ is reduced by the formation of the π -complexes, the self-ionisation equilibrium is moved to the left and the concentration of ions is reduced correspondingly. The fact that for a pure solution (e.g. C9) the conductivity decreases nearly to zero indicates that the $\text{AlBr}_3 + \text{Me}_2\text{C}=\text{CH}_2$ complex does not participate in an ionogenic reaction.

It seems clear that the ions which give rise to the conductivity during the slow addition of isobutylene, are not the same as those which cause the initiation of polymerisation.

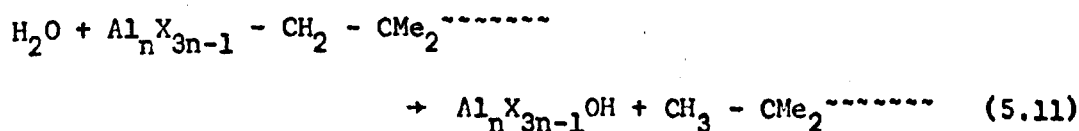
In looking for an explanation of this phenomenon one should consider the effect of the isobutylene on the polarity and dielectric constant of the solvent, (any reduction in dielectric constant would cause a reduction of the rate of ionisation and of the extent of ionisation), and the effect of the small amounts of impurities such as water.

The reaction of aluminium halides with impurities may give oxonium ions, and these are generally not able to initiate the polymerisation of hydrocarbons, as has already been suggested in § 4.

5.4 The Test of the Self-Ionisation theory

5.4.1 Introduction. As has been stated before in this chapter, the most important premise of the Self-Ionisation theory is that the $Al_n X_{3n-1}^+$ cation, which arises from the self-ionisation of an aluminium halide, reacts with isobutylene (or any olefin) and thus generates a carbenium ion in the way represented by reaction 5.3. If this reaction occurs, a carbon-aluminium bond is formed. If the carbenium ions formed in reaction 5.3, initiate polymer chains, then some of the polymer will have $Al_n X_{3n-1}-C$ end-groups. If the olefinic end-groups created by transfer reactions in the polymerisation of isobutylene for instance are also subject to attack by the $Al_n X_{3n-1}^+$ cation as was suggested in § 5.2.2.5, then an initial or terminal $Al_n X_{3n-1}$ group should be present in nearly every polymer molecule.

The aluminium-carbon bond will be hydrolysed easily in the way shown in reaction 5.11.



If the water is labelled with tritium, then some tritium should be incorporated into the polymer by reaction 5.11. Thus the hydrolysis of a freshly prepared polymer solution, with enough tritiated water to hydrolyse completely all the aluminium halide, and all the Al-C bonds, places labelled hydrogens on the polymer where Al-C bonds existed previously. From measurements of the content of tritium in the polymer with the scintillation counting method described in

§ 2.2.1.2. the number of aluminium-carbon bonds which were present in the polymer before killing, can be calculated.

This type of analysis was first used in cationic polymerisation by Colclough⁹ who used labelled antimony to detect initiator fragments in polystyrene which had been initiated by antimony pentachloride.

5.4.2 Results. The method of polymerisation and hydrolysis has been described in § 2.2.3.3.

At the end of a polymerisation, tritiated water was added in a ca. tenfold excess over the initiator to hydrolyse the aluminium halide to $\text{Al}(\text{OH})_3$, and the carbon-aluminium bonds in the polymer to carbon-tritium bonds. The polymer was isolated by precipitation in methanol. It was dried in a vacuum oven, weighed, and re-dissolved in toluene. The count-rate was then determined in the way described in § 2.2.1.2. The polymer was then re-precipitated in methanol, dried, weighed, redissolved in toluene and recounted. This process of re-precipitation etc., was continued until the polymer had a constant count-rate per mg. Usually two or three re-precipitation were sufficient, but when high molecular weight (ca. 250,000) polyisobutylene was examined, seven re-precipitations were required.

A liquid-liquid extraction method, tried first, in which the toluene solution of polymer was washed with distilled water to remove the excess of tritiated water was not successful. Although steady count rates were achieved, catalyst fragments which contained a considerable amount of tritium remained in the polymer solution.

Table 5.3

Details of the experiments. The ionic concentration in column 10 is the value at the end of the polymerisation, and it is compared to the number of polymer molecules, calculated from the yield and D.P. In column 11 the amount of tritium in g.-atoms is compared with the number of polymer molecules.

Expt. R3 was an early expt. in which an inefficient method of removing the excess of tritiated water was used. It is included because of the information it yields concerning the concentration of ions.

Table 5.3

Expt. No.	Monomer (P ₁)	10[P ₁]/mole l ⁻¹	AlX ₃	10 ³ [AlX ₃]/mole l ⁻¹	Solvent	Temp. of Polymn. /°C	Yield %	D.P.	No. of ions per polymer chain	No. of g.atoms of T per g. polymer	Polymn Reaction Time/min	Notes
R3	IB	1.1	AlBr ₃	48	MeBr	-63	95	~100	~1.1	~(4)	80	Most of the polymer in soln. during polymerisation
R8	IB	3.25	AlBr ₃	12.8	MeBr	-63	98	450	1.4	1.5	110	"
R15	IB	4.34	AlBr ₃	21.4	MeBr	-78	99	3900	0.12	0.66	25	Little polymer in soln.
R9	IB	3.3	AlCl ₃	2.0	EtCl	-78	96	430	0.13	1.0	30	"
R10	NBD	6.8	AlBr ₃	9.4	MeBr EtBr	-125	20	460	0.3±.2	42	50	"
R12	St	2.9	AlBr ₃	7.2	MeBr	-63	76	44	1.7x10 ⁻⁴	4x10 ⁻²	33	"
R14	St	2.4	AlBr ₃	2.6	MeBr	-78	99	44	1.4x10 ⁻²	5x10 ⁻²	37	"
*R11	IB	1.4	AlBr ₃	6.1	MeBr	-63	97	400	1.2	No of ¹⁴ C incorp <0.01	74	Most of the polymer in soln. during polymerisation

* This polymer was killed with ¹⁴C labelled isopropanol

Later re-precipitation of polymer solutions which had been extracted with water removed the excess of tritium. The methanol used in the latter re-precipitation was evaporated, and aluminium was detected in the residue by the aluminium test § 2.2.3.4, which showed the liquid-liquid extraction method to be very ineffective at removing the catalyst residues.

Three properties of each expt. were measured and compared:

- (i) The total number of free ions present before hydrolysis, calculated in the way described in § 5.2.1:
- (ii) The total number of polymeric end-groups, calculated from the yield and the D.P. which was measured as described in § 2.2.1;
- (iii) The number of moles of tritium incorporated per mole of polymer.

The results of the successful expts. are shown in Table 5.3.

Polymerisation of Isobutylene. Expts. were performed at -63° and -78° , and high yields of polymer with values of the D.P. in the range ca. 400 to 4,000 were obtained.

The polymers from expts. R15, R9 and R8 contained ca. 1 tritium atom, and therefore originally 1 aluminium-carbon bond, per molecule. When it was possible to keep the polymer in solution, the final value of the conductivity suggested a minimum of 1 g. ion for 1 g. mole of polymer!

When aluminium chloride was used as initiator, the results obtained resembled closely those obtained when aluminium bromide was

used, as is demonstrated by the results of expts. R9 and R15.

In expt. R11 the reaction mixture was treated with ^{14}C -labelled isopropanol, and the polymer obtained contained negligible activity. It follows that the reaction of the carbenium ion with the alcohol produces a terminal double bond rather than an isopropyl ether group. If the carbenium ion reacts in this way with isopropanol, then the analogous behaviour with water is likely. When the alcohol was added to the reaction mixture, the conductivity fell to zero within half a minute, which indicated a rapid destruction of ions, (see Figs 5.1 - 5.5).

It can be concluded that (a) the polymers contain C-Al bonds during the polymerisation; (b) that the number of these bonds is ca. one per molecule; and (c) that the number of ions in solution grows subsequent to completion of the polymerisation and is finally about equal to the number of polymer molecules.

The polymerisation of styrene and norbornadiene. Once it had been established that aluminium-carbon bonds were involved in the initiation of the polymerisation of isobutylene, other monomers were tested, namely norbornadiene (NBD) and styrene (St).

Neither behaves quite like isobutylene during polymerisation because both give polymers which are precipitated to a greater extent than polyisobutylene (see Table 5.1).

The polystyrene gave a gel-like material which adhered to the walls of the vessel, whereas norbornadiene gave a white crusty material. For the expts. with NBD a very low temp. (-125°C) was used so as to obtain a polymer free from cross-links. As the polymer was formed, the conductivity of the system dropped steadily. The ionic concentration could not be calculated exactly, because the polymerisation was carried out in an approximately equimolar mixture of ethyl and methyl bromides, the viscosity of which is not known, and is difficult to estimate.

St was dosed in small amounts at ca. 5 min. intervals and the conductivity varied as described in § 5.2.2.3 and both the precipitated polymer and the reaction mixture in the cell became yellow; this colour disappeared rapidly on hydrolysis.

In expt. R14 the polymer was allowed to dissolve after it had been formed, and the conductivity of the solution so formed increased as the dissolution proceeded. The final value of the conductance, when not all the polymer had dissolved indicates a number of g. ions which is of the same order as the number of carbon-aluminium bonds. In the St polymerisation the incorporation of tritium after hydrolysis was rather low. It is very likely that the carbon-aluminium bonds are those formed in the initiating process.

The polymerisation of NBD gave a polymer with a large incorporation of tritium.

Table 5.4

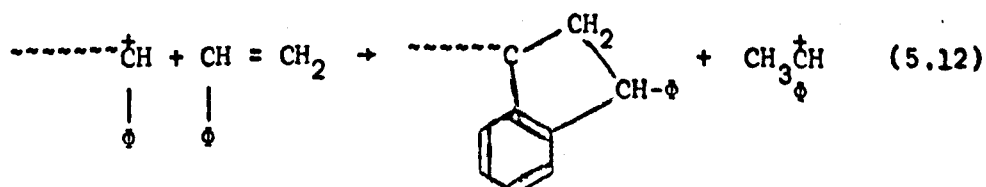
Expt. No.	Polymer	D.P.	No of g. atoms of tritium per g. mole. polymer
R5	PIB	1,300	1.3
R6	PIB	3,600	1.8
R7	Nonadecane	- (M.W. = 268.5)	0

Check and blank experiments, showing levels of
incorporation of tritium into "dead" polymer.

Check and Blank experiments. To ascertain whether tritium could have entered the polymer by a process other than the hydrolysis of a carbon-aluminium bond, we tested the reaction of suitable polymers with aluminium bromide. The polymers were dissolved in ethyl bromide, and phials of aluminium bromide were crushed into these solutions, which were subsequently kept at 0° for ca. 15 min., and then hydrolysed in the usual way with tritiated water. The three substances examined in this way were polyisobutylenes of high and low D.P., and nonadecane. Each poly-isobutylene molecule contains one double bond, hence the concentration per g. of polymer is inversely proportional to the D.P. The results in Table 5.4 show that ca. one molecule of tritium per polymer molecule was incorporated. In the expt. with nonadecane, which is a completely saturated material, no tritium was incorporated into the hydrocarbon. It therefore seems established that Al-C bonds are formed only from double bonds, and the expts. in which non-polymerising mixtures were obtained show that it must be Al-ions and not Al-molecules which produce them.

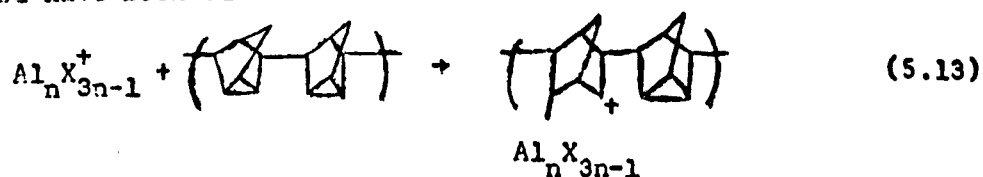
5.4.3 Discussion. The radiochemical analysis showed that polyisobutylene produced by the above method contained ca. 1 tritium and hence one carbon-aluminium bond per polymer chain. This surprising result is easily understood if the idea that the terminal double bonds, which are formed in a chain-transfer reaction are subject to aluminatation (c.f. § 5.2.2.5). Further evidence for this came from the expts. with dead material where double bonds were shown to be aluminated.

For polystyrene the chain-ends are mostly terminal indanyl groups:



As this terminal indanyl group cannot be aluminated like a double bond, the amount of tritium incorporated comes only from the initial $\text{AlBr}_2\text{CH}_2\text{CHPh-}$ groups and therefore represents the total number of growing chains.

For polynorbornadiene, the high level of incorporation suggests that the three-membered rings in the polymer behave like double bonds and have been aluminated.



One puzzling feature of the results obtained is that a very high concentration of free ions has been found, ca. 1 per polymer chain for the isobutylene polymerisation. It would be expected from the equilibrium constant of reaction 5.6, that the value ought to be much lower. However, as was stated before, the quantitative interpretation of conductivity results is very dubious, and in addition the value of K_p calculated for reaction 5.6 was for aluminium chloride initiation, and as the results in Table 5.3 show, the polymerisation by aluminium chloride produced rather less free ions per polymer chain than did the polymerisation by aluminium bromide.

5.4.4 Comparison of the radiochemical expts. with the results of other workers. Ghanem and Marek have recently published a paper,⁶ in which they described the effect of adding tritiated water before, during and after the polymerisation of isobutylene by aluminium bromide in heptane at ca. -70° . They analysed their polymers for tritium with a scintillation counting method, which was very similar to that described in this thesis. However, the work is not really comparable to that described here, because they used very small amounts of tritiated water ($[AlBr_3] : [T_2O] = 100:1$), and consequently they discovered very little tritium in the polymer. The fact that they found some incorporation of tritium, is taken by the writer to indicate that these results are an additional confirmation of the existence of the carbon-aluminium bond.

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Suggestions for Further Work

The work described above was, in many respects, of an exploratory nature, and for this reason it is possible to make a lot of suggestions for further work.

One of the main problems with which we were faced often during the work was the lack of basic information about the physical properties of the compounds used. For instance, the viscosity of methyl bromide and ethyl chloride has never been measured properly, and the variation of density with temp. has never been determined for many compounds.

One simple measurement which would be of great use, would be the determination of the solubility of aluminium chloride in pure methylene dichloride, ethyl chloride and methyl chloride; an impure solvent can accept a much higher concentration than can the pure solvent. There are many reports in the literature of "pure" aluminium chloride solutions, in which the authors have claimed concentrations which are so much higher than those predicted by the ideal solubility, that it would appear that the solvents were anything but pure! The measurement would therefore provide us with a useful discriminator.

A problem which interests me greatly, is the reaction of aluminium halides and titanium halides with water. Hitherto, this has been a totally neglected reaction, although it has been commonly regarded as being of great significance in the initiation of cationic polymerisations.

In this work we have shown that conductivity, which is often regarded as an unrevealing measurement, is, in fact not so; it can be used to reveal a) The nature of an ionogenic equilibrium; b) The kinetics of ionogenic processes; c) The state of purity; and hence the nature of the ionic species in solution may often be deduced. These methods could be used effectively in the studies of many cationic polymerisation systems.

With regard to the work on ether and aluminium halides, it would be very interesting to know whether the change in conductivity at the transition point is reversible. This would help to confirm the explanation which was offered concerning the remarkable conductivity behaviour in these systems.

Since I have shown that non-polymerising solutions of aluminium halides and isobutylene can be prepared (§ 5), it should be possible now to obtain the freezing point phase-diagram of the binary mixture. If so, this would show the existence and composition of any complexes. Perhaps work in this area could be extended to the i.r. study of the interaction of isobutylene and aluminium halides and the investigation of the vapour pressure of the solution, so that the high strength of the complex which we found may be confirmed.

Appendix 1

A Generalised Treatment of Ionogenic Equilibria

A Generalised Treatment of Ionogenic Equilibria

Part I Theory

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This paper is concerned with a very general treatment (hitherto lacking in the Literature) of equilibria in which n molecules generate 2 or n ions. Equations are developed for the dependence of the specific conductance on the total concentration of solute in terms of the equilibrium constants and the true equivalent conductances of the electrolytes. After the "simple" systems those involving ion-pairs are considered, and in a separate Section the influence of ionic strength effects on a few systems is discussed.

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Introduction

Amongst the most common equilibria in solution are those involving molecules and ions and in particular those in which only molecules react to give completely ionic products. In principle any number of molecules could generate any number of ions. We will be concerned here mainly with those equilibria in which only two ions are generated from different numbers of molecules. Such equilibria have been known for a very long time, yet the only systems for which an algebraic treatment is to be found in standard textbooks are those in which one molecule (or other non-conducting species, such as an ion-pair) generates two ions (Ostwald Dilution Law, Kraus-Bray equation etc.) The neglect of all other types of ionogenic equilibria has polarised the thinking of electro-chemists and others in such a manner, that even the symptoms by which other types of ionogenic equilibria can be recognised are not widely known, and their consideration is generally omitted from discussions of the state of metal halides in solutions (e.g. TiCl_4 or AlCl_3) of equilibria between organic halides and metal halides, (e.g. $\text{Ph}_3\text{CCl} + \text{HgCl}_2$ or $\text{MeCOF} + \text{SbF}_5$) and other types of systems where they are relevant.

We are concerned here especially with the electrochemical aspects of ionogenic equilibria, in other words with the manner in which they manifest themselves in studies of the electrical conductance of solutions. The adaption of our equations for studies in which the concentration of one or more of the species involved is monitored by optical or other means, follows from our various equations as a series of trivial corollaries, and many of the resultant equations are well known.

Equilibria in which two molecules generate two ions first came to the notice of the senior author in connection with the self-ionisation of titanium tetrachloride, and subsequently in the context of several other equilibria involving metal halides. The present work was prompted by an apparently complete absence of a comprehensive and systematic treatment of ionogenic equilibria; in Part I we deal in Section A with a series of ideal

systems, i.e. those which do not involve ionic strength effects, and then in Section B we consider some real systems. In Part II we will examine the electrochemical behaviour of actual systems mostly taken from the literature and show how our considerations can be applied to these. We will also consider there the very few treatments of actual systems along lines similar to ours which have been put forward by other authors.

A Ideal Systems

1. n Molecules of one Type generate Two Ions.

1.1 General treatment.

Let \underline{n} molecules of a substance A react to generate the ions R^+ and Q^-



Let the total, initial concentration of A be \underline{c}_0 , let its concentration at equilibrium be \underline{c} , and let the concentration of each ion be \underline{i} , then the mass-balance is

$$\underline{c}_0 = \underline{c} + \underline{n.i} \quad (A.1)$$

The degree of ionisation is defined as

$$\alpha = \underline{i}/\underline{c}_0 \quad (A.2)$$

and the specific conductance κ is related to \underline{i} by the usual equation

$$\kappa = 10^{-3} \Lambda_T \underline{i}, \quad (A.3)$$

(if \underline{i} is in mol. l^{-1} and κ is in ohm $^{-1}$ cm $^{-1}$)

where Λ_T is the true equivalent conductance of the pair of ions R^+ and Q^- at the concentration \underline{i} . Thus in general,

$$\kappa = \alpha \cdot 10^{-3} \Lambda_T \underline{c}_0 \quad (A.4a)$$

$$\alpha = 10^3 \kappa / \Lambda_T \underline{c}_0 \quad (A.4b)$$

The conventional equivalent conductance Λ defined as $\Lambda = 10^3 \kappa / \underline{c}_0$ has a very limited utility, and that only in systems in which $\underline{n} = 1$, and for that reason we have eschewed its use completely. The reason that Λ is not generally very useful is that its difference from Λ_0 can be due to two completely different effects: incomplete ionisation of the electrolyte and departure from ideality (ionic strength effects). It is of course the ionic strength effects which account for the difference between Λ_T and Λ_0 .

From these considerations and others it follows that it is more useful to frame all equations in terms of the independent variable(s) which may be one or more concentrations, and the directly observed dependent variable κ .

The argument can be started conveniently with an expression for the equilibrium constant of reaction (I) which, by means of eqn (A.1) and (A.2), can be written as

$$\underline{K}_n = \alpha^2 / (1 - n\alpha) \frac{n}{c_0} - 2 \quad (\text{A.5})$$

From this general starting-point we now proceed to consider some specific cases.

1.2 Specific cases

1.2.1 $n = 1$ This is the case which is treated in all text-books of Physical Chemistry, and it thus needs little comment. The substitution of eqn (A.4) into eqn (A.5) leads directly to the Kraus-Bray equation in the slightly unfamiliar forms (A.6a) and (A.6b) which avoid the use of the derived quantity Λ :

$$10^3 \kappa = 10^{-3} \underline{K}_1 \Lambda_T^2 \frac{c_0}{\kappa} - \underline{K}_1 \Lambda_T \quad (\text{A.6a})$$

$$\text{or } 10^{-3} \frac{c_0}{\kappa} = 10^3 \kappa / \Lambda_T^2 \underline{K}_1 + 1 / \Lambda_T \quad (\text{A.6b})$$

As is well known, approximate values of both \underline{K}_1 and Λ_T can be obtained from appropriate plots of $\kappa - c_0$ data, and accurate values of \underline{K}_1^θ and Λ^θ (\underline{K}_1 and Λ_T at $c_0 = 0$) can be obtained by standard methods.

For many purposes it is useful to have an explicit equation for the dependence of κ on c_0 , which is given by eqn (A.7). This equation, which is of course equivalent to eqn (A.6), is not generally given in text books.

$$\kappa = 5 \times 10^{-4} \Lambda_T \underline{K}_1 \left[(1 + 4 \frac{c_0}{\underline{K}_1})^{\frac{1}{2}} - 1 \right] \quad (\text{A.7})$$

When $4c_0/\underline{K}_1 \gg 1$,

$$\kappa \approx 10^{-3} \Lambda_T \underline{K}_1^{\frac{1}{2}} c_0^{\frac{1}{2}} \quad (\text{A.8})$$

In real systems at ionic strengths in excess of ca. 10^{-4} M (depending on polarity of solvent) eqn (A.7) must of course be modified by taking account of the effects of ionic strength on Λ_T and K_1 . This can be done as for eqn (A.6) by standard methods.

1.2.2. $\underline{n} = 2$

The case $\underline{n} = 2$ is in many ways more interesting than the previous one, because it has been ignored almost completely and yet corresponds to an appreciable number of real systems. According to eqn (A.5), when $\underline{n} = 2$,

$$\underline{K}_2 = \alpha^2 / (1 - 2\alpha)^2, \quad (\text{A.9})$$

so that, as expected from Le Chatelier's Principle, α does not depend on \underline{c}_0 . In other words, in an ideal system of this kind the extent of ionisation does not tend to any limit with varying concentration, and in real systems it is only influenced slightly by ionic-strength effects; this feature will be discussed below. Systems in which dilution does not affect the degree of ionisation are so unfamiliar to most chemists that their existence often comes as a shock. Unfortunately, the one type of " $\underline{n} = 2$ system" which is widely familiar is the self-ionising liquid, e.g. water or liquid ammonia, and in these the absence of the concentration variable obscures the fact that α is independent of \underline{c}_0 .

It follows from eqn (A.9) that

$$\alpha = \underline{K}_2^{1/2} / (1 + 2\underline{K}_2^{1/2}) \quad (\text{A.10})$$

and then from eqn (A.4) that

$$\kappa = 10^{-3} \Lambda_{T\underline{K}_2}^{1/2} \underline{c}_0 / (1 + 2\underline{K}_2^{1/2}) \quad (\text{A.11})$$

Eqn (A.11) means that (in ideal systems) κ is a linear function of \underline{c}_0 , and in fact a linear dependence of κ on \underline{c}_0 is the most obvious symptom signalling the existence of a 2:2 equilibrium. It is obvious that these systems also differ from 1:2 equilibria in that \underline{K}_2 and Λ_T cannot be determined separately from a set of $\kappa - \underline{c}_0$ data.

1.2.3. $n \geq 3$

For $n = 3$, combination of eqn (A.4) and (A.5) gives

$$\underline{c}_0/\kappa = 3 \times 10^3/\Lambda_T + 10^2/\Lambda_T^{2/3} \underline{K}_3^{1/3} \kappa^{1/3} \quad (\text{A.12})$$

so that for this type of system both Λ_T and \underline{K}_3 can be found from the intercept and slope of a plot of \underline{c}_0/κ against $\kappa^{1/3}$.

Under conditions where the r.h.s. term in κ is negligibly small, this might simulate an $n : n$ ionisation. (i.e. $\kappa \propto \underline{c}_0$) However under these conditions the solute is almost totally ionised and this should be easily detectable.

For $n = 4$

$$\underline{K}_4 = \alpha^2/(1 - 4\alpha)^4 \underline{c}_0^2 \quad (\text{A.13})$$

and the usual substitutions give

$$1.6 \times 10^{-7} \kappa^2 - 8 \times 10^{-3} \Lambda_T \underline{c}_0 \kappa - \Lambda_T^2 \underline{c}_0^2 - 10^{-3} \Lambda_T / \underline{K}_4^{1/2} = 0 \quad (\text{A.14})$$

Although there is no convenient analytical solution of this equation, \underline{K}_4 and Λ_T can be found from it by computer.

For $n \geq 3$, α increases with increasing \underline{c}_0 . Thus at low values of \underline{c}_0 , and thus of α , eqn (A.5) can be given in the approximate form

$$\underline{K}_n \approx \alpha^2 / \underline{c}_0^{n-2} = 10^6 \kappa^2 / \Lambda_T^2 \underline{c}_0^n, \quad (\text{A.15})$$

so that

$$\kappa \approx 10^{-3} \underline{K}_n^{1/2} \Lambda_T \underline{c}_0^{n/2} \quad (\text{A.16})$$

1.2.4 The shapes of the conductivity curves and the limits of α

The general shapes of the curves relating κ to c_0 are shown in fig. 1.

- For $\underline{n} = 1$ it follows from eqn (A.6.b) that

$$dc_0/d\kappa = 2 \times 10^3 \kappa / \Lambda_T^2 K_1 + 1/\Lambda_T \quad (\text{A.17})$$

i.e. as c_0 and κ decrease, $dc_0/d\kappa$ decreases asymptotically to $1/\Lambda_T$.

(Although it would be more logical to consider $d\kappa/dc_0$, the algebraic expressions for its reciprocal are so much simpler, that nothing would be gained by inverting them).

For $\underline{n} = 2$,

$$dc_0/d\kappa = 10^3(1 + 2K_2)^{1/2} / \Lambda_T K_2^{1/2}, \quad (\text{A.18})$$

which means that the slope is independent of c_0 .

For $\underline{n} = 3$,

$$dc_0/d\kappa = 3 \times 10^3 / \Lambda_T + 2 \times 10^2 / 3 \Lambda_T^{2/3} K_3^{1/3} \kappa^{1/3}, \quad (\text{A.19})$$

i.e. as c_0 and κ increase, $dc_0/d\kappa$ decreases to an asymptotic value of

$$3 \times 10^3 / \Lambda_T.$$

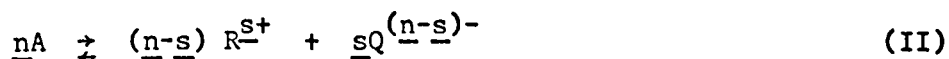
The asymptotic values which α approaches with changing c_0 can be found easily from eqn (A.5). As is well known, for $\underline{n} = 1$, $\alpha \rightarrow 1$ as $c_0 \rightarrow 0$.

For $\underline{n} = 2$, α is independent of c_0 . It follows directly from eqn (A.9) that as α is independent of c_0 , it can only vary with K_2 and that as $K_2 \rightarrow \infty$, $\alpha \rightarrow 1/2$.

For $\underline{n} = 3$, $\alpha \rightarrow 1/3$ as $c_0 \rightarrow \infty$ and for $\underline{n} = 4$, $\alpha \rightarrow 1/4$.

2. n Molecules of One Type generate n Ions

When n molecules of the same species are in equilibrium with n ions, of which s are anions and n-s are cations, (Equilibrium (II)),



the equilibrium constant $K_{\underline{ns}}$ is given by eqn (A.21)

$$K_{\underline{ns}} = \frac{[R_{\underline{s}}^{s+}]^{(n-s)} [Q_{\underline{n-s}}^{(n-s)-}]^s}{[A]^n} \quad (A.21)$$

The specific conductivity is given by eqn (A.22)

$$10^3 \kappa = \lambda_T^+ [R_{\underline{s}}^{s+}] \underline{s} + \lambda_T^- [Q_{\underline{n-s}}^{(n-s)-}] (\underline{n-s}) \quad (A.22)$$

The charge balance is given by eqn (A.23)

$$(\underline{n-s}) [R_{\underline{s}}^{s+}] = \underline{s} [Q_{\underline{n-s}}^{(n-s)-}] \quad (A.23)$$

Because n molecules generate n ions, the ionisation process does not alter the total number of "particles" in solution and for that reason the concentrations balance is expressed by eqn (A.24):

$$\underline{c}_0 = [A] + [R_{\underline{s}}^{s+}] + [Q_{\underline{n-s}}^{(n-s)-}] \quad (A.24)$$

The usual treatment of these four simultaneous equations yields the required expression for κ as a function of \underline{c}_0 :

$$10^3 \kappa = \underline{c}_0 K_{\underline{ns}}^{1/\underline{n}} (\lambda_T^+ \underline{s}^2 + \lambda_T^- [\underline{n-s}]^2) / (\underline{n} K_{\underline{ns}}^{1/\underline{n}} + [\underline{n-s}] \underline{s}/\underline{s} (\underline{s}/\underline{n}-1)) \quad (A.25)$$

As expected, eqn (A.25) reduces to (A.11) for n = 2 and s = 1.

It follows from eqn (A.25) that the linear correlation between κ and \underline{c}_0 is a general property of all systems in which the number of ions formed is equal to the number of molecules consumed in their formation.

3. Two Different Molecular Species Generate Two Ions

3.1 General Treatment

Consider the reaction



Let the initial concentrations of A and B be \underline{a}_0 and \underline{b}_0 respectively and let $[R^+] = [Q^-] = \underline{i}$. The degree of ionisation could be defined in different ways, and we will define it as

$$\alpha = \underline{i}/\underline{a}_0$$

The equilibrium constant for reaction (III) is then given by

$$\underline{K}_{nm} = \alpha^2 \underline{a}_0^2 / \underline{a}_0^n (1 - \underline{n}\alpha)^n (\underline{b}_0 - \underline{m}\alpha \underline{a}_0)^m$$

and the general conductance equation takes the form

$$\underline{K}_{nm} = (10^3 \kappa / \Lambda_T)^2 / (\underline{a}_0 - 10^3 \underline{n}\kappa / \Lambda_T)^n (\underline{b}_0 - 10^3 \underline{n}\kappa / \Lambda_T)^m \quad (\text{A.26})$$

3.2 $\underline{n} = \underline{m} = 1$

If $\underline{n} = \underline{m} = 1$, eqn (A.20) takes the form

$$[10^3 (1 - \underline{K}_{11}^{-1}) / \Lambda_T^2] \kappa \underline{X}_A / \underline{a}_0 = 1 / \Lambda_T - 10^{-3} \underline{a}_0 \underline{X}_B / \kappa \quad (\text{A.27})$$

where $\underline{X}_A = \underline{a}_0 / (\underline{a}_0 + \underline{b}_0)$ and $\underline{X}_B = \underline{b}_0 / (\underline{a}_0 + \underline{b}_0)$

This equation has a formal resemblance to the Kraus-Bray equation in the form (A.6a), and by means of it Λ_T and \underline{K}_{11} can be obtained from plots of $\kappa \underline{X}_A / \underline{a}_0$ against $\underline{a}_0 \underline{X}_B / \kappa$.

For the case $\underline{a}_0 = \underline{b}_0 = \underline{c}_0$ eqn (A.27) is reduced to the form

$$5 \times 10^{-2} (1 - \underline{K}_{11}^{-1}) \kappa / \Lambda_T^2 \underline{c}_0 + 5 \times 10^{-4} \underline{c}_0 / \kappa - 1 / \Lambda_T = 0 \quad (\text{A.28})$$

which is in fact identical with the much more tractable form (A.29)

obtainable from eqn (A.26) or by a method similar to that used in section

A.1.2.2, namely

$$\kappa = 10^{-3} \Lambda_{T-11} K_{-0}^{\frac{1}{2}} / (1 + K_{-11}^{\frac{1}{2}}) \quad (\text{A.29})$$

This differs from eqn (A.11) only by the absence of the factor 2 in the denominator.

4. The Participation of Ion-Pairs

4.1 n like molecules generate two ions

The chemical equation representing this situation is



The mass balance equation is

$$\underline{c}_o = [A] + \underline{n} ([R^+ Q^-] + [R^+]), \quad (A.30)$$

i.e. the total number of moles of compound A is the number which remains unionised plus the number which have formed ion-pairs plus the number which have formed free ions.

The charge balance and definition of α are

$$[R^+] = [Q^-] \equiv \underline{i} = \alpha \underline{c}_o \quad (A.31)$$

The fraction of the total solute which forms ion-pairs is

$$\alpha' = [R^+ Q^-] / \underline{c}_o \quad (A.32)$$

In these terms the general equation expressing equilibrium (IV) is

$$\frac{K_{np} K_F}{\underline{c}_o} = \alpha^2 \underline{c}_o^{2-n} / [1 - \underline{n}(\underline{i} + [R^+ Q^-]) / \underline{c}_o]^n \quad (A.33)$$

$$= \alpha^2 \underline{c}_o^{2-n} / [1 - \underline{n}(\alpha + \alpha')]^n \quad (A.34)$$

General considerations indicate that if only one property of such systems can be measured, such as the conductivity, the unknowns K_{np} , K_F , and Λ_o cannot be determined; but if other properties which are characteristic of species other than the free ions, e.g. the spectrum of the compound A, can be measured, all the unknowns could be determined.

4.1.1. n = 1

For this case we obtain eqn (A.35) by substituting from eqn (A.4b) into the appropriate version of eqn (A.34):

$$\kappa = 5 \times 10^{-4} \frac{K_{1P} K_F \Lambda_T}{\Lambda_T} \{ [1 + 2c_0(1 - \alpha')/K_{1P} K_F]^{\frac{1}{2}} - 1 \} \quad (\text{A.35})$$

This equation is not useful as it stands but can be transformed to

$$(1 - \alpha')c_0/\kappa - 10^3/\Lambda_T = 10^6 \kappa / K_{1P} K_F \Lambda_T^2 \quad (\text{A.35a})$$

which, by means of the mass-balance equation

$$c_0 = [A] + [R^+Q^-] + [R^+] \quad (\text{A.37.})$$

and eqn (A.35) can be given the useful form (A.35b):

$$(c_0 - [R^+Q^-])/\kappa - 10^3/\Lambda_T = 10^6 \kappa / K_{1P} K_F \Lambda_T^2 \quad (\text{A.35b})$$

If $[R^+Q^-]$ can be measured (e.g spectroscopically) for every value of c_0 for which κ is measured, then the appropriate plot would yield Λ_T and $K_{1P} K_F$.

- The two equilibrium constants cannot be separated unless either $[A]$ or $[R^+]$ (or $[Q^-]$) can also be determined.

4.1.2. $\underline{n} = 2$

For this case κ is given by eqn (A.38):

$$\kappa = 10^{-3} \underline{K}_{2P}^{\frac{1}{2}} \underline{K}_F^{\frac{1}{2}} \Lambda_T (\underline{c}_O - 2 [R^+ Q^-]) / (1 + 2 \underline{K}_{2P}^{\frac{1}{2}} \underline{K}_F^{\frac{1}{2}}) \quad (\text{A.38})$$

If both κ and $[R^+ Q^-]$ can be measured simultaneously for each value of \underline{c}_O , then the coefficient $10^{-3} \underline{K}_{2P}^{\frac{1}{2}} \underline{K}_F^{\frac{1}{2}} \Lambda_T / (1 + 2 \underline{K}_{2P}^{\frac{1}{2}} \underline{K}_F^{\frac{1}{2}})$ can be obtained. If, in addition, $[R^+]$ or $[Q^-]$ or $[A]$ could be determined, then the dissociation equilibrium of the ion-pairs could be treated separately so that \underline{K}_F could be found; but \underline{K}_{2P} and Λ_T cannot be separated.

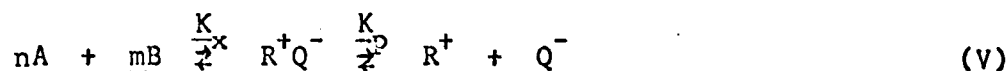
4.1.3. $\underline{n} > 2$

For $\underline{n} = 3$ the equation relating $\underline{K}_{3P} \underline{K}_F$ to α and α' is a cubic in both these variables, and for $\underline{n} = 4$ it is a bi-quadratic. The corresponding equations for κ can be derived by obvious, though tedious, methods, and the methods of obtaining Λ_T and the equilibrium constants follow directly from those used for simpler systems.

4.2 Two unlike molecular species generate two ions

4.2.1 General treatment

Consider the reaction



Let the initial concentrations of A and B be \underline{a}_0 and \underline{b}_0 respectively and let $[R^+] = [Q^-] = \underline{i}$. As before, the degree of ionisation can be defined in various ways, and it is defined here by

$$\alpha = \underline{i}/\underline{b}_0 \quad (A.39)$$

The fraction of total solute which forms ion-pairs is

$$\alpha' = [R^+Q^-]/\underline{b}_0$$

The general expression for the conductivity is given by eqn (A.40)

$$\kappa = 10^{-3} \Lambda_T \left[\underline{a}_0 \frac{\underline{n}}{\underline{b}_0} \frac{\underline{m}}{\underline{b}_0} \{1 - \underline{m}(\alpha' + \alpha)\}^{\underline{m}} \{1 - \underline{n}\underline{b}_0(\alpha' + \alpha)/\underline{a}_0\}^{\underline{n}} \frac{K}{\underline{x}} \frac{K_f}{\underline{f}} \right]^{\frac{1}{2}} \quad (A.40)$$

4.2.2 $\underline{n} = \underline{m} = 1$

By means of the methods used in previous cases, eqn (A.40) can be reduced to an expression which has a form similar to eqn (A.38):

$$\kappa = 10^{-3} \Lambda_T \left(\frac{K_f K_x}{\underline{f} \underline{x}} \right)^{\frac{1}{2}} \left[\underline{a}_0 \underline{b}_0 - (\underline{a}_0 + \underline{b}_0) \underline{y} + \underline{y}^2 \right]^{\frac{1}{2}} \quad (A.41)$$

where $\underline{y} = \underline{i} + [R^+Q^-]$.

If the total concentration \underline{y} of one kind of ion, say the cation, can be measured, then this is the most appropriate form of the equation. For instance, if \underline{y} can be measured spectroscopically, as was done for systems involving Ph_3C^+ and an anion $\text{MtX}_{\underline{z}+1}^-$ derived from a metal halide $\text{MtX}_{\underline{z}}$. If only \underline{i} or only $[R^+Q^-]$ can be measured, then the other one of these can be eliminated from eqn (A.41) by means of the following equation:

$$\frac{K_f}{\underline{f}} = \underline{i}^2/[R^+Q^-] \quad (A.42)$$

B Real Systems

1. Ionic Strength Effects on the $\underline{n} = 2$ Equilibria

The conductivity of real systems with $\underline{n} = 1$ has been dealt with adequately by many authors and need not concern us here. The behaviour of systems with $\underline{n} = 3$ and 4 is still too unexplored to make a detailed treatment worthwhile at present, but the behaviour of real $\underline{n} = 2$ systems of both types is of current interest and that is what we will consider next.

1.1 Two molecules of one type generate two ions

We start with eqn (A.11) and take into account that in a real system κ will differ from the value given by eqn (A.11) for two quite distinct reasons: Λ_T will depend on the ionic strength (given in this case by \underline{i}) in a manner which can probably be represented adequately by an equation of the type

$$\Lambda_T = \Lambda^0 - (\underline{A}\Lambda^0 + \underline{B})\underline{i}^{\frac{1}{2}} ; \quad (\text{B.1})$$

and \underline{K}_2 will depend on the ionic strength in a manner best expressed through the mean ionic activity coefficient $\bar{\gamma}_{\pm}$ and the thermodynamic ionisation constant \underline{K}_2^0 . However, since the relation between \underline{K}_2 and α does not involve the concentration of ions, it is not immediately obvious how \underline{K}_2 is related to $\bar{\gamma}_{\pm}$ and \underline{K}_2^0 but this can be clarified as follows: If we take the activity coefficient of the molecules A as unity, it follows that eqn (A.9) takes the form

$$\underline{K}_2^0 = \underline{i}^2 \bar{\gamma}_{\pm}^2 / (1 + 2\alpha)^2 \underline{c}_0^2 = \alpha^2 \bar{\gamma}_{\pm}^2 / (1 - 2\alpha)^2 = \underline{K}_2 \bar{\gamma}_{\pm}^2 \quad (\text{B.2})$$

and

$$\alpha = \underline{K}_2^{\frac{1}{2}} / (\bar{\gamma}_{\pm} + 2\underline{K}_2^{\frac{1}{2}}), \quad (\text{B.3})$$

so that $\alpha \rightarrow \alpha^0 = \underline{K}_2^{\frac{1}{2}} / (1 + 2\underline{K}_2^{\frac{1}{2}})$ as \underline{c}_0 and $\underline{i} \rightarrow 0$.

In order to obtain κ as a function of \underline{c}_0 we substitute into eqn (B.1) for Λ_T from eqn (A.4) and for \underline{i} from eqn (A.2), thus obtaining

$$10^3 \kappa / \underline{c}_0 = \Lambda^0 \alpha - (\underline{A} \Lambda^0 + \underline{B}) \alpha^{3/2} \underline{c}_0^{1/2} \quad (\text{B.4})$$

Thus a plot of $10^3 \kappa / \underline{c}_0$ against $\underline{c}_0^{1/2}$ should give a curve which tends asymptotically to the straight line

$$10^3 \kappa / \underline{c}_0 = \Lambda^0 \alpha^0 - (\underline{A} \Lambda^0 + \underline{B}) \alpha^{03/2} \underline{c}_0^{1/2} \quad (\text{B.5})$$

from the slope $\underline{S} = \Lambda^0 \alpha^0$ and intercept $\underline{I} = (\underline{A} \Lambda^0 + \underline{B}) \alpha^{03/2}$ of which Λ^0 , α^0 , and hence \underline{K}_2^0 can be obtained, since of course the constants \underline{A} and \underline{B} depend only on the nature of the system and can be calculated for each set of experimental conditions.

1.2 Two different molecules generate two ions

We start this treatment with eqn (B.1) and consider the appropriate substitutions, for Λ_T and \underline{i} . From the definition of $\Lambda_T = 10^3 \kappa / \underline{i}$ and the eqn (A.21) which relates \underline{i} to α we obtain

$$\Lambda_T = 10^3 \kappa / \alpha \underline{a}_O \quad (\text{B.6})$$

Therefore

$$10^3 \kappa / \alpha \underline{a}_O = \Lambda^O - (\underline{A} \Lambda^O + \underline{B}) \alpha^{\frac{1}{2}} \underline{a}_O^{\frac{1}{2}} \quad (\text{B.7})$$

This equation is of the same form as eqn (B.4), but the big difference is that in the present case α is given as the solution of eqn (B.8) which is eqn (A.22) for $\underline{n} = \underline{m} = 1$, and with the inclusion of the mean ionic activity coefficient γ_{\pm} , to give the thermodynamic equilibrium constant

$$\underline{K}_{11}^{\theta} = \alpha^2 \underline{a}_O \gamma_{\pm}^2 / (1 - \alpha)(\underline{b}_O - \alpha \underline{a}_O) \quad (\text{B.8})$$

This equation signifies that α varies not only because of the ionic strength effect but also as a result of changing \underline{a}_O and/or \underline{b}_O .

The explicit expression for α is so complicated that it serves no useful purpose, and the evaluation of Λ^O and $\underline{K}_{11}^{\theta}$ would probably be done best by iterative methods.

Fig.1

Curves of concentration versus conductivity
for various types of ionogenic equilibria.

$\underline{n} = 1$, the dissociation of methyltriethyl ammonium
iodide in methylene dichloride at 0°. ¹ $\underline{K}_1 = 0.902 \times 10^{-5} \text{M}$.

$\underline{n} = 2$, the ionisation of acetyl hexafluoroantimonate
in methylene dichloride at 0°. ² $\underline{K}_2 = 5 \times 10^{-2}$.

$\underline{n} = 3$, a theoretical curve for the situation in which
 $\underline{K}_3 = 16 \text{ M}^{-1}$ and $\Lambda_T = 50$.

1. J.H.Beard and P.H.Plesch, J.Chem.Soc., 1964, 4879.

2. O.Nuyken and P.H.Plesch, Chem.and Ind., 1973, 379.

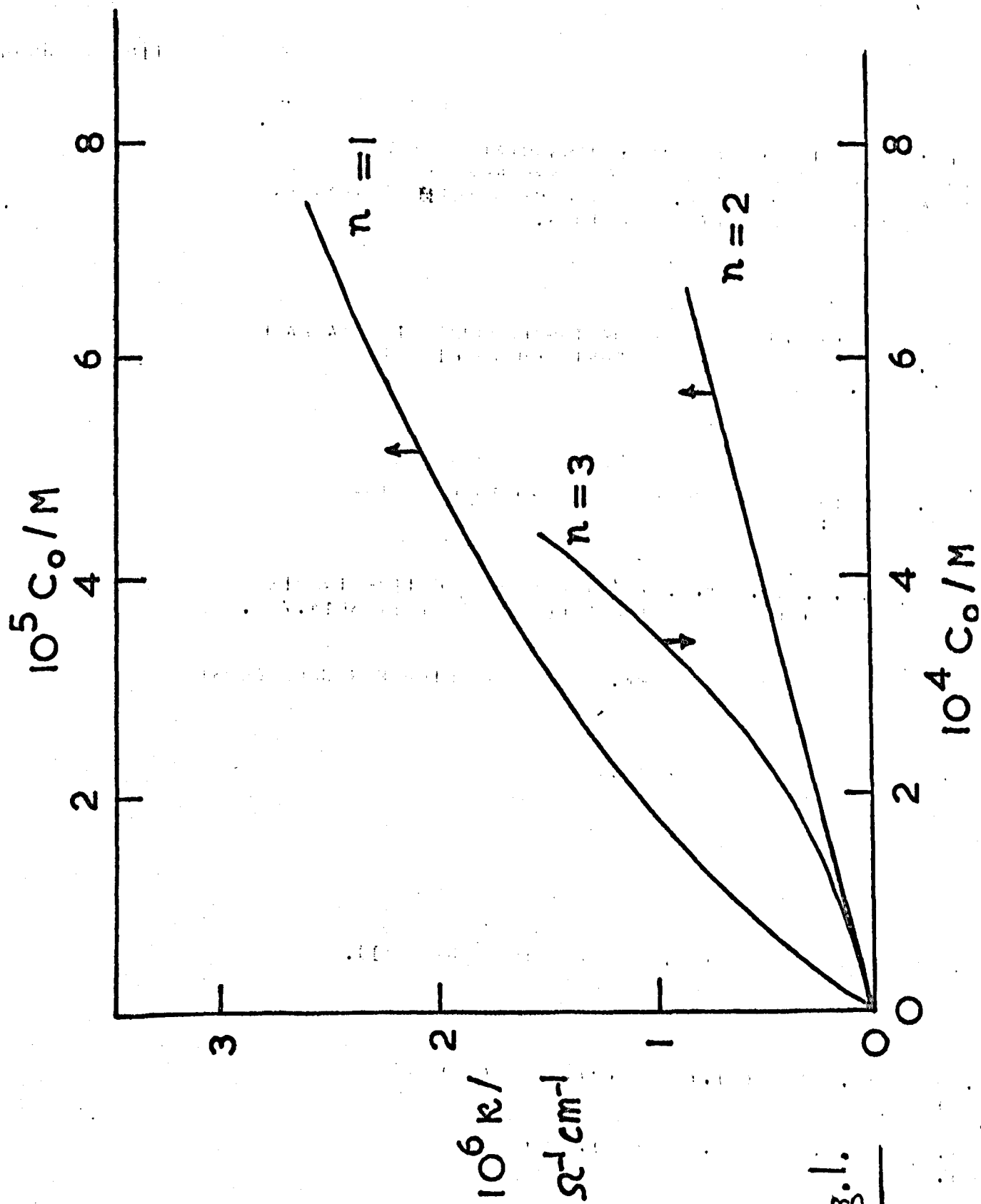


Fig.1.

Appendix 2

The computer programme which was used to estimate the value of κ_e . The programme is designed to print out the results on a line-printer and to plot the graph of $\ln(\kappa_e + \kappa_i)$ - $\ln(\kappa_e - \kappa_i)$ vs. t , the time. To do this the subroutine ISEASY is called to plot the points, and again to plot the least squares slope. If the least squares slope agrees well with the points, the result would be considered satisfactory.

If ISEASY is not available lines 149 to 162, should be omitted; the starred subscripted variables in line 18 should also be omitted; the statement in line 17 should be ignored.

&JOB;CHR012; KINETICS OF IONISATION AND CALCN OF FINAL CONDUCTANCE &PL
SWOP

&FORTRAN;

&LIST;

```
1* C GRATTANS KINETIC SCHEME
2* C TREATMENT OF THE KINETICS OF IONOGENIC REACTIONS.
3* C THE PROG IS DESIGNED TO ESTIMATE THE VALUE
4* C OF THE CONDUCTIVITY AT EQUILIBRIUM.
5* C THE FOLLOWING INPUTS ARE REQUIRED.
6* C NOTE ALL TIMES IN MINS, ALL CONDS UNCORRECTED, AND IN MICROMHO ]]].
7* C CARD 1 SPACE 1&2 NO OF RESULTS.
8* C SPACES 3&4 THE NO. 50.
9* C SPACES 5-13 INITIAL TIME MIN.
10* C SPACES 19-32 CONDUCTIVITY AT INITIAL TIME.
11* C SPACES 33-56 VALUE OF CELL-CONSTANT.
12* C CARD 2 SPACES 1-14 A VALUE OF THE EQUILIBRIUM VALUE OF
13* C CONDUCTIVITY, CHOSEN TOO LOW.
14* C NOW FOLLOW THE RESULTS. EACH CARD HAS THE
15* C TIME IN THE FIRST 14 SPACES & THE CONDUCTIVITY IN
16* C THE NEXT 14
17* C HEADING FOR PLOT ON LAST CARD UP TO 24 SPACES
18* C DIMENSION HEAD*(4),SHEAD*(3),XLABEL*(2),YLABEL*(2),AANSW(50)
19* C DIMENSION ATIME(50)
20* C DIMENSION X(2),Y(2)
21* C DIMENSION CONF(50),CAPF(50),TIM(50),CONN(50),DEV(50)
22* C DIMENSION SLOPE(50),ACFPT(50)
23* C
24* C
25* C I=0
26* C DI=0.0
27* C DINI=0.0
28* C ACAPI=0.0
29* C DELCAP=0.0
30* C DIVI=0.0
31* C DIGI=0.0
32* C ANA =0.0
33* C TO =0.0
34* C CONO=0.0
35* C CC =0.0
36* C DELTA= 0.0
37* C NUM=0
38* C NUMB=0.0
39* C NOCFS=0
40* C
41* C
42* C WRITE(2,10)
43* C 10 FORMAT(51H TREATMENT OF KINETICS OF LITTLE DISSOCIATED SYSTEM)
44* C
45* C
46* C READ(7,20)NUM,NOCFS,TO,CONO,CC
47* C 20 FORMAT(2I2,3F14.7)
48* C WRITE(2,21)NUM,NOCFS,TO,CONO,CC
```

```

49*      21 FORMAT(2I2,3F14.7)
50*          CAPO = CONO*CC
51*          DIVI = NOCFS
52*          DIGI = NUM
53*          READ(7,25)CONF(1)
54*      25  FORMAT(F14.7)
55*          WRITE(2,26)CONF(1)
56*      26  FORMAT(F14.7)
57*          DO 170 NC = 1,NUM
58*          READ(7,200)TIM(NC),CONN(NC)
59*      200  FORMAT(2F14.7)
60*          WRITE(2,171)TIM(NC),CONN(NC)
61*      171  FORMAT(2F14.7)
62*      170  CONTINUE
63*      64  CONTINUE
64*          I = I + 1
65*          DI = I
66*          WRITE(2,747)I
67*      747  FORMAT(I2,10H TH CYCLE )
68* C      CONDITION IF MIN HAS NOT BEEN FOUND IN 10 CYCLES.
69*          IF ( DI .LT.10)      GOTO 66
70*          WRITE(2,737)
71*      737  FORMAT(28H IS TOO HIGH CAPF 1 USED      )
72*          CAPF(1) = CONF(1)*CC - CAPO
73*          NUMB = 1
74*          GO TO 76
75*      66  CONTINUE
76*          CAPF(1) = CONF(1)*CC*DI - CAPO
77*          DELTA = CONF(1)/DIVI - CONO/DIVI
78*          DO 160 N3 = 2, NOCFS
79*          DINI = N3 - 1
80*          CONF(N3) = (CONF(1) - CONO)*DI + DELTA*DINI
81*          CAPF(N3) = CONF(N3)*CC
82*          WRITE(2,271)
83*      271  FORMAT(30H CAPPA F VALUE AFTER DELT ADN)
84*          WRITE(2,172)CAPF(N3)
85*      172  FORMAT(E14.7)
86*      160  CONTINUE
87* C      LEAST SQUARES ROUTINE 1, FOR ALL CAPPA F VALUES.
88*          DO 190 ND = 1, NOCFS
89*          SANSW = 0.0
90*          STIMSQ = 0.0
91*          SANTI = 0.0
92*          STIME = 0.0
93*          SANSQ = 0.0
94*          DO 150 N = 1, NUM
95*          ANSW = 0.0
96*          CAPP = 0.0
97*          TIME = 0.0
98*          CAPP = CONN(N)*CC - CAPO
99*          TIME = (TIM(N) - TO)*60.0
100*          ANSW = ALQ((CAPF(ND) + CAPP)/(CAPF(ND) - CAPP))
101*          SANSQ = ANSW**2 + SANSQ
102*          SANSW = ANSW + SANSW
103*          STIMSQ = TIME**2 + STIMSQ
104*          STIME = TIME + STIME
105*          SANTI = ANSW*TIME + SANTI
106*      150  CONTINUE
107*          ACCEPT(ND) = (STIME*SANTI - STIMSQ*SANSW)/(STIME**2 - DIGI*STIMSQ)
108*          SLOPE(ND) = SANSW/STIME - DIGI*ACCEPT(ND)/STIME

```

```

109* C THE RMS DEVIATION IS NOW BEING USED
110*     DEV(ND)=SQRT((SANSQ-ACEPT(ND)*SANSW-SLOPE(ND)*SANTI)**2)
111*     190 CONTINUE
112*     N=0
113*     999 N=N+1
114* C CONDITION FOR STOPPING LOOP IF N EXCEEDS NO IN ARRAY.
115*     IF (N.LT. NOCFS ) GOTO 888
116*     WRITE(2,707)
117*     707 FORMAT(14H NO MIN FOUND )
118*     GO TO 64
119* C IF THERE IS A MINIMUM IN THE DEVIATION THEN PRINT OUT*****
120*     888 IF ( DEV(N) .GT. DEV(N+1) ) GOTO 999
121*     NUMB = N
122*     76 CONTINUE
123* C BEGIN PRINT OUT
124*     WRITE(2,50)
125*     50 FORMAT(42H LOG TERM , TIME SECS , CAPPA MCMO)
126* C RECALCULATE VALUES IN ARRAY FOR PLOT, FOR CHOSEN CAPPA F.....
127*     DO 250 N=1,NUM
128*     ANSW=0.0
129*     CAPP=0.0
130*     TIME=0.0
131*     CAPP=CONV(N)*CC - CAPO
132*     TIME=(TIM(N)-TO)*60.0
133*     ANSW=ALOG((CAPF(NUMB)+CAPP)/(CAPF(NUMB)-CAPP))
134*     ATIME(N)=TIME
135*     AANSW(N)=ANSW
136*     WRITE(2,40)ANSW,TIME,CAPP
137*     40 FORMAT(3F14.7)
138*     250 CONTINUE
139* C CALC AND PRINT OUT SLOPE, INTERCEPT, DEVIATION, CAPPA F, THE INITIAL VAL
140* C A , AND DELCAP THE DIFFERENCE BETWEEN CAPPA F AND CAPPPA I***
141*     WRITE(2,303)
142*     303 FORMAT(55H DEVIATION , INTERCEPT , SLOPE , CAPPA F.)
143*     WRITE(2,404)DEV(NUMB),ACEPT(NUMB),SLOPE(NUMB),CAPF(NUMB)
144*     404 FORMAT(3F14.7,F13.6)
145*     ACAPI=CAPF(NUMB)*(EXP(ACEPT(NUMB))-1.0)/(EXP(ACEPT(NUMB))+1.0)
146*     DELCAP=CAPF(NUMB)-ACAPI
147*     WRITE(2,135)ACAPI,DELCAP
148*     135 FORMAT(12H CAPPA I IS ,F10.5,11H DELCAP IS ,F10.5)
149*     DATA SHEAD/8HMINIMISA,8HTION OF ,8HRMS DEVN/
150*     DATA XLABEL/8HTIME SE,8HCONDS /
151*     DATA YLABEL/8HLOG FUNC,8HTION /
152*     READ(7,97)HEAD
153*     97 FORMAT(4A8)
154* C BEGIN THE PLOTTER OUTPUT ****
155*     CALL ISEASY(NUM,ATIME,AANSW,1,1,1,1,0,0,0,0,4,HEAD,3,SHEAD,2,
156*     1XLABEL,2,YLABEL)
157*     X(1)=0.0
158*     X(2)=ATIME(NUM)
159*     Y(1)=ACEPT(NUMB)
160*     Y(2)=ACEPT(NUMB)+SLOPE(NUMB)*X(2)
161*     CALL ISEASY(2,X,Y,1,0,0,3,0,0,0,0,4,HEAD,3,SHEAD,2,XLABEL,2,
162*     1YLABEL)
163*     STOP
164*     END

```