To my Mother and Father

## PREFACE

Until quite recently, the chemistry of non-aqueous solvents was a relatively neglected field of research. Most solution chemistry was aqueous solution chemistry, for water is the most readily available and biologically most important of all solvents. While the study of non-aqueous media is now a thriving science, accurate data are still quite sparse, and the interpretation of the processes occurring in solution is often uncertain.

Trifluoroacetic acid is of interest as a solvent, since it combines moderately strong acidic character with a low dielectric constant. The acid has been investigated as a medium for both organic and inorganic reactions, but little is known about its basic solvent properties. The work reported here represents the beginning of a fundamental study of these properties, with a particular emphasis on conductance studies and the behaviour of electrolytes in the solvent.

## ACKNOWLEDGEMENTS

Very many people have helped toward the preparation of this work, and I would like to offer my thanks especially to the following:-

- to Dr. and Mrs. J. B. Milne, for their kindness and friendship in the last few years.
- to Dr. Milne in particular, for his invaluable advice and criticism, constant encouragement, and ability to distinguish the essential from the detail.
- to friends and colleagues within the Department.
- to the technical staff of the Department, and especially to Mr. Egon Christoff for his help with the design and fabrication of the apparatus.
- to the Government of Ontario and the National Research Council for generous financial support.
- to my wife, Anne.

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# CHAPTER 1

# INTRODUCTION

## A. General

Trifluoroacetic acid was originally prepared by oxidizing nitrotrifluoromethylcyclohexane or trifluorotoluidine with nitric acid (1), and is now made commercially by the electrochemical fluorination of acetic acid, acetic anhydride or acetyl fluoride in liquid hydrogen fluoride. The pure substance is a colourless, volatile, mobile liquid with a pungent smell. It is extremely hygroscopic, and the azeotrope formed with water boils at a higher temperature than either of the components (2). Although its derivatives are less poisonous than the corresponding monofluorocompounds (3), trifluoroacetic acid is not a pleasant substance to handle, and even its fumes have a vicious attack on the skin.

The solvent properties of trifluoroacetic acid have been the subject of a recent, brief review (4).

## B. Purification

The main impurity in the commercial acid is water. Simons and Lorentzen (5) used repeated fractional crystallization and obtained an acid freezing at -15.25°C, with a specific conductance of $\sim 4 \times 10^{-8}$ $ohms^{-1}$ $cm^{-1}$. Conway and Vijh (6) distilled the acid from boron trioxide to obtain a satisfactory product. Many workers have distilled the acid directly from phosphorus pentoxide, undoubtedly leading to contamination with the anhydride, and this may account for the slightly low values of the dielectric constant found by

TABLE I

Physical Properties of Trifluoroacetic Acid

(Values are at 25°C unless otherwise stated)

| Property | Value | Reference |
|---|---|---|
| Boiling Point (°C) | 71.78 | 10 |
| | 72.4 | 11 |
| | 71.0 | 5 |
| Melting Point (°C) | -15.25 | 5 |
| | -15.2±.05 | 10 |
| | -15.216 | present work |
| Enthalpy of Vapourization | 33,999[a] | 10 |
| at boiling point | 34,700[b] | 11 |
| (joules mole$^{-1}$) | | |
| Entropy of Vapourization | 98.53[c] | 10 |
| at boiling point | 100.8[d] | 11 |
| (joules mole$^{-1}$) | | |
| Molal Cryoscopic Constant (°C) | 6.458 | present work |
| Enthalpy of Fusion (calc) | 9,750[e] | present work |
| (joules mole$^{-1}$) | | |
| Enthalpy of Formation (liq.) | 1.059x10$^{6}$ [f] | 12 |
| (joules mole$^{-1}$) | | |

a 8.126 kcal mole$^{-1}$
b 8.30 kcal mole$^{-1}$
c 23.55 cal deg$^{-1}$ mole$^{-1}$
d 24.1 cal deg$^{-1}$ mole$^{-1}$
e 2.33 kcal mole$^{-1}$
f -253±.8 kcal mole$^{-1}$

TABLE I (cont.)

| Property | Value | Reference |
|---|---|---|
| Density (g $ml^{-1}$) | 1.4775 | 2 |
| | 1.4785 | 10 |
| | 1.4788 | 13 |
| | ($d=1.5375-.002346t^{o}C$) | " |
| | 1.489 | 14 |
| Molar Volume | 77.125 | 10 |
| (cc. $mole^{-1}$) | ($V=72.265+.10635t$ | |
| | $+3.253x10^{-4}t^{2}$) | |
| Refractive Index | 1.283 | 15 |
| ( $n_D^{25}$ ) | | |
| Dipole Moment (gas) | $2.28x10^{-18}$ | 20 |
| (e.s.u.) | | |
| Dielectric Constant | 8.40 | 17 |
| | 8.32 | 7 |
| | 8.25 | 8 |
| | 8.2 | 18 |
| | 40.8 | 19 |
| Viscosity (centipoise) | .8565 | 2 |
| | .880 | 14 |
| Surface Tension | 13.527 | 13 |
| (dynes $cm.^{-1}$) | ( $\gamma=15.638-.08444t^{o}C$) | |

TABLE I (cont.)

| Property | Value | Reference |
|---|---|---|
| Specific Conductance ($ohm^{-1}$ $cm.^{-1}$) | $.24 \times 10^{-6}$ | 14 |
| | $.3 \times 10^{-6}$ | 21 |
| | $.048 \times 10^{-6}$ | 5 |
| | $.0064 \times 10^{-6}$ | present work |
| Limiting Equivalent Conductivity in water ($cm.^2$ $ohm^{-1}$ $equiv.^{-1}$) | 388 | 22 |
| $pK_a$ in water | .175 | 22* |
| $H_o$ | -3.03 | 23 |
| | -2.77 | 9 |
| Critical Temperature (°C) | 218.13 | 25 |
| Critical Pressure (atm.) | 32.15 | 25 |
| Critical Volume (l $mole^{-1}$) | .204 | 25 |

* Data re-interpreted by present author.

Danhauser and Cole (7), and by Fialkov (8). Taylor et al. (9) have recommended distillation over silver trifluoroacetate to remove possible traces of hydrogen chloride. The purification procedures adopted in the present work are described later.

C. Physical Properties

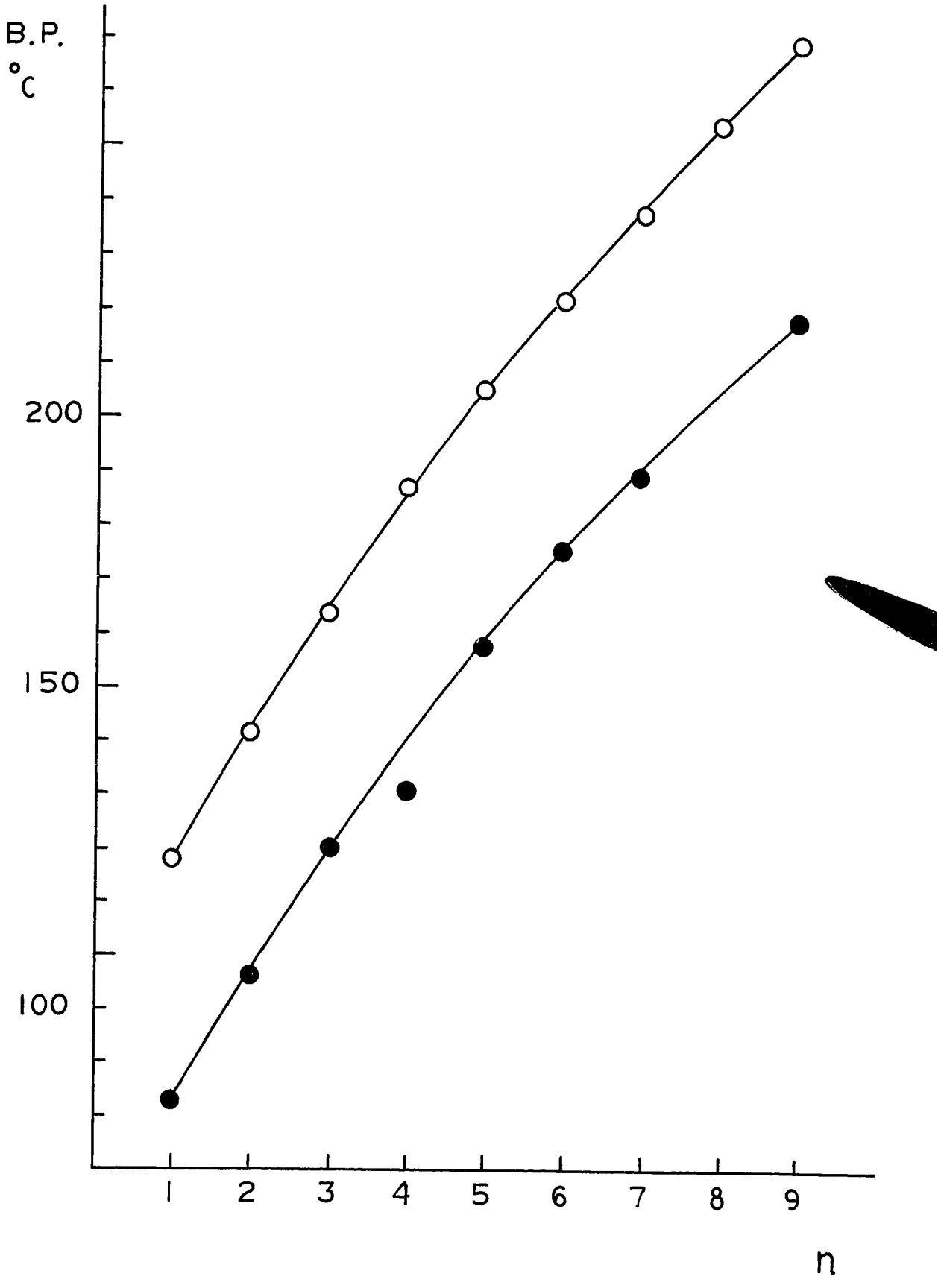
The physical properties of trifluoroacetic acid are summarized in Table I. The acid has a convenient liquid range of about 85°C, and the boiling point is 71.78°C. The higher value of 72.4°C was shown by Kreglewski (10) to be due to traces of water. The boiling points of perfluoro- acids are usually about 50°C lower than those of the parent hydrocarbon acids, and so trifluoroacetic acid is normal in this respect (Fig. 1).

A low boiling point reflects, among other things, low molecular polarizability, and consequently a low refractive index might be expected. That of trifluoroacetic acid is the lowest of all compounds listed in the "Handbook of Chemistry and Physics". The dielectric constant is related to refractive index, and most authors have found a value of about 8.3, the high value of Simons and Lorentzen (40.8) being attributed to electrode polarization. Though long recognized as seriously in error, Simons and Lorentzen's result has led to confusion in the literature as late as 1971 (26). Most of the other measurements are open to objection. Danhauser and Cole (7) used stainless steel electrodes which were attacked by the acid. Their results were frequency

Figure 1

Boiling points of alkyl- and perfluoroalkyl- carboxylic acids as a function of number of carbon atoms in the alkyl chain.

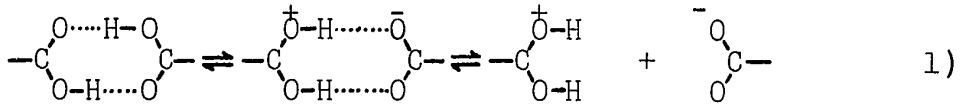
- o $C_nH_{2n+1}CO_2H$
- • $C_nF_{2n+1}CO_2H$


B.P.
°C
200
150
100
1
2
3
4
5
6
7
8
9
n

independent only above 1000 c.p.s., and showed a peculiar temperature variation. Fialkov (8) and Tedder (18) used acid of rather high conductance. The best value seems to be that of Harris and O'Konski (17), who used platinum electrodes and fairly pure acid. The dielectric constant they obtained was frequency independent above 50 c.p.s. and had a normal temperature coefficient.

Accurate knowledge of the dielectric constant of a medium is vital for electrochemical studies. It determines the upper limit of concentration for which current theoretical treatments of electrolyte solutions are applicable and is an important parameter in such treatments. Fuoss (27) has calculated that at concentrations above $3.2 \times 10^{-7} D^3$ solute ions associate, not only to ion pairs, but also to ion triplets and higher aggregates, and only approximate treatments are available. For trifluoroacetic acid (D=8.40), this means that useful information can be obtained only from measurements at concentrations below about $1.9 \times 10^{-4}$ molar, and raises enormous practical difficulties in so very hygroscopic a medium.

Even after rigorous purification, trifluoroacetic acid retains a slight conductance. This is probably due to self-ionization as suggested by Latimer (28) for other carboxylic acids, and may be represented schematically as:-



hydrogen-bonded ion pair

1)

It could also arise from ionic self-dehydration, similar to that found by Gillespie (29) for sulphuric acid:-

$$3CF_3CO_2H \rightleftharpoons H_3O^+ + CF_3CO_2^- + (CF_3CO)_2O \qquad 2)$$

trifluoroacetic anhydride

Conductimetric titrations of the anhydride with water (21, present work) are not sensitive enough to rule out the possibility of reaction 2) occuring to some extent, and no thermochemical data exist from which the position of equilibrium might be calculated. Throughout this work, reaction 1) is assumed to be the dominant one, but the evidence for this is neither more nor less conclusive than for other carboxylic acids.

In water, trifluoroacetic acid is moderately strong, and its $pK_a$ has been definitely established as 0.175 by conductance measurements (22). Unfortunately, the authors used the Ostwald dilution law to extrapolate their data, and obtained $pK_a$=0.231 (the value of 0.175 has been obtained using the Fuoss 1965 conductance equation (30)). The work of (22) has been criticized by Redlich et al. (31), who obtained a $pK_a$ of -0.255 by N.M.R. measurements, while Kreevoy and Mead (32) found $pK_a$=-0.51 from a Raman study. The N.M.R. work assumed that the proton resonance would be affected only by the relative amounts of $H_2O$, $H_3O^+$, and $CF_3CO_2H$. This seems unlikely in view of Peterson's report that the position of the $CF_3CO_2H$ proton signal in ether solutions is shifted as much as 0.3 p.p.m. by hydrogen bonding effects alone (33) Criticisms of the spectral measurements have received

extensive discussion (34). By indirect, empirical methods, Goulden (35) estimated $pK_a$=0.3, and Brownstein and Stillman (36) suggested a value of 4.75. Högfeldt (37) has proposed an elegant way of correlating $pK_a$ with $H_o$ values in aqueous solution, and found $pK_a$=-0.15. He used the $H_o$ values of Randles and Tedder (38), which are probably in error (24). Grunwald and Haley (16) used differential refractometry to estimate $pK_a$=-0.41 at 22°C, but the validity of the theoretical treatment is not clear.

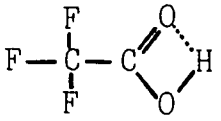
The exact value of the Hammelt acidity function is disputed ($\sim$-3.1 (23,24); -2.77 (9)), but it seems that the anhydrous medium is more acidic than formic acid ($H_o \sim$-2.2), and much less acidic than liquid hydrogen fluoride ($H_o \sim$-11) or sulphuric acid ($H_o$=-12.08), (39;40, pp. 64,158). Direct comparison with acetic acid is not possible, as a reliable value of $H_o$ for this solvent is not available (see discussion in (4), pp. 311-314).

D. Physical Properties and Structure

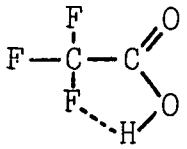
i) The molecule and the vapour state

Early electron diffraction work by Karle and Brockway showed that trifluoroacetic acid is largely associated in the vapour state as a cyclic dimer (41). They deduced the parameters listed in Table II. Gibbs and Smyth (20) estimated the dipole moment of the monomer as $2.28 \times 10^{-18}$ e.s.u., from dielectric constant measurements on the hot vapour. This is a higher value than would be expected from structure I below, where the $CF_3$ and carboxyl group moments

would oppose each other, and the alternative H-F bonded structure II has been proposed (42)



I



II

An infra-red and Raman study of the vapour by Josien et al. (44,45) gives $\nu_{OH}$ = 3587 cm.$^{-1}$ for the monomer and 3000 cm.$^{-1}$ for the dimer. The frequencies are reduced by a factor of about 1/1.3 in the deuterated compound.

TABLE II

Molecular parameters for trifluoroacetic acid

| Parameter | Monomer | Dimer |
|---|---|---|
| F - C distance | 1.36 ± .05Å | 1.36 ± .03Å |
| F–C–F angle | 110 ± 4° | |
| C - C distance | | 1.48 ± .03Å |
| O–H···O distance | | 2.73 ± .05Å |
| O–H···O angle | | 130 ± 3° |

Various estimates of the thermodynamics of the process:-

$$2\ CF_3CO_2H\ (g) \rightleftharpoons (CF_3CO_2H)_2\ (g)$$

have been made. Spectral measurements by Dunken and Marx (46) give $\Delta H = -17.0 \pm .7$ kcal/mole, $\Delta S = -41.6 \pm 3$ e.u., but Kagarise (47) suggests $\Delta H = -13.7$ kcal/mole. Vapour density measurements (48) give $\Delta H = -14.0$ kcal/mole and $\Delta S = -36.5$ e.u.

Lundin et al. (49) studied a number of carboxylic acids by a vapour pressure method, and deduced the parameters in Table III

TABLE III

Thermodynamics of the process:-

$$(RCO_2H)_2 \rightleftharpoons 2\ RCO_2H$$

at 160°C

| Acid | $K_{diss}$ | $\Delta H$ (kcal/mole) |
|---|---|---|
| $CF_3CO_2H$ | 7.4 | 14.0 |
| $HCO_2H$ | 5.5 | 14.1 |
| $CH_3CO_2H$ | 1.8 | 13.8 |
| $n\text{-}C_3H_7CO_2H$ | 1.6 | 13.9 |
| $n\text{-}C_6H_{13}CO_2H$ | 1.65 | 13.3 |
| $(CH_3)_3CCO_2H$ | 1.1 | 14.0 |

The very small variation in $\Delta H$ (hydrogen bond strength of the dimer) is surprizing, and has not been convincingly explained.

Both the vapour pressure and the vapour density measurements showed significant deviation at lower temperatures from the predicted values for a monomer/dimer equilibrium. The authors suggested the existence of more highly associated forms in the vapour near the boiling point of the liquid, perhaps analogous to the tetramers established for acetic acid (50).

ii) The liquid state

While classical theory treated liquids by an extension of the concepts of an ideal gas, modern theory regards them as disordered solids. There are, however, virtually no data for solid trifluoroacetic acid, not even a direct measurement of the heat of fusion. The structures of many salts have been determined, but that of the solid acid is unknown, although an N.M.R. study suggests that it is different from those of trichloro- and tribromoacetic acids (51). Some information on the liquid may be obtained from the published physical properties and spectral data, as below.

The molar refraction of a substance is defined as:-

$$[R] = \frac{M}{d} \frac{(n^2-1)}{(n^2+2)}$$

where M is the molecular weight, d the density, n the refractive index. It is often taken as a measure of the

actual space occupied by the molecules. With $n_D^{25} = 1.283$, $[R] = 12.7$ ml. for trifluoroacetic acid. This implies that about 83% of the bulk of the liquid is 'empty space' at room temperature. If the 12.7 ml. were made up of N similar spheres (N = Avogadro number), then each sphere would have a radius of 1.72Å, a figure remarkably close to the "average effective molecular radius" of 1.84Å found by Marks from the velocity of sound in the acid (52).

Othmer (53) has found linear relations between the physical properties and various functions of the critical constants of a liquid, often using an intermediate reference substance as standard. Not only may such relations be used for the extrapolation of data, but, providing the reference substance is well chosen, slight changes in the liquid state show up as discontinuities in the otherwise linear plots. Thus plots for water all show a discontinuity at about 30°C, which Raman and N.M.R. studies indicate is due to the rather sudden onset of free rotation of the water molecules (54, p.4; 55). Fig. 2 shows two such plots for trifluoroacetic acid.

a) is a graph of log $P'_{acid}$ against log $P'_{ref}$ where $P'_{acid}$ is the reduced vapour pressure of trifluoroacetic acid (vapour pressure/critical pressure) at a particular reduced temperature ($T/T_{critical}$), and $P'_{ref}$ is the reduced vapour pressure of the reference substance (here $C_2F_6$) at the same reduced temperature. The plot is accurately linear over the entire liquid range of the acid (-15 to +70°C), with a

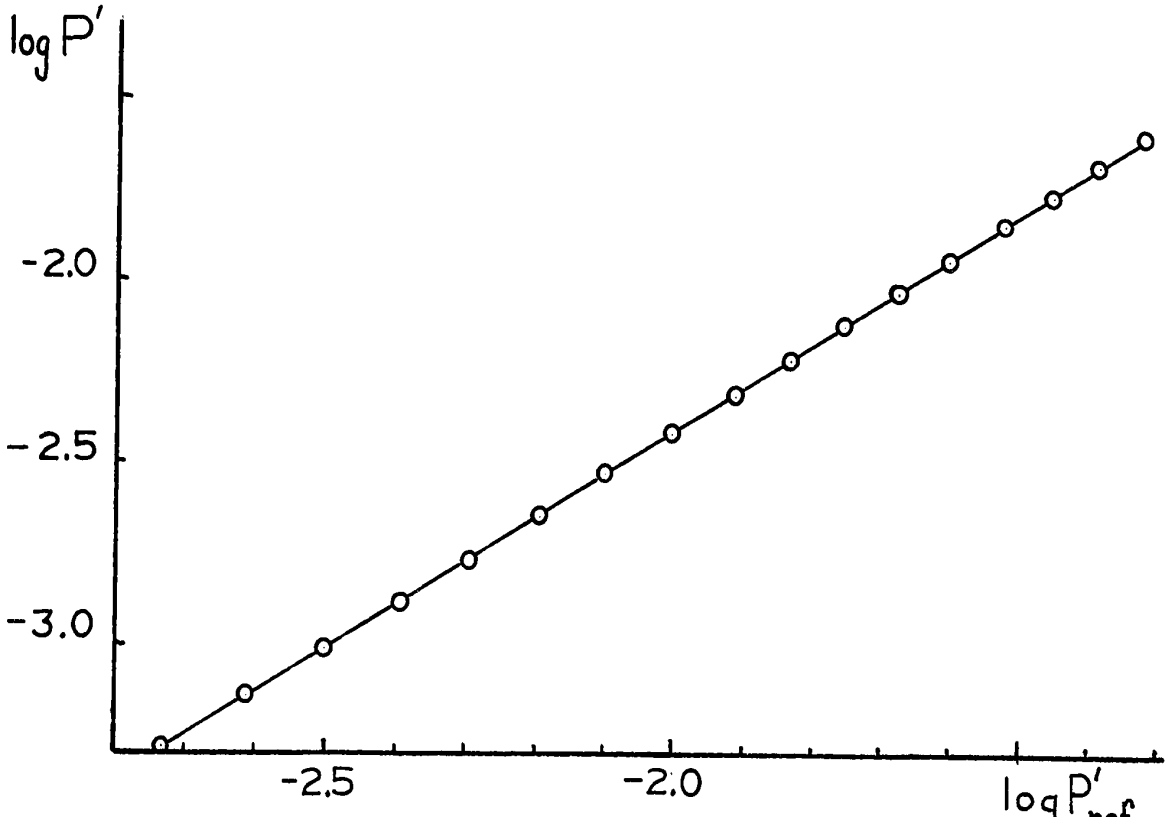
Figure 2

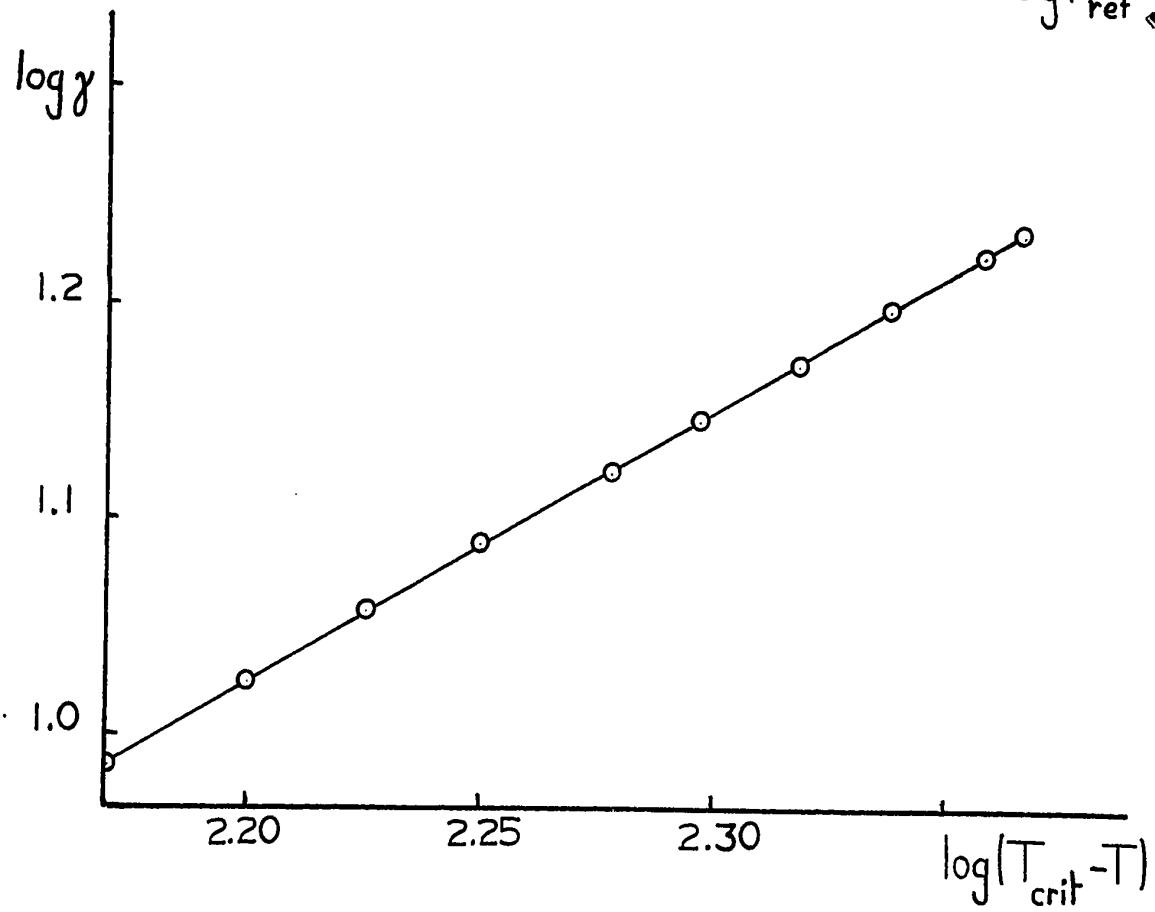
Othmer-type plots for trifluoroacetic acid

a) $\log P'_{acid}$ vs. $\log P'_{ref}$

b) $\log \gamma$ vs. $\log(T_{crit}-T)$

(see text for explanation of symbols)


log P'
-2.0
-2.5
-3.0
-2.5
-2.0
log P'ref


log γ
1.2
1.1
1.0
2.20
2.25
2.30
log (Tcrit - T)

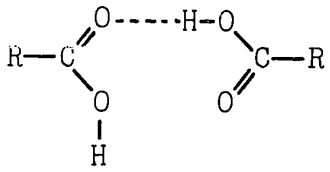
standard deviation of only ±.024% from the best straight line.

b) is a graph of $\log\gamma$ against $\log(T_{crit}-T)$ where $\gamma$ is the surface tension of the acid, and is also linear.

The Othmer-type plots, then, establish that the structure of trifluoroacetic acid is essentially unchanged over the entire liquid range. Unfortunately they do not say what that structure actually is, and it has usually been supposed that the liquid consists of the same monomers and cyclic dimers found in the vapour phase. By comparing the infra-red spectra of a number of substituted carboxylic acids in the liquid and vapour phases and in carbon tetrachloride solution, Barceló and Otero were able to make detailed assignments of the main bands (56). The sharp band found at 3587 $cm.^{-1}$ in the hot vapour and 3668 $cm.^{-1}$ in $CCl_4$ is attributed to the O-H stretch of the monomer, and is entirely absent in the pure liquid. The O-H---O stretching vibration of the dimer occurs at 3150 $cm.^{-1}$ in the hot vapour, 3144 $cm.^{-1}$ in $CCl_4$, and 3240 $cm.^{-1}$ in the liquid. The carbonyl stretch is found at the unusually high frequency of 1843 $cm.^{-1}$ in the monomer, and 1776 $cm.^{-1}$ in the dimer, while other frequencies down to 261 $cm.^{-1}$ have also been accounted for. A study of the far infra-red spectrum has also been made (57), but detailed assignments are not offered by the authors.

A more recent infra-red investigation by Murty and Pitzer (58) led to a rather different picture of the liquid. While admitting that cyclic dimers predominate in

the vapour and in very dilute solution in non polar solvents, the authors claim that linear polymers and open dimers of the type:-



are the most probable species at concentrations above $10^{-3}$ molar, and in the pure liquid. The argument turns on the breadth of the O-H dimer stretching frequency, the presence of a shoulder on the carbonyl band, and change of the spectrum when the acid is diluted. The interpretation has been criticized by Josien et al. (59) whose careful and extensive study showed that some of Murty's results were due to the formation of complexes with the solvents used, but later work by Murty (60) tends to support his original idea.

Some insight may be gained from dielectric studies. Thyrion and Decrooq (61) measured the dielectric constant of solutions of trifluoroacetic acid in cyclohexane over the concentration range $4.5 \times 10^{-3}$ to $6 \times 10^{-2}$ molar. They assumed that the acid dimerizes, and deduced:-

$$\frac{(D-D')}{C} \approx (D_m-D_d)V\sqrt{\frac{1}{2K}}\cdot\sqrt{\frac{1}{C}} + (D_d-D')V$$

where D is the dielectric constant of the mixture

D' " " " " " " " solvent

$D_m$, $D_d$ are the dielectric constants of the

monomer and dimer at infinite dilution.

V is the molar volume of the solute, and C its concentration

$$K = [\text{Dimer}] / [\text{Monomer}]^2$$

They found that a plot of $(D-D')/C$ against $\sqrt{1/C}$ was indeed linear, and from slope and intercept deduced that

$$D_{dimer} = 1.62$$
$$K \approx 320$$

This value for the dielectric constant of the dimer is approximately equal to the square of the refractive index of the acid ($(n_D^{25})^2 = 1.646$), as would be expected if the dipole moment of the dimer were zero. The work seems to contradict the conclusions of Murty mentioned above, but the linearity of Thyrion's plots may be fortuitous.

If the acid does indeed consist largely of cyclic dimers, then the observed dielectric constant of 8.4 is much larger than anticipated. Harris and Alder (62) have suggested that the high value arises from the presence of hydrogen-bonded ion pairs in the liquid,

$$(CF_3CO_2H)_2 \rightleftharpoons CF_3CO_2H_2^+ \cdot {}^-O_2CCF_3$$

and have deduced $\Delta H$ and $\Delta S$ for the ionization from the temperature coefficient of the dielectric constant. Their values lead to an ionization constant of about $1.13 \times 10^{-2}$, and hence an ion pair concentration of $\sim 0.74$ molar in the pure liquid. There are two serious objections to this.

First, additional infra-red bands from the O-H stretching vibration should be observed, and are not. Although unexplained 'satellite' lines do occur in the OH region, these persist in the vapour phase, and cannot be due to ion pairs. Second, the supposition predicts an impossibly high conductance of the liquid. Fuoss (27, p.213) has calculated that the dissociation constant of an ion pair in a solvent of dielectric constant, D, is given by

$$\frac{1}{K_{diss}} = \frac{4\pi Na^3}{3000} \times \exp(e^2/DkTa)$$

where 'e' is the charge on the electron, and 'a' the distance of closest approach of the ions, approximately equal to the sum of the ionic radii. Substituting a value of 'a' = 3.64Å ( = twice molecular radius of $CF_3CO_2H$) leads to $K_{diss} = 3.5 \times 10^{-7}$. Assuming that

$$[\text{ions}] \approx \sqrt{\{K_{diss} \times [\text{ion pair}]\}}$$

then

$$[\text{ions}] \approx \sqrt{\{3.5 \times 10^{-7} \times 0.743\}}$$
$$\approx 6 \times 10^{-4}$$

With the equivalent conductivity conservatively estimated as about 30, a specific conductivity of $\sim 18 \times 10^{-6}$ ohm$^{-1}$ cm.$^{-1}$ is predicted some 3000 times greater than the observed value of $\sim 0.006 \times 10^{-6}$ ohm$^{-1}$ cm.$^{-1}$.

It thus seems difficult to reconcile the observed dielectric constant of trifluoroacetic acid with the hypothesis of extensive cyclic dimer formation in the liquid. If

on the other hand, no assumption is made about the nature of the species present, then the Harris-Alder equation for dielectric constant (54, p. 10) may be used.

$$\frac{D_o-1}{D_o+2} = \frac{D_\infty-1}{D_\infty+2} + \frac{4\pi Nd\mu^2}{3MkT} \cdot \frac{3D_o}{(D_o+1)(D_o+2)} \quad g$$

where $D_o$ is the observed (static) dielectric constant

$D_\infty$ " " dielectric constant at optical frequencies, $\approx 1.1(n_D)^2$ (63)

$$\mu = \left(\frac{D+2}{3}\right)^2 \mu_o \qquad (64)$$

$\mu_o$ is the dipole moment of the gaseous molecule

M is the molecular weight

d is the density

g is a structural correlation factor.

With the data for trifluoroacetic acid, this gives g = 0.55. g is expected to be 1.0 for non-associated liquids, greater than 1 for liquids associated in a 'head to tail' manner, and less than 1 where dipoles are oriented against each other. The value for the acid may be compared with the figures 0.7 (pyridine, contra-association), 1.0 (chloroform, unassociated), 2.5 and 3.6 (water, HCN, 'normal' association).

Summarizing, liquid trifluoroacetic acid was at first thought to consist mainly of closed cyclic dimers, but this is not consistent with the latest spectroscopic work, or the dielectric constant. The latter may be interpreted in terms of extensive 'contra-association' of the molecules

without necessarily invoking closed dimeric species.

E. Donor Properties, Solubilities, Compound Formation

The presence of a $CF_3$- group drastically reduces the availability of the carbonyl oxygen's lone pair of electrons and trifluoroacetic acid has essentially no donor properties. This reduction of basicity seems to be quite general for groups alpha to a perfluoro-alkyl group. Simons and Lorentzen, for example, have shown that $(C_4F_9)_3N$ is a non-electrolyte in trifluoroacetic acid, whereas $(C_4H_9)_3N$ seems to be fully protonated (5). From studies in $HSO_3F/SbF_5$ mixtures, Levy et al. (65) estimated the $pK_b$ of $CF_3CO.CH_3$ as 14.9. Satchell (66) studied the proton availability in carboxylic acid/$SnCl_4$ mixtures, which he concluded decreases in the order:-

$$CH_3CO_2H > ClCH_2CO_2H > Cl_2CHCO_2H > CF_3CO_2H$$

This was interpreted by the author as suggesting increasing reluctance of the carbonyl oxygen to co-ordinate to the tin. Olofssohn (67-69) has measured the heats of reaction of various esters with antimony pentachloride to give 1:1 complexes. A selection of the results is given in Table IV.

Iodine dissolves in trifluoroacetic acid to give a pale violet solution, not the intense brown colour (charge transfer) usually associated with oxygenated solvents. Buckles and Mills (70) have measured the wavelength of the absorption maximum of $I_2$, ICl, and $Br_2$ in various solvents, and have also shown that the compounds $R_4NI_3$ exist entirely

TABLE IV

Heat of reaction for the process:-

$RCO_2R' + SbCl_5 \longrightarrow RCO_2R'.SbCl_5$

| Ester | $\Delta H$ (kcal/mole) |
|---|---|
| $HCO_2Et$ | 17.22 |
| $CH_3CO_2Me$ | 16.60 |
| $CH_2ClCO_2Et$ | 12.80 |
| $CHCl_2CO_2Et$ | 9.35 |
| $CCl_3CO_2Et$ | 3.05 |
| $CF_3CO_2Me$ | 2.70 |

as $R_4NI$ and $I_2$ in trifluoroacetic acid (71). Table V shows some typical results.

TABLE V

Wavelength of the absorption maximum (m.micron) of halogen compounds in solution

| Solvent | $I_2$ | | ICl | $Br_2$ |
|---|---|---|---|---|
| $H_2SO_4$ | 502) | brown | 442 | 405 |
| $CH_3CO_2H$ | 478) | | 362 | 400 |
| $CF_3CO_2H$ | 512) | | 450 | 411 |
| $CCl_4$ | 517) | violet | 460 | 417 |
| Vapour phase | 520) | | - | |

It is seen that $CF_3CO_2H$ more nearly resembles $CCl_4$ than $CH_3CO_2H$. Voigt (72) has shown that the position of the maximum is directly related to the ionization potential of the solvent.

The experimental evidence makes it clear that trifluoroacetic acid is a very weak base, unlikely to be protonated except by the strongest of acids, and its low conductance ($6 \times 10^{-8}$ ohm$^{-1}$ cm.$^{-1}$) is not surprizing. Semi-empirical calculations of the charge distribution in the molecule (42,43) suggest that the hydroxyl oxygen atom may be more susceptible to protonation than that of the carbonyl function.

Solubility phenomena are intimately related to the donor properties of the solvent, but quantitative treatments are possible only for the simplest cases. Two trends, however, may be expected for trifluoroacetic acid. Because of the poor donor properties of the solvent, lattice energy effects will be more pronounced. For the same reason cation solvation will be rather small, but solvation of the anion (or of the negative end of the ion pair) could be important. These features are illustrated by the data of Cady and Hara (73), reproduced in Table VI. Salts of high lattice energy (e.g. divalent metal sulphates) or with anions of low polarizability (perchlorates, periodates) are almost insoluble, as are many salts with some covalent character (e.g. $HgCl_2$). The solubility rises with polarizability of the anion, but here another effect enters; the salt may react with the solvent. Thus evaporation of solutions of the alkali metal chlorides gives the trifluoroacetates and hydrogen chloride.

In view of the low solubilities of the perchlorates ($Na < 0.1$ g/100 g) the solubility of lithium perchlorate (11.6 g/100 g) is anomalous (74). Lithium salts, however, are well known to be peculiar. The solubility of the perchlorate corresponds to a mole fraction of 0.111, which may be compared to the value of 0.3 - 0.5 found in non-fluorinated carboxylic acids, and in alcohols, ethers and ketones. The interest is not so much in the high solubility of lithium perchlorate relative to other perchlorates, but in its rather

TABLE VI

Approximate solubilities of salts in trifluoroacetic acid

25°C

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Amount dissolved greater than 10 g anhydrous salt per 100 g $CF_3COOH$

Acetates: Na, K, $NH_4$, Sr, Ba, Cd, Hg(II), Cu(II), Co(II), Ni, Pb(II).

Other salts: CsCl, $NH_4NO_3$, $K_2SO_4$, $K_3PO_4$

Amount dissolved from 1 to 10 g anhydrous salt per 100 g $CF_3COOH$

Fluorides: Na, K, Ba, Cu(II), Ag(I), Cd

Chlorides: Na, K, Mg, Ca, Fe(III)

Bromides and iodides: Na, K, Ca

Sulfates: Na, $NH_4$

Nitrates, nitrites, oxalates, chlorates, bromates, iodates, acid sulfates, and dichromates of Na and K

Thiocyanates: Na, K, $NH_4$

Phosphates: Na, Ca, Co, Zn, $HPO_4$ and $H_2PO_4$ salts of Na, K, Ca

Chromates: Na, K, Ca, Ba, Pb, Co, Zn

Others: $KMnO_4$, $K_4Fe(CN)_6$, $CrO_3$, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_6]Cl_2$, $[Co(NH_3)_5H_2O](NO_3)_3$, trans-$[Co(NH_3)_4(NO_2)_2]Cl$, trans-$[Co(NH_3)_4NO_2Cl]Cl$, $[Co(NH_3)_3(NO_3)_3]$

Amount dissolved from 0.1 to 1 g per 100 g $CF_3COOH$

Halogenides: $BeCl_2$, $SrCl_2$, $BaCl_2$, $CdCl_2$, $CoCl_2$, $CrCl_3$, $CdBr_2$, $CdI_2$, $MgF_2$, $NiF_2$

TABLE VI (cont.)

Others: $Ca(NO_3)_2$, $Ba(NO_3)_2$, $Cr_2(SO_4)_3$

Amount dissolved less than 0.1 g per 100 g $CF_3COOH$

Halogenides: $CaF_2$, $PbF_2$, $MnF_2$, $FeF_3$, AgCl, $ZnCl_2$, $AlCl_3$, $PbCl_2$, $HgCl_2$

Perchlorates: Na, K, Zn

Periodates: Na, K

Sulfates: Be, Mg, Ca, Ba, Zn, Ni, Co, Fe(II), Cu(II)

Other: $Ce_2(C_2O_4)_3 \cdot 9H_2O$, $BaS_2O_6 \cdot 2H_2O$

low solubility in trifluoroacetic acid compared to other solvents. This again is explained by the poor donor properties of the acid.

Cady (73) also measured the solubility of various trifluoroacetates in the anhydrous acid. The results are given in Table VII, together with n, the number of moles of solvent associated with one mole of the undissolved solid residue. The solubility decreases as the cation radius decreases, and as the oxidation state increases, i.e. with increasing surface potential of the cation. This is consistent with lattice energy being the dominant effect, but it should be remembered that the ion pair dipoles will be solvated and that both contact and solvent separated ion pairs may be present, together with single ions, triple ions, and perhaps higher aggregates. A quantitative treatment would be difficult.

The degree of solvation in the solid phase (n in Table VII) deserves attention. The existence of the solvates $CF_3CO_2Na.nCF_3CO_2H$, n= 1 or 2, has been confirmed by vapour pressure studies (75). A value of $\Delta H = 16 \pm 2$ kcal/mole was found for the monosolvate (c.f. $\Delta H = 14$ kcal/mole for dissociation of the acid dimer), and the second solvent molecule is much more weakly bound. The infra-red spectrum of the mono-solvate shows that the acid acquires considerable anionic, carboxylate character, and a more correct formulation is probably $NaH(O_2CCF_3)_2$. This would be consistent with the work of Golič and Speakman (76) who carried out an

TABLE VII

Solubilities of Trifluoroacetates at 29.8°C

| Solute trifluoroacetate of | Solubility g anhydrous salt/100 g $CF_3COOH$ | Solid phase apparent no. moles $CF_3COOH$/ mole of salt, n |
|---|---|---|
| Na | 13.10 ± 0.05 | 2.1 |
| K | 50.13 ± 0.31 | 1.0 |
| Mg | 0.57 ± 0.009 | 1.9 |
| Ca | 6.26 ± 0.07 | 3.8 |
| Sr | 23.19 ± 0.32 | 2.2 |
| Ba | 41.66 ± 0.66 | 3.5 |
| Zn | 0.87 ± 0.01 | 0.2 |
| Cd | 7.61 ± 0.12 | 0.1 |
| Hg(II) | 49.72 ± 0.20 | 0.4 |
| Ag(I) | 15.15 ± 0.08 | 0.1 |
| Cu(II) | 19.73 ± 0.08 | 0.1 |
| Al | 0.01 | 0.0 |
| La | 0.142 ± 0.006 | 3.1 |
| Ce(III) | 0.101 ± 0.004 | |
| Pr(III) | 0.084 ± 0.005 | 3.0 |
| Nd | 0.059 ± 0.002 | 2.6 |
| Th(IV) | 0.016 ± 0.002 | 0.4 |
| $UO_2^{2+}$ | 0.035 ± 0.003 | |
| Co(II) | 16.65 ± 0.17 | 1.7 |
| Ni(II) | 16.48 ± 0.24 | 1.7 |

X-ray study of the crystal structures of the salts $MH(O_2CCF_3)_2$, M= K, Rb, Cs. All three salts were monoclinic, with alternating layers of cations and anions. The rubidium and potassium salts were isomorphous, with a rather different structure from the caesium salt. Table VII suggests that the La, Ce, Pr and Nd salts may be $M^{III}(H(O_2CCF_3)_2)_3$, the Ni and Co salts $M^{II}(H(O_2CCF_3)_2)_2$. One can likewise account for two of the acid molecules in the alkaline earth salts. The curious alternation of n (2,4,2,4) in the series Mg, Ca, Sr, Ba may be an accident of the experimental conditions.

Zinc trifluoroacetate is unique among the compounds studied, apparently being amphoteric. By saturating trifluoroacetic acid simultaneously with the zinc and sodium salts, Cady increased the solubility of the former from 0.87 to 13.0 g/100 g, of the latter from 13.1 to 23.0 g/100 g. These increases are much larger than can be explained by ion association effects of the type discussed by Griswold et al. for acetic acid (77), and the solubilities of Mg, Nd, and surprizingly, Al trifluoroacetates were unaffected under the same conditions. In terms of moles, the increases are 0.0417 moles/100 g for Zn, 0.0727 moles/100 g for Na, a ratio of sodium to zinc of 1.75 to 1. This ratio is compatible with the equilibria:-

$$NaO_2CCF_3 + Zn(O_2CCF_3)_2 \rightleftharpoons Na\left[Zn(O_2CCF_3)_3\right]$$

$$NaO_2CCF_3 + Na\left[Zn(O_2CCF_3)_3\right] \rightleftharpoons Na_2\left[Zn(O_2CCF_3)_4\right]$$

but the extensive ionic association that occurs with even

TABLE VIII

Solubilities of gases in trifluoroacetic acid

| Gas | Temp., °C | Partial Pressure cm. Hg. | Solubility ml/ml | Solubility millimole/mole |
|---|---|---|---|---|
| $CO_2$ | 27 | 65.2 | 3.5 | 11.7 |
| CO | 26 | 64.6 | 0.0 | 0 |
| $Cl_2$ | 25.5 | 65.6 | 9.3 | 31 |
| HBr | 26 | 65.7 | 6.6 | 22 |
| HCl | 26 | 65.2 | 4.1 | 14 |
| $H_2S$ | 26 | 65.7 | 8.6 | 28.7 |
| $N_2$ | 26 | 63.6 | 0.1 | .33 |
| $N_2O$ | 24.5 | 66.5 | 4.3 | 14.3 |
| $O_2$ | 27 | 64.2 | 0.2 | .67 |
| $PH_3$ | 26 | 65.3 | 15.9 | 53 |
| $SO_2$ | 26 | 66.7 | 23.4 | 78 |

simple solutes in this solvent makes such an interpretation uncertain.

The approximate solubilities of a number of gases in trifluoroacetic acid have also been reported by Cady (78), and are reproduced in Table VIII. The absence of temperature or pressure data make thermodynamic interpretation impossible, and attempts to correlate the solubilities with the dipole moment or heat of sublimation of the gas give a fairly even scattering of points on the graph paper. Several qualitative observations may be made, however. Predictably, gases which react with water (e.g. HCl, $SO_2$, $CO_2$) are much less soluble in trifluoroacetic acid. Other gases have solubilities comparable to those found in benzene and carbon tetrachloride, and rather lower than in fluorocarbons (79). Gerrard and Macklen (80,81) have found that the solubility of hydrogen choloride in oxygenated solvents is a function of the electron density on the oxygen atom, and it is not surprizing that Cady's value for the gas in trifluoroacetic acid at 26°C (0.014 mole/mole), is much less than for formic, acetic, mono- or tri-chloroacetic acids (0.055, 0.125, 0.086*, 0.089* mole/mole respectively).

Although not a particularly strong acid, and with essentially no donor properties, trifluoroacetic acid forms a number of addition compounds, many of which appear to be hydrogen bonded. The compounds are listed in Table IX, together with the evidence for their existence.

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* Extrapolation to 26°C of data in (80)

TABLE IX

Molecular Addition Compounds of Trifluoroacetic Acid

| Compound | Evidence | Reference |
|---|---|---|
| $CF_3CO_2H.H_2O$ | 1) Freezing point<br>*2) Conductance etc. | 82<br>87 |
| $CF_3CO_2H.2H_2O$ | 1) Vapour density<br>*2) Conductance etc. | 83<br>87 |
| $CF_3CO_2H.4H_2O$ | Freezing point | 82 |
| $CF_3CO_2H.Dioxane$ | Vapour density | 83 |
| $CF_3CO_2H.CH_3CO_2H$ | 1) Vapour density<br>*2) Conductance, viscosity | 83<br>84 |
| $CF_3CO_2H.2CH_3CO_2H$ | * Viscosity | 84 |
| $CF_3CO_2H.CH_2ClCO_2H$ | * Viscosity | 84 |
| $CF_3CO_2H.H_2SO_4$ | * Density | 14 |
| $CF_3CO_2H.H_2S_2O_7$ | * Density | 85 |
| $CF_3CO_2H.2H_2S_2O_7$ | * Viscosity | 85 |
| $CF_3CO_2H.HClO_4$ | * Visc., and temp. coeff. of visc. | 86 |
| $CF_3CO_2H.2HClO_4$ | * " " | 86 |

* Compound claimed, to explain deviation of physical properties of mixture from additivity. Data are not internally consistent, and should be treated with caution

F. Reactions in Trifluoroacetic Acid

Trifluoroacetic acid is quite often used as a solvent for organic reactions, and offers considerable advantages where a moderately acidic, non-oxidizing medium is required. Peterson (88) has shown that solvolysis of 2-hexyl tosylate is about four times faster in trifluoroacetic than in formic acid, hitherto considered the best medium, this in spite of the difference in dielectric constant ($CF_3CO_2H$, 8.40; $HCO_2H$, 56.1 at 25°C). Brown (89) found that nitration, mercuration, and bromination of aryl compounds were much faster in trifluoroacetic than in acetic acid, showed simpler kinetics, and could be carried out on de-activated aryl rings even in the absence of mineral acid catalysts. It seems that trifluoroacetic acid may be a better solvating agent for nucleophilic leaving groups, and that a reaction such as:-

$$HNO_3 + 2CF_3CO_2H \rightleftharpoons NO_2^+ + H_3O^+ + 2CF_3CO_2^-$$

may occur spontaneously. The participation of ions, or at least ion pairs, is not inconsistent with the low dielectric constant of the solvent. Setkina (90) has shown by deuterium exchange that tertiary esters, for example, are extensively ionized in the acid.

The use of trifluoroacetic anhydride to acetylate sugars is commonplace, and the behaviour of the mixed anyhdride, $CF_3CO.O.OCCH_3$ has recently been investigated. Bonner (91,92) found that phenols react with the mixed anhydride to give the acetylated derivative almost exclusively, while alcohols give a mixture, with the trifluoroacetate

predominating. The kinetics are complicated but appear to rule out the participation of $CH_3CO^+$. The differences between alcohols and phenols are attributed to their relative nucleophilicities.

Trifluoroacetic acid, and especially its mixture with liquid sulphur dioxide, is a good solvent for proteins in the absence of air (93), and is even claimed to dissolve cell walls without extensive breakdown of the material (94). In the presence of air, the solutions turn purple. This surprizingly mild behaviour recalls that of liquid hydrogen fluoride (40,p. 76). The analysis of amino-acids by conductimetric titration in trifluoroacetic acid is discussed later.

The acid has not been used extensively as a medium for inorganic reactions, but Cady and Fujioka (78) have studied the action of a large number of substances on a total of twenty-five dissolved trifluoroacetates. Their results are summarized in Table X. The most surprizing feature is the failure of lead sulphide to precipitate (solubility product in water $3.4 \times 10^{-28}$ at 18°C) and this may be due to the formation of a complex with the solvent. The solubility of many lead salts in aqueous sodium acetate may be recalled.

The oxidizing powers of chromate and permanganate ions are rather less than in water. Potassium permanganate reacted with the solvent to give $CO_2$, $CF_3COF$, $COF_2$ and $SiF_4$. It has been shown that the initial product is $Mn_2O_7$ (95).

TABLE X

Reactions of Metal Trifluoroacetates

in Trifluoroacetic Acid Solutions

| Reactant | Product |
|---|---|
| HCl | Chloride ppt: |
| | Reaction, complete: Cd(II), Cu(II), Pb(II), Hg(II), Hg(I), Ni(II), Zn(II). All the ppt colors were white except for Ni(II) which was amber |
| | Reaction, nearly complete: Bi(III), Co(II), Mn(II), Sn(II). The Co(II) ppt was light blue, but the others were white. |
| | Reaction, partial: Fe(II), olive color |
| | Colloidal ppt: Ag(I), white, orange $CrO_2$ soln was converted to a red soln probably $CrO_2Cl_2$ |
| $H_2S$ | Sulfide ppt: |
| | Reaction, complete: Sb(III), Cd(II), Cu(II), Hg(II), and Hg from Hg(I), Ag(I) |
| | Reaction, nearly complete: Fe(II) soln and S from Fe(III), Sn(II), Zn(II) |
| | Reaction, partial: Bi(III) |
| | Colloidal ppt: As(III), orange $CrO_3$ soln was converted to a green soln of Cr(III) and $H_2SO_4$ |
| | The colors of the sulfides were the same as the colors obtained from ppt from aqueous media |

TABLE X (cont.)

| Reactant | Product |
|---|---|
| $HClO_4$ | Perchlorate ppt:<br>Reaction, complete: K<br>Reaction, nearly complete: $NH_4^+$, Cd(II), Hg(I), Ag(I), Na(I), Sr(II), Zn(II)<br>Reaction, partial: Sb(III), Ba(II), Bi(III), Cr(III), Co(II), Cu(II), Fe(III), Pb(II), Mg(II), Mn(II), Hg(II), Ni(II)<br>Colloidal ppt: As(III) (solid not identified)<br>Colbalt perchlorate was pink, copper perchlorate was light blue, nickel perchlorate was light green. All the other perchlorates were white. |

Sartori et al. (96-98) have prepared the tetrakis-trifluoroacetates of Si, Zr, Th and Hf by refluxing the chlorides in anhydrous trifluoroacetic acid. Titanium tetrachloride gave $3TiO(O_2CCF_3)_2.2CF_3CO_2H$ under the same conditions. The 4-valent tin and germanium compounds were obtained by the action of $Hg^I(O_2CCF_3)$ on the chlorides.

G. Electrochemistry and Acid-Base Equilibria

Since trifluoroacetic acid is moderately strong, it should be possible to use it as a solvent to differentiate the strengths of various acids which would be fully dissociated in water. This has been put to practical use by Kresze and Schmidt (99), who carried out conductimetric titrations of amino acids and peptides against anhydrous perchloric acid ($\sim$0.5N dissolved in $CF_3CO_2H$). The titration curves consisted of two straight lines, intersecting at 1:1. Ammonium chloride was found to act as a base, and the results were unaffected by small amounts (0-5%) of water. DeVries (100) has made successful potentiometric titrations of such weak bases as thiourea and nitroguanidine, using bimetallic Pt/Pt electrodes, but obtained erratic results when acetic acid was used as the medium.

These are practical uses. A fundamental study has been undertaken by Bessière (101,102), but his results are of doubtful use. The dissociation constants of a number of acids and bases were estimated by spectrophotometric methods using indicators, and the pK values used to calibrate glass and $Ag/AgClO_4$ electrodes in trifluoroacetic acid. A

scale of acid and base strengths in the solvent was derived. The methodology is sound, and the results have been commended in a recent review (4), but several very serious objections can be raised:-

1) The indicator method used (Kolthoff and Bruckenstein, (103)) contains assumptions of unproven validity in trifluoroacetic acid.

2) The measurements were made at high concentrations where the concentrations of triple ions of the type $M_2A^+$ and $MA_2^-$ are appreciable.

3) The solvent contained water ( ~36 p.p.m. or $10^{-3}$ molar) which may affect the results.

4) The effect of liquid junction potentials was ignored. Though this is understandable in so difficult a medium, the liquid junction between anhydrous trifluoroacetic acid and the aqueous filling of the glass electrode can hardly be dismissed.

5) The authors admit that the electrode potentials were not reproducible from one run to another.

These unattractive features invalidate most of the conclusions based on this work, including the claim that water (virtually a non-electrolyte, (5)) is a stronger base than the trifluoroacetates of sodium or potassium. A polarographic study by the same author has been mentioned, (private communication in (4)), but is not yet published.

The most careful attempt to study ionic processes in the acid is by Simons and Lorentzen (5), who measured the conductivities of several substances in trifluoroacetic acid,

both above and below the concentration limit for the formation of triple ions. The increases in conductivity produced by $(C_4F_9)_3N$, $(C_4H_9)_2O$ and water were negligible. The remarkable result for water is similar to that found in 100% nitric acid (104, and references therein), and will be discussed in detail when the results of the present work are discussed. It is possible that isolated $H_2O$ molecules are much less basic than bulk water, and are largely unprotonated.

The salt, $CF_3CO_2K$, and the amine, $(C_4H_9)_3N$ were both found to be electrolytes, though highly associated because of the low dielectric constant of the solvent. Simons and Lorentzen used a dielectric constant of 40.8, instead of 8.40, to extrapolate their results. Re-calculation by the 1965 method of Fuoss (30) leads to the following results:-

| | $\Lambda_o$ | $10^6$xDiss Const. | $\mathring{a}$ (Å) |
|---|---|---|---|
| $CF_3CO_2K$ | 59.5 | 4.19 | 4.9 |
| $(C_4H_9)_3N$ | 41.1 | 266 | 8.6 |

The exact values are uncertain, since the solutions certainly contained traces of water, and were in contact with mercury of unreported purity. However, it may be noted that the salt with the larger cation ($(C_4H_9)_3N^+$) has the smaller mobility and larger dissociation constant.

Fialkov (14) has found that $H_2SO_4$ raises the conductivity of 100% trifluoroacetic acid only very slightly, and concludes that $H_2SO_4$ is a non-electolyte in this solvent.

The same author (105) also claims that the $pK_a$ of $H_2S_2O_7$ in trifluoroacetic acid is 3.1, but the table of data to which he refers is unfortunately not included in the article. Gillespie (29) finds that $CF_3CO_2H$ lowers the conductance of 100% $H_2SO_4$, and attributes this to a decrease in the number of self-dissociation ions. Hyman (106) found that $CF_3CO_2H$ slightly raises the conductance of liquid hydrogen fluoride, but the results are erratic, and may be due to impurities.

Like other carboxylic acids, trifluoroacetic acid undergoes the Kolbe reaction, which has been carefully studied by Conway and Vijh (6,107). Electrolysis of $CF_3CO_2K$ in the anhydrous acid gave a 96% yield of $C_2F_6$. This yield was diminished by traces of water, due to the formation of an oxide film on the platinum electrodes The authors found no evidence for the participation of acyl or hydrogen peroxides, and established the mechanism as:-

$$CF_3CO_2^- \longrightarrow CF_3CO_2\cdot \longrightarrow CF_3\cdot + CO_2$$
$$\downarrow$$
$$C_2F_6$$

H. Miscellaneous

This section contains the results of a number of reports in the literature which have influenced the choice or interpretation of our experiments, or imposed limits on the experimental conditions.

Acyl derivatives

The most important acyl derivative is trifluoro-

acetic anhydride, which is easily prepared by distilling the acid from phosphorous pentoxide. It boils at 39.15°C, melts at -63.5°C and has a density of 1.464 g/cm.$^3$ at 25°C (10). The substance reacts vigorously with cold water (cf. acetic anhydride, which may be used in aqueous solution), and is excellent for drying solutions of the acid. Mixed anhydrides with other carboxylic acids may be prepared by mixing the anhydride with the appropriate acid, or preferably by the action of the acid on an acid imidazolide (108):-

$$CF_3CO_2H + \begin{matrix} N{=}C \\ | \quad N\text{-}CO\text{-}R \\ C{=}C \end{matrix} \longrightarrow RCO.O.COCF_3 + \begin{matrix} N{=}C \\ | \quad N\text{-}H \\ C{=}C \end{matrix}$$

A number of anhydrides with inorganic acids have also been characterized. The fluorosulphate derivative may be prepared by the oxidation of $CF_3COBr$ (109) or $(CF_3CO)_2O$ (110) with $S_2O_6F_2$

$$2CF_3COBr + S_2O_6F_2 \xrightarrow[12\ hr.]{3°C} 2CF_3CO.OSO_2F$$

$$(CF_3CO)_2O + S_2O_6F_2 \xrightarrow[20\ min.]{100°C} CF_3OSO_2F + CF_3CO.OSO_2F + CO_2$$

The physical properties of the compound have been extensively investigated. $^{19}F$ nuclear magnetic resonance gives the F(C) and F(S) peaks at +73.1 and -47.8 p.p.m. relative to $CFCl_3$ (109) and at +2.0 and -123.7 p.p.m. relative to $CF_3CO_2H$ external (110). The expected ratio of 3:1 is observed.

Delfino and Shreeve (109) find that $CF_3CO.OSO_2F$ is hydrolysed only slowly by 0.1 N sodium hydroxide at 100°C.

This is in marked contrast to trifluoroacetic anhydride itself, and to the compound $CF_3CO.OSO_2.OH$, prepared by mixing equimolar proportions of $SO_3$ and $CF_3CO_2H$, and distilling under reduced pressure (111). The latter compound reacts rapidly with water or alcohols to give the corresponding acids or esters, and with trifluoroacetic acid to give the anhydride and $H_2SO_4$.

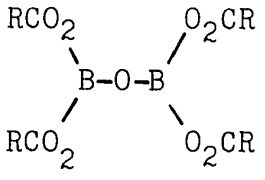
Park et al. (112) have prepared a mixed anhydride with nitrous acid by irradiating a mixture of $(CF_3CO)_2O$ and nitrosyl chloride.

$$(CF_3CO)_2O + NOCl \longrightarrow CF_3CO.ONO \quad (+CF_3COCl?)$$

The compound is a yellow liquid, boiling at 46°C (80 mm.), and decomposing at 200°C to trifluoronitrosomethane, $CF_3-N=O$. When trifluoroacetic anhydride and nitric acid are heated together to 100°C in a bomb, a 7% yield of fluoropicrin, $CF_3-NO_2$ is obtained (113). A mixed anhydride has also been prepared from iso-cyanic acid, though the structure has not been established (114)

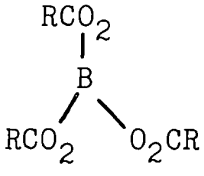
$$HNCO + (CF_3CO)_2O \longrightarrow CF_3CO.NCO + CF_3CO_2H$$

A number of compounds exist which may be regarded formally as mixed anhydrides. These include the trifluoroacetates of the group IV elements mentioned above (96-98) and the compounds $B_2O(O_2CCF_3)_4$ and $B(O_2CCF_3)_3$ claimed by Gerrard et al. (115,116). These can presumably be formulated as:-



I

and



II

The compound II is interesting, since it is a potential acid in trifluoroacetic acid as solvent:-

$$HO_2CCF_3 + B(O_2CCF_3)_3 \rightleftharpoons H^+\left[B(O_2CCF_3)_4\right]^-$$

Gerrard prepared the compounds by mixing $BCl_3$ and a carboxylic acid in a 1:3 molar ratio in n-pentane. All carboxylic acids except trifluoroacetic gave compounds of type I, which is also the product from the reaction of anhydrides with boric acid (120,121 and references contained in 115). The evidence for the compound II (R= $CF_3$) is not entirely satisfactory. The analyses lie between those expected for I and II, and the infra-red frequencies of II differ from those of I by only a few wave numbers. Kibbel (117-119) has repeated much of the work, confirmed the existence of compounds of type I, and prepared salts of the type $MB(O_2CR)_4$ and $MB_2O(O_2CR)_5$. He has also prepared ether derivatives of the compounds, and formulates the diethyl ether complex as $Et_3O^+\left[B(O_2CR)_3OEt\right]^-$. While apparently accepting Gerrard's claim for $B(O_2CCF_3)_3$, he seems to avoid discussion of the result.

Trifluoroacetic acid forms the amide, the nitrile, the acetanilide and a series of esters quite normally, and all the halides have been prepared (2). The bromide and

chloride are made by the action of $PCl_3$ or $PBr_3$ on barium trifluoroacetate, or from the benzoyl halide and the free acid the iodide by reacting $CF_3COCl$ with HI, and the fluoride by the electrochemical fluorination of acetyl fluoride. The bromide has also been prepared by the reaction of trifluoroacetic anhydride with bromine at high temperatures in the presence of carbon (122).

$$(CF_3CO)_2O + Br_2 + C \xrightarrow{150\text{-}650°C} CF_3CO.Br + CF_3Br + 2CO$$

All halides except the iodide (b.p. 22°C) are gases at room temperature.

What may be iodine trifluoroacetate, $IO_2CCF_3$, has been obtained as a silver complex, $AgI(O_2CCF_3)_2$, but never isolated (123-126). The tris-trifluoroacetate, $I(O_2CCF_3)_3$, has been made by the action of fuming nitric acid and trifluoroacetic anhydride on iodine (127).

Lindner and Krantz (128) have prepared thermally unstable adducts of the type:-

$$R_fCOF.MF_5 \quad (R_f = CF_3,\ C_2F_5;\ M = P,\ As,\ Sb)$$

by metathesis between RCOBr and $AgMF_6$.

They formulate the antimony compound as $CF_3COF.SbF_5$ at room temperature, but ionic $CF_3CO^+SbF_6^-$ in liquid sulphur dioxide below -25°C. If this is correct, the compound would be the only known cationic trifluoroacetyl derivative, analagous to the $CH_3CO^+$ salts studied by Olah et al. (129,130), but the evidence, which turns on the anomalous temperature variation of solution conductance, is not entirely satisfactory.

Salts

Swarts prepared a large number of trifluoroacetates by standard techniques (1,131,132) and many others have since been added (e.g. 73,133). Baillie (133) measured the magnetic properties of the solid salts, and the infra-red and ultra-violet spectra of solutions in nitromethane. The results indicate that salts have essentially octahedral co-ordination of the cations by oxygen. The infra-red spectra of the potassium and caesium salts are particularly simple, consisting of the spectrum of the $CF_3CO_2^-$ ion, with an additional band assigned to the metal-oxygen stretch at 150 $cm.^{-1}$ (K) or 115 $cm.^{-1}$ (Cs). Magnetic measurements by Thompson and Yawney (134) show that $Cu(O_2CCF_3)_2$ is not dimeric, unlike $Cu(O_2CCH_3)_2$. An X-ray study by Cruickshank (135) shows that the ammonium salt is strongly hydrogen bonded. Among the more exotic salts prepared are trifluoroacetates of xenon (136), plutonium (137) and graphite (95).

Pyrolysis

Trifluoroacetic acid is not particularly sensitive to heat, but is decomposed at high temperatures to a variety of products, including $CF_3COF$, $COF_2$, $(CF_2)_n$, and $CF_3CO_2CHF_2$ (138). Pyrolysis of the anhydride does not lead to difluoroketene (139).

The trifluoroacetate salts are much less stable to heat than the acid, and are best dried in vacuo at temperatures not exceeding 50°C. Baillie (133) has characterized the major decomposition products. Although Swarts (131) reported that the well-known reaction of carboxylic acids:-

$$RCO_2Na + NaOH \longrightarrow RH + Na_2CO_3$$

did not appear to work for sodium trifluoroacetate, La Zerte (140) obtained $CHF_3$ in 5 moles % yield by heating the materials together in a sealed tube. Other products were $CO_2$, $C_2F_4$ and $CF_3COF$ in yields of 75, 15 and 5 moles % respectively. Trifluoroacetates of Ag, $Tl^{I}$, $Hg^{I}$, $Si^{IV}$, $Sn^{IV}$, $Hf^{IV}$, $Zr^{IV}$ and $Ge^{IV}$ can be sublimed in vacuo without decomposition (132,96-98).

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The present work is chiefly a conductivity and N.M.R. study. The conductance measurements (Chapters IV, V, VI) yielded valuable information about the behaviour of acids and bases in the solvent, demonstrated the association of simple ions to higher aggregates, and enabled the self-ionization constant of the solvent to be determined. Transport number studies gave individual ionic mobilities, and freezing point determinations were made to further investigate the processes of ionic association. The N.M.R. experiments (Chapter III) were undertaken to study the reaction of some common mineral acids with trifluoroacetic anhydride, and hence to set a limit on the experimental conditions for conductivity studies.

# CHAPTER II

## Experimental details and preparative studies

This chapter contains details of preparative and purification methods, experimental technique, instrumentation and analyses. Since the success or failure of some of the preparative work is relevant to the understanding of the N.M.R. and conductance studies described in chapters III and V, this chapter contains a little more interpretation than is customary in an experimental section. This is particularly true of the description of efforts to make triacyl derivatives of boric acid (section C(iv)).

### A. Routine preparations and purifications

i) Glassware

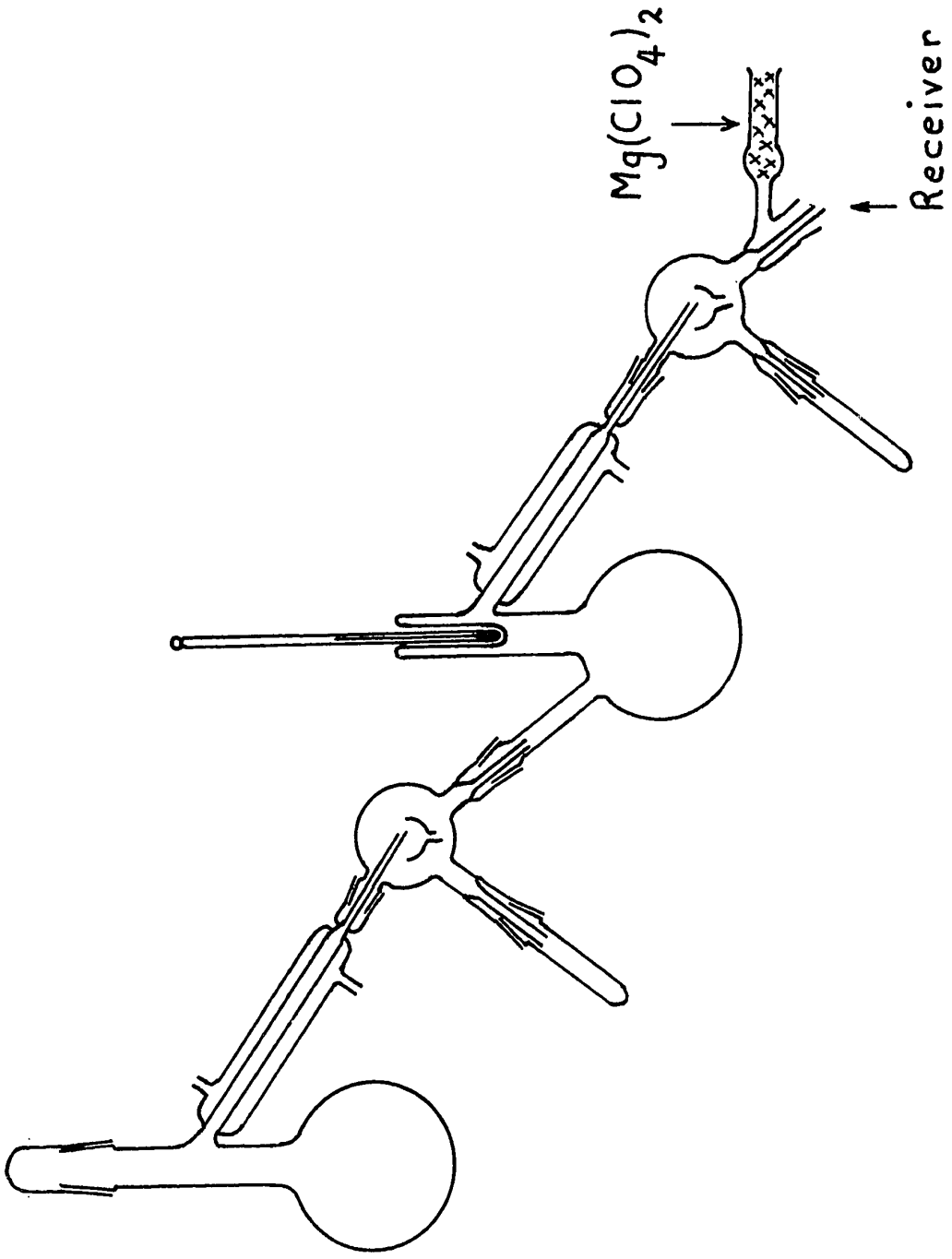
All glassware was routinely cleaned by washing with distilled water, followed by acetone (to remove any grease), 95% ethanol, distilled water, 10% nitric acid, distilled water, and conductivity water, then finally dried in an oven at ~180°C for 1-2 hours.

ii) Trifluoroacetic acid

The best grade acid from Matheson, Coleman and Bell was used. Two methods were adopted for its purification. In the first, the acid was mixed with about 5% of its weight of trifluoroacetic anhydride and subjected to a preliminary fractional distillation through a 40 cm. glass column packed with glass helices. The fraction distilling at 71.5 to 72°C was then mixed with about 1% of anhydride

Figure 3

Still for the final distillation of trifluoroacetic acid.


$Mg(ClO_4)_2$
Receiver

and transferred to a one-piece double distillation apparatus, previously flamed out in a current of dry nitrogen (Figure 3). Distillation could be made directly into the conductivity cell or into another receiver. Acid prepared in this way had a specific conductivity of 0.041 - 0.079 x $10^{-6}$ $ohm^{-1}$ $cm.^{-1}$, and a freezing point of -15.26°C.

In a second method the double distillation step was omitted, and the receiver attached directly to the fractionation apparatus (Figure 4). The receiver could be filled with the first fraction of acid, and then drained into a vessel underneath (not shown) by opening the Teflon tap A. This procedure was repeated until about 800-1000 ml had been passed, then about 200 ml were collected (b.p. 71.5-72.0°C). For direct distillation into the conductivity cell the siphon arrangement shown in Figure 5 was designed. The pressure in the waste vessel, A, could be reduced by the rubber bulb, B, causing acid to flow from the cell to the vessel, A, where it formed a liquid seal preventing back diffusion of damp air into the cell. The method has several advantages. Contact of the solvent with the atmosphere is minimized, and the first fraction of the acid (which contains anhydride) not only ensures a thorough rinsing of all parts of the apparatus, but also removes any moisture bonded to the surface of the glass. The boiling point (71.5- 2.0°C), melting point (-15.215°C) and specific conductivity (0.6 - 1.0 x $10^{-8}$ $ohms^{-1}$ $cm.^{-1}$) may be compared with the best available published values (b.p. 71.78°C (10),

Figure 4

Weight dropper for receiving
and dispensing trifluoroacetic acid.

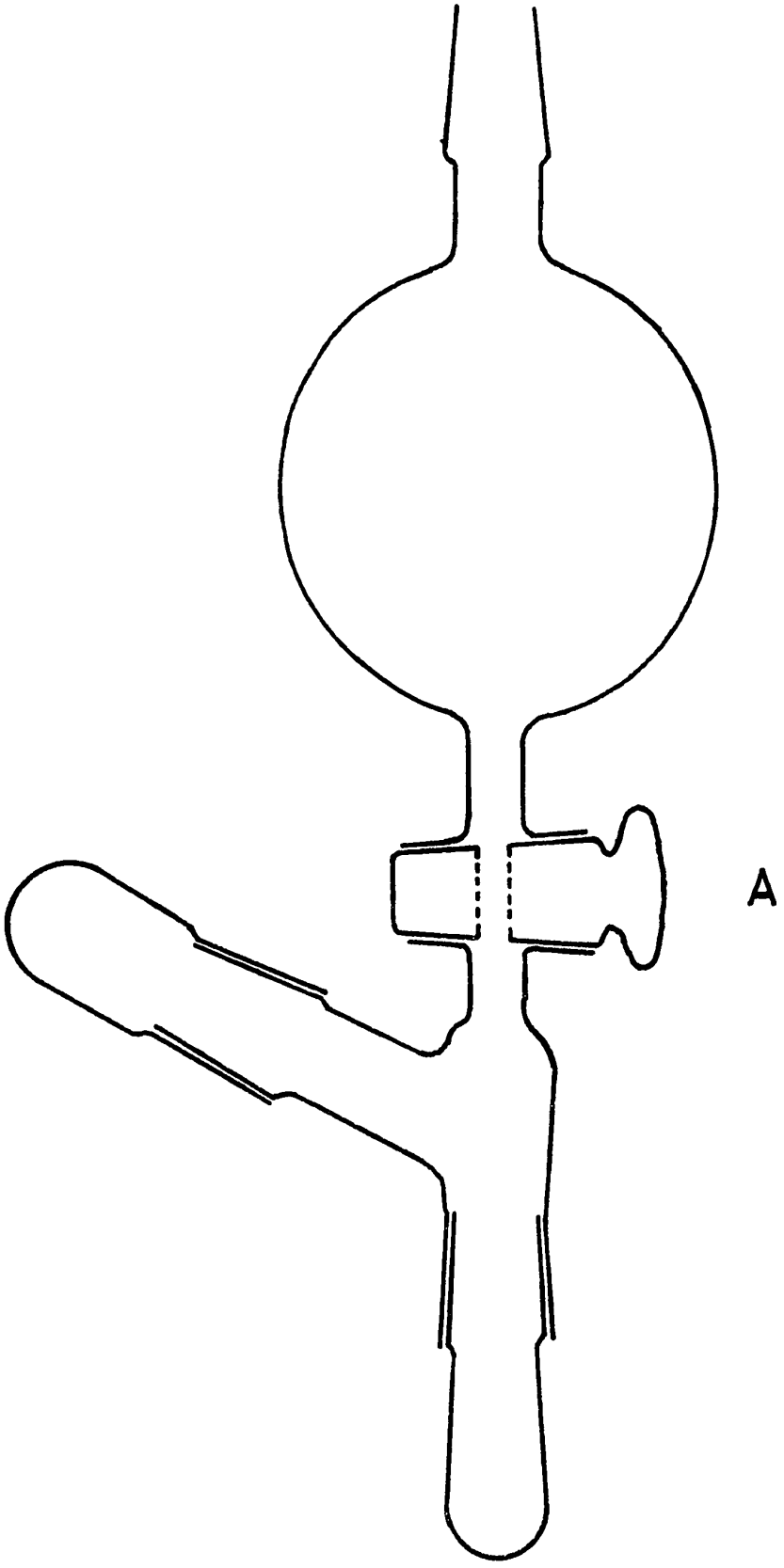
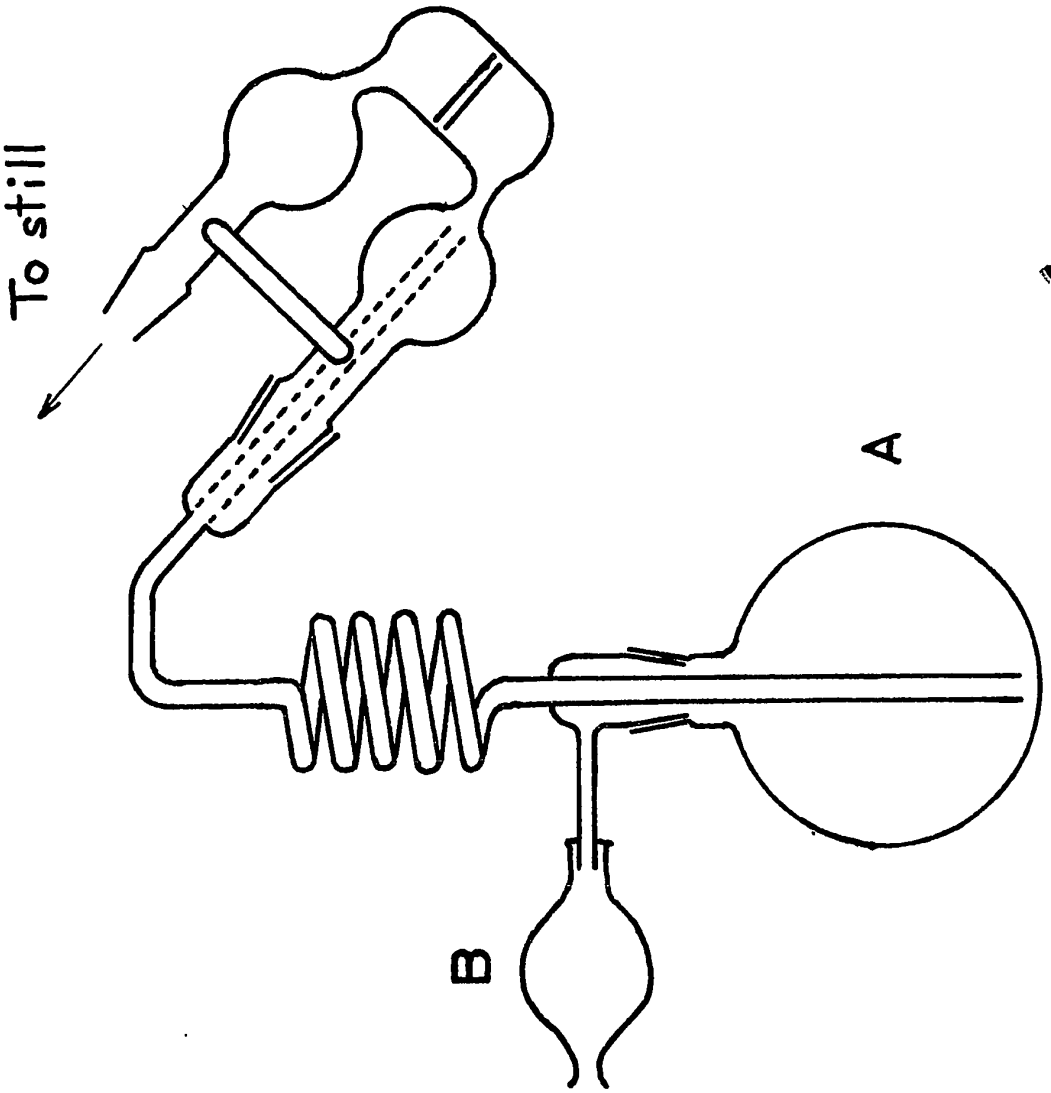

A

Figure 5

System for collecting trifluoroacetic acid in the conductivity cell.


To still
A
B

m.p. - 15.25°C (5), $K_{sp}$ 4.8 x $10^{-8}$ $ohm^{-1}$ $cm.^{-1}$ (5)).

iii) Trifluoroacetic anhydride

The anhydride was obtained by refluxing the parent acid with phosphorus pentoxide and distilling. The product was redistilled from fresh $P_2O_5$, and the fraction boiling at 39-39.5°C collected (b.p. 39.15°C (10))

iv) Water

Conductivity water used for final rinsing of glassware, for conductance studies and for the recrystallization of salts The water was prepared by simple distillation, followed by distillation from alkaline permanganate. The product had a specific conductivity of 1-2 x $10^{-6}$ $ohm^{-1}$ $cm.^{-1}$.

v) Salts

The trifluoroacetates of Na, K, Rb and Cs were prepared from aqueous solutions of the metal carbonate and trifluoroacetic acid, the salts of Li and $NH_4$ from the respective hydroxides. All the salts except that of lithium were recrystallized from conductivity water and dried at 40-50°C under vacuum. The lithium salt was too soluble to be recrystallized, and was obtained by evaporation of an aqueous solution to dryness at 100°C, then dried as for the other trifluoroacetates. All the salts were deliquescent, particularly those of Li and Na. Analyses of the first samples were made by Alfred Bernhardt Analytical

Laboratories, Elbach, Germany. Results are given in Table XI. The cation content of each salt was checked periodically, using atomic absorption spectrophotometry for Li, Na and K (with a Unicam SP90A Atomic Absorption Spectrophotometer), conversion to tetraphenylborate for Rb and Cs (171, p. 561) and a standard distillation and titration method for $NH_4$ (171, p.254).

vi) Acids

Solutions of several mineral acids were required for nuclear magnetic resonance studies, and the commerical acids were used without further purification. Concentrated nitric, hydrofluoric and perchloric acids were analyzed by titration of diluted samples with standard alkali. The following results were obtained:-

| | | |
|---|---|---|
| $HNO_3$ | 69.30% | (w/w) |
| HF | 47.97% | |
| $HClO_4$ | 71.49% | |

Sulphuric acid was analyzed by conversion to barium sulphate, and was found to contain 94.39% $H_2SO_4$.

Tetrafluoroboric acid was prepared by dissolving the calculated amount of boron trioxide in concentrated hydrofluoric acid and filtering the product, as described by Brauer (172) The reaction is very exothermic, and was carried out in plastic apparatus immersed in an ice/salt bath. Analysis for $BF_4^-$ by the nitron method (171 p. 578) was unsuccessful; titration with standard alkali gave $HBF_4$ 52.62% by weight, assuming that $HBF_4$ is the only

TABLE XI

Analyses of some trifluoroacetates

| Compound $MO_2CCF_3$ | % M | | % F | |
|---|---|---|---|---|
| | Found | Calc. | Found | Calc. |
| $LiO_2CCF_3$ | - | 5.76 | 47.35 | 47.50 |
| $NaO_2CCF_3$ | 16.77 | 16.91 | 41.68 | 41.96 |
| $KO_2CCF_3$ | 25.82 | 25.68 | 37.14 | 37.43 |
| $RbO_2CCF_3$ | 43.22 | 43.10 | 28.59 | 28.71 |
| $CsO_2CCF_3$ | 53.45 | 53.90 | 23.47 | 23.18 |
| $NH_4O_2CCF_3$ | 13.75 | 13.77 | 43.81 | 43.50 |

strong acid present.

Fluorosulphuric acid was obtained from Allied Chemicals and antimony pentafluoride from Ozark-Mahoning. Each was purified by distillation in a flamed-out apparatus before use (b.p., $HSO_3F$, 160°C; $SbF_5$, 142°C)

Solutions of $B(O_2CCF_3)_3$ were prepared from AnalaR grade boric acid. The calculated amounts of boric acid, $(CF_3CO)_2O$ and $CF_3CO_2H$ were mixed in a glass tube which was then sealed off and shaken mechanically until a clear solution was obtained.

vii) Solutions for cryoscopy

Spectral grade carbon tetrachloride from the Baker Chemical Company and methanesulphonyl fluoride from Eastman Organic Chemicals were used without further purification as non-electrolytes for cryoscopic studies.

B. Procedures, apparatus and instrumentation

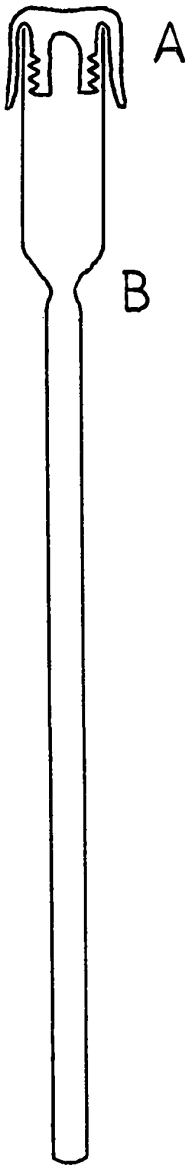
i) Nuclear Magnetic Resonance studies

Samples were prepared as follows. A piece of glass tubing about 7 mm. in diameter was sealed to the N.M.R. tube (Figure 6) and fitted with a rubber cap, A. The reactants were weighed into the tube and then frozen solid in liquid nitrogen. The tube was evacuated on a vacuum line, and melted off at the constriction, B.

Spectra were taken on a Varian Associates HA-100 spectrometer, and except for the antimony pentafluoride solutions, were all run at ~25°C.

Figure 6

The preparation of samples for N.M.R. studies.


A
B

ii) Conductance studies

Electrical conductivities were measured with a Beckman RC-18A conductivity bridge, using the glass cell shown in Figure 7. The electrodes consisted of 1" diameter lightly platinized platinum discs, separated by about 1 mm. A cell constant of $1.769 \times 10^{-2}$ was found by calibration with standard aqueous potassium chloride solution.

Solutions were made up in a weight pipette. The density of trifluoroacetic acid was taken as 1.4775 g/cc (2) and the molarity of the solution was calculated by assuming that the volume of the solution was equal to the weight of the solvent divided by the density of the solvent, i.e. volume changes produced by the electrolyte were neglected. The solutions contained ~0.2-0.5% of trifluoroacetic anhydride to remove any water present in the freshly distilled acid or introduced from the atmosphere. With this precaution, there was no observable change in conductivity when a dummy addition was made to the cell. The temperature for all measurements was maintained at 25 ± 0.005°C by means of an oil bath.

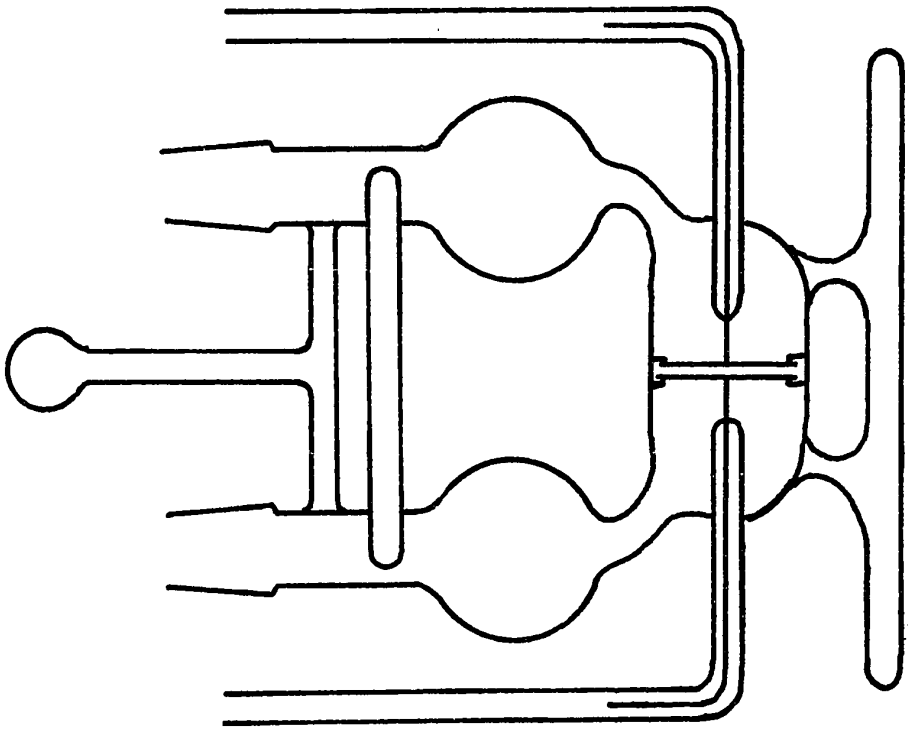
The analysis of the data is described in chapter IV. The dielectric constant of the solvent was taken as 8.40 (17), and the viscosity as 0.8565 cP (2). Programs were run on an IBM-360 computer.

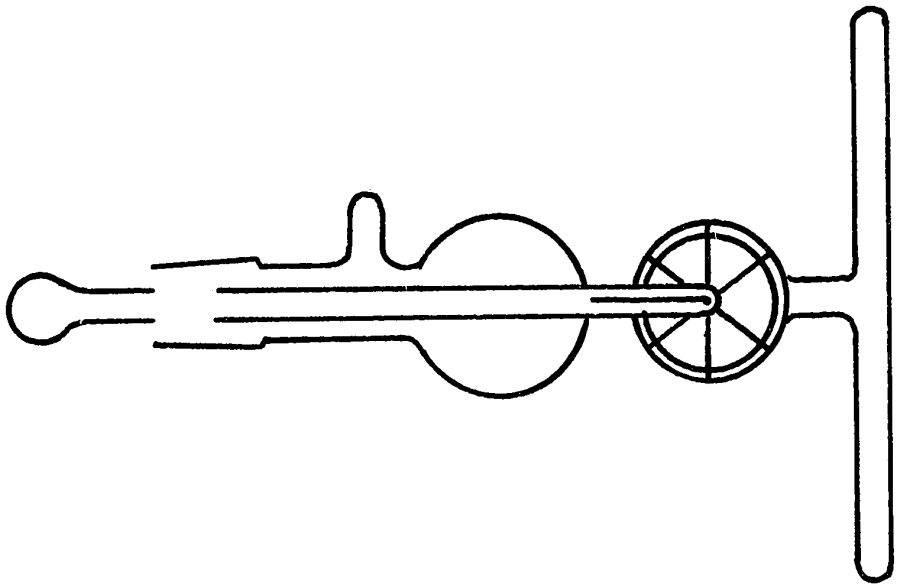
iii) Transference numbers

Transference numbers for caesium and potassium trifluoroacetates in trifluoroacetic acid were measured by

Figure 7

The conductance cell.





a modification of the Hittorf method, and the very small concentrations of electrolyte were measured conductimetrically. The apparatus is shown in Figure 8. Basically it consists of three conductivity cells E, F and G which can be isolated from each other by the hollow tap T2. The cell constants of E, F and G were $2.918 \times 10^{-2}$, $2.803 \times 10^{-2}$ and $2.887 \times 10^{-2}$ respectively. The bulbs B and C provide 'dead space' to allow thorough mixing of solutions after electrolysis. The neck of each bulb carries a scale which had previously been calibrated in terms of the volumes of the compartments on either side of the tap T2. All taps were made of teflon and were used without lubrication. For reasons of clarity, the diagram does not show the electrical connections to each of the six electrodes (two electrodes in each compartment).

To avoid interference from triple ions, measurements had to be made with electrolyte concentrations of only about $1.5 \times 10^{-4}$ molar. Under these conditions the resistance of the electrolyte between the two compartments E and G is of the order of $15 \times 10^{6}$ ohms, and an applied potential difference of several thousand volts was necessary to cause a measurable change within a reasonable time. The electrical circuit is shown in Figure 9. R1 is a variable resistance ('Variac'), allowing modulation of the input to HV, a Universal Voltronics 25 kV high voltage supply. R2 is a large resistance ( $\sim$20 M $\Omega$ ) chosen so that HV can be used at its optimum output ( $\sim$15 kV). R3 is a dummy

Figure 8

Hittorf cell for the measurement of transference numbers.

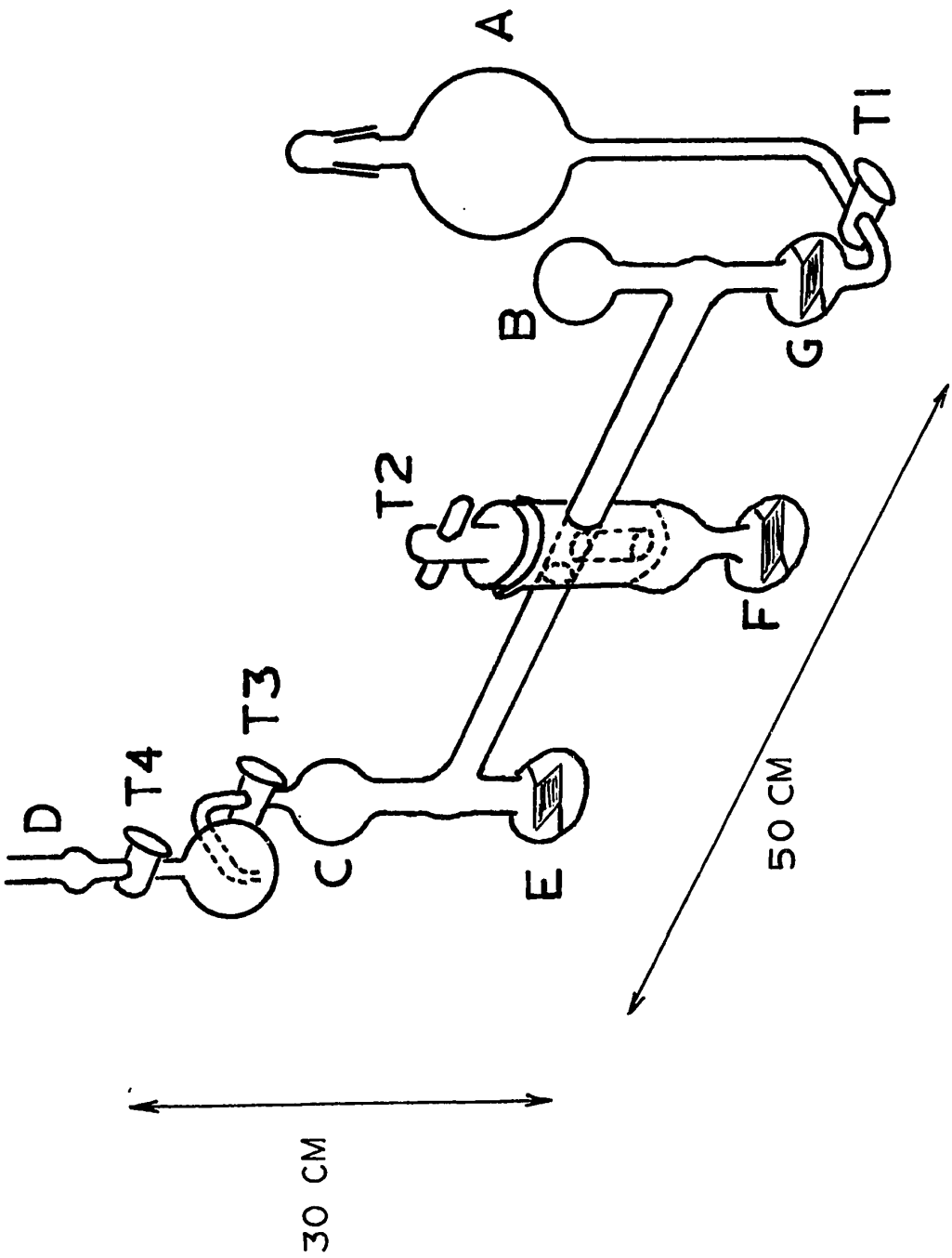
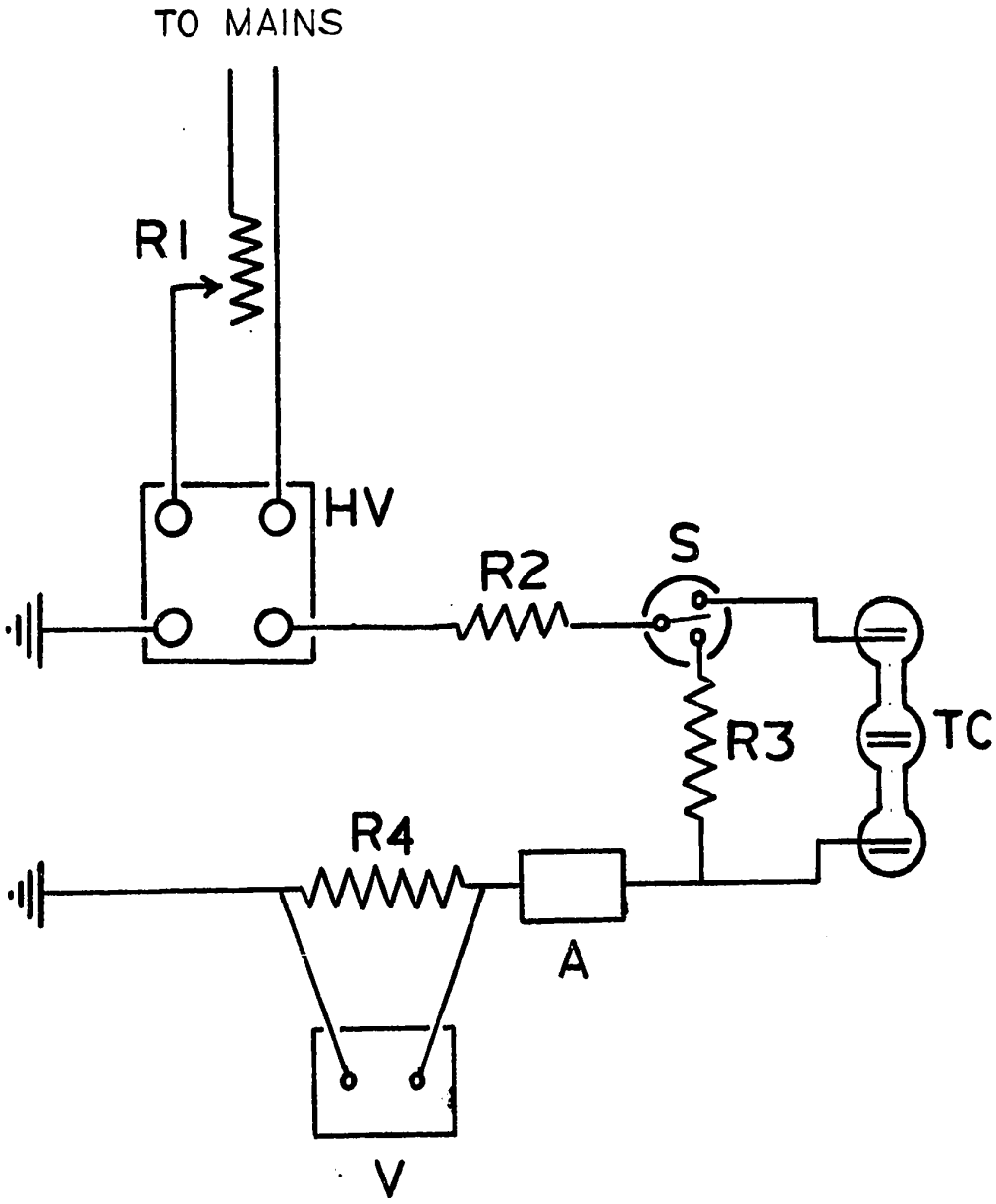

A
T1
B
G
T2
F
T3
T4
D
C
E
50 CM
30 CM

Figure 9

Electrical circuit for transference number studies.


TO MAINS
R1
HV
R2
S
R3
TC
R4
A
V

load, whose resistance is approximately equal to that of the electrolyte in the transference cell, TC ( ~15 MΩ ). A is a microammeter used to monitor the current, S a mercury switch, V a potentiometer (model PHM4c, manufactured by Radiometer, Copenhagen). $R_4$ is a standard resistance which is chosen to give the optimum reading of the potentiometer, V, and is immersed in the oil bath at 25°C.

The experiment was conducted as follows. About 300 ml. of the solution to be studied was made up by weight, the tap T1 (Figure 8) closed and the bulb A filled with the liquid. Some of the solution was then allowed through T1, used to rinse the inside of the cell, and finally discarded into the waste trap W. The three compartments were then filled with solution up to about half way on the two calibrated scales, the taps T1 and T3 were closed, and the solution thoroughly mixed until the liquid in all three compartments had the same specific conductivity when the apparatus had come to thermal equilibrium in the oil bath. If this conductivity differed by more than 1% from the value expected from previous conductance studies, the solution was discarded, and the experiment recommenced. Taps T2, T3 and T4 were opened and the apparatus mounted on a vibration-free stand in the oil bath. The electrical circuit was allowed to warm up through the dummy load R3. After about 20 minutes the chronometer was started, and the mercury switch S thrown to connect the transference cell and cut out R3. Readings of the potential difference across

R4 were taken every few minutes. After a suitable period (10 to 30 minutes) the circuit was switched off, and the taps T2 and T3 (Figure 8) closed to isolate the compartments. The liquid in each compartment was thoroughly mixed by removing the cell from the oil bath and inverting it several times. The cell was then replaced, the conductance measured in each compartment, and the volumes of the solutions found from the position of the liquid levels on the calibrated scales. The change in number of equivalents of electrolyte in each compartment, $\Delta n$, was found from the volume of solution in the compartment and the previously established relationship between specific conductance and concentration. The total quantity of electricity passed, Q, was found from the value of the resistance R4 (checked before and after the experiment) and a graph of the voltage across R4 against time. The transference number of the cation is given by

$$t_+ = \frac{\Delta n}{Q \mathcal{F}} \qquad \text{(see chapter VII)}$$

where $\Delta n$ is the change in the number of equivalents in either cathode or anode compartment,

Q is the total charge passed in coulombs

$\mathcal{F}$ is the Faraday.

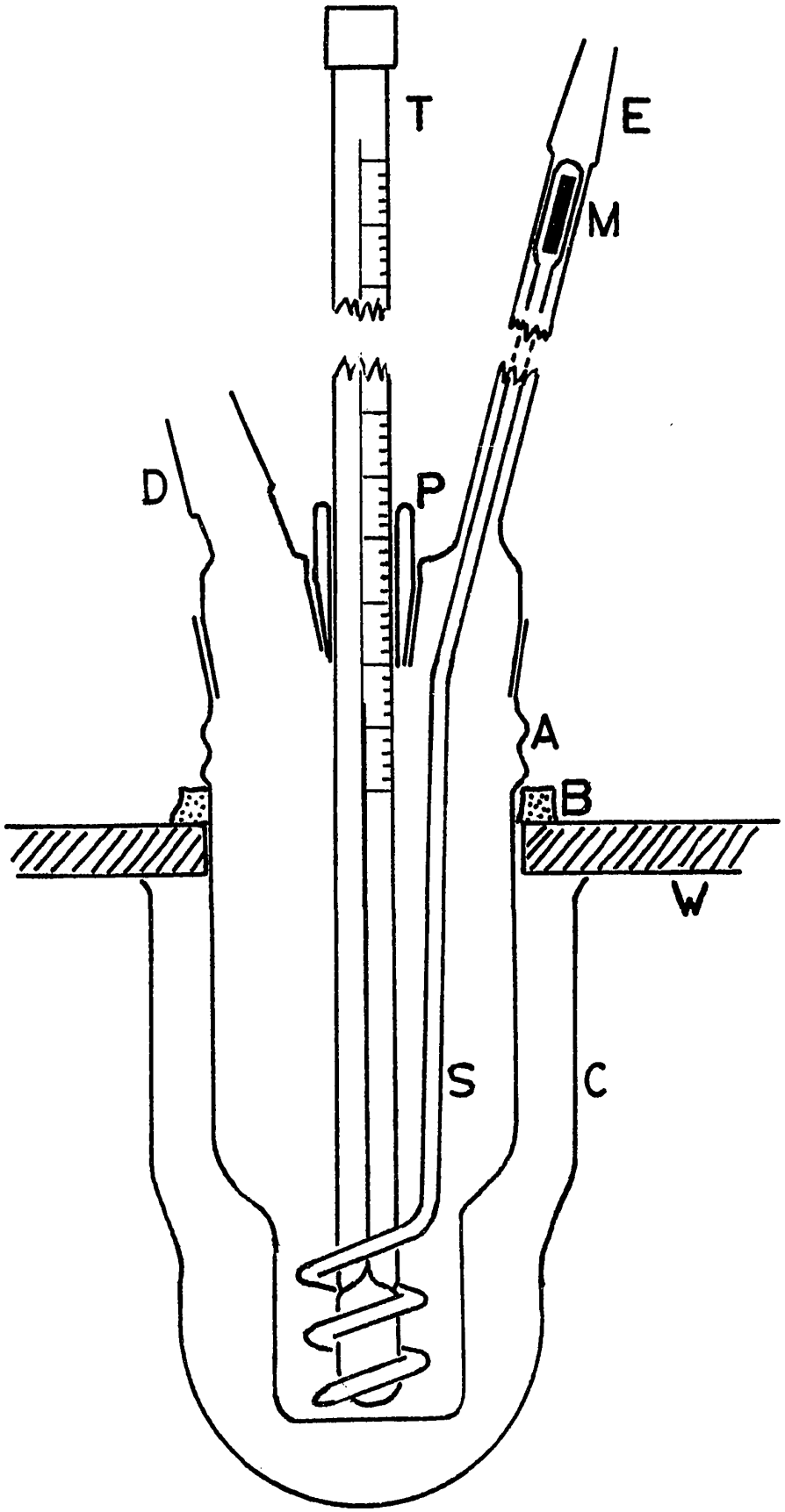
iv) Cryoscopy

The apparatus used for the measurement of freezing point is shown in Figure 10. It consists of a glass vessel (A) held firmly by a rubber strip (B), and supported on a plywood frame (W). The vessel is fitted with a ground glass top, and its lower part is surrounded by an air jacket (C) Samples or solvent can be introduced through the ground glass joint (D) and a sensitive thermometer (T) is held securely by a plastic insert (P). Stirring is acheived automatically by a stirrer fitted with a small magnet (M). The magnet can be raised or lowered by a solenoid (not shown) powered by a variable speed make-and-break circuit.

To carry out an experiment, the apparatus is first assembled without the thermometer or air jacket and flamed out in a stream of dry nitrogen introduced through E. When the glassware is cool the thermometer is replaced and solvent introduced from a large weight burette until the lower well of A is nearly full. The freezing point of pure solvent is taken as follows. The liquid is cooled almost to its freezing point by immersing the vessel A directly in an ice/salt slush bath. The bath is then removed, the air-jacket C replaced, and surrounded by a second ice/salt bath at a temperature such that the temperature of the liquid in A falls at a rate of 0.1-0.2°C per minute. When the solvent has supercooled by about 1°C, a small piece of platinum foil is cooled in liquid nitrogen,

Figure 10

Apparatus for the measurement of freezing points.


T
E
M
D
P
A
B
W
S
C

and dropped into the solvent via the ground glass joint D. Crystallization of the solvent occurs immediately, and the latent heat evolved causes the temperature to rise rapidly to the true freezing point.

Samples to be studied were added as concentrated solutions in trifluoroacetic acid, and allowance for the added solvent made in the calculation of concentration. Freezing points were measured in the same way as for the pure solvent. In one experiment the observed freezing point was plotted against the degree of super-cooling for each point and extrapolated to zero super-cooling, thus correcting for the increased concentration in the liquid phase as pure solvent freezes out. The corrections were very small ( $\sim$.001°C) and were not made in other experiments.

Freezing points were measured with a thermometer supplied by Thermoschneider Ltd., Wertheim, Germany.

C. General preparative studies

i) The reaction of $(CF_3CO)_2O$ with $CF_3CO_2NH_4$

The electrical conductance of ammonium trifluoroacetate solutions containing a little trifluoroacetic anhydride decreases slowly with time, (chapter III) and some reaction between the salt and the anhydride was suspected. To test this, 4 g of ammonium trifluoroacetate was refluxed overnight with 150 g of trifluoroacetic anhydride. The solid dissolved slowly, and beautiful white crystals were obtained on pumping off the excess liquid. The crystals

sublimed readily at room temperature when left in a closed container for a few hours. Both the sublimed product and the residue melted sharply at 86°C (m.p. $CF_3CO_2NH_4$ 123.7°C)

The nitrogen content of the compound was found as 6.75% by displacing the ammonia with sodium hydroxide, absorbing it in standard acid, and titrating with standard alkali. This suggests that the compound is the di-acyl amide $(CF_3CO)_2NH$ (req'd. N content 6.70%). 1 g of the compound neutralized $4.74 \times 10^{-4}$ equivalents of sodium hydroxide in the cold, and a further $4.58 \times 10^{-4}$ equivalents on boiling, a total of $9.32 \times 10^{-4}$ equivalents. The amount calculated for $(CF_3CO)_2NH$ is $9.67 \times 10^{-4}$ equivalents per gram.

ii) The reaction of $SbF_5$ with $CF_3CO_2K$

2.9 g of $SbF_5$ (.013 moles) were dissolved in 25 g of trifluoroacetic acid and added to a solution of 2.0 g of potassium trifluoroacetate (0.013 moles) in 25 g of acid. The dense white precipitate was filtered off in the dry-box on a sintered glass funnel, washed with trifluoroacetic acid, and dried in vacuo at room temperature. An X-ray powder photograph identified the solid as potassium hexafluoroantimonate. Table XII compares the principal lines observed for the sample with the published values for $KSbF_6$ (173). The substance was analyzed for potassium by flame emission spectrophotometry, using a Unicam model SP90A spectrophotometer (found 13.2%, req'd. 14.2%).

TABLE XII

X-ray powder photograph of product of reaction of $SbF_5$ with $CF_3CO_2K$

| Sample | | $KSbF_6$ | |
|---|---|---|---|
| d | Intensity | d | Intensity |
| 5.12 | 70 | 4.98 | 62 |
| - | | 4.07 | 9 |
| 3.61 | 100 | 3.51 | 100 |
| 2.95 | 20 | 2.90 | 11 |
| 2.51 | 10 | 2.51 | 5 |
| - | | 2.41 | 5 |
| 2.27 | 10 | 2.26 | 4 |
| - | | 2.15 | 3 |
| 2.09 | 60 | 2.05 | 38 |
| - | | 1.98 | 4 |
| 1.805 | 30 | 1.784 | 22 |
| 1.701 | 20 | 1.685 | 11 |
| 1.626 | 20 | 1.595 | 11 |
| - | | 1.522 | 5 |
| 1.47 | 3 | 1.463 | 4 |
| 1.42 | 3 | 1.404 | 4 |
| 1.364 | 30 | 1.350 | 13 |
| 1.21 | 5 | | |

iii) The reaction of $SbCl_5$ with $CF_3CO_2H$ and $Hg(O_2CCF_3)_2$

Satori's preparations (96-98) of group IV metal trifluoroacetates from the corresponding chlorides and trifluoroacetic acid or a heavy metal trifluoroacetate suggested that a similar reaction might be carried out on $SbCl_5$.

a) reaction with $CF_3CO_2H$

22 g of $SbCl_5$ was refluxed for 24 hours with 7 g of trifluoroacetic anhydride and 44 g trifluoroacetic acid in a flask fitted with a condenser and a drying tube. The two phases slowly merged to give a clear colourless solution. Excess solvent was pumped off on the vacuum line to leave a colourless involatile liquid. At ~-20°C, this gave colourless crystals in a thick liquid. The liquid showed no tendency to crystallize further, and gave a glass at dry ice temperatures.

A sample of the mixture was withdrawn hydrolysed with water and the resulting aqueous solution filtered free of the white precipitate of $Sb_2O_5$. The clear liquid was analyzed for total acid and for chloride, and a fresh sample analyzed for $Sb^V$, all by standard techniques (171). The results suggest that the product was a mixture of $HSbCl_5(O_2CCF_3)$ and $HSbCl_4(O_2CCF_3)_2$. A mixture containing 76.7% of the former to 23.3% of the latter by weight should have 39.3% Cl, 28.3% Sb, and neutralize $1.39 \times 10^{-2}$ equivalents of base per gram of substance: the values found were respectively 39.3%, 28.7%, and $1.34 \times 10^{-2}$ equivalents/g.

b) Reaction with mercuric trifluoroacetate.

Mercuric trifluoroacetate dihydrate was prepared from mercuric oxide and aqueous trifluoroacetic acid. A two-fold excess of acid was used, since the salt is extensively hydrolysed in aqueous solution. The anhydrous salt was obtained by treating the dihydrate with trifluoroacetic anhydride and crystallizing from trifluoroacetic acid. The salt was analysed for mercury by conversion to bis(ethylenediamine) copper (II) tetra-iodomercurate (found 47.2%, req'd 46.~%).

20 g of $SbCl_5$ ( ~.1 mole) were dissolved in about 50 ml of $CF_3CO_2H$ contained in a flask fitted with a reflux condenser and a drying tube, and a solution of 90 g $Hg(O_2CCF_3)_2$ ( ~.25 moles) in 150 ml of anhydrous acid slowly added. An immediate dense white precipitate was formed. The solution became very hot and refluxed gently. After cooling, the mixture was centrifuged, and the supernatant liquid concentrated on the vacuum line to give a very poor yield ( ~1 g) of white crystals, probably $Sb(O_2CCF_3)_5$. Analysis for total acid content and for antimony (171, p. 366 ) showed that 1 g of the product neutralized $7.35 \times 10^{-3}$ equivalents of base and contained 18.2% Sb. The values required for $Sb(O_2CCF_3)_5$ are $7.28 \times 10^{-3}$ equivalents/g and 17.8% Sb, those for $HSb(O_2CCF_3)_6$ are $7.49 \times 10^{-3}$ equivalents/g and 15.0% Sb.

iv) experiments with boric acid

N.M.R. and conductance studies (chapters III and V) established that the compound $B(O_2CCF_3)_3$ exists in solution. A large number of attempts were made to isolate this compound, but none were successful. The usual product was a mixture of $B(O_2CCF_3)_3$ with $B_2O(O_2CCF_3)_4$. Analysis of the products was acheived by a modification of the procedure described by Gerrard et al. (115). The sample was hydrolysed by dissolving it in water, and the trifluoroacetic acid produced was titrated to methyl red with standard sodium hydroxide. A few grams of mannitol were added, and the boric acid titrated to phenolphthalein. The procedure was shown to be reliable by using it to analyse a standard aqueous solution containing known amounts of boric and trifluoroacetic acids.

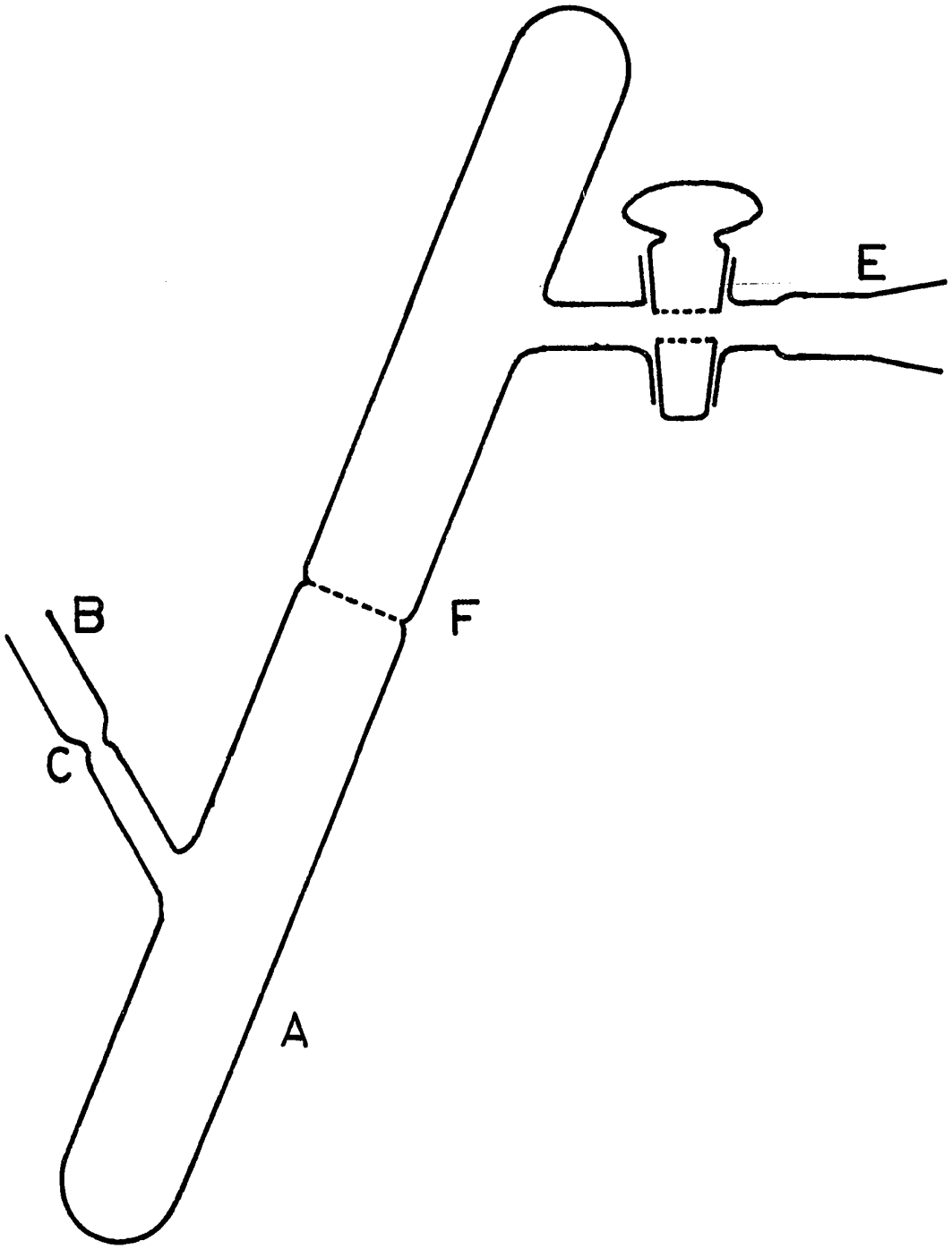
a) the reaction of $H_3BO_3$, $CF_3CO_2Cs$ and $(CF_3CO)_2O$

The apparatus used for this preparation is shown in Figure 11. F is a sintered glass disc.

Caesium trifluoroacetate (2.93 g, 0.012 moles), boric acid (0.78 g, 0.012 moles), trifluoroacetic anhydride (3( g, 0.14 moles) and trifluoroacetic acid (23 g, .2 moles) were weighed into the lower half of the vessel via the side-arm B, which was then sealed off at the constriction, C. The mixture was shaken for several days, and gave a clear solution. The vessel was connected to a vacuum line at the ground glass joint E, and the solution concentrated until crystals appeared. The tube was then rotated about E so

Figure 11

Apparatus for the preparation of $CsB(O_2CCF_3)_4$


E
B
F
C
A

that the mother liquor was sucked into the other end of the container, and the crystals collected on the sintered glass frit F. The contents were then pumped to dryness, and the tube cut open in the dry-box. Analysis showed the crystals to be $CsB(O_2CCF_3)_4$ (Found: Cs, 22.6%, 22.0%; B, 1.80%; hydrolysable trifluoroacetate, 56.3%. Calc: Cs 22.3%; B, 1.81%; hydrolysable trifluoroacetate, 56.8%).

b) The reaction of $H_3BO_3$ and $(CF_3CO)_2O$

The procedure was identical with that for the preparation of the caesium salt above, except that $CsO_2CCF_3$ and trifluoroacetic acid were omitted. 2.6 g (.042 moles) of $H_3BO_3$ and 48 g (.23 moles) of $(CF_3CO)_2O$ were used. The reaction took several weeks. Concentration of the solution gave hexagonal plates of $B_2O(O_2CCF_3)_4$. (Analysis:- Found; B, 4.28%; $CF_3CO_2^-$, 90.46%. Calc. for $B_2O(O_2CCF_3)_4$; B, 4.42%, $CF_3CO_2^-$, 92.3%).

c) The reaction of $BCl_3$ with $CF_3CO_2H$

The procedure of Gerrard et al. (115) was followed exactly. Approximately 6 g ($\frac{1}{20}$ mole) of $BCl_3$ were condensed in a weighed flask fitted with a side-arm and a magnesium perchlorate guard tube. The flask was stoppered tightly and reweighed, then 10 ml. of n-pentane added to the mixture. The amount of trifluoroacetic acid to give a molar ratio $CF_3CO_2H/BCl_3$ of 3:1 was calculated, weighed out exactly, dissolved in 10 ml. of n-pentane, and added slowly to the $BCl_3$ solution. Considerable heat was evolved, and vigorous effervescence of HCl was observed. The resulting

pasty mass was pumped down at ~10 mm Hg pressure, to give a dry yellowish solid. The reaction was carried out at room temperature and at 0°C, and was varied by omitting the n-pentane and by substituting trifluoroacetic anhydride or methyl trifluoroacetate for the acid. In all cases the analyses lay between those expected for $B(O_2CCF_3)_3$ (B, 3.10%; $CF_3CO_2$, 96.91%) and $B_2O(O_2CCF_3)_4$ (B, 4.42%; $CF_3CO_2$, 92.3%), and the reaction product was probably a mixture of the two. A similar reaction between trimethyl borate and $(CF_3CO)_2O$ gave a fine white precipitate containing 22.4% B and 19.8% $CF_3CO_2$. The product was presumably a highly condensed species, and the boron analysis approaches that of pure $B_2O_3$ (31.1%).

d) The reaction of $KB(O_2CFF_3)_4$ with $HClO_4$

A solution of $KB(O_2CCF_3)_4$ was prepared by mixing 1.677 g $H_3BO_3$ and 4.138 g $CF_3CO_2K$ (4.130 g required for equimolar amounts of K and B) with about 45 g of $(CF_3CO)_2O$, sealing the tube , and shaking until a clear solution was obtained. The solution was transferred to a flask fitted with a side-arm and an $Mg(ClO_4)_2$ guard tube. A standard solution of anhydrous $HClO_4$ in $CF_3CO_2H$ was added to the $KB(O_2CCF_3)_4$ solution in an amount calculated to precipitate all the potassium present as $KClO_4$. An immediate white precipitate was obtained. The mixture was centrifuged in stoppered tubes and the supernatant liquid concentrated on the vacuum line. No crystals were obtained, but only an oily liquid, which formed a glass at about -15°C. Attempts

to remove solvent by pumping at about 40°C gave a white solid residue, and a white crystalline sublimate. The sublimate contained 4.838% B and 89.46% trifluoroacetate, a $CF_3CO_2$/B ratio of 7:4, and is presumably some more highly condensed species. The residue contained 3.53% B and 76.7% $CF_3CO_2$.

e) Other reactions

In one experiment gaseous diborane was bubbled directly into 100% trifluoroacetic acid, and in another, gaseous $CF_3COCl$ was bubbled through a solution of methyl borate in n-pentane. In both experiments all the products were volatile at 20°C and 20 mm Hg pressure. It seems that no reaction had taken place.

# CHAPTER III

## $^{19}F$ Nuclear Magnetic Resonance Studies

### A. General

Trifluoroacetic acid is a good solvent for quite a wide range of substances, and yet is itself an extremely weak base (see Chapter I). This combination of properties makes it an attractive medium for the titration of such weak bases as amino-acids and other organic nitrogen compounds, in spite of the unpleasant, corrosive nature of the solvent. Thus both conductimetric and potentiometric titrations have been reported (99,100), using anhydrous perchloric acid as titrant.

Quantitative investigation of acid/base equilibria in trifluoroacetic acid, and in particular the measurement of $pK_a$ for various acids, is much more difficult. Measurements must be made at concentrations of less than about $2 \times 10^{-4}$ molar to avoid interference from triple ions, and water, which may react with the solute, must be rigorously excluded. Neglect of one or both of these considerations invalidates much of the previous work in this and other solvents. Thus one author finds that $H_2SO_4$ is a non-electrolyte in trifluoroacetic acid (conductance, 105), another that it has a $pK_a$ of 6.3 (indicator studies, 101). Pyrosulphuric, methanesulphonic and perchloric acids are also claimed to behave as acids in the solvent (101,102).

The conductances studies reported in Chapters IV and V were all made in the presence of about 0.1% ( ~.007

molar) trifluoroacetic anhydride to remove traces of water. Since this represents a concentration considerably greater than that of the electrolyte to be studied ( $\sim 2 \times 10^{-4}$ molar), it was essential to know if the electrolyte would react with the anhydride. While it was safe to assume that bases such as the alkali metal trifluoroacetates would be unaffected, the N.M.R. studies established that all the conventional strong mineral acids did indeed react with the anhydride, and are therefore unsuitable for conductance studies. This does not, of course, mean that the substances are not acids in the solvent, but simply that practical difficulties make quantitative measurements impossible by the techniques reported here. Two acids, however, were found to stable to trifluoroacetic anhydride, antimony pentafluoride (as $HSbF_5(O_2CCF_3)$) and boron tris(trifluoroacetate) (as $HB(O_2CCF_3)_4$). Several other substances were also investigated. The experimental details have been given in Chapter II. Basically, a substance was mixed with the anhydride in an N.M.R. tube which was then sealed off under vaccuum and the mixture allowed to react. All transfers were made in a dry-box.

B. The system $H_2O/HClO_4/(CF_3CO)_2O$

Perchloric acid was used as the concentrated (71.4%) aqueous solution. On addition of the anhydride two distinct phases were formed, the lower, oily one containing the aqueous acid; after shaking for several hours, a homogeneous solution was obtained. Possible reactions are:-

$$(CF_3CO)_2O + H_2O \rightarrow 2CF_3CO_2H \quad 1)$$

$$(CF_3CO)_2O + HClO_4 \rightarrow CF_3CO_2H + CF_3CO.O.ClO_3 \quad 2)$$

$$(CF_3CO)_2O + 2HClO_4 \rightarrow 2CF_3CO_2H + Cl_2O_7 \quad 3)$$

In one experiment, insufficient anhydride was added to react with the water present, and the spectrum run before the two phases had disappeared. Two peaks were observed corresponding to trifluoroacetic acid and un-reacted anhydride. When the same sample was run a few hours later, a single peak (trifluoroacetic acid) was seen. This indicates that the anhydride reacts slowly, but completely, with the water present, and that reaction with water is preferred to reaction with perchloric acid.

In a second experiment, the mole fractions of $H_2O/(CF_3CO)_2O/HClO_4$ were 0.286/0.585/0.129. Three peaks were found and assigned to $CF_3CO_2H$, $CF_3CO.OClO_3$ and excess $(CF_3CO)_2O$. The observed peak areas were in excellent agreement with those predicted if reactions 1) and 2) go to completion. Results are given in Table XIII. It will be noticed that the signal for $CF_3CO.O.ClO_3$ is to low field of those for the anhydride and the acid. This is consistent with the electronegativity of the group attached to $CF_3CO^-$ in each case.

The products of the reaction are not indefinitely stable, and decompose slowly to oxides of chlorine. One of the solutions produced a greenish-yellow gas after a few days, but became a bright ginger colour on freezing in liquid nitrogen. Although the tube was opened without difficulty, the sample exploded violently when allowed to warm up. The

TABLE XIII

Chemical shifts and peak areas for the system $H_2O/HClO_4/(CF_3CO)_2O$

| Product | Chemical Shift (p.p.m) | Observed Area | Calculated Area (reaction 2) |
|---|---|---|---|
| $CF_3CO_2H$ | .00 | 1.00 | 1.00 |
| $(CF_3CO)_2O$ | -.54 | .483 | .485 |
| $CF_3CO.ClO_4$ | -2.95 | .184 | .184 |

colour change, yellowish gas to red-brown solid, and the explosion suggest the presence of $Cl_2O_6$ (or possibly $ClO_2$), produced by the decomposition of the mixed anhydride.

$$4\,CF_3CO.O.ClO_3 \longrightarrow 2(CF_3CO)_2O + 2Cl_2O_6 + O_2 \qquad 4)$$

The compound $CF_3CO.O.ClO_3$ was not isolated, but more likely to be the mixed anhydride, as formulated, than the ionic perchlorate, $CF_3CO^+.ClO_4^-$. The cation $CF_3CO^+$ has been claimed to exist at low temperatures (128) but is very unstable. The $CF_3CO_2H$, $(CF_3CO)_2O$ and $CF_3CO.O.ClO_3$ resonances were observed as separate signals, whereas exchange via the $CF_3CO^+$ ion would have collapsed the spectrum to one single peak. In addition, solutions of perchloric acid containing excess anhydride were non-conducting, eliminating the possibility of an ionic perchlorate (See Chapter V). Thus if trifluoroacetic anhydride is present, perchloric acid solutions are decomposed; if anhydride is absent, the principal ionic species undoubtedly will be $H_3O^+.ClO_4^-$; if one uses sufficient $HClO_4$ to swamp the effects of adventitous water (inevitably present at ~.005% concentration if anhydride is omitted) or added anhydride (necessarily added at ~0.1% concentration to remove water), then the concentration of electrolyte required are so high that triple ion formation makes the accurate analysis of conductivity data quite impossible.

C. The system $HSO_3F/(CF_3CO)_2O/CF_3CO_2H$

Fluorosulphuric and perchloric acids are iso-

electronic. One might expect them to show similar behaviour toward trifluoroacetic anhydride, with the difference that $HSO_3F$ could perhaps be solvolysed by the hydroxyl function of $CF_3CO_2H$.

$$CF_3CO_2H + FSO_3H \longrightarrow HF + CF_3CO.SO_3H$$

In fact, solvolysis does not occur, for a mixture of fluorosulphuric and trifluoroacetic acids (mole fractions 0.62, 0.38) showed two peaks in the N.M.R. spectrum separated by 116.3 p.p.m., and these may be assigned to the F-C (high field) and F-S (low field) signals of $CF_3CO_2H$ and $HSO_3F$ respectively. Peak areas were exactly as expected from the stoicheiometry of the mixture (observed F(C)/F(S), 0.545; expected, 0.543).

The reaction of fluorosulphuric acid with trifluoroacetic anhydride gives a total of five peaks in the N.M.R. spectrum. Details of the spectra for three different solutions are given in Table XIV, and can be fully explained by the equilibrium:-

$$(CF_3CO)_2O + HSO_3F \rightleftharpoons CF_3COSO_3F + CF_3CO_2H \qquad 5)$$

The peaks are assigned as:-

A $CF_3CO_2H$

B $(CF_3CO)_2O$

C $CF_3CO.SO_3F$

D $HSO_3F$

E $CF_3COSO_3F$

TABLE XIV

Chemical shifts (p.p.m.) and relative intensities (bracketed figures) for mixtures of $HSO_3F$ and $(CF_3CO)_2O$

| Sample | Mole Fraction $HSO_3F/(CF_3CO)_2O$ | Peak A | B | C | D | E | K |
|---|---|---|---|---|---|---|---|
| 1 | .370/.630 | +.21 (4.79) | 0.0 (30.1) | -1.47 (3.08) | -116.4 (2.68) | -122.5 (1.00) | .12 |
| 2 | .595/.405 | +.13 (4.36) | 0.0 (13.7) | -1.47 (3.17) | -116.3 (4.06) | -122.5 (1.00) | .16 |
| 3 | .796/.204 | +.08 (3.32) | 0.0 (5.76) | -1.46 (3.10) | -116.2 (6.83) | -122.2 (1.00) | .17 |

and this may be justified as follows. None of the peaks shows any fine structure, ruling out products such as $CF_3SO_3F$ or $CF_3SO_2F$, where the two kinds of fluorine atoms are known to interact and produce a splitting of the signals (110). In all three spectra the ratio of C to E is 3:1 within the experimental error for peaks so far apart; the chemical shifts of the peaks are in good agreement with the literature values for neat $CF_3CO.SO_3F$ (109,110). Peak B can be attributed to $(CF_3CO)_2O$, since it is at its most intense for the solutions containing the most anhydride. This leaves A, the only other peak in the F on C region, for $CF_3CO_2H$. The assignments for A, B, and C then follow the sequence that one would expect from the relative electronegativities of the -OH, $-O_2CCF_3$ and $-OSO_2F$ groups. Since equation 5) requires that $CF_3CO_2H$ and $CF_3CO.SO_3F$ be produced in equal amounts, then the ratio of the peaks A/E should also be 3:1. This ratio is approached in solution 3), but the results for the first two solutions are in rather poor agreement with the theoretical values. Slight traces of water would of course increase the intensity of A by hydrolysis of the anhydride, but hardly enough to account for so large a discrepancy. More important is the fact that A is a relatively small peak lying very close to a peak about seven times its own size, and integration is known to be rather unreliable under these conditions. Finally, peak D must be assigned to $HSO_3F$; the separation of A and D agrees well with the results of the first experiment, where $CF_3CO_2H$ and $HSO_3F$ were the only species

present in solution.

In no case did the reaction go to completion, and even in sample 1), where the concentration of anhydride was almost double the required amount, most of the fluorosulphuric acid stays unchanged. This is not a kinetic effect, for the spectra remained the same after the solutions had been left standing for several weeks, and kept at 100°C for two or three days. Reaction 5) must be an equilibrium involving all four species. This is totally unexpected, for the corresponding reaction with perchloric acid proceeds quantitatively, and the back reaction, i.e.

$$CF_3CO.SO_3F + CF_3CO_2H \longrightarrow (CF_3CO)_2O + HSO_3F$$

seems particularly unlikely, since Delfino and Shreeve (109) have shown that hydrolysis of $CF_3CO.SO_3F$ is very slow, even with boiling 0.1 normal sodium hydroxide. Nevertheless, the evidence for an equilibrium is very strong. As the initial concentration of the reactants is known, the equilibrium constant, defined by:-

$$K = \left[CF_3CO.SO_3F\right]\left[CF_3CO_2H\right] / \left[(CF_3CO)_2O\right]\left[HSO_3F\right]$$

can be derived from the relative intensities of the N.M.R. signals. The values of K (last column, Table XIV) are satisfactorily constant for the three samples, considering the change in composition of the medium.

The N.M.R. spectrum also furnishes indirect evidence that $HSO_3F$ is strong enough to protonate trifluoro-

acetic acid. Four of the signals occurred at the same position in each spectrum, but that due to $CF_3CO_2H$ moves systematically to low field as the proportion of $HSO_3F$ in the mixture is increased. While hydrogen-bonding effects would modify the proton N.M.R. spectrum, they would have little effect on the resonance of the more remote $^{19}F$ nucleus, and the cation $CF_3CO_2H_2^+$ could be present in the solutions. Protonation will cause deshielding of the fluorine nucleus, and the signal (peak A) should move down-field as the $HSO_3F/CF_3CO_2H$ (D/A) ratio is increased. This is exactly what is observed. At the same time an equivalent amount of $SO_3F^-$ ion should be produced, and the $HSO_3F$ resonance (peak D) should move to higher fields. Such a movement can be seen, but the errors in measurement are larger than for the $CF_3CO_2H$ peak and the result may be spurious.

D. The system $(CF_3CO)_2O/H_2O/H_2SO_4$

Spectra were taken of mixtures of concentrated (94.4%) sulphuric acid* with trifluoroacetic anhydride. The first stage of the reaction is undoubtedly removal of the small amount of water present (5.6%), and this might be followed by dehydration of the sulphuric acid. Only two signals were observed in the spectra, and the one at higher field can safely be assigned to the anhydride from the variation of relative intensities with composition of the mixture. The other peak must then arise from the acid,

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* for analysis, see Chapter II.

$CF_3CO_2H$, perhaps exchanging with such species as $CF_3CO.HSO_4$ or $(CF_3CO)_2.SO_4$.

Table XV shows the results of the experiments, and also gives the intensity ratios calculated for various possible reactions. It is obvious that the anhydride does more than just remove the water present in the concentrated sulphuric acid, and also clear that the results do not correspond quantitatively to any of the reactions 7-9 in Table XV . To fit the observed intensities to an equilibrium involving either or both of the species $CF_3CO.HSO_4$ or $(CF_3CO)_2.SO_4$ (analogous to the $HSO_3F$ system) requires equilibrium 'constants' that vary by more than an order of magnitude for the four samples, and are even negative in some cases. The participation of the mixed anhydrides (perfluoroacyl sulphates) can, in fact, be eliminated on other grounds. Firstly, if these species are present, they must be exchanging with $CF_3CO_2H$ since only two peaks are seen in the spectrum and yet $CF_3CO.ClO_4$ and $CF_3CO.SO_3F$ give separate, distinct signals. Secondly, at least one mole of $CF_3CO_2H$ would be produced for each mole of $CF_3CO.HSO_4$, and Dowdall, who has actually isolated the compound $CF_3CO.SO_3OH$ ($=CF_3CO.HSO_4$), has shown that the acyl hydrogen sulphate reacts quantitatively with trifluoroacetic acid to give $H_2SO_4$ and the anhydride (111).

As the possibility of mixed anhydride formation can be discounted, Table XV suggests that the most likely reaction is dehydration of the sulphuric acid to $SO_3$, and for the highest concentration of anhydride, the difference between the observed intensity and that calculated for complete

TABLE XV

Chemical Shifts, and the ratio (product peak)/(anhydride peak)

for solutions of $H_2SO_4$ in $(CF_3CO)_2O$

| Sample | Mole fraction $H_2O/H_2SO_4/(CF_3CO)_2O$ | Peak ratio (Observed) | Peak ratio (calculated) 6 | 7 | 8 | 9 | Peak Separation (c.p.s.) |
|---|---|---|---|---|---|---|---|
| 1 | .139/.439/.422 | 6.5 | .49 | ∞ | ∞ | ∞ | 5.5 |
| 2 | .105/.330/.565 | 2.1 | .23 | 3.2 | ∞ | 3.2 | 8.7 |
| 3 | .090/.283/.627 | 1.3 | .17 | 1.5 | ∞ | 1.5 | 10.1 |
| 4 | .078/.245/.677 | .87 | .13 | .91 | 5.2 | .91 | 9.1 |

Key to reactions

6 $(CF_3CO)_2O + H_2O \rightarrow 2CF_3CO_2H$

7 $(CF_3CO)_2O + H_2SO_4 \rightarrow CF_3CO_2H + CF_3CO.HSO_4$

8 $2(CF_3CO)_2O + H_2SO_4 \rightarrow 2CF_3CO_2H + (CF_3CO)_2.SO_4$

9 $(CF_3CO)_2O + H_2SO_4 \rightarrow 2CF_3CO_2H + SO_3$

Intensity ratios calculated assuming $CF_3CO.HSO_4$ and $(CF_3CO)_2SO_4$ exchange with $CF_3CO_2H$ to give a single peak.

dehydration is less than 5%. The reaction would not be quantitative. for sulphur trioxide and $(CF_3CO)_2O$ compete for the sulphuric acid. One can write:-

$$nH_2SO_4 + (n-1)\ (CF_3CO)_2O \rightleftharpoons H_2S_nO_{2n+1} + 2(n-1)\ CF_3CO_2H \quad 10)$$

Raman studies of oleums (169; 40, p. 163), have shown that n can take the values 2, 3, 4 or higher, while free $SO_3$ may exist in the solution as cyclic trimers. There is also the possibility of the adducts $SO_3.n(CF_3CO)_2O$, n= 1 or 2, and $SO_3.nCF_3CO_2H$, n= 2 or 3, analogous to the acetic acid derivatives described by Ram Chand Paul et al. (161,162). Half a dozen or more different species might be present in solution, involving a corresponding number of entirely unknown equilibrium constants. Thus, while the reactions 10) are probably the most important ones in the $H_2SO_4/(CF_3CO)_2O$ system, quantititave interpretation would need further experiments.

It will be noticed that the $CF_3CO_2H$ signal shifts considerably as the composition of the mixture is changed, just as in the $HSO_3F$ system, and again this is probably caused by protonation of the trifluoroacetic acid. Protonation must be quite extensive, for even at the lowest concentrations of anhydride the $CF_3CO_2H$ signal is already 5.5 c.p.s. to <u>low</u> field of $(CF_3CO)_2O$, whereas in the absence of $H_2SO_4$, it occurs at about 45 to 50 c.p.s. (the exact position depending on concentration) to <u>high</u> field. The strength of polysulphuric acids is generally believed to increase with the number of sulphur atoms per molecule; higher concentrations of anhydride

should produce greater amounts of the stronger acids, and this is consistent with the gradual movement of the $CF_3CO_2H$ signal to low field. However, at very high concentrations the higher acids will disappear as free $SO_3$ is produced, protonation of $CF_3CO_2H$ will be reduced and the signal should retreat to higher fields. This point seems to have been reached in sample number 4.

E. The system $H_2O/HNO_3/(CF_3CO)_2O$

Only one $^{19}F$ N.M.R. signal was observed for a solution of composition $H_2O/HNO_3/(CF_3CO)_2O$: .337/.217/.446, mole fraction, although there was enough anhydride to react with the water present and to leave some over. There must have been a further reaction with the nitric acid itself, probably according to one of the equations:-

$$HNO_3 + (CF_3CO)_2O \longrightarrow CF_3CO_2H + CF_3CO.O.NO_2 \qquad 11)$$

or

$$2HNO_3 + (CF_3CO)_2O \longrightarrow 2CF_3CO_2H + N_2O_5 \qquad 12)$$

A solution of the composition $H_2O/HNO_3/(CF_3CO)_2O$: .264/.170/.566 mole fraction (i.e. more than sufficient anhydride for completion of reactions 11 or 12) showed two peaks, areas 3.42:1.0, with the weaker signal 10.4 c.p.s. to low field. The weaker signal is assigned to excess anhydride, and the stronger to $CF_3CO_2H$, or $CF_3CO_2H$ exchanging with other species. The theoretical intensity ratios are 3.31:1 for reaction 11), assuming exchange between the products, or 1.61:1 for reaction 12), indicating the formation of the mixed anhydride,

$CF_3CO.O.NO_2$. Exchange with the trifluoroacetic acid could proceed via the ionic form $NO_2^+.^-O_2CCF_3$, nitryl trifluoroacetate.

After several days, some brown gas ($NO_2$) was observed over the first solution studied ($H_2O/HNO_3/(CF_3CO)_2O$: 0.337/0.217/0.446), but not in the second solution where the amount of anhydride was sufficient to react with all the nitric acid according to equation 11). Large, colourless crystals appeared in this second solution, but their analysis was prevented by the violent explosion of the sample. Though not conclusive, this is at least consistent with the presence of $CF3CONO_3$, for acyl nitrates are known to be highly unstable.

F. The system $H_2O/HBF_4/(CF_3CO)_2O$

Tetrafluoroboric acid was used as an aqueous solution, prepared by dissolving a stoicheiometric quantity of boron trioxide in concentrated hydrofluoric acid. In a preliminary experiment, a mixture was made containing $H_2O/HBF_4/(CF_3CO)_2O$ in mole fractions .474/.076/.450, i.e. the solution had insufficient anhydride to react with all the water present. The two resonances observed were assigned to $CF_3CO_2H$ and $BF_4^-$. The ratio of the peak areas ($BF_4^-/CF_3CO_2H$ = 0.116) is close to that predicted from the stoicheiometry of the mixture (0.113) and the chemical shift of the $BF_4^-$ peak (70.0 p.p.m. to high field of $CF_3CO_2H$) is in good agreement with the literature values (163).

In a second sample the mole fractions $H_2O/HBF_4/(CF_3CO)_2O$ were .380/.060/.560. The spectrum is

entirely consistent with the reaction:-

$$(CF_3CO)_2O + HBF_4 \longrightarrow CF_3CO_2H + CF_3COF + BF_3 \qquad 13)$$

Details of the spectrum are recorded in Table XVI, where the intensities are compared with those calculated from the stoicheiometry of the mixture assuming that reaction 13) goes to completion. Agreement is remarkably good in view of the difficulty of integrating the smaller peaks accurately. The coupling constants found from the doublet and from the quartet (6.2 and 5.6 c.p.s.) are probably as close as can be expected for peaks so far apart. It is surprizing that there is no published spectrum for the compound $CF_3COF$, but the shifts and coupling constants found (-1.25 p.p.m. ($CF_3$), - 90.6 p.p.m. (CFO); J 5.6-6.2 c.p.s.) are fairly close to the values given by Prager (164) for the rather similar compound $ClCF_2CF_2'C(O)F''$ ( $\delta_F$ = -7.4 p.p.m., $\delta_{F'}$ = 3.8.7 p.p.m., $\delta_{F''}$ = -103.7 p.p.m. relative to $CF_3CO_2H$, $J_{F'-F''}$ = 8.0 c.p.s.).

No coupling was observed between B and F in the spectrum of $BF_3$, but the chemical shift (+53.1 p.p.m. relative to internal $CF_3CO_2H$) was close to the published value (+48.4 p.p.m. to external $CF_3CO_2H$, 163).

Reaction 13) may proceed via the formation of $CF_3CO.BF_4$. The analogous hexafluoro-phosphate, -arsenate and -antimonate derivatives have been claimed, but are all unstable at room temperature (128).

G. The system $(CF_3CO)_2O/CF_3CO_2H/SbF_5$

$^{19}F$ N.M.R was used to investigate the reaction of trifluoroacetic acid with antimony pentafluoride. A small

TABLE XVI

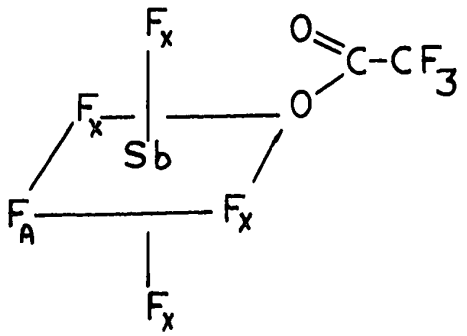
Chemical shifts (p.p.m.), coupling constants (c.p.s.) and relative intensities for the solution $H_2O/HBF_4/(CF_3CO)_2O$: .380/.060/.560

| Peak | Chemical shift | Intensity Observed | Intensity Calculated | Assignment |
|---|---|---|---|---|
| A | -90.6 (quartet, J=5.6) | .02 | .024 | $CF_3COF$ |
| B | -1.25 (doublet, J=6.2) | .069 | .073 | $CF_3COF$ |
| C | -.50 | .304 | .293 | $(CF_3CO)_2O$ |
| D | 0.0 | 1.00 | 1.00 | $CF_3CO_2H$ |
| E | +53.1 | .07 | .073 | $BF_3$ |

amount of trifluoracetic anhydride was added to the solutions to ensure anhydrous conditions. Figure 12 reproduces the spectra at 25°C and -15°C of a mixture containing $SbF_5/(CF_3CO)_2O/CF_3CO_2H$ in mole fractions of .338/.023/.639 and Table XVI a) summarizes the observations. Spectra of more dilute solutions were very similar, but failed to show the small peaks I and J. The results closely resemble those found for $SbF_5$ in other solvents (165,166), and are consistent with the reaction:-

$$SbF_5 + CF_3CO_2H \longrightarrow HSbF_5(O_2CCF_3) \qquad 14)$$

At 25°C, the broad peak A can be attributed to the $CF_3$ group of $HSbF_5(O_2CCF_3)$ exchanging with $CF_3CO_2H$, the sharp peak B to anhydride, and peak C (also broadened by the exchange process) to F on Sb. These assignments are confirmed by the spectrum at -15°C, where exchange is slow enough to permit resolution of peak A into the separate signals D($HSbF_5O_2CC\underline{F}_3$) and E ($CF_3CO_2H$). In the F on Sb region a doublet and a quintet can be distinguished (peaks G and H). Together these represent a typical $AX_4$ spectrum arising from the acid $HSbF_5(O_2CCF_3)$ or the anion (i) derived from it:-




i)

Figure 12

The $^{19}F$ nuclear magnetic resonance spectrum of $SbF_5$ in trifluoroacetic acid.

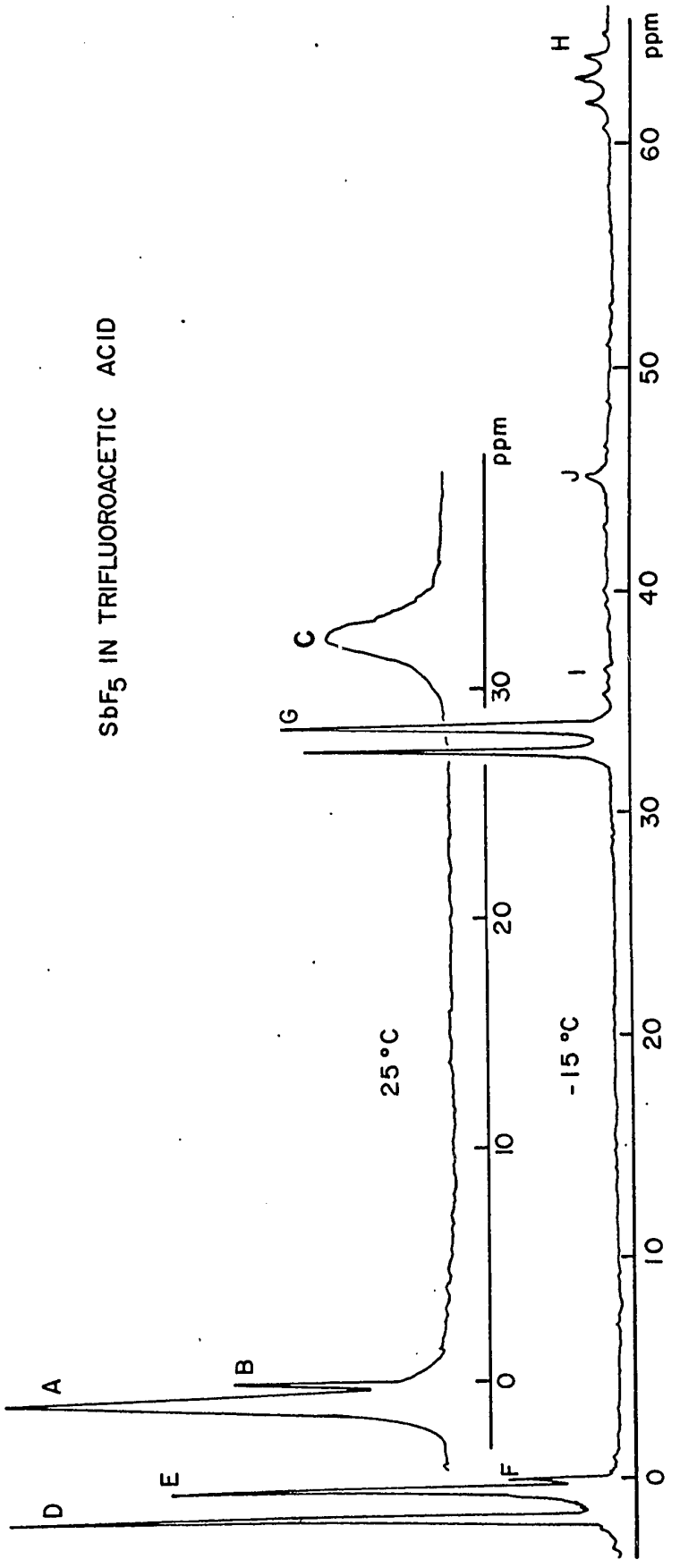

SbF5 IN TRIFLUOROACETIC ACID
A
B
C
D
E
F
G
H
I
J
25 °C
-15 °C
ppm
ppm
0
10
20
30
40
50
60
0
10
20
30

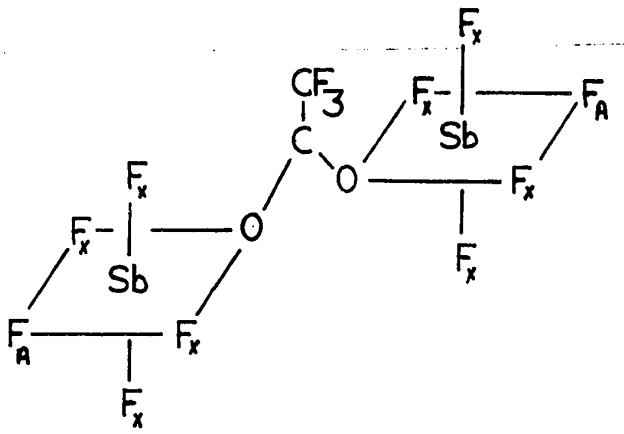
TABLE XVI a)

$^{19}F$ N.M.R. chemical shifts for the system

$SbF_5/CF_3CO_2H/(CF_3CO)_2O$, mole fractions .338/.023/.639

| Peak | Assignment | Chemical shift (p.p.m. from $(CF_3CO)_2O$) |
|---|---|---|
| A | F on C in $HO_2CCF_3$ and $HSbF_5(O_2CCF_3)$ | - 0.82 |
| B | $(CF_3CO)_2O$ - internal | 0.0 |
| C | F on Sb | + 32.3 |
| D | F on C in $HSbF_5(O_2CCF_3)$ | - 1.65 |
| E | bulk $HO_2CCF_3$ | - 0.37 |
| F | $(CF_3CO)_2O$ | 0.0 |
| G | $F_x$ on Sb in $HSbF_5(O_2CCF_3)$ | + 33.3 ($J_{ax}$ = 98.6 c.p.s.) |
| H | $F_a$ on Sb in $HSbF_5(O_2CCF_3)$ | + 60.4 ($J_{ax}$ = 97.5 c.p.s.) |
| I | $F_x$ on Sb in $H(SbF_5)_2O_2CCF_3$ | + 35.8 ($J_{ax}$ = 100.1 c.p.s.) |
| J | $HSbF_6$ | + 45.1 |

The relative intensities and chemical shifts of peak D, G and H are consistent with this formulation, while the coupling constant $J_{Fa-Fx}$ (98.0 c.p.s.) is similar to that found for the analogous derivatives of $SbF_5$ with $H_2O$ and $HSO_3F$ (165 166). The doublet peak, I, in the F on Sb region is probably one part of an $AX_4$ spectrum arising from the dimeric ion (ii) below:-




ii)

Similar associated species have been observed in other solvents (165,166). The quintet of the second $AX_4$ spectrum would be too weak to observe.

Peak J is attributed to $SbF_6^-$; its chemical shift is close to the literature values (163). The signal is broadened by quadrupole relaxation of the $^{121}Sb$ and $^{123}Sb$ nuclei (I = 5/2, 7/2). $SbF_6^-$ could be produced by a ligand redistribution reaction:-

$$2SbF_5(O_2CCF_3)^- \longrightarrow SbF_6^- + SbF_4(O_2CCF_3)_2^- \qquad 15)$$

By analogy with other known $SbF_4X_2^-$ species, the second product of reaction 15) is expected to have a cis structure

(165,166), and to give two triplets in the N.M.R. spectrum. These peaks were not observed, for the intensity of each signal would be only 2/3 that of the $SbF_6^-$ peak, and would be distributed among the three component peaks of the triplet and lost in the base-line. When a trifluoroacetic acid solution of $SbF_5$ was mixed with a solution of potassium trifluoroacetate, a dense white precipitate was obtained. This was identified as $KSbF_6$ by its X-ray powder diffraction pattern, although the potassium analysis was slightly low (found 13.2%; required, 14.2%, $KSbF_6$; 10.6%, $KSbF_5(O_2CCF_3)$). The N.M.R. spectrum of the supernatant liquid showed several peaks in the F on C region, but no fluorine on antimony could be detected.

H. The system $H_3BO_3/(CF_3CO)_2O/CF_3CO_2H$

Gillespie (40, p. 164) has prepared sulphuric acid solutions of the complex acid, $HB(HSO_4)_4$, by reacting $H_3BO_3$ with $SO_3$. It was hoped that a similar reaction with $(CF_3CO)_2O$ would give an acid in trifluoroacetic acid. The literature contains many claims for triacyl borates, but only one of these can be supported (115). As described in Chapter II, attempts to isolate the compounds $HB(O_2CCF_3)_4$ or $B(O_2CCF_3)_3$ led to mixtures of $B(O_2CCF_3)_3$ with the diborate, $(CF_3CO_2)_2B.O.B(O_2CCF_3)_2$.

In order to investigate the reaction in solution, N.M.R. studies were made on solutions prepared from boric acid and trifluoroacetic anhydride, sometimes with added trifluoroacetic acid. A clear solution was obtained usually

after about ten days. Two peaks were observed in the $^{19}F$ N.M.R. spectrum one of which was assigned to $(CF_3CO)_2O$, and the other (about 40-45 c.p.s. to high field depending on concentration) to $CF_3CO_2H$ exchanging with the boron species. The exchange could not be slowed down enough to permit resolution of separate $CF_3CO_2H$ and acyl borate resonances although the spectrum was investigated at temperatures down to about -20°C. The results of the study are recorded in Table XVII, where the observed ratio of (product peak)/(anhydride peak) can be compared with that predicted from the reactions:-

$$B(OH)_3 + 3(CF_3CO)_2O \longrightarrow B(O_2CCF_3)_3 + 3CF_3CO_2H \qquad 16)$$

$$2B(OH)_3 + 5(CF_3CO)_2O \longrightarrow B_2O.(O_2CCF_3)_4 + 6CF_3CO_2H \qquad 17)$$

Table XVII also gives the percentage of the total boron that is present as $B(O_2CCF_3)_3$, and the time elapsed between making up the solutions and running the spectra. Since the reaction between $H_3BO_3$ and $(CF_3CO)_2O$ is a heterogeneous one then a smooth variation of the results with time cannot be expected; nevertheless, a general trend is apparent. Sample 1) shows that reaction 16) occurs quantitatively, and that the solution is stable for up to about three weeks after preparation. After this time, spontaneous decomposition to $B_2O(O_2CCF_3)_4$ becomes serious. Sample 2) and 3) are particularly useful, since spectra were run on two separate occasions. There was usually a considerable delay (about 10 days) between complete

TABLE XVII

Chemical shifts and intensity ratios

for solutions of $H_3BO_3$ in $(CF_3CO)_2O$

| Sample | Mole fraction $H_3BO_3/(CF_3CO)_2O/CF_3CO_2H$ | Peak Separation (c.p.s.) | Intensities (product/anhydride) Obs. | Eq.16 | Eq.17 | $B(O_2CCF_3)_3$ (%) | Time elapsed (days) |
|---|---|---|---|---|---|---|---|
| 1 | .128/.872/0.0 | 43.7 | .792 | .787 | .497 | 100 | 24 |
| 2 | .118/.882/0.0 | 41.6 | .582 | .668 | .500 | 54 | 27 |
| 2a | " | 44.3 | .550 | " | " | 32 | 65 |
| 3 | .173/.827/0.0 | 42.0 | 1.24 | 1.69 | 1.08 | 28 | 27 |
| 3a | " | 42.4 | 1.20 | " | " | 20 | 65 |
| 4 | .144/.856/0.0 | 42.4 | .823 | 1.02 | .729 | 35 | 34 |
| 5 | .099/.615/.286 | 44.2 | 1.11 | 1.38 | 1.06 | 18 | 34 |
| 6 | .122/.340/.538 | 45.0 | 2.94 | 5.00 | 2.84 | 13 | 34 |
| 7 | .0873/.384/.528 | 43.6 | 3.24 | 4.31 | 2.91 | 29 | 34 |

dissolution of the boric acid and running the spectra. For conductivity studies (Chapter V) the measurements could be made as soon as reaction was complete, and under these conditions, concentrations of the diborate, $B_2O.(O_2CCF_3)_4$ are thought to be negligible.

Since it was not possible to separate the signals due to the boron species and the solvent, $CF_3CO_2H$, there is no sure way of distinguishing between $B(O_2CCF_3)_3$ (or $B_2O(O_2CCF_3)_4$) and the acid derived from it, $HB(O_2CCF_3)_4$ (or $HB_2O(O_2CCF_3)_5$). The protonic acid form is much more probable, however, for it explains the rapid exchange between $CF_3CO_2H$ and boron species as well as the fact that $B(O_2CCF_3)_3$ is an electrolyte that can be titrated with caesium trifluoroacetate. In addition, the salts $MB(O_2CR)_4$ and $MB_2O(O_2CR)_5$ are known (present work, 117-119).

I. Miscellaneous

A few experiments were made to investigate the action of trifluoroacetic anhydride on some common substances, but these were only partially successful.

Chromic anhydride, $CrO_3$, dissolved readily in $(CF_3CO)_2O$ to give a dark orange, almost black solution, but the $^{19}F$ N.M.R. showed only a single broad resonance in the F on C region. It is likely that the solution (which turned green after several weeks) contained some paramagnetic $Cr^{3+}$ ion which would explain the width of the absorption.

Sodium nitrite reacted with $(CF_3CO)_2O$ to give a brilliant yellow solution and a white residue (probably

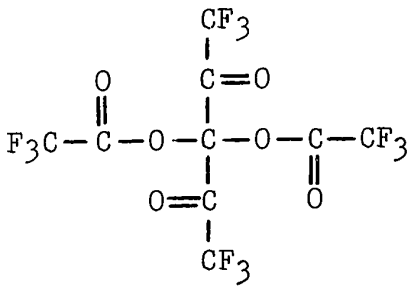
$CF_3CO_2Na$ and unchanged $NaNO_2$). The solution was forced through a sintered glass frit into an N.M.R. tube, but again only a single broad peak was observed in the spectrum. The product was probably nitrosyl trifluoroacetate, $NO.O_2CCF_3$, which has also been prepared by irradiation of a mixture of $(CF_3CO)_2O$ and NOCl (112) and is described as a yellow, explosive liquid. This substance is not expected to exchange with anhydride, and the fact that only one signal is observed may be due to paramagnetic broadening of the peak by traces of free NO or $NO_2$ in the solution.

Formaldehyde (as the solid polymer, paraformaldehyde) dissolves slowly in $(CF_3CO)_2O$, and one can envisage the reactions:-

$$2(CF_3CO)_2O + H_2CO \longrightarrow \underset{\text{I}}{CF_3CO.CO.CO.CF_3} + 2CF_3CO_2H \qquad 18)$$

$$3(CF_3CO)_2O + H_2CO \longrightarrow \underset{\text{II}}{(CF_3CO)_2.C.(CF_3CO_2)_2} + 2CF_3CO_2H \qquad 19)$$

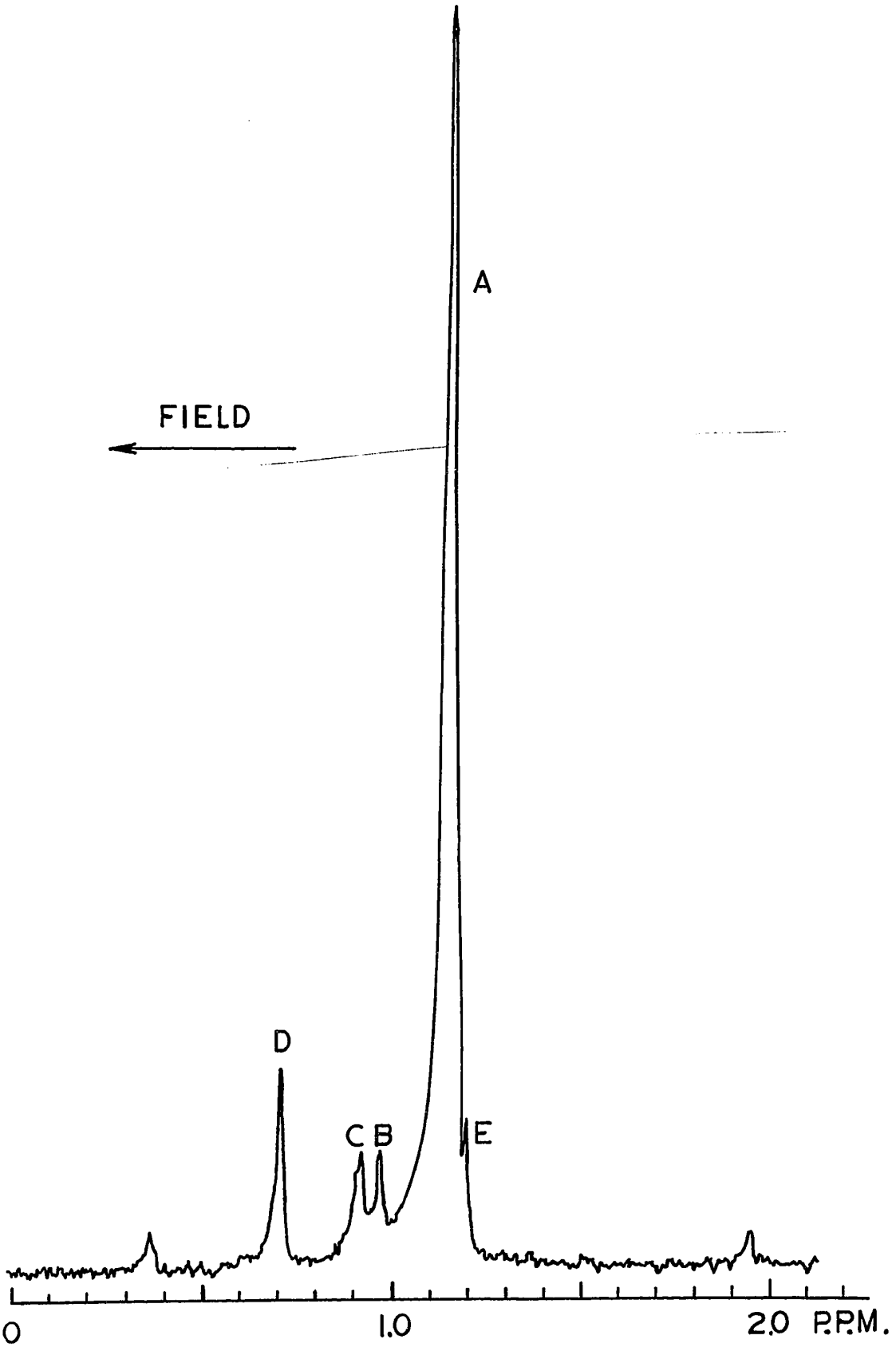
The diagram shows that compound II would have two types of fluorine in different chemical environments and present in equal amounts.



II

Figure 13

The $^{19}F$ nuclear magnetic resonance spectrum of formaldehyde in $(CF_3CO)_2O$.


A
FIELD
D
C
B
E
0
1.0
2.0 P.P.M.

A solution with mole ratios $H_2CO/(CF_3CO)_2O$ equal to 1:4.65 gave the spectrum shown in Figure 13. While accurate integration was not possible, the large peak A can be assigned to $(CF_3CO)_2O$, and D to $CF_3CO_2H$. The two equal peaks B and C probably arise from compound (II), and the peak E from compound (I). Without further work, a definite interpretation cannot be made.

Summary

Reliable conductivity measurements in trifluoroacetic acid must be carried out at low concentrations of electrolyte to avoid interference from triple ions, and in the presence of trifluoroacetic anhydride to remove adventitious water. The conventional strong mineral acids are unsuitable as electrolytes, because they react with the anhydride. $^{19}F$ nuclear magnetic resonance has established the following reactions

1. $HClO_4 + (CF_3CO)_2O \longrightarrow CF_3CO.O.ClO_3 + CF_3CO_2H$
   $CF_3CO.ClO_4$ is unstable, decomposing to oxides of chlorine, probably $Cl_2O_6$.

2. $HSO_3F + (CF_3CO)_2O \longrightarrow CF_3CO.OSO_2F + CF_3CO_2H$
   The reaction is an equilibrium, and a constant of 0.12 to 0.17 was estimated.

3. $nH_2SO_4 + (n-1)\ (CF_3CO)_2O \longrightarrow H_2S_nO_{2n+1} + 2(n-1)\ CF_3CO_2H$

4. $HNO_3 + (CF_3CO)_2O \longrightarrow CF_3CO.ONO_2 + CF_3CO_2H$
   Crystals of what is probably $CF_3CO.NO_3$ were obtained, but

were lost in an explosion.

5. $HBF_4 + (CF_3CO)_2O \longrightarrow CF_3COF + BF_3 + CF_3CO_2H$

6. $CF_3CO_2H + SbF_5 \longrightarrow H.SbF_5(O_2CCF_3)$

7. $H_3BO_3 + 3(CF_3CO)_2O \longrightarrow B(O_2CCF_3)_3 + 3CF_3CO_2H$

   $B(O_2CCF_3)_3$ probably exists as $HB(O_2CCF_3)_4$, and decomposes slowly to give $B_2O.(O_2CCF_3)_4$

The acids $HSbF_5(O_2CCF_3)$ and $HB(O_2CCF_3)_4$ are suitable for conductance studies. Some evidence was found that $(CF_3CO)_2O$ gives nitrosyl trifluoroacetate with sodium nitrite, and a novel compound with formaldehyde.

# CHAPTER IV

## Bases in trifluoroacetic acid - electrical conductivity at low concentrations

### A. General

The strongest base that can exist in a solution is the solvent anion. The alkali metal trifluoroacetates are therefore expected to be strong bases in trifluoroacetic acid, and a study of their electrical conductivities was undertaken. The results of the study (141) have helped to understand the nature of the solvent, and have added to the very sparse data available on electrical conductivity in non-aqueous solutions.

Solvents of low dielectric constant are difficult to work with. At very low concentrations an electrolyte can exist as covalent molecules, ion pairs (contact or solvent-separated), and free (solvated) ions.

$$MA \rightleftharpoons M^+A^- \rightleftharpoons M^+ + A^-$$

Even strong (fully ionized) electrolytes may be only slightly dissociated. At higher concentrations, ion triplets and higher aggregates occur, making accurate, quantitative interpretation of conductance data impossible. This particular difficulty can be avoided by working at concentrations of less then $2 \times 10^{-4}$ molar for trifluoroacetic acid ($\sim 3.2 \times 10^{-7} D^3$, $D = 8.40$ at 25°C), when triple ions form less than about one percent of the total conducting species. A lower concentration limit ($\sim 10^{-5}$ molar) is imposed by the conductance of the solvent itself. Below this concentration, the conductance of solute and solvent are comparable, and large errors arise.

The uncertaintities are particularly serious where solvent and solute share a common ion, since there will be a mutual repression of dissociation, the extent of which is unknown. The conductivity measurements reported here, then, covered the concentration range $10^{-5}$ to 2 x $10^{-4}$ molar.

Precise work at such low concentrations raises enormous experimental difficulties in so hygroscopic a medium. A concentration of $\sim$2.5 p.p.m. in water would be equal to the highest concentration of electrolyte studied, and could affect the measurements both by contributing conducting ions to the solution, and also by selective solvation of the electrolyte. A special case of selective solvation could arise in studies of acids, where the reaction:-

$$HX + H_2O \longrightarrow H_3O^+ + X^-$$

is likely to be preferred to:-

$$HX + CF_3CO_2H \longrightarrow CF_3CO_2H_2^+ + X^-$$

The precautions taken to avoid interference by adventitious water have been detailed in Chapter II, but a necessary preliminary to conductance studies is to investigate the behaviour of water in the system.

When the experimental difficulties are solved, there remains the problem of interpretation. The electrolytes studied were all incompletely dissociated, and the dissociation is governed by a constant:-

$$K = f^2 c\gamma^2/(1-\gamma) \qquad 1)$$

where f is the activity coefficient

$\gamma$ is the degree of dissociation

Fuoss (27, p. 213) has derived a theoretical expression for the dissociation constant:-

$$1/K = \frac{4\pi N\mathring{a}^3}{3000} \cdot \exp(e^2/kTD\mathring{a}) \qquad 2)$$

where e is the charge on the electron (e.s.u.)

k is Boltzmann constant

T is the temperature (°K)

D is the dielectric constant.

The parameter, $\mathring{a}$, the distance of closest approach between ions, has been the subject of much discussion in the literature, and is, in many cases, approximately equal to the sum of the radii of cation and anion.

The equivalent conductivity of an electrolyte, $\Lambda$, is related to the conductivity at infinite dilution, $\Lambda_o$, by an equation proposed by Fuoss, Onsager and Skinner (142):-

$$\Lambda = \gamma(\Lambda_o - (B_1\Lambda_o + B_2)\, c\gamma + (E_1\Lambda_o - E_2)c\gamma \cdot \log_e(6E_1 c\gamma) + Lc\gamma) \qquad 3)$$

The constants $B_1$, $B_2$, $E_1$, $E_2$ are functions of the dielectric constant and viscosity of the solvent and of the temperature only, while L contains $\Lambda_o$ and $\mathring{a}$. Expressions for the coefficients are given in Appendix I. It will be noticed that if the $E_1$, $E_2$ and L terms are ignored, equation 3) reduces to the Onsager limiting law for a weak electrolyte, while if ionic strength effects are neglected so that f = 1 and the coefficients $B_1$, $B_2$, etc. are all zero, then $\gamma = \Lambda/\Lambda_o$, and

substitution in 1) gives the familiar Ostwald dilution law.

With these equations, conductivity data can be analyzed quite easily. Equation 3) is rearranged to:-

$$\gamma = \Lambda/(\Lambda_o - G(\Lambda_o, \mathring{a}, c, \gamma)) \qquad 3a)$$

$G(\Lambda_o, \mathring{a}, c, \gamma)$ is simply convenient shorthand for the mobility correction written out in full in equation 3). An initial guess is made for $\Lambda_o$ ($=\Lambda_o'$, say) and for $\mathring{a}$, with $\gamma$ put equal to $\Lambda/\Lambda_o'$ as a first approximation Iteration of 3a) leads to a self-consistent value for $\gamma$. The activity coefficient is calculated from the extended Debye-Hückel equation, thus allowing for ionic volume.

$$\log f = -A(c\gamma)^{\frac{1}{2}}/(1+B\mathring{a}(c\gamma)^{\frac{1}{2}}) \qquad 4)$$

where A and B are constants (see Appendix I). Substitution in 1) shows that a plot of $1/\gamma\Lambda_o'$ against $cf^2\Lambda_o'\gamma$ is a straight line, slope $1/\Lambda_o$, intercept $1/K(\Lambda_o)^2$, where K is the dissociation constant, and $\Lambda_o$ a better approximation to the limiting equivalent conductivity. From 2), a better value of $\mathring{a}$ is calculated, and the entire process repeated until $\Lambda_o$ changes by no more than one part in ten thousand. A computer program was written to accomplish this automatically (Appendix II), and differs in detail from the program given by Kay (143). The method is essentially that of the Fuoss 1935 paper (144), using a more accurate expression for the activity coefficient, and retaining the higher terms of the conductance equation.

B. Experiments with water and trifluoroacetic anhydride

Table XVIII shows the results of an experiment in which small portions of the anhydride were added to trifluoroacetic acid in the conductivity cell, and then small portions of water. The same results are given graphically in Figure 14. For convenience, the points for water are plotted as negative on the anhydride concentration axis, since within the limits of the experiment, water appears to remove anhydride completely:-

$$(CF_3CO)_2O + H_2O \longrightarrow 2CF_3CO_2H$$

No attempt was made to study water at the very low concentrations to which the Fuoss-Onsager analysis is applicable, since the conductances would have been far too small to measure reliably; nevertheless, very valuable conclusions may be drawn from Figure 14. The first addition of anhydride produces a sharp decrease in conductance, due to the removal of traces of water in the freshly distilled acid. Further anhydride gives a very slight decrease, which could be due to dielectric effects, or a reduction in the number of self-dissociation ions. The back-titration of the anhydride with water causes the specific conductivity curve to be retraced very well, and when all anhydride is consumed, the conductance rises sharply. From the point of intersection of the two curves, it can be calculated that the original, freshly distilled acid was about .005 molar in water. The conductance of the water solutions was approximately the same as that found by Simons and Lorentzen (5), while the sharp break at

TABLE XVIII

Specific conductances ($K_{sp}$) for trifluoroacetic anhydride and for water in trifluoroacetic acid at 25°C  Solvent $K_{sp}$ = .0949 $ohm^{-1}$ $cm^{-1}$

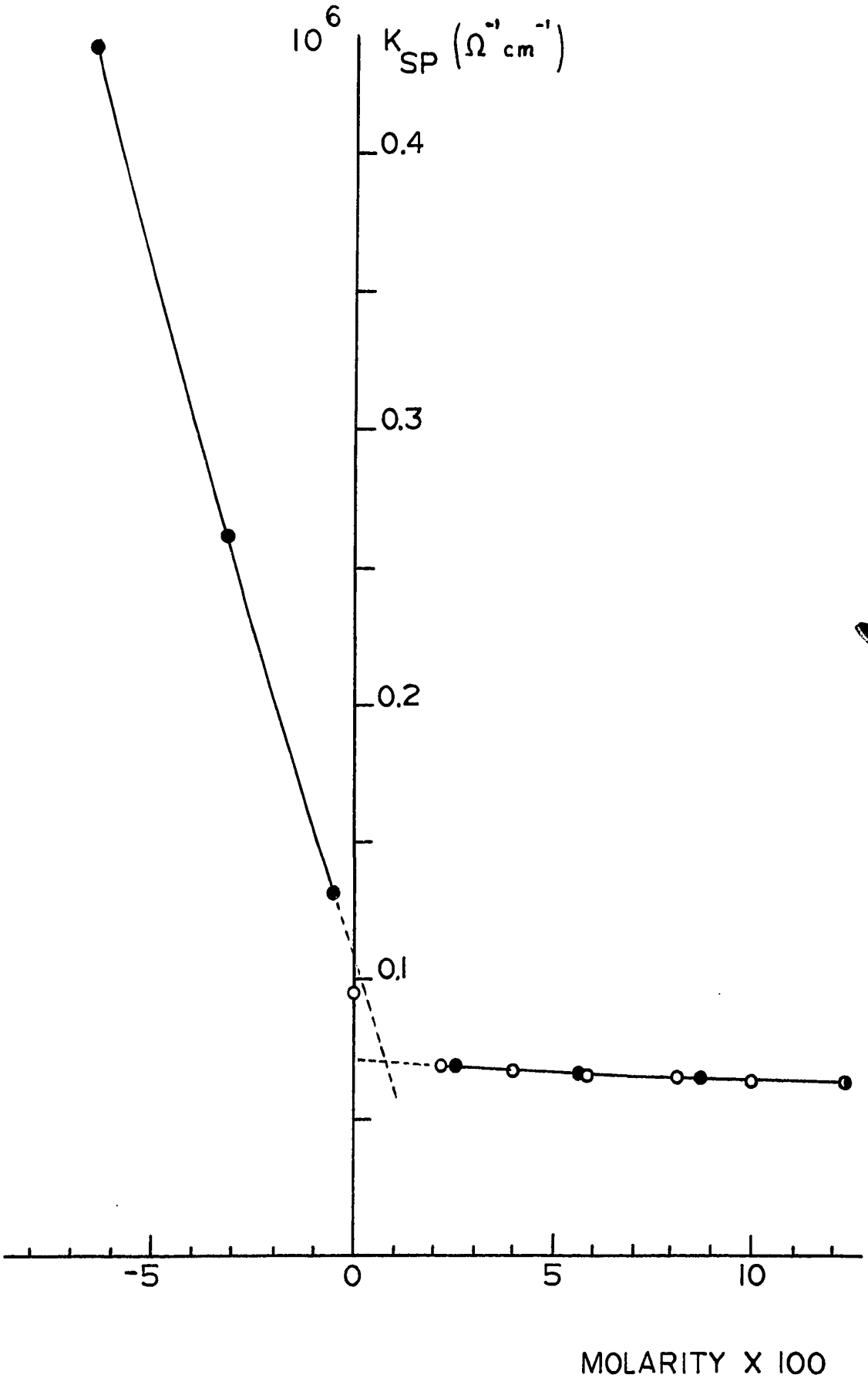
| Solute | $10^2$ x molarity | | $10^6$ x $K_{sp}$ |
|---|---|---|---|
| | Anhydride | Water | ($ohm^{-1}$ $cm^{-1}$) |
| Anhydride | 2.185 | | .0688 |
| additions | 4.025 | | .0672 |
| | 5.870 | | .0660 |
| | 8.102 | | .0644 |
| | 9.959 | | .0636 |
| | 12.26 | | .0631 |
| Water | 8.706 | | .0641 |
| additions | 5.703 | | .0661 |
| | 2.549 | | .0686 |
| * | - | .5801 | .1320 |
| | | 3.177 | .2610 |
| | | 6.448 | .4364 |
| | | 9.512 | .6240 |
| | | 12.56 | .8365 |
| | | 15.31 | 1.053 |
| | | 18.47 | 1.337 |
| | | 21.78 | 1.666 |

* All anhydride consumed at this point, water in excess.

Figure 14

The conductimetric titration of trifluoroacetic anhydride with water.

- o anhydride additions (read left to right)
- • water additions (read right to left)


$10^6$ $K_{SP}$ $(\Omega^{-1} cm^{-1})$
0.4
0.3
0.2
0.1
-5
0
5
10
MOLARITY X 100

an anhydride/water ration of 1:1 is qualitatively in agreement with the work of Tedder et al. (21), though their conductivities were higher than ours by an order of magnitude.

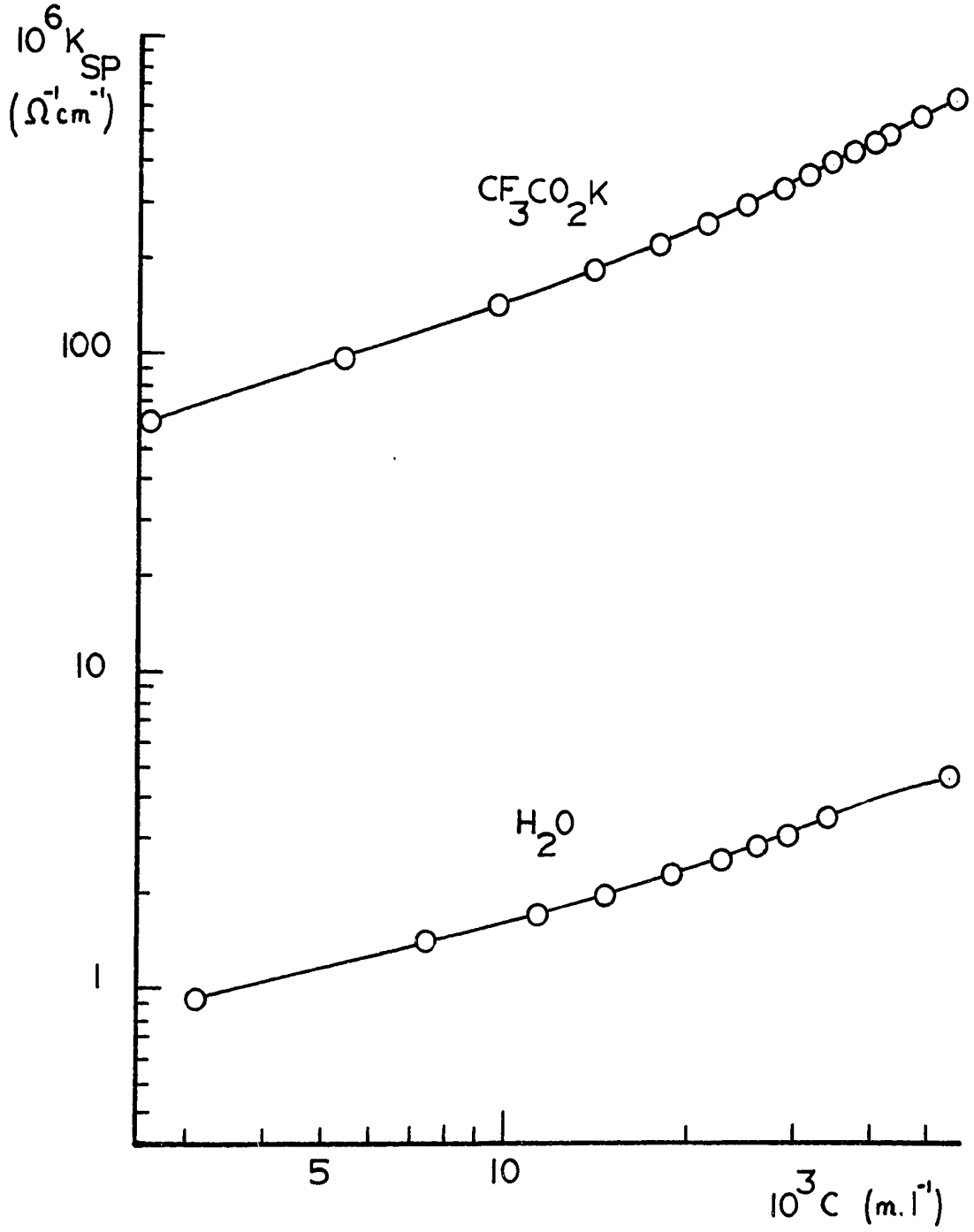
The reaction of water with anhydride in trifluoroacetic acid is not particularly rapid. When water was added to the solution of anhydride, the conductance jumped to a high value which fell slowly and reached a steady value after about 50 minutes. The variation of conductance with time suggested that the reaction was probably first order in water and in anhydride, with a rate constant of about 1.45 $mole^{-1}$ $min^{-1}$.

Figure 14 emphasizes that water has a much greater effect on the conductance of trifluoroacetic acid than does the anhydride, but in fact water is itself a very weak electrolyte. Figure 15 shows a comparison of the specific conductivity of water with that of potassium trifluoroacetate over the same concentration range, using the results of a more extensive experiment with water. It is seen that the conductance of water is less than that of the potassium salt by 2-3 orders of magnitude. This remarkable result recalls work in nitric acid (145, and references therein) and liquid hydrogen fluoride (40, p. 68), where the conductance of water solutions is also less than expected. Several explanations might be considered:-

a) that water is associated to polymers carrying a single proton, i.e. $\left[(H_2O)n.H_3O^+\right].CF_3CO_2^-$, as suggested by Hyman for water in liquid HF (40), resulting in a rather

Figure 15

Comparison of the specific conductances ($K_{sp}$) of water and potassium trifluoroacetate in trifluoroacetic acid.


$10^6 K_{SP}$
$(\Omega^{-1} cm^{-1})$
100
10
1
$CF_3CO_2K$
$H_2O$
5
10
$10^3 C$ $(m.l^{-1})$

small concentration of ions.

b) that the ions $H_3O^+$ and $CF_3CO_2^-$ each have a very small conductivity, owing to strong hydrogen bonding with the solvent.

c) that the ion pair $H_3O^+ . {}^-O_2CCF_3$ is almost undissociated.

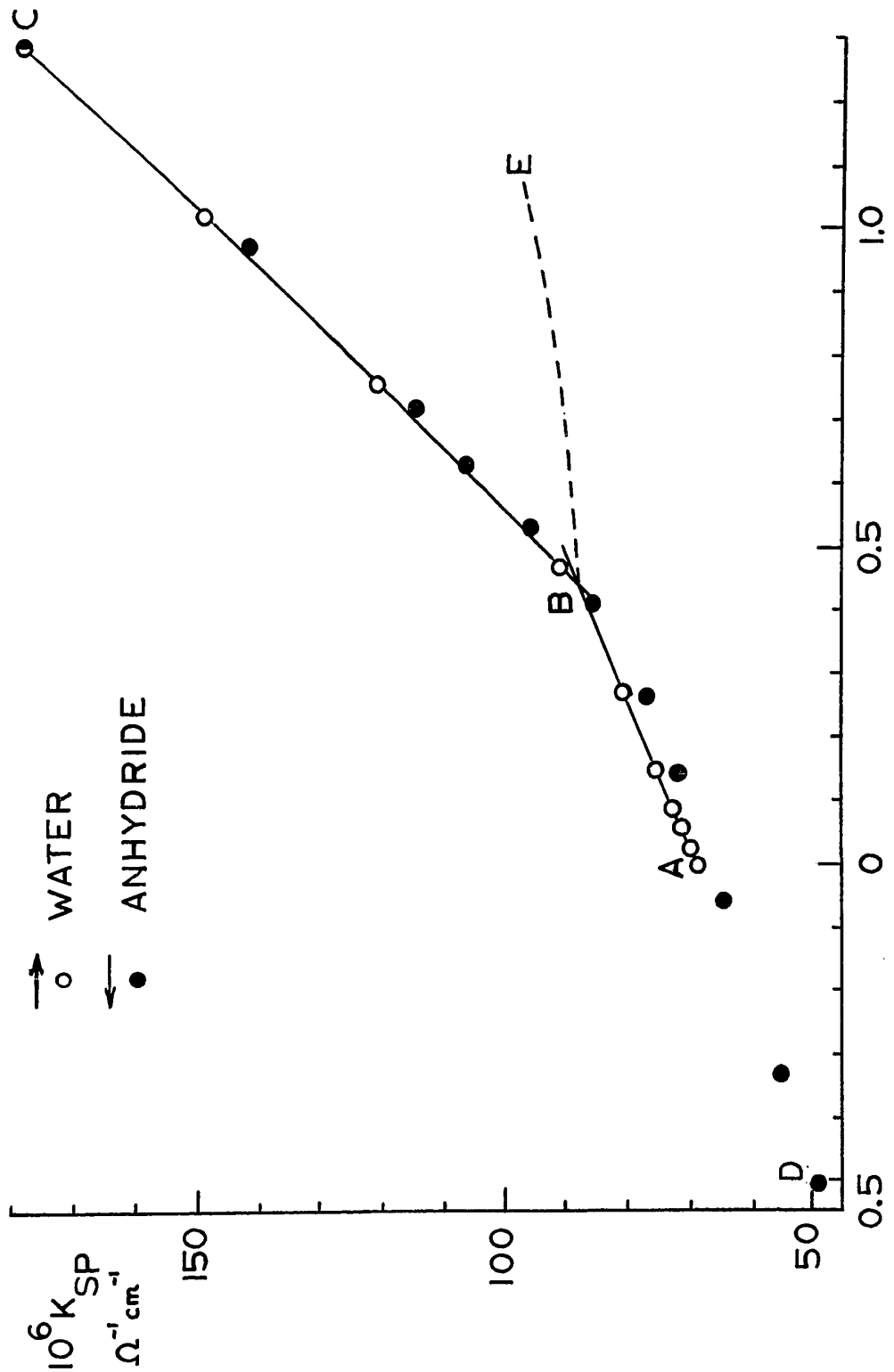
d) that water is not protonated.

The explanations a), b) and c) may be dismissed. Cryoscopy in $CF_3CO_2H$ and in $HNO_3$ (present work, 145), two solvents in which water is virtually a non-electrolyte, show that water neither associates to polymers nor produces dissociated ions i.e. it has a molecular weight of 18 in these solvents: the conductance of the alkali metal trifluoroacetates shows that whatever the mobility of the $H_3O^+$ ion may be, that of $CF_3CO_2^-$ is normal: Fuoss' theoretical expression for the dissociation constant of an electrolyte predicts that $H_3O^+ . {}^-O_2CCF_3$ should be dissociated to about the same extent as the ammonium salt.

It seems then, that water is simply not protonated in trifluoroacetic acid, which at first seems surprizing, for the acid is moderately strong in water ($pK_a$ = .175). However the situations are not analogous, for while 0.01 molar trifluoroacetic acid in 55 molar water may well dissociate, with the charge of the proton spread over the bulk of the solvent, this says nothing about the basicity of an isolated water molecule in 100% trifluoroacetic acid. It is possible that the acid is just not strong enough to protonate the water. Although ionic, crystalline derivatives of water are known

Figure 16

The effect of trifluoroacetic anhydride and water on the conductivity of caesium trifluoroacetate solutions.


C
E
B
A
D
WATER
ANHYDRIDE
$10^6 K_{SP}$
$\Omega^{-1}$ cm$^{-1}$
150
100
50
0.5
0
0.5
1.0
MOLARITY

with some strong acids, for example $H_3O^+ \cdot ClO_4^-$, no such compounds have been isolated for hydrogen fluoride or trifluoroacetic acid. The compound $CF_3CO_2H \cdot H_2O$ is known (82,83,87), but in the vapour phase at least this is a hydrogen-bonded hetero-dimer. and the system $H_2O/CF_3CO_2H$ is liquid above 0°C over the entire composition range.

It has sometimes been argued that when water is non-electrolyte, small traces may be permitted in measurements on more highly conducting species (147). This is not true for trifluoroacetic acid; Fig. 16 shows the effect of water and anhydride on the conductance of caesium trifluoroacetate. The solution was initially 0.032 m in the salt, and ~ 0.44 molar in anhydride. As water is added the conductance rises, and a sharp break occurs when all the anhydride is used up (points A-B). The curve is approximately retraced (C-D) when the water is back-titrated with anhydride, though the points are somewhat lower, as the titration produces solvent which dilutes the salt. The broken line (B-E) shows the expected curve if water simply contributes conducting ions to the solution, and the increase observed is obviously much more dramatic. The rather steep slope is probably due to changes in the bulk dielectric constant of the medium. Similar measurements on a more dilute solution of the caesium salt ($1.8 \times 10^{-4}$ molar) gave much the same sort of curve.

C. Alkali metal trifluoroacetates

The experimental conductivities of ammonium and the alkali metal trifluoroacetates are given in Table XIX for the concentration range $10^{-5}$ to $2 \times 10^{-4}$ molar. They are

TABLE XIX

Specific conductances ($K_{sp}$) and equivalent conductivities ( $\Lambda$ ) for ammonium and the alkali metal trifluoroacetates in trifluoroacetic acid at 25°C

| Solute ($K_{sp}$ pure solvent) | Concentration ($10^4$xmolarity) | $10^6 x K_{sp}$ (ohm$^{-1}$ cm$^{-1}$) | $\Lambda$ |
|---|---|---|---|
| $CF_3CO_2Li$ ($K_{sp}$ solvent = .0428 x $10^{-6}$ ohm$^{-1}$ cm$^{-1}$) | | | |
| | .1232 | .1288 | 10.46 |
| | .2359 | .1777 | 7.530 |
| | .4032 | .2315 | 5.741 |
| | .5119 | .2607 | 5.093 |
| | .6403 | .2917 | 4.556 |
| | .8172 | .3298 | 4.036 |
| | 1.035 | .3721 | 3.594 |
| | 1.249 | .4090 | 3.275 |
| | 1.452 | .4417 | 3.042 |
| | 1.639 | .4708 | 2.873 |
| | 1.797 | .4906 | 2.731 |
| $CF_3CO_2Na$ ($K_{sp}$ solvent = .0418 x $10^{-6}$ ohm$^{-1}$ cm$^{-1}$) | | | |
| | .2480 | .2273 | 9.167 |
| | .4568 | .3152 | 6.899 |
| | .6738 | .3872 | 5.747 |
| | .9000 | .4522 | 5.024 |
| | 1.133 | .5118 | 4.516 |
| | 1.292 | .5487 | 4.247 |
| | 1.479 | .5895 | 3.986 |
| | 1.670 | .6286 | 3.764 |
| | 1.927 | .6787 | 3 522 |
| $CF_3CO_2K$ ($K_{sp}$ solvent = .0586 x $10^{-6}$ ohm$^{-1}$ cm$^{-1}$) | | | |
| | .0961 | .2492 | 25.94 |
| | .2090 | .3852 | 18.43 |
| | .3695 | .5370 | 14.53 |
| | .5031 | .6423 | 12.77 |
| | .6129 | .7195 | 11.74 |
| | .7497 | .8075 | 10.77 |
| | .8998 | .8946 | 9.9411 |

TABLE XIX (cont.)

| Solute ($K_{sp}$ pure solvent) | Concentration ($10^4$xmolarity) | $10^6 x K_{sp}$ ($ohm^{-1}$ $cm^{-1}$) | $\Lambda$ |
|---|---|---|---|
| $CF_3CO_2K$ | 1.029 | .9654 | 9.381 |
| | 1.142 | 1.025 | 8.970 |
| | 1.356 | 1.129 | 8.322 |
| | 1.541 | 1.212 | 7.867 |
| | 1.707 | 1.284 | 7.520 |
| $CF_3CO_2Rb$ ($K_{sp}$ = .0799 x $10^{-6}$ $ohm^{-1}$ $cm^{-1}$) | | | |
| | .1347 | .3546 | 26.33 |
| | .3204 | .6010 | 18.76 |
| | .5533 | .8374 | 15.13 |
| | .7573 | 1.007 | 13.30 |
| | .9489 | 1.150 | 12.12 |
| | 1.166 | 1.297 | 11.12 |
| | 1.381 | 1.431 | 10.36 |
| | 1.574 | 1.544 | 9.813 |
| | 1.741 | 1.637 | 9 400 |
| $CF_3CO_2Cs$ ($K_{sp}$ = .066 x $10^{-6}$ $ohm^{-1}$ $cm^{-1}$) | | | |
| #1 | .1838 | .5159 | 28.07 |
| | .5461 | 1.052 | 18.74 |
| | .8558 | 1.397 | 16.32 |
| | 1.191 | 1.714 | 14.40 |
| | 1.493 | 1.970 | 13.19 |
| | 1.728 | 2.153 | 12.46 |
| $CF_3CO_2Cs$ ($K_{sp}$ = .0764 x $10^{-6}$ $ohm^{-1}$ $cm^{-1}$) | | | |
| #2 | .1901 | .5331 | 28.03 |
| | .3436 | .7889 | 22.96 |
| | .5869 | 1.114 | 18.99 |
| | .7267 | 1.315 | 17.25 |
| | .8778 | 1.431 | 16.30 |
| | 1.016 | 1.568 | 15.44 |
| | 1.184 | 1.726 | 14.57 |
| | 1.304 | 1.831 | 14.05 |
| | 1.481 | 1.982 | 13.38 |
| | 1.597 | 2.076 | 13.00 |
| | 1.741 | 2.814 | 12.54 |

TABLE XIX (cont.)

| Solute ($K_{sp}$ pure solvent) | Concentration ($10^4$xmolarity) | $10^6 x K_{sp}$ (ohm$^{-1}$ cm$^{-1}$) | $\Lambda$ |
|---|---|---|---|
| $CF_3CO_2NH_4$ ($K_{sp}$ = .0629 x $10^{-6}$ ohm$^{-1}$ cm$^{-1}$) | | | |
| | .1431 | .3551 | 24.81 |
| | .3062 | .5640 | 18.42 |
| | .5053 | .7631 | 15.10 |
| | .6757 | .9078 | 13.44 |
| | .9078 | 1.081 | 11.91 |
| | 1.059 | 1.184 | 11.18 |
| | 1.223 | 1.288 | 10.53 |
| | 1.385 | 1.384 | 10.00 |
| | 1.547 | 1.478 | 9.553 |
| | 1.711 | 1.567 | 9.162 |

obviously rather small, and the equivalent conductivities fall off rapidly because of increasing association of the ions to pairs.

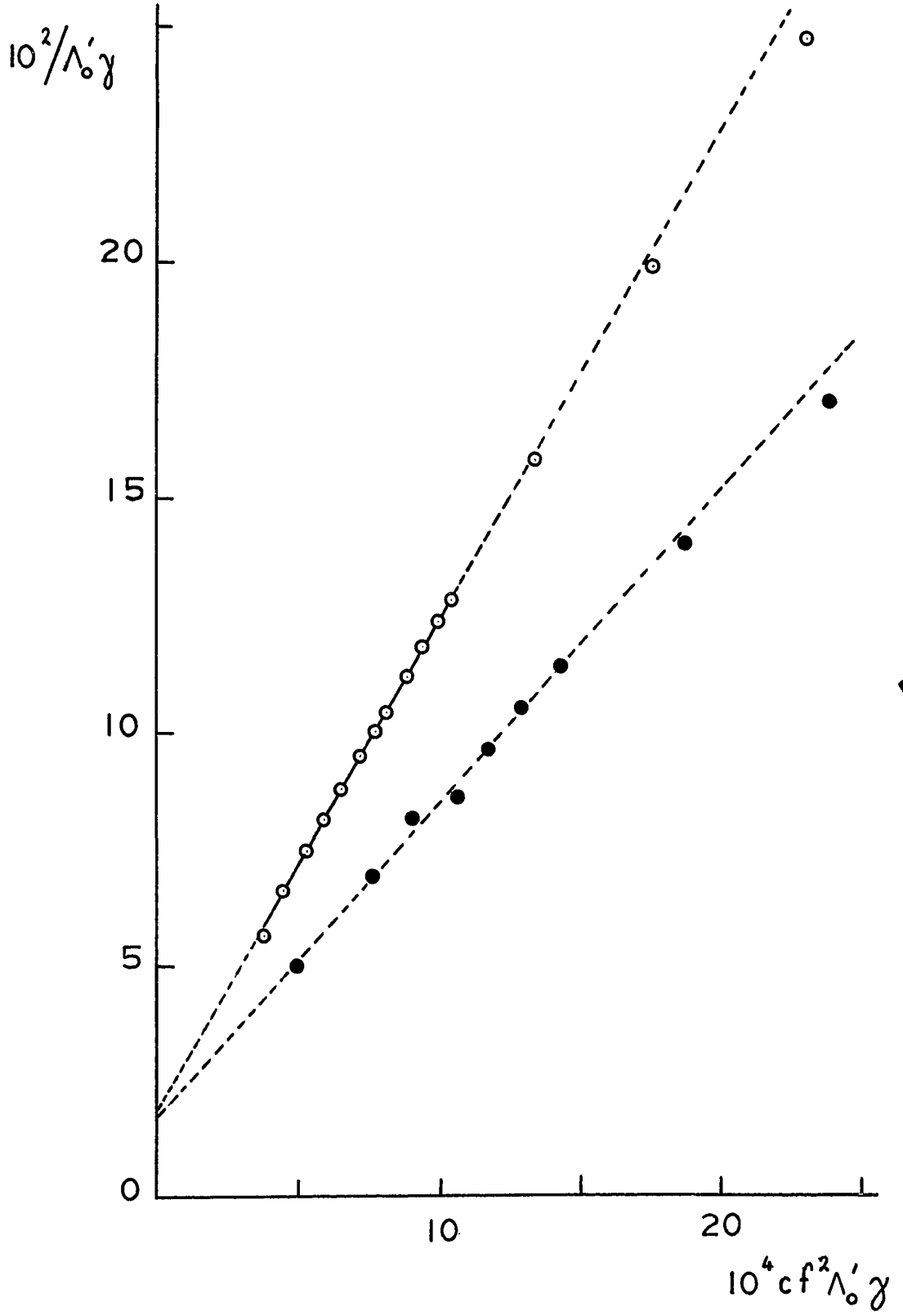
The data were analyzed by the method outlined at the beginning of this chapter, using the computer program in Appendix II. Figure 17 is a plot of such an extrapolation for potassium trifluoroacetate. Although the theoretical upper limit of concentration is $\sim 2 \times 10^{-4}$ molar, the curve is reasonably linear up to about three times this concentration, after which points appear with negative deviations from the line. This is because triple ions are beginning to contribute to the conductance; the apparent value of $\gamma$ is increased, leading to a smaller ordinate $(1/\Lambda_o\gamma)$ and larger abscissa $(cf^2\Lambda_o\gamma)$. Points at very low concentrations also show slight negative deviations, caused by the conductance of the solvent itself. At first it was thought that this arose from incomplete repression of the solvent self-dissociation, but later techniques for preparing the acid reduced its conductivity by nearly an order of magnitude. The low concentration deviations must therefore be due to traces of impurity, possibly electrolyte leached from the glass of the cell. These very small deviations are not sufficient to affect the results seriously, but as a precaution, neither the lowest point, nor any point above a concentration of $1.9 \times 10^{-4}$ molar were included in the final extrapolation.

The results of Simons and Lorentzen for potassium trifluoroacetate (5) are also included in Figure 17. These

Figure 17

Fuoss-type plot for the conductivity of potassium trifluoroacetate.

- o results of present study
- ● data of Simons and Lorentzen.


$10^2/\Lambda_0'\gamma$
20
15
10
5
0
10
20
$10^4 c f^2 \Lambda_0' \gamma$

authors found conductivities about 25% greater than those reported here. Their experimental conditions were such that the solvent certainly contained traces of water, and perhaps also some mercurous trifluoroacetate, since the solutions were in contact with mercury of unreported purity.

Table XX lists the parameters derived from conductivity measurements, using Fuoss' (1965) expression for conductance (equation 3) above). The extrapolation is not very sensitive to the value of $\mathring{a}$, and putting $\mathring{a}$ equal to the sum of the cation and anion radii made very little difference to the result. Use of the Onsager limiting law instead of the more exact equation 3) increased the values of $\Lambda^{\circ}$ by about 10%, but left the relative order unchanged. The difference is due not to large discrepancies between the limiting law and equation 3), but to the fact that $\Lambda^{\circ}$ is obtained as the reciprocal of a very small intercept after a rather long extrapolation. It was not thought worthwhile to repeat the extrapolations with the multitude of alternative conductance equations (e.g. 148, 149) that are to be found in the literature.

The good agreement ($\sim$3%) for the two runs with caesium trifluoroacetate is extremely pleasing, for it represents a drastic test of the reproducibility of the data. The dissociation constants increase with increasing cation radius, in accord with both intuitive feeling, and Fuoss' theoretical expression (equation 2) above). The ammonium and rubidium salts, which have the same crystal cation radius

TABLE XX

Limiting equivalent conductivities ( $\Lambda_o$), dissociation constants ($K_d$) and distance of closest approach (å) for electrolytes at 25°C

| Solute | $\Lambda_o$ (ohm$^{-1}$ cm$^2$ equiv.$^{-1}$) | $10^6 \times K_d$ (m l$^{-1}$) | $10^8 \times$ å (cm) | Standard Deviation (%)* |
|---|---|---|---|---|
| $CF_3CO_2Na$ | 62.28 | .573 | 4.15 | .14 |
| $CF_3CO_2K$ | 55.58 | 3.06 | 4.77 | .15 |
| $CF_3CO_2K$** | 59.47 | 4.19 | 4.91 | 2.01 |
| $CF_3CO_2Rb$ | 52.95 | 5.57 | 5.04 | .24 |
| $CF_3CO_2Cs$ (#1) | 47.06 | 13.7 | 5.54 | .16 |
| $CF_3CO_2Cs$ (#2) | 48.78 | 12.9 | 5.50 | .41 |
| $CF_3CO_2NH_4$ | 49.70 | 5.95 | 5.08 | .40 |

* Standard deviation of points from the Fuoss extrapolation

** Data of Simons and Lorentzen (5).

(1.48Å) have almost identical dissociation constants. The constants are smaller by nearly two orders of magnitude than those derived by Bessière (101,102) from electrode potential and colorimetric measurements. The discrepancy probably arises from the fact that Bessière's work was done at concentrations where interference from triple ions is appreciable.

The order of limiting equivalent conductivities

$$Na > K > Rb > Cs$$

is extremely surprizing, and appears to be unique in the literature. It is exactly the reverse of that found in such diverse solvents as liquid $SO_2$, methanol, acetone (150), tetrahydrofuran (151) and trifluoroethanol (152). The order is complex in water. The only cases where $\Lambda_o$ systematically decreases with increasing cation radius are the large tetraalkylammonium salts in various solvents (e.g. 153). Application of Stokes law to the motion of an ion leads to the conclusion that

$$\lambda_i^\circ = 10^7 \mathcal{F}^2/6\eta \, Nr_i \qquad 5)$$

where $\lambda_i^\circ$ is the limiting equivalent conductivity of the ion

$\mathcal{F}$ is the Faraday (coulombs)

$\eta$ is the viscosity of the solvent (poise)

$r_i$ is the radius of the ion.

The 'normal' order of conductances is then explained by assuming that the solvated radius of the cation increases as the crystal radius decreases, owing to the increasing surface

potential of the ion. Where the solvated radius turns out to be less than the crystal radius (e.g. for $K^+$, $Rb^+$, $Cs^+$ in water), other effects have been proposed such as structure-breaking in the solvent by the ion.

When these ideas are applied to the alkali metal trifluoroacetates, difficulties immediately arise. The order of the equivalent conductivities suggests that solvation of the cation is unimportant, consistent with the poor donor properties of the solvent, but substitution of the crystal radii of the ions in 5) predicts values of $\Lambda_o$ much greater than observed. Fuoss (154) pointed out that a solute ion causes orientation of the solvent dipoles around it, and when the ion moves, a finite time is taken for the dipoles to relax. Boyd (155,156) and Zwanzig (157,158) attempted to put this on a quantitative footing, and ultimately derived the equation:-

$$\lambda_i^\circ = \frac{10^7 \mathcal{F}^2}{N(Ar_i + B/r_i^3)} \qquad 6)$$

The constants A and B are functions of the viscosity, dielectric constant, refractive index and dielectric relaxation time of the solvent. The relaxation time can be approximated by the Debye formula

$$= 4\pi\eta r_s^3/kT \qquad 7)$$

where $r_s$ is the radius of the solvent molecule. Substitution in 6) predicts the values 3.1, 7.4, 9.6 and 13.0 for the ionic mobilities of $Na^+$, $K^+$, $Rb^+$ and $Cs^+$ respectively. Not only are these smaller than seems reasonable, but they are

also in the wrong order.

A survey by Fernández-Prini and Atkinson (159) showed that the Boyd-Zwanzig theory of dynamic dielectric effects is, in fact, inadequate for predicting ionic mobilities. These authors introduced a correction for the change in local dielectric constant around the ion. Further theories may be envisaged to embrace dynamic viscosity effects, and the local viscosity near the ion. The latter would be equivalent to including the structure-making and -breaking effects which have already received a semi-quantitative treatment in the work of Engel and Hertz (55). Such theories are not available at present, and thus while the limiting equivalent conductivities reported here suggest that solvation of the cations is relatively unimportant, a quantitative interpretation cannot as yet be given.

The limiting conductance of ammonium trifluoroacetate is rather less than that of the rubidium salt, although the cationic radii are the same. The exact value is a little uncertain, for the conductance of the ammonium compound decreased slightly with time, and it was subsequently shown that ammonium trifluoroacetate reacts with trifluoroacetic anhydride to give bis(trifluoroacetyl)amide, $(CF_3CO)_2NH$. The decrease observed, however, was very small, and the rather low mobility of $NH_4^+$ may be due to specific hydrogen bonding between the ion and the solvent.

The parameters $\Lambda_o$, K and $\mathring{a}$ could not be derived for lithium trifluoroacetate, as the Fuoss-type extrapolation

led to negative intercepts whatever the initial trial value of $\Lambda_o$. The lithium salt is expected to be much less dissociated than the other trifluoroacetates, and the contribution to the conductance from the solvent probably remains important until concentrations at which triple ion formation is appreciable. All points will then appear with negative deviations from the theoretical line. This, combined with the very steep slope and rather long extrapolation could easily cause the intercept to become negative. Some information, however, may be obtained as follows. The slope of the extrapolation, $(1/K\Lambda_o^2)$, is much less sensitive to experimental error than is the intercept, and a value of about 840 was found when the extrapolation was performed with a trial $\Lambda_o$ of 70. This is confirmed by studies of triple ion equilibria which also give an estimate of $K\Lambda_o^2$ (see Chapter VI). The radius of the trifluoroacetate ion, $r_-$, may be estimated as about 1.65Å, and a plot of logK against $\log(r_+ + r_-)$ was found to be accurately linear for the trifluoroacetates of Na, K, Rb and Cs. The plot is simply an empirical correlation of the dissociation constant with the cation crystal radius, but has some theoretical justification in that K is an exponential function of the distance of closest approach between the ions. Extrapolation of the plot led to $K \sim 1.1 \times 10^{-7}$ for lithium trifluoroacetate, and combined with the approximate slope of the Fuoss plot, yields $\Lambda_o \sim 104$. The value is not, of course, very accurate, but probably of the right order. It is consistent with the trend in $\Lambda_o$

$$Li > Na > K > Rb > Cs$$

The interpretation of the $\mathring{a}$ values given in Table XX is not entirely clear; the values are somewhat larger than the sum of the crystal radii. While this may be due to interpenetration of solvent sheaths as is suggested for water (54, p. 247), it is more likely that it arises from the inadequacy of the theoretical treatment. Fuoss himself has pointed out that a more complete expression for the ion pair dissociation constant is:-

$$1/K = \frac{4\pi N\mathring{a}^3}{3000} \cdot \exp(e^2/kTD\mathring{a}) \times \exp(E/RT) \qquad 8)$$

where E is the difference in solvation energies of the separate ions and of the ion pair. If $\mathring{a}$ is put equal to the sum of the cation and anion radii, then equation 8) can be used to calculate the solvation energy differences. For the sodium, potassium, rubidium and caesium salts, these are -13.2, -11.6, -11.0 and -10.3 kcal/mole respectively. The values seem reasonable, show the expected cation dependence, and are interestingly close to the heat of dissociation of the trifluoroacetic acid dimer (14.0 kcal/mole). This treatment, of course, suggests that the $\mathring{a}$ values used in calculating the coefficients of the conductivity equation may be in error. Fortunately, the extrapolation is not very sensitive to the chosen value of $\mathring{a}$, and the derived values of $\Lambda_o$ and K change by only about 1%.

A recent paper (152) has attempted to include equilibria between contact ion pairs and solvent-separated ion pairs in the dissociation constant. The authors' treatment is open to very serious objections and no attempt has been made to apply it to the present work.

D. Summary

The electrical conductivities of a number of substances were measured. Trifluoroacetic anhydride is a non-electrolyte in trifluoroacetic acid and water an extremely weak base. Ammonium and the alkali metal trifluoroacetates are strong (fully ionized) bases, but highly associated in solution. Data were analyzed by the Fuoss-Onsager-Skinner conductance equation. The ion pair dissociation constants of the salts showed the expected variation with ionic size. Ionic mobilities were found to be in the order:-

$$Na > K > Rb > NH_4 > Cs$$

The position for lithium is not certain, but an approximate calculation shows that it may lie even higher than sodium. This order is extremely unusual, and indicates that cation solvation may be relatively unimportant in trifluoroacetic acid.

# CHAPTER V

## Acids and solvent self-dissociation

### A. General

One of the aims of this study was to measure the concentration of ions present in the pure solvent, that is, the extent of the reaction:-

$$2CF_3CO_2H \rightleftharpoons CF_3CO_2H_2^+ . {}^-O_2CCF_3 \rightleftharpoons CF_3CO_2H_2^+ + CF_3CO_2^-$$

ion pair

If the limiting equivalent conductivity of the ions is known, then their concentration can be calculated from the observed specificic conductance of the solvent.

The limiting equivalent conductivity, $\Lambda^\circ_{HA}$, of the solvent can be found from the well-known Kohlrausch relationship:-

$$\Lambda^\circ_{HA} = \Lambda^\circ_{HX} + \Lambda^\circ_{MA} - \Lambda^\circ_{MX}$$

where HX is an acid in the solvent, MA a base, and MX the salt formed from the two. While many substances act as bases in the trifluoroacetic acid (Chapter IV), the problem of finding a suitable acid for the system is a considerable one. For practical reasons, it is necessary to work in the presence of small amounts of trifluoroacetic anhydride, and N.M.R. studies (Chapter III) showed that this reacts with the common strong acids $H_2SO_4$, $HClO_4$, $HSO_3F$ and $HBF_4$. The same studies however, showed that the compounds $HSbF_5(O_2CCF_3)$

TABLE XXI

Specific conductances ($K_{sp}$) and equivalent conductivities ( $\Lambda$ ) for some acids and salts in trifluoroacetic acid at 25°C

| Solute | Concentration ($10^4$xmolarity) | $10^6 x K_{sp}$ (ohm$^{-1}$ cm$^{-1}$) | $\Lambda$ (ohm$^{-1}$ cm$^2$ equiv.$^{-1}$) |
|---|---|---|---|
| $HSbF_5(O_2CCF_3)$ ($K_{sp}$ solvent = .0760 x $10^{-6}$ ohm$^{-1}$ cm$^{-1}$) | | | |
| #1 | .1490 | .1745 | 11.71 |
| | .2799 | .2849 | 10.18 |
| | .4085 | .3693 | 9.039 |
| | .5395 | .4433 | 8.218 |
| | .7027 | .5236 | 7.451 |
| | .8131 | .6042 | 7.430 |
| | .9962 | .6774 | 6.800 |
| | 1.178 | .7420 | 6.296 |
| | 1.345 | .7979 | 5.934 |
| | 1.498 | .8493 | 5.671 |
| $HSbF_5(O_2CCF_3)$ ($K_{sp}$ solvent = .0375 x $10^{-6}$ ohm$^{-1}$ cm$^{-1}$) | | | |
| #2 | .2113 | .2516 | 11.90 |
| | .4257 | .4096 | 9.621 |
| | .6152 | .5249 | 8.532 |
| | .8509 | .6483 | 7.618 |
| | 1.082 | .7585 | 7.007 |
| | 1.275 | .8413 | 6.597 |
| | 1.513 | .9402 | 6.214 |
| | 1.759 | 1.035 | 5.882 |
| | 1.981 | 1.115 | 5.627 |
| *$KSbF_5(O_2CCF_3)$ (Solvent $K_{sp}$ = .0630 x $10^{-6}$ ohm$^{-1}$ cm$^{-1}$) | | | |
| | .1597 | .2357 | 14.76 |
| | .3646 | .3964 | 10.87 |
| | .4978 | .4791 | 9.626 |
| | .7134 | .5980 | 8.376 |
| | .9042 | .6880 | 7.609 |

* corrected for solvent conductance, since solvent and electrolyte have no common ion.

TABLE XXI (cont.)

| Solute | Concentration ($10^4$xmolarity) | $10^6 x K_{sp}$ (ohm$^{-1}$ cm$^{-1}$) | $\Lambda$ (ohm$^{-1}$ cm$^2$ equiv.$^{-1}$) |
|---|---|---|---|
| $KSbF_5(O_2CCF_3)$ | 1.074 | .7602 | 7.078 |
| | 1.232 | .8230 | 6.678 |
| | 1.465 | .9091 | 6.204 |
| | 1.695 | .9867 | 5.822 |
| | 1.962 | 1.074 | 5.476 |
| $HB(O_2CCF_3)_4$ (Solvent $K_{sp}$ = .00734 x $10^{-6}$ ohm$^{-1}$ cm$^{-1}$) | | | |
| #1 | .2971 | .1264 | 4.255 |
| | .4882 | .1660 | 3.401 |
| | .7596 | .2126 | 2.798 |
| | .9765 | .2432 | 2.490 |
| | 1.156 | .2661 | 2.302 |
| | 1.337 | .2882 | 2.157 |
| | 1.483 | .3056 | 2.061 |
| | 1.615 | .3208 | 1.986 |
| $HB(O_2CCF_3)_4$ (Solvent $K_{sp}$ = .0142 x $10^{-6}$ ohm$^{-1}$ cm$^{-1}$ | | | |
| #2 | .2201 | .1102 | 5.007 |
| | .4395 | .1588 | 3.612 |
| | .6356 | .1939 | 3.050 |
| | .8843 | .2345 | 2.652 |
| | 1.116 | .2664 | 2.388 |
| | 1.308 | .2903 | 2.220 |
| | 1.507 | .3121 | 2.072 |
| | 1.652 | .3269 | 1.979 |
| *$CsB(O_2CCF_3)_4$ (Solvent $K_{sp}$ = .00607 x $10^{-6}$ ohm$^{-1}$ cm$^{-1}$) | | | |
| | .1726 | .5190 | 30.07 |
| | .3778 | .9316 | 24.66 |
| | .6054 | 1.296 | 21.41 |
| | .8517 | 1.633 | 19.17 |
| | 1.081 | 1.907 | 17.65 |
| | 1.282 | 2.130 | 16.62 |
| | 1.496 | 2.351 | 15.71 |
| | 1.710 | 2.556 | 14.95 |
| | 1.913 | 2.740 | 14.32 |

* corrected for solvent conductance, since solvent and electolyte have no common ion.

and $B(C_2CCF_3)_3$ can be prepared in solution and these could possibly act as the acid required. The investigation is in several parts:-

1) to find whether the compounds $HSbF_5(O_2CCF_3)$ and $B(O_2CCF_3)_3$ are electolytes (conductance measurements)
2) to find whether the compounds are acids in trifluoroacetic acid (conductimetric titration with a base)
3) to prepare salts of the acids, and measure their conductivities.

Anticipating the results somewhat, both $HSbF_5(O_2CCF_3)$ and $B(O_2CCF_3)_3$ were electrolytes, and it was possible to prepare and isolate the salt $CsB(O_2CCF_3)_4$ (see Chapter II). What may have been the potassium salt $KSbF_5(O_2CCF_3)$ was prepared in dilute solution, but the results were unsatisfactory and the compound could not be isolated. The measured specific and equivalent conductivities of the compounds studied are given in Table XXI, and the parameters derived from them ($\Lambda_o$, K, $\mathring{a}$) in Table XXII. Since the two systems (the one based on boron, the other on antimony) differed considerably, the results for each are discussed separately.

B. The antimony pentafluoride system

Solutions of antimony pentafluoride in trifluoroacetic acid conduct electricity at least as well as do solutions of the alkali metal trifluoroacetates. The results in Table XXII show excellent agreement between two different

TABLE XXII

Limiting equivalent conductivities ( $\Lambda_o$ ), dissociation constants ($K_d$) and distance of closest approach (å) for some acids and salts at 25°C

| Solute | $\Lambda_o$ ($ohm^{-1}$ $cm^2$ $equiv.^{-1}$) | $10^6 x K_d$ ($m\ l^{-1}$) | $10^8 x$ å (cm) | Standard Deviation (%)* |
|---|---|---|---|---|
| $HSbF_5(O_2CCF_3)$ #1 | 17.97 | 21.1 | 5.82 | 2.25 |
| $HSbF_5(O_2CCF_3)$ #2 | 17.91 | 26.7 | 5.98 | .51 |
| $KSbF_5(O_2CCF_3)$ | 31.42 | 6.16 | 5.09 | .46 |
| $HB(O_2CCF_3)_4$ #1 | 19.92 | 1.61 | 4.51 | .46 |
| $HB(O_2CCF_3)_4$ #2 | 19.13 | 1.81 | 4.55 | .61 |
| $CsB(O_2CCF_3)_4$ | 46.32 | 21.4 | 5.83 | 2.15 |

sets of measurements. The limiting equivalent conductivity is lower than for the bases $CF_3CO_2M$, while the dissociation constant K and distance of closest approach å are rather higher; this is consistent with the larger ions involved. The standard deviation of the points is larger than for the bases because of greater experimental difficulties, particularly the extreme sensitivity of the compounds to atmospheric moisture. On the basis of the conductance studies and the N.M.R. results the principal reaction at low concentrations is thus established as:-

$$SbF_5 + CF_3CO_2H \xrightarrow{1)} H^+[SbF_5(O_2CCF_3)]^- \overset{2)}{\rightleftharpoons} \underset{\text{solvated}}{H^+} + SbF_5(O_2CCF_3)^-$$

The first step (ionization) goes to completion within experimental error.

The potassium salt of the acid is much more difficult to prepare, and the formula '$KSbF_5(O_2CCF_3)$' in Tables XXI and XXII is convenient rather than accurate. On mixing concentrated solutions of $SbF_5$ and $CF_3CO_2K$ in equivalent amounts, a dense white precipitate was obtained, which appears to be highly insoluble in trifluoroacetic acid. Successive dilutions of the slurry with pure solvent gave a liquid containing about $5 \times 10^{-5}$ moles of the product per litre of solvent, and with a negligible conductance. An X-ray powder photograph showed the white substance to be potassium hexafluoroantimonate, $KSbF_6$, and this is confirmed by the potassium analysis (found 13.2%; req'd. for $KSbF_6$ 14.2%). The other products of the reaction were not identi-

fied. When more dilute solutions were mixed ( $\sim 10^{-3}$ molar), the same result was usually obtained, but on one occasion no precipitate was observed. It is this solution that was used to find the results given above. The reason for the sudden change of behaviour is not understood, for the preparations were all attempted under the same conditions.

The results for the $KSbF_5(O_2CCF_3)$ run are not in fact, satisfactory. When all the $\Lambda_o$ values in Table XXII are combined, it appears that the mobility of the potassium ion is less than that of the caesium ion by about 14.4 units, while the values for the alkali metal trifluoroacetates show that potassium is actually more mobile than caesium by about 7.5 units. Since the results for the boric acid system are thought to be reliable, it seems that the value of 31.43 for the limiting equivalent conductivity of $KSbF_5(O_2CCF_3)$ is far too low. Other species are probably present in the solution, and some of the electrolyte may have been removed as $KSbF_6$. The amount of precipitate would have been too small to observe, even with complete conversion to $KSbF_6$. The conductimetric titration of $SbF_5$ against potassium trifluoroacetate showed no discontinuity at the expected equivalence point. The estimation of $\Lambda^\circ$ for the solvent requires conductivity data on an acid, a base and a salt. The antimony pentafluoride system provides an acid, but data for the salt are not useful.

C. The boric acid system

This system is much more reliable than the previous one, although the results should be interpreted with care.

Nuclear magnetic resonance studies (Chapter III) showed that boric acid reacts with trifluoroacetic anhydride to give tris(trifluoroacetyl) borate, $(CF_3CO_2)_3B$, and that this compound decomposes slowly to tetrakis(trifluoroacetyl) diborate, $(CF_3CO_2)_2B.O.B(O_2CCF_3)_2$. The conductance results established that the reaction product was an electrolyte, and finally a conductimetric titration with caesium trifluoroacetate (discussed in detail in the next section) gave the conductance at the equivalence point in almost perfect agreement with that expected from independent measurements on the salt, $CsB(O_2CCF_3)_4$.

By far the most likely explanation is that the boron compound co-ordinates with a solvent anion, and thus acts as an acid which can be titrated.

$$CF_3CO_2H + B(O_2CCF_3)_3 \longrightarrow H^+\left[B(O_2CCF_3)_4\right]^-$$

$$H^+\left[B(O_2CCF_3)_4\right]^- + CF_3CO_2Cs \longrightarrow Cs^+\left[B(O_2CCF_3)_4\right]^- + CF_3CO_2H$$

Two other possibilities could be suggested. The borate might undergo self-ionization:-

$$2(CF_3CO_2)_3B \rightleftharpoons (CF_3CO_2)_2B^+ + (CF_3CO_2)_4B^-$$

but since three-coordinate boron is already electron-

deficient. any reaction that produces a two-coordinate positive boron species is highly improbable. Alternatively, the boron might be present as the diborate compound, which could also behave as an acid.

$$CF_3CO_2H + (CF_3CO_2)_4B_2O \rightleftharpoons H^+\left[(CF_3CO_2)_5B_2O\right]^-$$

This possibility can be rejected for several reasons. The conductance measurements were made as soon as possible after the boric acid $H_3BO_3$, had dissolved in the anhydride, i.e. before extensive decomposition had taken place. The limiting equivalent conductivity of the substance (19.1 or 19.9) was quite close to that of antimony pentafluoride (17.9) as expected, for the anions $\left[B(O_2CCF_3)_4\right]^-$ and $\left[SbF_5(O_2CCF_3)\right]^-$ are roughly comparable in size. Any anion derived from $B_2O(O_2CCF_3)_4$ would be much larger, and a smaller $\Lambda^\circ$ is expected. Measurements on a solution of boric acid that had been left to stand for some weeks, and in which some amount of decomposition had taken place, did indeed lead to a lower value of $\Lambda^\circ$ ( 14) and a conductimetric titration showed that this solution required only about 0.7 moles of caesium trifluoroacetate to neutralize one mole of borate.

The reaction of tris(trifluoroacetyl) borate with trifluoroacetic acid is thus satisfactorily established as:-

$$(CF_3CO)_3B + CF_3CO_2H \rightleftharpoons HB(O_2CCF_3)_4 \underset{\text{solvated}}{\rightleftharpoons} H^+ + \left[B(OCCF_3)_4\right]^-$$

The agreement between the values derived from the two different sets of measurements (Table XXII) is excellent, and the value of $\Lambda^{\circ}$ is roughly what might be expected. The dissociation constant, however, and the value of $\mathring{a}$ derived from it, are smaller than anticipated. This is interpreted as meaning that the boron acid is a weak acid. Not only is there incomplete dissociation of the ion pair (as is the case for all electrolytes in this solvent), but actual formation of the ion pair from $B(O_2CCF_3)_3$ and the solvent is also incomplete. Fortunately, this makes no difference to the mathematical treatment of the results. K is simply re-interpreted as the overall dissociation constant, equal to the product of the ionization constant and the ion pair dissociation constant. This is possible since the concentration of solvent is constant. The error introduced into the parameter $\mathring{a}$ makes only a very small difference ($\sim$1%) in the extrapolation of the data.

The interpretation of the results for the caesium salt, $CsB(O_2CCF_3)_4$, is simpler. The value of $\Lambda^{\circ}$ for the salt is only slightly less than that of caesium trifluoroacetate, in spite of the difference in anionic sizes; presumably the mobility of the larger anion is affected much less by dielectric friction (Zwanzig) effects. The dissociation constant of the salt is about twice that of caesium trifluoroacetate.

D. Conductimetric titration

The interpretation given above is amply confirmed by the conductimetric titration of the boron acid with caesium trifluoroacetate. Small portions of a solution of the base were added to a dilute solution ($1.615 \times 10^{-4}$ molar) of $HB(O_2CCF_3)_4$ in the conductivity cell. The results are given in Table XXIII, and plotted in Figure 18. The stoicheiometric concentration of the acid appears to decrease (Table XXIII) because the base was added as a solution, and the extra solvent diluted the mixture. A dramatic change is not expected in the conductivity, for the reaction is between partially dissociated electrolytes with ions of rather similar mobilities. Nevertheless, a slight but definite discontinuity can be seen at a 1:1 ratio. The conductivity at the equivalence point is what would be expected from separate measurements on the salt, $CsB(O_2CCF_3)_4$. Furthermore, every point on the curve can be fitted assuming the reaction:-

$$H^+[B(O_2CCF_3)_4]^- + CF_3CO_2Cs \longrightarrow Cs^+[B(O_2CCF_3)_4]^- + CF_3CO_2H$$

The method can be outlined as follows.
Writing the acid, base, salt and solvent as HX, MA, MX, and HA respectively, the reaction is:-

$$HX + MA \longrightarrow MX + HA$$

Denoting concentrations by small letters for convenience, and the activity coefficient by f, the various dissociation

TABLE XXIII

Conductimetric titration of $HB(O_2CCF_3)_4$ with $CF_3CO_2Cs$. Concentrations are in moles/litre, the specific conductivity ($K_{sp}$) in $ohms^{-1}\ cm^{-1}$.

| $10^4$ x [Acid] | $10^4$ x [Base] | [Base]/[Acid] | $10^6$ x $K_{sp}$ Observed | $10^6$ x $K_{sp}$ Predicted |
|---|---|---|---|---|
| 1.580 | .2238 | .1416 | .7394 | .7384 |
| 1.528 | .5587 | .3656 | 1.226 | 1.253 |
| 1.489 | 8083 | 5430 | 1.556 | 1.578 |
| 1.453 | 1.034 | .7117 | 1.831 | 1.842 |
| 1.420 | 1.248 | .8787 | 2.067 | 2.072 |
| 1.379 | 1.512 | 1.097 | 2.266 | 2.316 |
| 1.344 | 1.731 | 1.288 | 2.425 | 2.458 |
| 1.305 | 1.985 | 1.521 | 2.598 | 2.623 |
| 1.266 | 2.234 | 1.765 | 2.753 | 2.777 |
| 1.240 | 2.399 | 1.935 | 2.860 | 2.875 |
| 1.207 | 2.612 | 2.165 | 2.988 | 2.998 |
| 1.169 | 2.854 | 2.442 | 3.126 | 3.132 |
| 1.131 | 3.098 | 2.740 | 3.262 | 3.262 |

constants are defined as:-

$$P \equiv f^2[M^+][X^-]/[MX] \equiv f^2 m.x/mx \qquad 1)$$

$$Q \equiv f^2[H^+][X^-]/[HX] \equiv f^2 h.x/hx \qquad 2)$$

$$R \equiv f^2[M^+][A^-]/[MA] \equiv f^2 m.a/ma \qquad 3)$$

The solvent HA is assumed undissociated.

When the initial concentration of base, $C_m$, is less than the initial concentration of acid, $C_x$, the ionic strength of the solution is equal to the concentration of acid anion, x.

Equations 1), 2) and 3) can be combined with the requirements of electrical neutrality and conservation of matter to give a cubic expression for x, which can be written

$$x = \sqrt[3]{\left\{\frac{PQC_x - x(f^2(Q(C_m-C_x)-PC_m)+PQ)-x^2f^2(Q+P)}{f^4}\right\}} \qquad 4)$$

One can also derive:-

$$x = \frac{-\beta + \sqrt{\beta^2-4\alpha\gamma}}{2\alpha} \qquad 5)$$

where

$\alpha = f^2\Lambda_{MX}$

$\beta = Q\,\Lambda_{MX} - f^2\sigma$

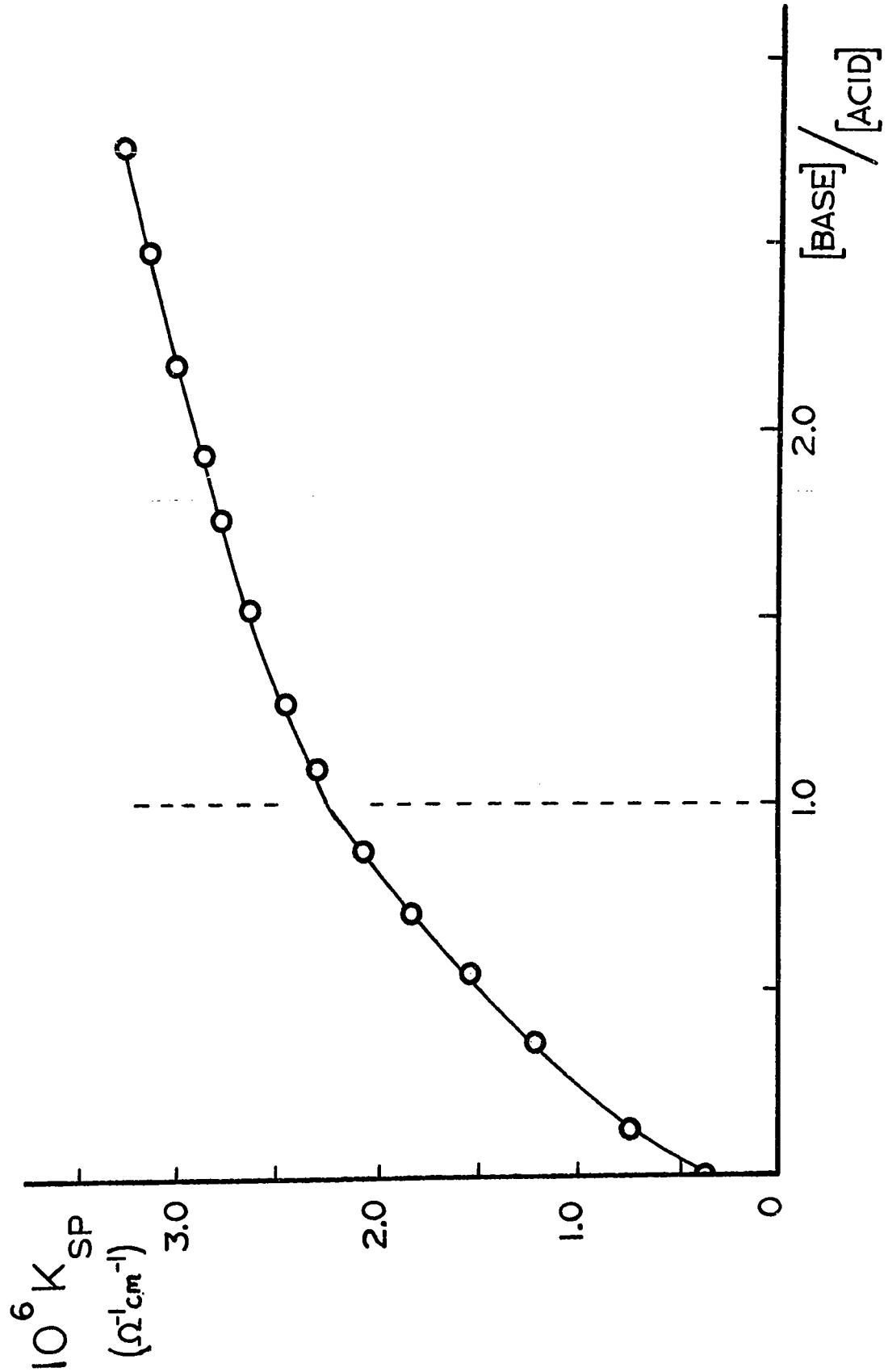
$\gamma = Q(C - C_m)(\Lambda_{HX} - \Lambda_{MX}) - Q\sigma$

$\sigma$ = 1000 x observed specific conductance of solution

$\Lambda$ is the equivalent conductivity of the electrolyte to which the subscript refers

Figure 18

The conductimetric titration of the acid, $HB(O_2CCF_3)_4$, against the base, $CF_3CO_2Cs$. The specific conductivity of the solution, $K_{sp}$, is plotted against the ratio of base to acid. The solid line shows the calculated curve.


$10^6 K_{SP}$
$(\Omega^{-1}cm^{-1})$
3.0
2.0
1.0
0
1.0
2.0
[BASE]/[ACID]

An initial value of x is found from equation 5) by putting f = 1, and the equivalent conductivities $\Lambda_{MX}$ and $\Lambda_{HX}$ equal to their values at infinite dilution. The estimate is refined by iteration in equation 4), using the extended Debye-Hückel equation for the activity coefficient, and taking $\mathring{a}$ as the weighted mean (for details, see Appendix III) of the $\mathring{a}$ values of the acid and salt. The final value of x from 4) is independent of the observed specific conductivity. Once x is known, all other ionic concentrations are easily derived. The observed specific conductance must be equal to the sum of the contributions from acid and salt (or from salt and base when $C_m > C_x$ )

i.e. Specific Conductivity = $10^{-3}$ $(h.\Lambda_{HX} + m.\Lambda_{MX})$

The values of $\Lambda$ are calculated from the values at infinite dilution and the ionic strength, by means of the Fuoss 1965 equation (142). Thus the concentrations of all ions in the system HX/MX/MA can be calculated from the dissociation constants for the various species, and the titration curve can be predicted from a knowledge of the $\Lambda^{\circ}$ values. A program was written to accomplish this automatically, and is given in Appendix III. The results are plotted in Figure 18. and agreement with experimental values is excellent, confirming both the validity of the interpretation, and the reliability of the conductance results.

E. The solvent self-dissociation

The limiting equivalent conductivities found for the boron acid system can be combined through the Kohlrausch

law of independent ionic mobilities to give $\Lambda^{\circ} = 21.13$ for the electrolyte $CF_3CO_2H_2^{+}.^{-}O_2CCF_3$. Since the specific conductance of the pure solvent is $0.0064 \times 10^{-6}$ $ohm^{-1}$ $cm^{-1}$, and

$$\Lambda = 1000 \times \text{Sp. Cond./C}$$

this gives the concentration of ions in the pure solvent as $3.03 \times 10^{-7}$, ionic strength effects being ignored at such a low concentration. The ionic product in the acid is then $\sim 9.1 \times 10^{-14}$, and an overall equilibrium constant of $\sim 5.6 \times 10^{-16}$ is derived for the reaction:-

$$2CF_3CO_2H \rightleftharpoons CF_3CO_2H_2^{+} + CF_3CO_2^{-}$$

The overall constant is the product of the ionization constant, $K_i$, and the ion pair dissociation constant, $K_d$ applicable to the reactions:-

$$2CF_3CO_2H \overset{K_i}{\rightleftharpoons} CF_3CO_2H_2^{+}.^{-}O_2CCF_3 \overset{K_d}{\rightleftharpoons} CF_3CO_2H_2^{+} + CF_3CO_2^{-}$$

$K_d$ may be approximated by putting it equal to the dissociation constant of caesium trifluoroacetate ($1.3 \times 10^{-5}$), since the radius of the $CF_3CO_2H$ molecule (and hence of the $CF_3CO_2H_2^{+}$ cation) is probably about 1.7 - 1.8 Å (see Chapter I), close to that of the caesium ion (1.69 Å). This gives $K_i \sim 4.3 \times 10^{-11}$, which is thought to be a more reasonable figure than the value of $1.1 \times 10^{-2}$ estimated by Harris and Alder (62) from the variation of the dielectric constant

with temperature.

It will be noticed that the value of 21.1 for the limiting equivalent conductivity of $CF_3CO_2H_2^+ \cdot {}^-O_2CCF_3$ means that the cation $CF_3CO_2H_2^+$ is less mobile than even the slowest-moving of the alkali metal ions ($Cs^+$), and this indicates that the solvent conducts by a normal diffusion process, and not by the special proton-transfer mechanism established for water, sulphuric acid (40, p. 142) and formic acid (4, p. 356). This is not surprizing for these three substances all have a three-dimensional hydrogen bonded structure, while trifluoroacetic acid seems to have much less long-range order. It is interesting that the mobility of the solvent cation in acetic acid ($CH_3CO_2H_2^+$) was found by Martin (167) to be greater than that of the sodium ion. Martin's measurements were made at 105.7°C, and a direct comparison of his results with those reported here for trifluoroacetic acid cannot be made.

F. Summary

Two systems of acids and salts have been investigated, one based on antimony pentafluoride, the other on boric acid. The first proved to be unsatisfactory because of difficulties in preparing a salt. Results for the second system were reproducible and internally consistent. In particular a conductimetric titration gave results in excellent agreement with those predicted from entirely independent measurements.

From the conductance data it was possible to estimate the extent of auto-protolysis of the solvent and also the dissociation constant and limiting equivalent conductivity of the electrolyte $CF_3CO_2H_2^+ . {}^-O_2CCF_3$. Denoting the solvent as HA, the relevant constants are:-

| | |
|---|---|
| $\Lambda^\circ$ $(H_2A^+.A^-)$ | 21.1 |
| Concentration of ions | $3.03 \times 10^{-7}$ |
| Ionic Product, $[H_2A^+][A^-]$ | $9.1 \times 10^{-14}$ |
| Overall dissociation constant, $[H_2A^+][A^-]/[HA]^2$ | $5.6 \times 10^{-16}$ |
| Dissociation constant of ion pair, $[H_2A^+][A^-]/[H_2A^+.A^-]$ | $1.3 \times 10^{-5}$ |
| Ionization constant of solvent, $[H_2A^+.A^-]/[HA]^2$ | $4.3 \times 10^{-11}$ |

A proton-transfer mechanism for conductance seems unlikely for trifluoroacetic acid.

# CHAPTER VI

## Conductance measurements at higher concentrations: triple ion equilibria

### A. General

Fuoss and Accascina (27) have described the general features of conductance/concentration curves for electrolytes in solvents of low dielectric constant. At very low concentrations the electrolyte should be completely dissociated. and the equivalent conductivity, $\Lambda$, should fall off from its value at infinte dilution with the slope predicted by the Onsager limiting law. As the concentration is raised, $\Lambda$ decreases much more rapidly since ions associate to form non-conducting pairs, but then at higher concentrations the curve begins to flatten, and may even go through a minimum. This is because ionic association now begins to produce triple ions of the type $M_2A^+$ and $MA_2^-$, and since these are charged, they contribute to the conductivity of the solution. At very high concentrations more complex behaviour is often observed. Chapters IV and V describe the results of conductivity studies at low concentrations, where only ions and ion pairs need be considered. This chapter deals with triple ions.

### B. Results and discussion

Table XXIV gives the conductances of several substances in the region where ion triplet formation is likely to be important. With the exception of the compounds

TABLE XXIV

Specific conductances ($K_{sp}$) and equivalent conductivities ( $\Lambda$ ) at 25°C, in the region of the conductivity minimum. (The concentration at the lowest observed conductivity is marked *).

| Solute | Concentration ($10^3$ x molarity) | $10^6$ $K_{sp}$ ($ohm^{-1}cm^{-1}$) | $\Lambda$ ($ohm^{-1}cm.^2$ $equiv.^{-1}$) |
|---|---|---|---|
| $CF_3CO_2Li$ | .3165 | .6516 | 2.059 |
| | .4004 | .7334 | 1.832 |
| | .5166 | .8352 | 1.616 |
| | .6506 | .9407 | 1.446 |
| | .7714 | 1.028 | 1.332 |
| | .8890 | 1.107 | 1.245 |
| | 1.010 | 1.183 | 1.171 |
| | 1.114 | 1.245 | 1.117 |
| | 1.241 | 1.318 | 1.062 |
| | 1.370 | 1.388 | 1.014 |
| | 1.536 | 1.476 | .9605 |
| | 1.692 | 1.552 | .9177 |
| | 3.466 | 2.301 | .6637 |
| | 7.985 | 3.719 | .4657 |
| | 25.64 | 7.901 | .3081 |
| | 43.77 | 11.92 | .2725 |
| | 66.72 | 17.34 | .2600 |
| | *83.95 | 21.82 | .2599 |
| | 103.6 | 27.43 | .2648 |
| | 124.3 | 33.99 | .2735 |
| | 153.8 | 44.62 | .2901 |
| | 210.2 | 69 32 | .3298 |
| | 289.3 | 114.0 | .3940 |
| $CF_3CO_2Na$ | .6764 | 1.335 | 1.974 |
| | 1.403 | 1.990 | 1.418 |
| | 2.695 | 2.864 | 1.063 |
| | 5.420 | 4.282 | .7901 |
| | 12.42 | 7.093 | .5713 |
| | 25.94 | 11.66 | .4496 |
| | 37.07 | 15.26 | .4116 |
| | 58.61 | 22.89 | .3906 |
| | *70.96 | 27.70 | 3903 |
| | 81.78 | 32.23 | .3941 |

TABLE XXIV (cont.)

| Solute | Concentration ($10^3$xmolarity) | $10^6$ $K_{sp}$ (ohm$^{-1}$ cm$^{-1}$) | $\Lambda$ (ohm$^{-1}$cm$^2$ equiv.$^{-1}$) |
|---|---|---|---|
| $CF_3CO_2Na$ | 100.6 | 40.88 | .4064 |
| | 130.6 | 57.00 | .4364 |
| $CF_3CO_2K$ | .3085 | 1.777 | 5.760 |
| | .5498 | 2.459 | 4.472 |
| | .9791 | 3.412 | 3.485 |
| | 2.624 | 6.085 | 2.319 |
| | 5.425 | 9.560 | 1.762 |
| | 9 722 | 14.14 | 1.455 |
| | 13.87 | 18.33 | 1.321 |
| | 17.81 | 22.28 | 1.251 |
| | 21.36 | 25.91 | 1.213 |
| | 24.77 | 29.45 | 1.189 |
| | 28.05 | 32.96 | 1.175 |
| | 31.10 | 36.33 | 1.168 |
| | 34.12 | 39.75 | 1.165 |
| | *36.12 | 42.99 | 1.164 |
| | 39 63 | 46.27 | 1.167 |
| | 42.29 | 49.56 | 1.172 |
| | 47.49 | 56.11 | 1.182 |
| | 54.17 | 65.18 | 1.203 |
| $CF_3CO_2Rb$ | .5003 | 3.042 | 6.080 |
| | 1.143 | 4.965 | 4.344 |
| | 2.315 | 7.624 | 3.294 |
| | 6.590 | 15.08 | 2.288 |
| | 11.97 | 23.36 | 1.952 |
| | 17.16 | 31.34 | 1.826 |
| | 21.55 | 38.31 | 1.778 |
| | 26.40 | 46.36 | 1.756 |
| | *30.11 | 52.81 | 1.754 |
| | 33.80 | 59.54 | 1.762 |
| | 39.46 | 70.42 | 1.785 |
| | 44.80 | 81.35 | 1.816 |
| | 54.47 | 103.0 | 1.890 |
| | 67.32 | 135.0 | 2.005 |
| $CF_3CO_2Cs$ | .2019 | 2.357 | 11.68 |
| | .8139 | 5.526 | 6.789 |
| | 1.832 | 9.143 | 4.990 |
| | 6.241 | 20.83 | 3.337 |

TABLE XXIV (cont.)

| Solute | Concentration ($10^3$xmolarity) | $10^6$ $K_{sp}$ ($ohm^{-1}$ $cm^{-1}$) | $\Lambda$ ($ohm^{-1}cm^2$ $equiv.^{-1}$) |
|---|---|---|---|
| $CF_3CO_2Cs$ | 11.31 | 32.92 | 2.909 |
| | 17.92 | 49.05 | 2.738 |
| | *22.50 | 60.96 | 2.710 |
| | 25.96 | 70.41 | 2.712 |
| | 28.71 | 78.20 | 2.723 |
| | 31.84 | 87.41 | 2.745 |
| | 37.27 | 104.3 | 2.798 |
| | 42.43 | 121.4 | 2.862 |
| $CF_3CO_2NH_4$ | .2120 | 1.779 | 8.394 |
| | .6239 | 3.327 | 5.333 |
| | 1.391 | 5.299 | 3.908 |
| | 2.146 | 6.864 | 3 197 |
| | 4.293 | 10.60 | 2.470 |
| | 8.373 | 16.64 | 1.987 |
| | 11.45 | 20.90 | 1.826 |
| | 15.75 | 26.82 | 1.703 |
| | 19.74 | 32.40 | 1.642 |
| | 22.88 | 36.93 | 1.614 |
| | 27.15 | 43 27 | 1.594 |
| | *31.51 | 50.01 | 1.587 |
| | 35.43 | 56.34 | 1.590 |
| | 39.30 | 62.90 | 1.600 |
| $HSbF_5(O_2CCF_3)$ | .2862 | 1.396 | 4.876 |
| | .3349 | 1.551 | 4.631 |
| | 1.031 | 3.218 | 3.121 |
| | 2.251 | 5.210 | 2.314 |
| | 3.568 | 6.935 | 1.944 |
| | 4.767 | 8.334 | 1.748 |
| | 9.704 | 13.29 | 1.370 |
| | 18.34 | 20.97 | 1.144 |
| | 29.67 | 30.78 | 1.037 |
| | 37.35 | 37.63 | 1.008 |
| | 43.57 | 43 36 | .9948 |
| | *51.98 | 51.45 | .9898 |
| | 57 02 | 56.45 | .9899 |
| | 62.56 | 62.13 | .9932 |
| | 71.55 | 71.79 | 1.003 |
| | 84.41 | 86.56 | 1.026 |
| | 99.94 | 105.8 | 1.059 |

TABLE XXIV (cont.)

| Solute | Concentration ($10^3$ xmolarity) | $10^6$ $K_{sp}$ (ohm$^{-1}$ cm$^{-1}$) | $\Lambda$ (ohm$^{-1}$ cm$^2$ equiv.$^{-1}$) |
|---|---|---|---|
| $HB(O_2CCF_3)_4$ | .3848 | .4545 | 1.181 |
| | .9063 | .5957 | .6573 |
| | 1.822 | .7387 | .4053 |
| | 6.438 | 1.200 | .1864 |
| | 13.28 | 1.692 | .1274 |
| | 22.83 | 2.230 | 0977 |
| | 40.55 | 2.999 | .0740 |
| | 56.12 | 3.535 | .0630 |
| | 70 87 | 3.968 | .0560 |
| | 83.56 | 4.299 | .0514 |
| | 95.66 | 4.587 | .0480 |
| | 106.7 | 4.828 | .0452 |
| $CsB(O_2CCF_3)_4$ | .3395 | 3.947 | 11.63 |
| | 6348 | 5.840 | 9.200 |
| | 1.343 | 9.248 | 6.886 |
| | 2.977 | 14.84 | 4.985 |
| | 5.075 | 21.00 | 4.137 |
| | 8.387 | 29.86 | 2.560 |
| | 13.08 | 42.30 | 3.235 |
| | 18.31 | 56.09 | 3.063 |
| | 23.24 | 69.51 | 2.990 |
| | 27.42 | 81.31 | 2.963 |
| | 31.23 | 92.45 | 2.960 |
| | *34.48 | 102.2 | 2.963 |
| $H_2O$ | 3.129 | 0926 | .0296 |
| | 7.410 | 1364 | .0184 |
| | 11.30 | .1653 | .0146 |
| | 14.56 | .1876 | .0129 |
| | 18.77 | .2183 | .0116 |
| | 25.77 | .2712 | .0105 |
| | 31.52 | .3167 | .0100 |
| | 53.76 | .4547 | .0085 |
| | 72.46 | .5687 | .0078 |
| | 98.96 | .7387 | .0075 |
| | *122.7 | .9059 | .0074 |
| | 137.1 | 1.018 | .0074 |
| | 154.2 | 1.155 | .0075 |
| | 177.8 | 1.354 | .0076 |
| | 201.2 | 1.568 | .0078 |

TABLE XXIV (cont.)

| Solute | Concentration ($10^3$ xmolarity) | $10^6$ $K_{sp}$ ($ohm^{-1}$ $cm^{-1}$) | $\Lambda$ ($ohm^{-1}$ $cm^2$ $equiv.^{-1}$) |
|---|---|---|---|
| $H_2O$ | 267.0 | 2.222 | .0083 |
| | 320.2 | 2.871 | .0090 |
| | 423.2 | 4.449 | .0105 |
| | 598.6 | 8.350 | .0139 |

$B(O_2CCF_3)_3$ and $CsB(O_2CCF_3)_4$ where the concentrations reached may not have been high enough, all the compounds studied show a minimum in the equivalent conductivity curve. In most cases this can be taken as evidence for triple ion formation, but the interpretation of the data for water must be made very carefully, since the solute may cause significant changes in the dielectric constant of the medium.

The equilibria governing triple ion formation may be written:-

$$MA \rightleftharpoons M^+ + A^-$$
$$MA + M^+ \rightleftharpoons M_2A^+$$
$$MA + A^- \rightleftharpoons MA_2^-$$

Writing the activity coefficient as f, dissociation constants are defined by:-

$$K = f^2[M^+][A^-]/[MA]$$
$$P = [M^+][MA]/[M_2A^+]$$
$$Q = [A^-][MA]/[MA_2^-]$$

The equivalent conductivity of the solution, $\Lambda$, can be expressed in terms of the individual mobilities of the single ions ( $\Lambda^+$, $\Lambda^-$) and of the triple ions ( $\lambda^+$, $\lambda^-$):-

$$= \frac{1}{C}\left\{[M^+].\Lambda^+ + [A^-].\Lambda^- + [M_2A^+].\lambda^+ + [MA_2^-].\lambda^-\right\} \quad 1)$$

Thus even if the individual mobilities of the single ions are known, the occurrence of triple ions in the system intro-

duces four new parameters into the conductance equation, the two dissociation constants P and Q, and the triple ion mobilities, $\lambda^+$ and $\lambda^-$. A complete solution of equation 1) has never been achieved, and approximate methods must be used. If the two dissociation constants, P and Q, have the same value (= k, say) and ionic strength effects are entirely ignored, then it has been shown (27) that equation 1) reduces to:-

$$\Lambda c^{\frac{1}{2}} = \alpha c + \beta \qquad 2)$$

where $\Lambda$ is the observed equivalent conductivity,

$$\alpha = \lambda_o K^{\frac{1}{2}}/k$$
$$\beta = \Lambda_o K^{\frac{1}{2}}$$

$\Lambda_o$ and $\lambda_o$ are the limiting equivalent conductivities of the electrolytes $M^+A^-$ and $M_2A^+.MA_2^-$.

A less approximate equation (27) makes some corrections for the effect of ionic strength on the activity and mobilities:-

$$\Lambda c^{\frac{1}{2}}.f.\frac{1}{1-S(c\Lambda/\Lambda_o^3)^{\frac{1}{2}}}\cdot\frac{1}{(1-\Lambda/\Lambda_o)^{\frac{1}{2}}} = \alpha c(1-\Lambda/\Lambda_o)+\beta \qquad 3)$$

f is calculated from the Debye-Hückel equation

$$\log f = -A(c\Lambda/\Lambda_o)^{\frac{1}{2}}/(1+B\mathring{a}(c\Lambda/\Lambda_o)^{\frac{1}{2}})$$

and $S = B_1\Lambda_o + B_2$ (see Appendix I)

Figure 19

A triple ion plot for various trifluoroacetates in trifluoroacetic acid.

$$Y = \Lambda c^{\frac{1}{2}}.f \frac{1}{1-S(c\Lambda / \Lambda o)^{\frac{3}{2}}} \cdot \frac{1}{(1-\Lambda/\Lambda o)^{\frac{1}{2}}}$$

$$X = c(1-\Lambda / \Lambda o)$$

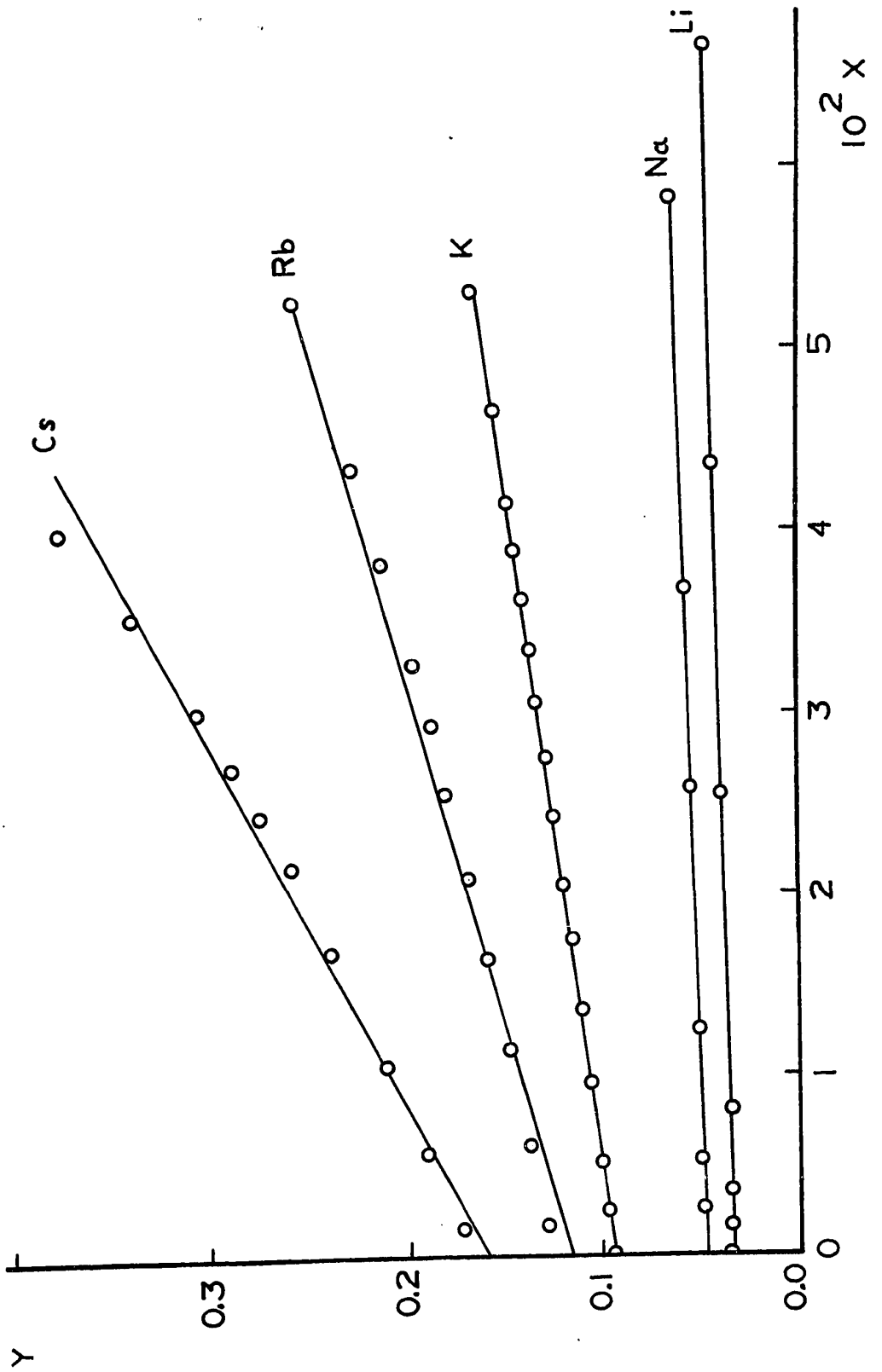

Cs
Rb
K
Na
Li
Y
0.3
0.2
0.1
0.0
0
1
2
3
4
5
$10^2$ X

Figure 19 shows a plot of equation 3) for the alkali metal trifluoroacetates in the region where triple ion formation is expected to be important, and the points approximate to a straight line quite well. The deviations are most marked for caesium trifluoroacetate, and while they may reflect a genuine, chemical effect, are most likely to be caused by the approximate nature of the mobility correction. This point will be discussed more fully when the case of antimony pentafluoride is considered, since the results for this compound reveal the limits of the mathematical treatment.

Table XXV gives the parameters derived from the conductivity measurements by use of equation 3). The best straight line to fit the points was calculated by a least squares method, and the last column gives the standard deviation from this line. The value of the intercept (column 3) should be equal to $\Lambda_o K^{\frac{1}{2}}$ (column 4) derived from the slope of the Fuoss-type plot ($1/\Lambda_o^2 k$) for measurements at very low concentrations (see chapters IV, V); the agreement is excellent. Column 5 gives the function $k\Lambda_o/\lambda_o$, found by dividing the intercept by the slope. Unfortunately, the plot cannot be made to give k and $\lambda_o$ separately, and the values of k in column 6 have been derived by following the suggestion of Fuoss and Kraus that triple ions are probably about one third as mobile as the single ions, i.e. that $\lambda_o/\Lambda_o = 1/3$. In fact a more likely value is

$$\lambda_o/\Lambda_o \approx \sqrt[3]{(1/3)} \approx 0.69$$

TABLE XXV

Parameters for triple ion equilibria obtained from equation 2)

| Substance | Slope | $10^2$ x Intercept | $10^2$ x $\Lambda_o K^{\frac{1}{2}}$ | $10^2$ x $k\Lambda_o/\lambda_o$ | $10^2$ x k | Std. Dev. |
|---|---|---|---|---|---|---|
| $CF_3CO_2Li$ | .254 | 3.33 | 3.44 | 13.1 | 4.37 | 2.48 % |
| $CF_3CO_2Na$ | .343 | 4.62 | 4.72 | 13.5 | 4.50 | 1.46 % |
| $CF_3CO_2K$ | 1.33 | 9.35 | 9.72 | 7.05 | 2.35 | .61 % |
| $CF_3CO_2NH_4$ | 1.97 | 11.7 | 12.1 | 5.93 | 1.98 | .59 % |
| $CF_3CO_2Rb$ | 2.62 | 11.8 | 12.5 | 4.51 | 1.50 | 2.67 % |
| $CF_3CO_2Cs$ | 5.02 | 16.0 | 17.6 | 3 19 | 1.06 | 2.56 % |
| $CsB(O_2CCF_3)_4$ | 4.48 | 19.9 | 21.4 | 4.34 | 1.45 | 2.11 % |
| *$SbF_5$ | 2.12 | 11.5 | 9.25 | 5.42 | 1.81 | - |

* Approximate values, derived from equation 2)

since triple ions have about three times the volume of single ions, whereas the conductivity depends inversely on the radius of the ion.

From studies of the temperature variation of the conductance of tetra-alkyl ammonium salts in anisole, Fuoss et al. proposed $\lambda_o/\Lambda_o = 0.82$ (168).

Whatever the exact value of $\lambda_o/\Lambda_o$ may be, the choice is unlikely to change the relative order of the values of k in Table XXV. Remembering that k is defined by:-

$$k = \frac{[M^+][MA]}{[M_2A^+]} = \frac{[A^-][MA]}{[MA_2^-]}$$

then the order of the triple ion dissociation constants for the trifluoroacetates ($Li > Na > K > NH_4 > Rb > Cs$) is surprizing. It is exactly the reverse of the trend found for the ion pair dissociation constants. Both elementary electrostatics and the theoretical expression for k devized by Fuoss (27) suggest that the smaller triple ions should be the more stable. The most probable explanation is a steric one; it seems quite likely that an ion as small as Na would have more difficulty in accomodating two bulky trifluoro-acetate ions around it than would a larger ion such as Cs. This is highly speculative, however, and one would have to suppose that electric effects become dominant after a certain point, since the triple ion dissociation constant of $CsB(O_2CCF_3)_4$ is larger than that of $CsO_2CCF_3$.

The case of water is interesting. Although

water is a very much weaker electrolyte than the other substances studied, it shows a minimum equivalent conductivity at a concentration of only ~0.1 molar, not much greater than that for the alkali metal trifluoroacetate. The minimum probably arises from the change in the dielectric constant of the medium as the concentration of water is increased. Using Fuoss' theoretical expression for the dissociation constant of an ion pair (see chapter IV) and assuming that the dielectric constant of the medium is proportional to the volume fractions of the constituents (water and trifluoroacetic acid), it can be estimated that the dissociation constant of an electrolyte with $\mathring{a} \sim 4\text{-}5$ Å will be increased by about 25% at a water concentration of 0.1 molar, and by about 550% at about 1 molar. Thus water is expected to react with the solvent according to the equations

$$H_2O + CF_3CO_2H \overset{K_i}{\rightleftharpoons} H_3O^+.^-O_2CCF_3 \overset{K_d}{\rightleftharpoons} H_3O^+ + CF_3CO_2^-$$

At very low concentrations the degree of dissociation of the ion pair $H_3O^+.^-O_2CCF_3$ will decrease with increasing concentration, as for any electrolyte, but eventually the changes in bulk dielectric constant produced by the presence of free water will cause a sharp rise in the concentration of $H_3O^+$ and $CF_3CO_2^-$ ions, and this is probably the principal cause of the minimum in the equivalent conductivity curve for water. Equilibria involving triple ions may also

be present, but any attempt to use equation 2) or 3) without allowing for the effect of the changing dielectric constant would be unjustified.

Equation 3) led to absurd results when applied to the data for $SbF_5$ ($HSbF_5(O_2CCF_3)$), and this is probably caused by the approximate nature of the mobility and activity corrections. The left-hand side of equation 3) contains a term $1-S(c\Lambda/\Lambda_o^3)^{\frac{1}{2}}$ in the denominator, and there is a possibility of division by zero at some stage. This will happen when

$$1 = S^2 c\Lambda/\Lambda_o^3$$

or

$$\text{Specific conductivity} = \frac{10^{-3}\Lambda_o^3}{S^2} \text{ ohm}^{-1} \text{ cm.}^{-1}$$

The most severe deviations from linearity will occur for electrolytes with large ions, for then $\Lambda_o$ will be small but the dissociation large, and the specific conductance will approach its critical value quite quickly. The results for the alkali metal trifluoroacetates are reliable because the measurements were well below the critical region, but for $SbF_5$ the critical specific conductance is calculated as only 59.8 $\mu$mhos, at a concentration of $6.03 \times 10^{-2}$ molar, whereas measurements were made to higher concentrations than this. Equation 3) is obviously inapplicable to this system, and the parameters listed in Table XXV were derived

from the simpler equation 2), which is plotted in Figure 20. While this avoids the difficulty of division by zero, the values derived are very approximate, since all ionic strength effects are neglected.

The acid $HB(O_2CCF_3)_4$ shows a different type of behaviour. No minimum was observed in the conductance curve, although measurements were made up to 0.1 molar, and triple ion plots using either of the equations 2) or 3) had slopes that were zero or slightly negative. It could be that triple ions are simply not formed, (very large dissociation constant), in which case equation 2) reduces to:-

$$\Lambda c^{\frac{1}{2}} = \text{constant}$$

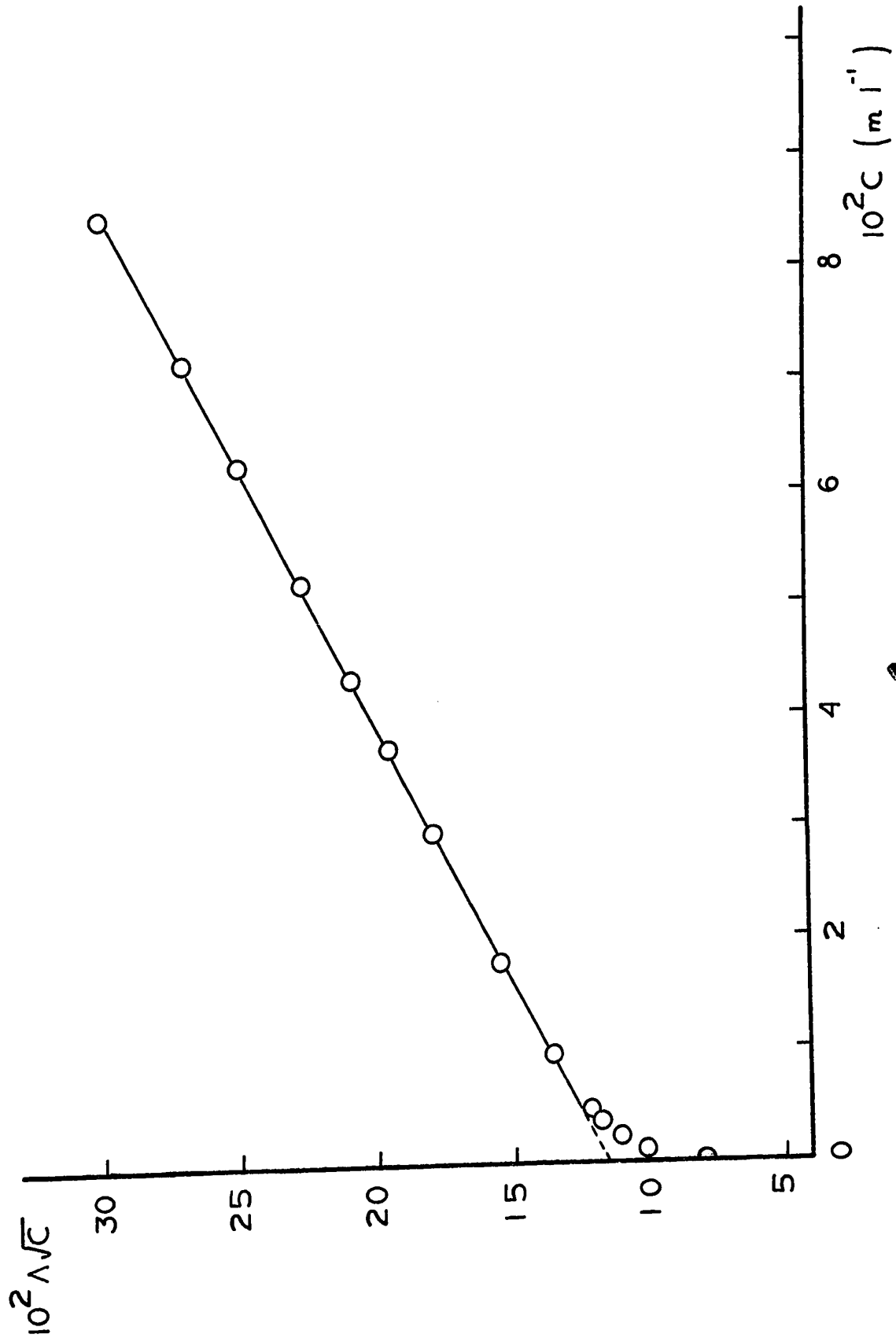
This is difficult to reconcile with the fact that the caesium salt $CsB(O_2CCF_3)_4$ gives a normal triple ion plot. Conductance studies at low concentrations (Chapter V) suggested that the reaction of $B(O_2CCF_3)_3$ with $CF_3CO_2H$ to give $HB(O_2CCF_3)_4$ is not quantitative, and the presence of uncomplexed $B(O_2CCF_3)_3$ can be expected to affect the triple ion equilibria. In addition, the more concentrated solutions might contain condensed species such as $\left[B_2O(O_2CCF_3)_5\right]^-$ which would affect the results.

C. Other approaches to the conductance minimum

The Fuoss-Kraus theory discussed above leads to an equation for a straight line expressed in terms of the two parameters $\Lambda_o K^{\frac{1}{2}}$ and k/n , where $n = \lambda_o/\Lambda_o$. Martin (167 b) modified the equation to obtain k and n separately,

Figure 20

Triple ion plot for antimony pentafluoride, using the more approximate equation 2 (see text).


$10^2 \Lambda\sqrt{C}$
30
25
20
15
10
5
0
2
4
6
8
$10^2 C$ (m l$^{-1}$)

and was partially successful in applying the method to triple ion equilibria in acetic acid. The values of k and n are obtained essentially from the rather small deviations of the experimental points from the straight line predicted by the simpler equations of Fuoss and Kraus, and thus the accuracy of the estimates is limited although the method is fundamentally sound. Fuoss (168) has described how $\lambda_o$ and k may be estimated from conductance studies over a wide range of temperatures. Neither of the methods was attempted in the present work.

All of the current treatments of triple ion equilibria assume equal dissociation constants for the two types of triple ion, and thus preclude examination of the relative stabilities of the ions $M_2A^+$ and $MA_2^-$.

Davies has offered an entirely different explanation of the conductance minimum (169). The minimum is usually interpreted as arising from the formation of triple ions, but for the solute water (see above) a minimum in the degree of dissociation itself, caused by changes in the dielectric constant, is thought to be more likely. Davies suggested that a dissociation minimum is quite general, and could arise from activity effects. The dissociation constant of an electrolyte is given by:-

$$K = f^2 c \gamma^2/(1-\gamma)$$

If the function $f^2c$ goes through a maximum value, $\gamma$ must show a minimum to maintain the constancy of K. The theory has been criticized by Fuoss (170) as quite unsubstantiated,

and Davies himself admits the possibility of triple ion formation in non-aqueous solvents. The results of the present study could not be fitted to Davies' theory, and in trifluoroacetic acid at least, triple ion formation is important.

D. Summary

The conductivities of several substances in trifluoroacetic acid go through a minimum at moderate concentrations, and this is consistent with the hypothesis of triple ion formation. The data can be fitted quite well to the equations of Fuoss and Kraus, but approximations made in the derivation lead to absurd results when the equations are applied to substances with a large dissociation constant and small limiting equivalent conductivity. Triple ion equilibria for the acid $HB(O_2CCF_3)_4$ are either unimportant, or complicated at high concentrations by the presence of other species. The minimum in the equivalent conductivity curve for water is probably due to changes in the bulk dielectric constant of the medium, and not to triple ion formation. Davies' theory of the dissociation minimum is not applicable in trifluoroacetic acid.

# CHAPTER VII

## Supplementary techniques -transference numbers and cryoscopy

### A. General

The conductance studies reported in Chapters IV - VI gave useful information about the behaviour of electrolytes in trifluoroacetic acid. It was hoped to increase the value of the results by using transference number measurements to find individual ionic mobilities, and cryoscopy to investigate the association of electrolytes at high concentrations. While not completely successful in this respect, the experiments yielded extremely interesting results.

### B. Transference numbers: introduction

Direct measurements of transference numbers in non-aqueous media is difficult, and has rarely been undertaken; the low dielectric constant of most solvents causes extensive association of the ions. Fuoss and Kraus have used an indirect method, which consists of measuring the conductivity of an electrolyte whose cation and anion have equal radii, and presumably equal mobilities (e.g. 174). Comparison with the few direct measurements available has shown that the method can be accurate to about 0.5% (175). The electolyte most frequently used is tetra(iso-amyl)ammonium tetraphenylborate. Unfortunately, this cannot be used in trifluoroacetic acid since the tetraphenylborate ion (as $NaBPh_4$) was decomposed by the solvent to give a purple

solution.

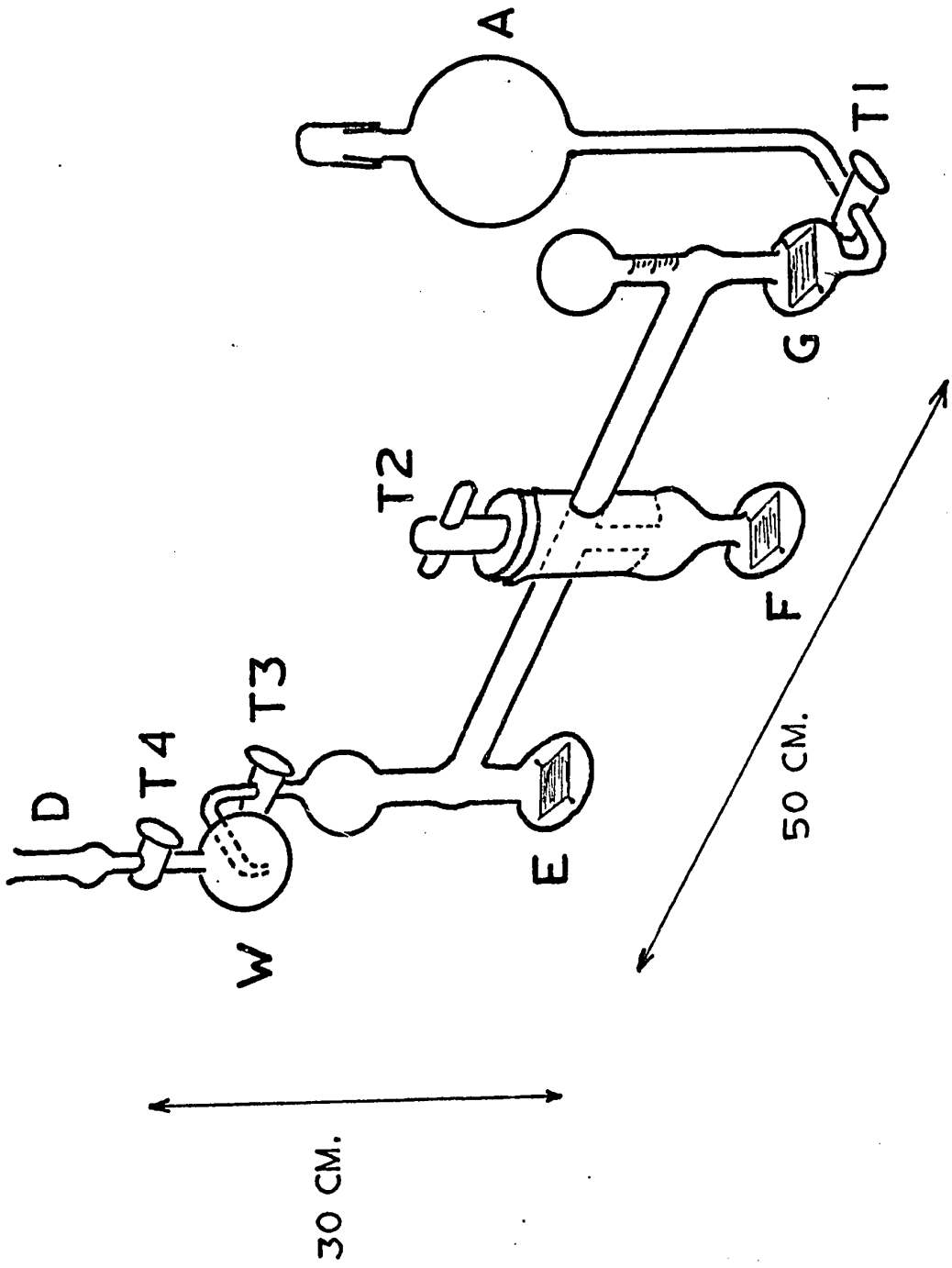
Lorimer et al. (176) adapted the moving boundary method to measure transference numbers in methanol and ethanol, and detected the boundary by the change in conductance as it swept past a pair of micro-electodes. They found that results were erratic at concentrations below $5 \times 10^{-4}$ molar, and since measurements in trifluoroacetic acid must be made at less than $2 \times 10^{-4}$ molar, the method was not considered suitable for the present work.

A modification of the Hittorf method was adopted for studies of the alkali metal trifluoroacetates, and concentration changes were followed conductimetrically. Since low concentrations of electrolyte were essential, the resistivity of the solutions was extremely high. The dimensions of the apparatus (Figure 21 ) represent a compromise between the long distances required between the anode and cathode compartments to prevent diffusion of the electolyte due to concentration differences, and the very short distances needed to pass any observable current through the cell. The apparatus and procedure have been described in detail in Chapter II.

It is usually stated that one, or preferably both, of the electrodes should be reversible, otherwise the electolysis products will contaminate the solution, and gassing at the electrodes may cause unwanted stirring. Since the amounts of material electrolysed were typically about 1 $\mu$mole these effects were expected to be negligible.

Figure 21

Hittorf cell for the measurement of transference numbers.


A
T1
G
T2
F
T3
T4
D
W
E
50 CM.
30 CM.

This was confirmed by mixing the solution in the cathode and anode compartments after electrolysis, and comparing the conductance of the solution with that measured before electrolysis. No change could be detected. The irreversible platinum electrodes were therefore considered satisfactory.

Conway and Vijh (6) have shown that electrolysis of solutions of potassium trifluoroacetate in trifluoroacetic acid gives virtually quantitative yields of hydrogen and $C_2F_6$. Since the conductance of the solutions is many times that of the pure solvent, it is assumed that the current is carried by metal and trifluoroacetate ions, and that the hydrogen is produced by preferential discharge of $H^+$ at the cathode. Under these conditions, it can be shown that the transference number of the metal cation is given by:-

$$t_+ = \Delta n/Q\mathcal{F}$$

where $\Delta n$ is the change in number of moles of electrolyte in either the cathode or the anode compartment, Q is the total charge passed (in coulombs), and $\mathcal{F}$ is the Faraday. The treatment differs from that for measurements with reversible electrodes, where the transference number of the cation is found from concentration changes in the anode compartment, and that of the anion can be calculated independantly from changes in the cathode compartment.

C. Transference numbers: results and discussion

Measurements were made on solutions of both caesium and potassium trifluoroacetates. Although no constant current circuit was included in the apparatus, the current fell by less than 2% during electrolysis, and the total charge passed was determined with a probable error of ~0.5%. The concentration changes were probably correct to about 3%. Table XXVI summarizes the results of the experiments, and also gives the duration of the experiment and the approximate potential difference applied between the electrodes E and G (Figure 21 ). The concentration in the central compartment, F, was found to remain constant throughout the experiment.

The transference number found for the caesium varies considerably in experiments 1 to 5, and the values are lowest for short experiments at low voltages. This implies that diffusion of the electrolyte due to the concentration gradient is affecting the results, and this was confirmed by measuring the conductivity of the solution in the cathode and anode compartments immediately after the experiment, and again about an hour later. As expected, the conductivity (and hence the concentration) of the solution around the cathode decreased (by about 10%), while that of the solution in the anode compartment increased by about the same amount. The experiments 6 and 7 were carried out for shorter times (to minimize diffusion) and at much

leaf 191 omitted
in page numbering.

TABLE XXVI

Results of transference number experiments at 25°C

| Electrolyte | Experiment | Concentration | Applied Voltage | Duration | $t_+$(cathode) | $t_+$(anode) |
|---|---|---|---|---|---|---|
| $CF_3CO_2Cs$ | 1 | $1.384 \times 10^{-4}$ | 120 | 5 hr. | .595 | .615 |
| " | 2 | $1.085 \times 10^{-4}$ | 120 | 1hr. 30min. | .535 | .532 |
| " | 3 | " | 237 | 2hr. 40min. | .570 | .584 |
| " | 4 | " | 237 | 4hr. 30min. | .559 | .544 |
| " | 5 | " | 510 | 2 hr. | .602 | .582 |
| " | 6 | " | 1100 | 1 hr. | .592 | .588 |
| " | 7 | " | 4400 | 15 min. | .591 | .594 |
| $CF_3CO_2K$ | 1 | $1.225 \times 10^{-4}$ | 2000 | 1 hr. | .519 | .517 |
| " | 2 | $1.193 \times 10^{-4}$ | 8000 | 15 min. | .515 | .505 |

higher voltages (to make concentration changes as large as possible) A satisfactorily constant value was obtained of .591 ± .003. Similarly, the transference number of the potassium ion was found to be .514 ± .009.

A difficulty immediately arises. The transference numbers show that the caesium ion is more mobile than the potassium, directly contradicting the results of the conductance studies reported in Chapter IV. If the transference numbers are combined with the known $\Lambda^{\circ}$ values for the trifluoroacetates of caesium and potassium, then a mobility of 19.6 (Cs) or 27.0 (K) is found for the trifluoroacetate ion, depending on which salt is used for the calculation. Even the smaller of these values must be too large, for the limiting equivalent conductivity of $CF_3CO_2H_2^+ . {}^-O_2CCF_3$ is itself only 21.1, and the mobility of the anion would probably be about one half of this value. The experiments thus give reproducible, but totally unreasonable values for the transference numbers. The author is quite unable to explain this. No current leakage could be detected in the apparatus. The voltages used are admittedly unprecedented in transference number measurements, although McBain et al. used 500 volts in their studies on aqueous acetic acid (177), but effects such as dielectric breakdown of the solvent, relaxation of the ionic atmosphere or increased dissociation of the electolyte due to the electric field are not expected until much higher

field strengths are reached. Further work is to be carried out on the system.

D. Cryoscopy: results and discussion

A suitable non-electrolyte was required to establish the cryoscopic constant of the solvant. Methanesulphonyl fluoride is a non-electrolyte in fluorosulphuric acid, and therefore unlikely to be protonated in trifluoroacetic acid (178). Carbon tetrachloride was also expected to be satisfactory. Conductance studies (Chapter IV) showed that trifluoroacetic anhydride is a non-electrolyte, but it has the disadvantage of being appreciably more volatile than the solvent. 1-3-5-trinitrobenzene is a non-electrolyte in $H_2SO_4$ (179), but was insoluble in trifluoroacetic acid.

The measured freezing point depressions for methanesulphonyl fluoride and for carbon tetrachloride are shown in Table XXVII, and plotted against the molality of the solution in Figure 22. Both the plots show a slight curvature at higher concentrations owing to the effects of non-ideality. The curves approach the same limiting tangent, and the slope of this line gives the cryoscopic constant as 6.46°C/(mole/1000 g). The latent heat of fusion of the solvent may be calculated from the equation:-

$$k_f = RT_f^2/1000\ L$$

where $k_f$ is the cryoscopic constant

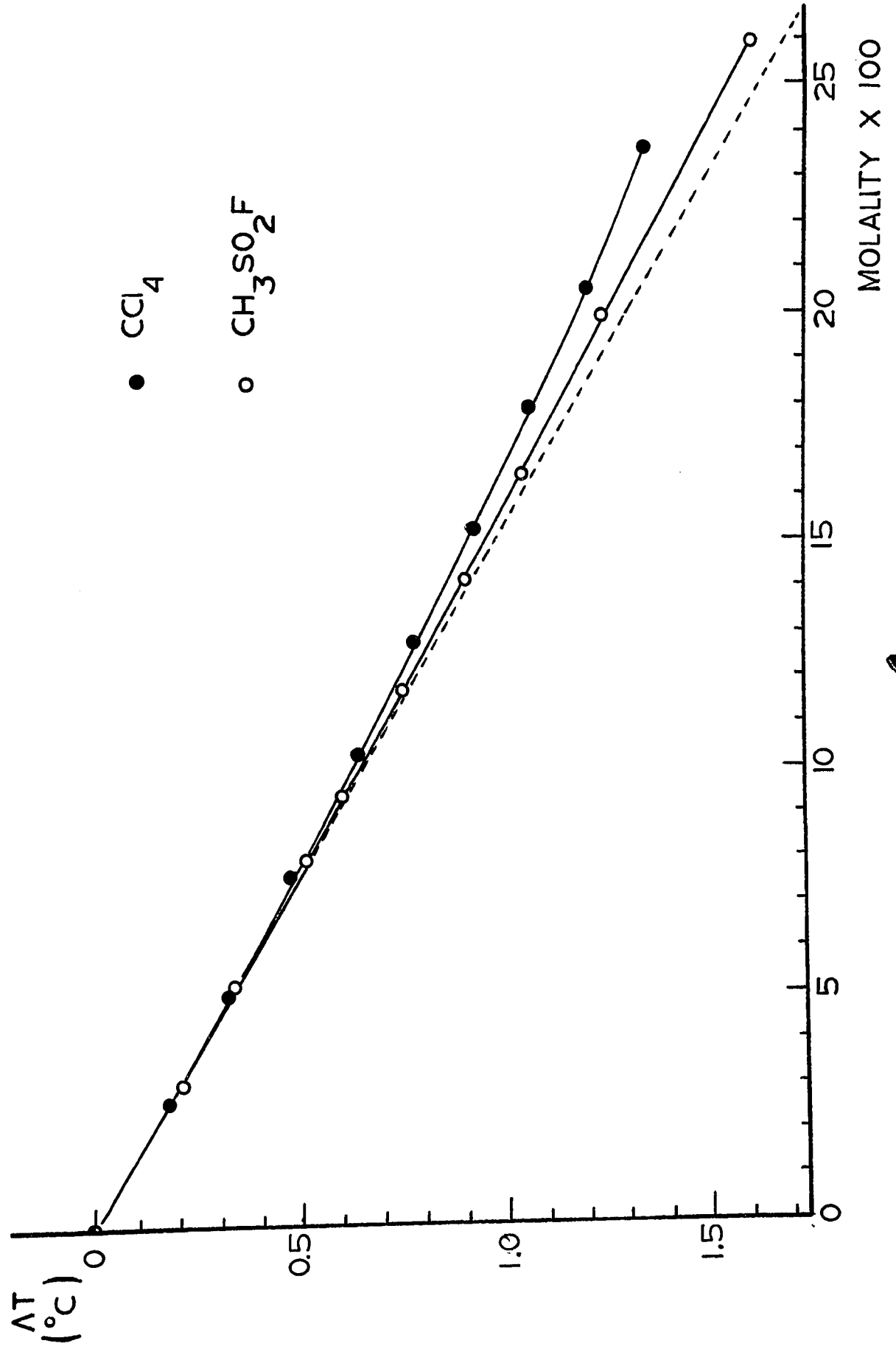
TABLE XXVII

Freezing point depressions in trifluoroacetic acid

| Solute (fr. pt. pure solvent) | $10^2$xConcentration (Molality) | Freezing point depression $\Delta T$, °C |
|---|---|---|
| $CH_3SO_2F$ (-15.261°C) | 3.184 | .209 |
| | 5.337 | .343 |
| | 8.090 | .516 |
| | 9.506 | .602 |
| | 11.788 | .749 |
| | 14.23 | .898 |
| | 16.52 | 1.039 |
| | 19.97 | 1.237 |
| | 26.03 | 1.603 |
| $CCl_4$ (-15.214°C) | 2.730 | .178 |
| | 5.129 | .324 |
| | 7.634 | .472 |
| | 10.427 | .638 |
| | 12.85 | .777 |
| | 15.38 | .922 |
| | 18.02 | 1.060 |
| | 20.59 | 1.200 |
| | 23.65 | 1.348 |

Figure 22

Freezing point depressions produced by carbon tetrachloride and methanesulphonyl fluoride in trifluoroacetic acid.


$CCl_4$
$CH_3SO_2F$
$\Delta T$ (°C)
0
0.5
1.0
1.5
0
5
10
15
20
25
MOLALITY X 100

$T_f$ the freezing point of the pure solvent

L the latent heat of fusion in calories per gram

The value found for the latent heat is 9750 joules $mole^{-1}$, or 2.33 $kcal.mole^{-1}$. There is unfortunately no direct measurement available in the literature for comparison.

Freezing point measurements were also carried out on solutions of trifluoroacetic anhydride, and at the end of the experiment, the anhydride was titrated with a solution of water. In calculating the concentration of water, allowance was made for the extra solvent produced by the reaction of anhydride with water. The results are given in Table XXVIII and plotted in Figure 23.

In Figure 23 the section A-B of the curve represents additions of anhydride, the part B-C additions of water, and the part C-D the effect of the water when all the anhydride is consumed. The depression produced by the very first addition of the anhydride is 0.210°C. This is in excellent agreement with the value of 0.211°C expected from the concentration at this point and the cryoscopic constant, and confirmed that the freshly distilled solvent contained negligible amounts of water.

The anhydride branch of the curve is retraced very well during the titration with water, but the intersection of the two branches is at a concentration of $1.30 \times 10^{-2}$ molal in anhydride, and not at zero. The error might arise from traces of water in the system, and the

TABLE XXVIII

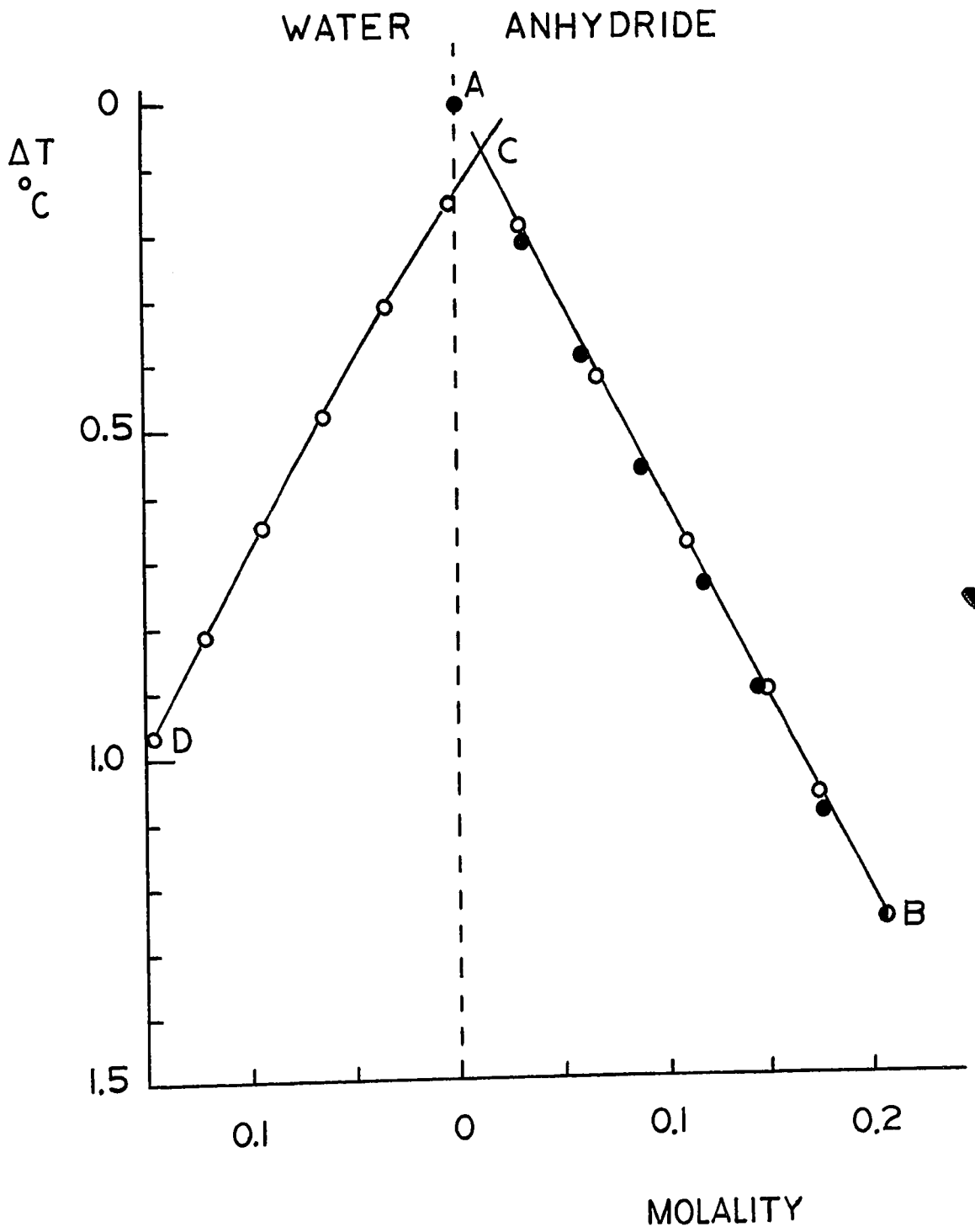
Cryoscopy of trifluoroacetic anhydride and titration with water

| Solute | Concn. of free anhydride (Molalityx100) | Concn. of free water (Molalityx100) | ΔT,°C |
|---|---|---|---|
| $(CF_3CO)_2O$ additions. (fr. pt. solvent -15.221°C) | 3.270 | - | .210 |
| | 6.069 | - | .384 |
| | 9.007 | - | .560 |
| | 11.93 | - | .737 |
| | 14.68 | - | .902 |
| | 17.92 | - | 1.093 |
| | 20.80 | - | 1.260 |
| $H_2O$ additions | 17.58 | - | 1.062 |
| | 15.05 | | .903 |
| | 11.07 | | .673 |
| | 6.864 | - | .420 |
| | 3.061 | | .185 |
| | - | .210 | .152 |
| | - | 3.338 | .313 |
| | | 6.401 | .479 |
| | | 9.408 | .647 |
| | | 12.22 | .812 |
| | | 14.74 | .968 |

Figure 23

Freezing point depressions produced by trifluoroacetic anhydride and by water in trifluoroacetic acid.

- ● Anhydride additions
- o Water additions.


WATER
ANHYDRIDE
A
C
D
B
0
0.5
1.0
1.5
ΔT
°C
0.1
0
0.1
0.2
MOLALITY

curve can be made to show the break at the theoretical point if it is assumed that the freshly distilled acid is $4.14 \times 10^{-2}$ molal in water ($7.5 \times 10^{-4}$ g water per gram of acid). This is obviously far too high, higher in fact than the concentration of anhydride at the first point on the curve. It requires that the first addition of anhydride should raise the freezing point, whereas the freezing point is in fact lowered by almost exactly the amount calculated from the cryoscopic constant. It therefore seems that the water must have entered during the course of the experiment. This is quite possible, since the experiment was a very long one. The reaction of trifluoroacetic anhydride with water is slow in dilute solution, and the titration alone took about six hours to accomplish. Other experiments were complete in $1\frac{1}{2}$ - 2 hours, and the effects of water diffusing into the apparatus are thought to be negligible in these cases.

The initial slope of the water branch of the curve is 6.40°C/(mole/1000 g), confirming that water neither dissociates nor associates to any appreciable extent in dilute solution. Thereafter the slope is somewhat greater, in agreement with the work of Cady and Cady (82) who studied a much wider concentration range.

Solutions of the trifluoroacetates of sodium, potassium and caesium were also investigated, and the results are given in Table XXIX. The last column of the table gives the value of $\nu$, the apparent number of moles of particles

TABLE XXIX

Depression of freezing point for various trifluoroacetates in trifluoroacetic acid

| Solute (fr. pt. pure solvent) | $10^2$xMolality | T,°C | $\nu$ |
|---|---|---|---|
| $CF_3CO_2Na$ | 1.651 | .105 | .971 |
| (-15.239°C) | 2.370 | .152 | .986 |
| | 3.373 | .223 | 1.02 |
| | 4.362 | .277 | .985 |
| | 5.246 | .333 | .987 |
| | 6.294 | .403 | .998 |
| | 7.356 | .481 | 1.02 |
| | 8.655 | .580 | 1.05 |
| | 9.976 | .672 | 1.06 |
| $CF_3CO_2K$ | .95 | .062 | .984 |
| (-15.250°C) | 2.004 | .129 | .987 |
| | 2.929 | .192 | 1.011 |
| | 3.799 | .246 | 1.002 |
| | 4.854 | .315 | 1.008 |
| | 5.931 | .383 | 1.006 |
| | 7.499 | .483 | 1.007 |
| | 9.267 | .599 | 1.015 |
| | 11.10 | .703 | .999 |
| | 14.36 | .923 | 1.020 |

TABLE XXIX(cont.)

| Solute (fr. pt. pure solvent) | $10^2$xMolality | T,°C | $\nu$ |
|---|---|---|---|
| $CF_3CO_2Cs$ | 2.572 | .171 | 1.023 |
| (-15.234°C) | 4.827 | .305 | .981 |
| | 9.713 | .587 | .950 |
| | 12.06 | .717 | .939 |
| | 14.19 | .849 | .950 |
| | 16.63 | .996 | .955 |
| | 18.94 | 1.150 | .973 |
| | 21.27 | 1.306 | .989 |

produced by one mole of solute. $\nu$ is calculated from the formula:-

$$\nu = \Delta T / \Delta T'$$

where $\Delta T$ is the lowering of freezing point produced by the sample, and $\Delta T'$ the depression produced by the same concentration of non-electrolyte, in this case, methanesulphonyl fluoride. Using the value of $\Delta T'$ actually observed, instead of calculating it from the cryoscopic constant, corrects for gross non-ideality effects. The validity of the correction depends on the suitability of the non-electrolyte used. Since methanesulphonyl fluoride, $CH_3SO_2F$, and the ion pair $CF_3CO_2M$ are structurally quite similar, the correction is thought to be an adequate one in this case. The significance of $\nu$ can be illustrated by the three extreme cases:-

1) The solute, MA, is completely undissociated

$$\nu = 1$$

2) The solute, MA, is completely dissociated to ions

$$MA \longrightarrow M^+ + A^-$$

$$\nu = 2$$

3) The solute, MA, exists entirely as triple ions

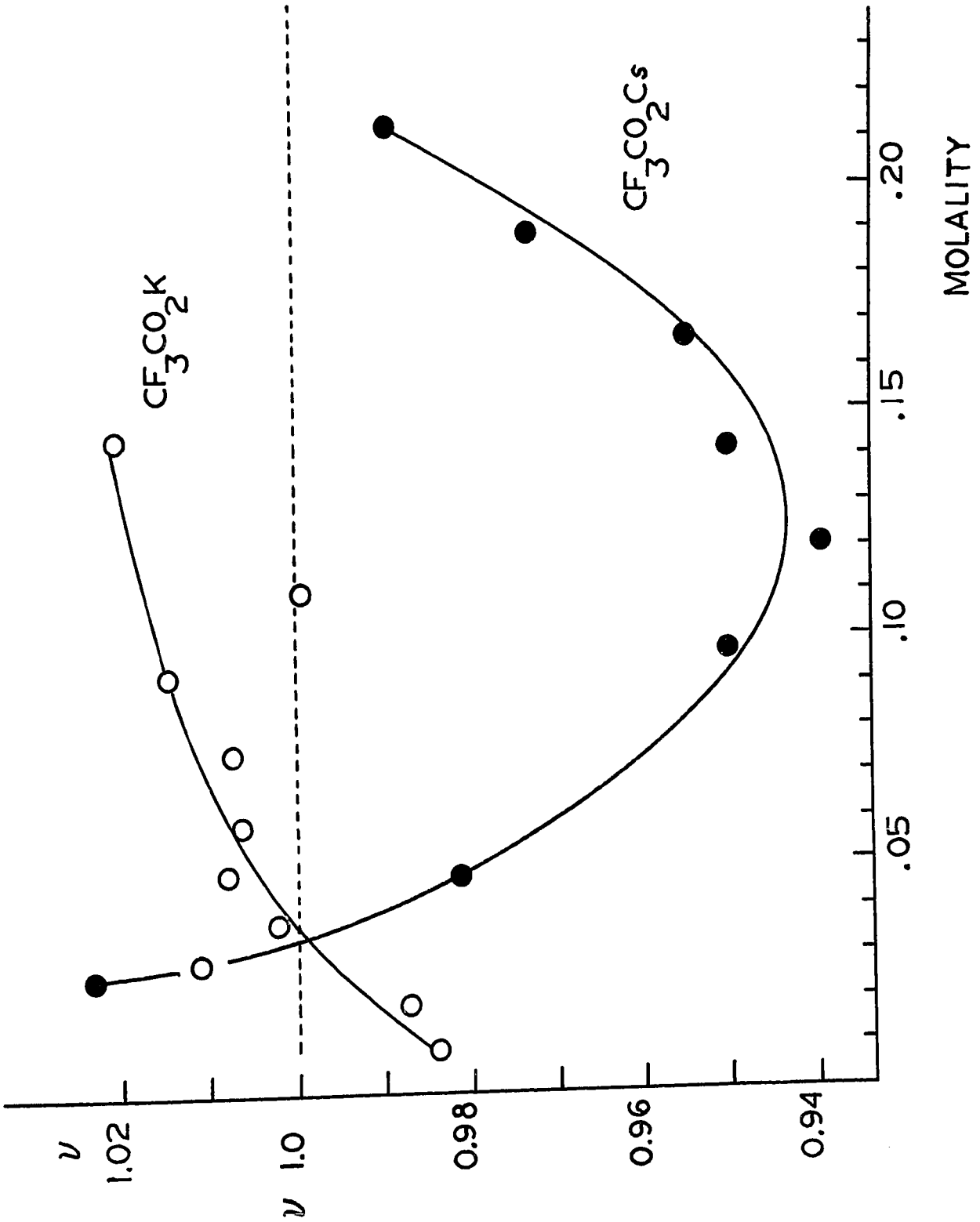
$$3MA \longrightarrow M_2A^+ + MA_2^-$$

$$\nu = 2/3$$

Figure 24 is a plot of $\nu$ against molality for the potassium

Figure 24

The parameter $\nu$ as a function of concentration for caesium and potassium trifluoroacetates.


$\nu$
1.02
$\nu$ 1.0
0.98
0.96
0.94
.05
.10
.15
.20
MOLALITY
$CF_3CO_2K$
$CF_3CO_2Cs$

and caesium salts, on a greatly magnified scale. The results for sodium trifluoroacetate are rather scattered, and have been omitted from the figure for the sake of clarity. A quantitative treatment is not possible, because the deviations of $\nu$ from unity are not much more than the experimental error ( $\sim 1\%$), and because the dissociation constants governing triple ion equilibria are not accurately known (see chapter VI). Nevertheless, the general pattern of the results is in accord with the conductivity studies. Caesium trifluoroacetate shows the best-defined behaviour. At the lowest concentration studied, $\nu$ is about 1.02, indicating dissociation to ions. The value of $\nu$ then falls sharply with increasing concentration because of association to triple ions, but goes through a minimum at about .12 molar, and begins to rise again. This may indicate that departures from ideality are progressively more marked, as would be expected if the electrolyte is co-ordinating to the solvent, reducing the amount of free solvent available, and thus increasing the effective concentration of the solute.

The results for the potassium, and particularly the sodium salts are more scattered, but the same increase in the slope of the curve is observed at higher concentrations, and attributed to solvation of the solute. At lower concentrations, $\nu$ is less than unity, probably indicating association to triple ions. It may be that at very low concentrations $\nu$ begins to increase again, as in the case of the caesium salt, but such behaviour was not observed in

the concentration range studied. This is in accord with the results of the conductance studies, which showed that dissociation of the solute to ions is much less extensive for the sodium and potassium salts than for the caesium.

Summary

Transference number experiments were carried out with solutions of caesium and potassium trifluoroacetates in trifluoroacetic acid. A modification of the Hittorf method was used, and concentration changes were followed conductimetrically. Extremely high voltages were necessary for electrolysis. The results were reproducible, but led to unsatisfactory estimates of the ionic mobilities. Further work is required.

Freezing point measurements established the cryoscopic constant of trifluoroacetic acid as 6.46°C/(mole /1000 g), and indirectly determined the latent heat of fusion of the acid as 2.335 kcal/mole. The behaviour of the solutes water and trifluoroacetic anhydride was also studied. The results obtained for solutions of the alkali metal trifluoroacetates were consistent with information derived from the conductance studies, but a quantitative interpretation was not possible.

## Summary of Conclusions

Trifluoroacetic acid is a moderately strong acid, with a dielectric constant of 8.40 at 25°C. A review of its solvent properties is presented. Conductance measurements at very low concentrations ( $\sim 2 \times 10^{-4}$ molar) established that the ammonium and alkali metal trifluoroacetates are strong bases, while the compounds $HB(O_2CCF_3)_4$ and $HSbF_5(O_2CCF_3)$ are acids. This was confirmed by a conductimetric titration. From these measurements, the concentration of the solvent self-dissociation ions $CF_3CO_2H_2^+$ and $CF_3CO_2^-$ was calculated as about $3.0 \times 10^{-7}$ molar in the pure solvent, and a proton-jump mechanism of conduction is thought to be unlikely.

All the electrolytes studied were highly associated, as expected in a low dielectric constant medium. Dissociation constants found for the ion pairs showed the expected dependance on ionic size, but the ionic mobilities for the alkali metal cations followed the unusual order:-

$$Na^+ > K^+ > Rb^+ > Cs^+$$

The order is the reverse of that found in most solvents, and may indicate that solvation of the cation is less important in trifluoroacetic acid than in other media.

Trifluoroacetic anhydride lowers the conductivity of the pure solvent very slightly, and reacts quantitatively

with water to give trifluoroacetic acid. The conductivity of water solutions is nearly three orders of magnitude less than that of solutions of the alkali metal trifluoroacetates at the same concentrations. It seems that an isolated water molecule is much less basic than the bulk liquid and that water is largely unprotonated in dilute solution in trifluoroacetic acid.

Conductance measurements were also made at higher concentrations ($2 \times 10^{-4}$ to 0.1 molar). Most of the electrolytes studied showed a minimum in the curve of equivalent conductivity versus concentration, owing to the formation of triple ions of the type $M_2A^+$ and $MA_2^-$. Dissociation constants for the triple ions are calculated and discussed.

$^{19}F$ nuclear magnetic resonance studies showed that trifluoroacetic anhydride reacts with many of the common mineral acids to form an interesting series of mixed anhydrides, and confirmed the existence of the acids $HSbF_5(O_2CCF_3)$ and $HB(O_2CCF_3)_4$. Numerous attempts were made to isolate $HB(O_2CCF_3)_4$, but none were successful. In many cases the product was the condensed species, $B_2O(O_2CCF_3)_4$.

A preliminary attempt was made to measure the transference numbers of electrolytes in trifluoroacetic acid. The results were reproducible, but not internally consistent.

Freezing point measurements established a value

of 6.46 °C/(mole/1000 g) as the cryoscopic constant of the solvent, and 2.335 kcal/mole (9750 joules/mole) as the latent heat of fusion. Water appears to have a normal molecular weight in trifluoroacetic acid. The results for the alkali metal trifluoroacetates could not be treated quantitatively, but followed the pattern predicted by the conductance studies.

## Appendix I

i) Coefficients of the Fuoss (1965) conductance equation.

$$\Lambda = \gamma(\Lambda_o - Sc^{\frac{1}{2}}\gamma^{\frac{1}{2}} + E c\gamma \log_e(6E_1 c\gamma) + Lc\gamma)$$

If D, T and $\eta$ are the dielectric constant, temperature and viscosity of the solvent respectively, then:-

$S = B_1 \Lambda_o + B_2$

$B_1 = 8.204 \times 10^5/(DT)^{3/2}$

$B_2 = 82.5/\eta\,(DT)^{\frac{1}{2}}$

$E_1 = 2.942 \times 10^{12}/(DT)^3$

$E_2 = 0.4333 \times 10^8/\eta\,(DT)^2$

$E = E_1 \Lambda_o - E_2$

$L_1 = 3.202E_1 \Lambda_o - 3.420E_2 + B_1B_2$

$b = 16.708 \times 10^{-4}/DT\mathring{a}$

$H(b) = (2b^2 + 2b - 1)/b^3$

$L_2 = 2E_1 \Lambda_o H(b) + 44E_2/3b - 2E\log_e b$

$L = L_1 + L_2$

ii) Coefficients of the Debye-Hückel activity equation.

$$\log f = -A\sqrt{c\gamma}\,/(1+B\mathring{a}\sqrt{c\gamma})$$

$A = 1.8246 \times 10^6/(DT)^{3/2}$

$B = 50.29 \times 10^8/(DT)^{\frac{1}{2}}$

## Appendix II

Program to extrapolate conductance data.

The following information must be supplied:-

| | |
|---|---|
| L | the number of sets of data (number of independant experiments) to be extrapolated. |
| D | the dielectric constant of the solvent |
| VISC | the viscosity of the solvent |
| T | the temperature (°K) |
| TITLE | the title of each individual experiment |
| N | the number of readings in one set of data |
| AMDO | an initial estimate of $\Lambda_o$ |
| AO | an initial estimate of $\mathring{a}$ |
| C(I) | the concentration at each point |
| AMDA(I) | the equivalent conductivity at each point. |

The language used is FORTRAN IV G

```
0001          DIMENSION C(100),AMDA(100),X(100),Y(100),GAMMA(100),TITLE(20),
             1F2(100)
0002          READ(1,1)L
0003        1 FORMAT(I4)
0004          M=1
0005          READ(1,2)D,VISC,T
0006        2 FORMAT(3F10.0)
0007          Z=D*T
0008          A=1.8246E6/Z**1.5
0009          B=50.29E8/Z**0.5
0010          B1=8.204E5/Z**1.5
0011          B2=82.50/VISC/Z**0.5
0012          E1=2.942E12/Z**3.
0013          E2=0.4333E8/VISC/Z**2.
0014          P=560.37E-8/D
0015          Q=25.2324E20
0016       76 CONTINUE
0017          READ(1,20,END=77)TITLE
0018       20 FORMAT(20A4)
0019          READ(1,3)N
0020        3 FORMAT(I4)
0021          READ(1,100)AMDO,AO
0022      100 FORMAT(2F10.0)
0023          READ(1,4)(C(I),AMDA(I),I=1,N)
0024        4 FORMAT(2F10.0)
0025          K=1
0026       16 S=B1*AMDO+B2
0027          IF(K.EQ.11) GOTO 47
0028          L=E1*AMDO-E2
0029          BO=16.708E-4/Z/AO
0030          H=(2.*BO*BO+2.*BO-1.)/BO**3.
0031          EL1=3.202*E1*AMDO-3.420*E2+B1*B2
0032          EL2=2.*E1*AMDO*H+44.*E2/3./BO-2.*E*ALOG(BO)
0033          EL=EL1+EL2
0034          DO 17 I=1,N
0035       19 GAMMO=AMDA(I)/AMDO
0036        7 U=C(I)*GAMMO
```

```
0037            AMDOC=AMDO-S*U**0.5+E*U*ALOG(6.*E1*U)+EL*U
0038            GAMMA(I)=AMDA(I)/AMDOC
0039            IF(ABS(GAMMA(I)-GAMMO)-GAMMA(I)*1.E-5)5,6,6
0040          6 GAMMO=GAMMA(I)
0041            GOTO 7
0042          5 F2(I)=10.**(-2.*A*U**0.5/(1.+B*AO*U**0.5))
0043            X(I)=C(I)*F2(I)*AMDO*GAMMA(I)
0044            Y(I)=1./GAMMA(I)/AMDO
0045         17 CONTINUE
0046            CALL LINE(X,Y,N,SLOPE,AINTER,STDER)
0047            AMDO2=1./AINTER
0048            DISCON=AINTER**2./SLOPE
0049            IF((AMDO2.LT.0.).OR.(DISCON.LT.0.)) GOTO 43
0050            IF((M.EQ.15).OR.(M.EQ.16)) GOTO 43
0051.        10 AO2=P/(ALOG(1./DISCON/Q/AO**3.))
0052            IF(ABS(AO2-AO)-AO2*1.E-5)9,8,8
0053          8 AO=AO2
0054            GOTO 10
0055         43 AO2=AO
0056          9 WRITE(3,11)TITLE,K
0057         11 FORMAT(1H1,1X,20A4,//,2X,'ITERATION #',I2)
0058            WRITE(3,12)(C(I),AMDA(I),GAMMA(I),F2(I),X(I),Y(I),I=1,N)
0059         12 FORMAT(//,2X,'CONCENTRATION',7X,'EQUIV. COND.',8X,'GAMMA',9X,
                1'ACT.COEFF.SOD.',10X,'X',17X,'Y',/,(6(2X,E14.7,2X)))
0060            WRITE(3,13)AMDO2,STDER,DISCON,AO2
0061         13 FORMAT(//,4X,'LT.EQ.COND.',8X,'STD.ERROR',8X,'DISS. CONST.',6X,
                1'LEAST DISTANCE',/,2X,E14.7,3X,E14.7,'8',1X,2(2X,E14.7,2X))
0062            WRITE(3,23)SLOPE,AINTER
0063         23 FORMAT(/////,2X,'SLOPE=',E14.7,/,2X,'INTERSEPT=',E14.7)
0064            IF((AMDO2.LT.0.).OR.(DISCON.LT.0.)) GOTO 47
0065            IF(ABS(AMDO2-AMDO)-AMDO2*1.E-4)47,15,15
0066         47 M=M+1
0067            IF(L-M)77,76,76
0068         15 AMDO=AMDO2
0069            K=K+1
0070            GOTO 16
0071         77 RETURN
0072            END
```

```
0001            SUBROUTINE LINE(X,Y,N,SLOPE,AINTER,STDER)
0002            DIMENSION X(100),Y(100)
0003            SUMX=0.
0004            SUMY=0.
0005            SUMXX=0.
0006            SUMXY=0.
0007            DO 1000 I=1,N
0008            SUMX=SUMX+X(I)
0009            SUMY=SUMY+Y(I)
0010            SUMXX=SUMXX+X(I)*X(I)
0011       1000 SUMXY=SUMXY+X(I)*Y(I)
0012            SLOPE=(SUMXY*FLOAT(N)-SUMX*SUMY)/(SUMXX*FLOAT(N)-SUMX*SUMX)
0013            AINTER=(SUMY-SLOPE*SUMX)/FLOAT(N)
0014            DEVSQ=0.
0015            DO 2000 I=1,N
0016            DEV=(Y(I)-SLOPE*X(I)-AINTER)*100./Y(I)
0017       2000 DEVSQ=DEVSQ+DEV*DEV
0018            STDER=(DEVSQ/FLOAT(N))**0.5
0019            RETURN
0020            END
```

## Appendix III

Program to calculate the specific conductance vs. concentration curve for the conductimetric titration of a partially dissociated acid with a partially dissociated base.

---

The following information must be supplied:-

| | |
|---|---|
| TITLE | the title of the experiment (optional) |
| D | the dielectric constant of the solvent |
| VISC | the viscosity of the solvent |
| T | the temperature (°K) |
| AMACID, AMBASE, AMSALT | the limiting equivalent conductivities of the acid, the base, and the salt formed from the two |
| DACID, DBASE, DSALT | the dissociation constants of the acid, base and salt |
| AOACID, AOBASE, AOSALT | the distances of closest approach of the ions found for the acid, base and salt. |
| N | the number of measurements to be processed |
| M | the number of these measurements made with the concentration of the base less than that of the acid |

CBASE(I) the added concentration of base at each point

CACID(I) the added concentration of acid at each point

SP(I) the observed specific conductance at each point

The language used is FORTRAN IV G

```
0001            DIMENSION TITLE(20),CACID(20),CBASE(20),R(20),SP1(20),SP2(20),
               1X(20),EM(20),Z(20),H(20),F(20)
0002            READ(1,1)TITLE
0003          1 FORMAT(20A4)
0004            READ(1,452)D,VISC,T
0005        452 FORMAT(3F10.0)
0006            READ(1,2)AMACID,DACID,AMSALT,DSALT,AMBASE,DBASE
0007          2 FORMAT(6F10.0)
0008            READ(1,3)AOACID,AOSALT,AOBASE,M,N
0009          3 FORMAT(3F10.0,2I4)
0010            DEVSQ=0.0
0011            S=D*T
0012            A=1.8246E6/S**1.5
0013            B=50.29E8/S**0.5
0014            B1=8.204E5/S**1.5
0015            B2=82.5/VISC/S**0.5
0016            E1=2.942E12/S**3.
0017            E2=0.4333E8/VISC/S**2.
0018            AO=(AOACID+AOBASE+AOSALT)/3.
0019            DO 1000 I=1,M
0020            READ(1,4)CACID(I),CBASE(I),SP1(I)
0021          4 FORMAT(3F10.0)
0022            SIGMA=SP1(I)*1000.
0023            BETA=DACID*AMSALT-SIGMA
0024            GAMMA=DACID*(CACID(I)-CBASE(I))*(AMACID-AMSALT)-DACID*SIGMA
0025            X1=(-BETA+SQRT(BETA*BETA-4.*AMSALT*GAMMA))/2./AMSALT
0026            F(I)=10.**(-A*SQRT(X1)/(1.+B*AO*SQRT(X1)))
0027          5 X(I)=((DSALT*DACID*CACID(I)-X1*(F(I)**2.*(DACID*(CBASE(I)-CACID(I)
               1)-DSALT*CBASE(I))+DSALT*DACID)-X1**2.*F(I)**2.*(DACID+DSALT))/
               2F(I)**4.)**(1./3.)
0028            H(I)=DACID*(CACID(I)-CBASE(I))/(F(I)**2.*X(I)+DACID)
0029            EM(I)=X(I)-H(I)
0030            Z(I)=0.0
0031            AO=(H(I)*AOACID+EM(I)*AOSALT)/(H(I)+EM(I))
0032            F(I)=10.**(-A*SQRT(X(I))/(1.+B*AO*SQRT(X(I))))
0033            IF(ABS(X(I)-X1)-X(I)*0.0001)7,6,6
0034          6 X1=X(I)
0035            GOTO 5
0036          7 ESALT=E1*AMSALT-E2
0037            BO=16.708E-4/S/AO
0038            ELSALT=3.202*E1*AMSALT-3.420*E2+B1*B2+2.*E1*AMSALT*(2.*BO*(BO+1.)-
               11.)/BO**3.+44.*E2/3./BO-2.*ESALT*ALOG(BO)
0039            EQSALT=AMSALT-(B1*AMSALT+B2)*X(I)**0.5+ESALT*X(I)*ALOG(6.*E1*X(I))
```

```
     1+ELSALT*X(I)
0040  EACID=E1*AMACID-E2
0041  ELACID=3.202*E1*AMACID-3.420*E2+B1*B2+2.*E1*AMACID*(2.*BO*(BO+1.)-
     11.)/BO**3.+44.*E2/3./BO-2.*EACID*ALOG(BO)
0042  EQACID=AMACID-(B1*AMACID+B2)*X(I)**0.5+EACID*X(I)*ALOG(6.*E1*X(I))
     1+ELACID*X(I)
0043  SP2(I)=(H(I)*EQACID+EM(I)*EQSALT)/1000.
0044  DEV=(SP2(I)-SP1(I))*100./SP1(I)
0045  DEVSQ=DEVSQ+DEV*DEV
0046  R(I)=CBASE(I)/CACID(I)
0047 1000 CONTINUE
0048  M=M+1
0049  DO 2000 I=M,N
0050  READ(1,4)CACID(I),CBASE(I),SP1(I)
0051  SIGMA=SP1(I)*1000.
0052  BETA=DBASE*AMSALT-SIGMA
0053  GAMMA=DBASE*(CBASE(I)-CACID(I))*(AMBASE-AMSALT)-DSALT*SIGMA
0054  EM1=(-BETA+SQRT(BETA*BETA-4.*GAMMA*AMSALT))/2./AMSALT
0055  F(I)=10.**(-A*SQRT(EM1)/(1.+B*AO*SQRT(EM1)))
0056  8 EM(I)=((DSALT*DBASE*CBASE(I)-EM1*(F(I)**2.*(DBASE*(CACID(I)-
     1CBASE(I))-DSALT*CACID(I))+DSALT*DBASE)-(EM1*F(I))**2.*(DSALT+
     2DBASE))/F(I)**4.)**(1./3.)
0057  Z(I)=DBASE*(CBASE(I)-CACID(I))/(DBASE+F(I)**2.*EM(I))
0058  X(I)=EM(I)-Z(I)
0059  H(I)=0.0
0060  AO=(X(I)*AOSALT+Z(I)*AOBASE)/(X(I)+Z(I))
0061  F(I)=10.**(-A*SQRT(EM(I))/(1.+B*AO*SQRT(EM(I))))
0062  IF(ABS(EM(I)-EM1)-EM1*0.0001)10,9,9
0063  9 EM1=EM(I)
0064  GOTO 8
0065 10 ESALT=E1*AMSALT-E2
0066  BO=16.708E-4/S/AO
0067  ELSALT=3.202*E1*AMSALT-3.420*E2+B1*B2+2.*E1*AMSALT*(2.*BO*(BO+1.)-
     11.)/BO**3.+44.*E2/3./BO-2.*ESALT*ALOG(BO)
0068  EQSALT=AMSALT-(B1*AMSALT+B2)*EM(I)**0.5+ESALT*EM(I)*ALOG(6.*E1*
     1EM(I))+ELSALT*EM(I)
0069  EBASE=E1*AMBASE-E2
0070  ELBASE=3.202*E1*AMBASE-3.420*E2+B1*B2+2.*E1*AMBASE*(2.*BO*(BO+1.)-
     11.)/BO**3.+44.*E2/3./BO-2.*EBASE*ALOG(BO)
0071  EQBASE=AMBASE-(B1*AMBASE+B2)*EM(I)**0.5+EBASE*EM(I)*ALOG(6.*E1*
     1EM(I))+ELBASE*EM(I)
0072  SP2(I)=(X(I)*EQSALT+Z(I)*EQBASE)/1000.
0073  R(I)=CBASE(I)/CACID(I)
```

```
0074              DEV=(SP2(I)-SP1(I))*100./SP1(I)
0075              DEVSQ=DEVSQ+DEV*DEV
0076         2000 CONTINUE
0077              STDEV=SQRT(DEVSQ/N)
0078              WRITE(3,11)TITLE
0079           11 FORMAT(1H1,2X,20A4)
0080              WRITE(3,12)AMACID,AMBASE,AMSALT,DACID,DBASE,DSALT,AO
0081           12 FORMAT(//,2X,
                 1'LT. EQ. COND. ACID =',E14.7,/,2X,
                 2'LT. EQ. COND. BASE =',E14.7,/,2X,
                 3'LT. EQ. COND. SALT =',E14.7,/,2X,
                 4'DISS. CONST. ACID  =',E14.7,/,2X,
                 5'DISS. CONST. BASE  =',E14.7,/,2X,
                 6'DISS. CONST. SALT  =',E14.7,/,2X,
                 7'AV. LEAST DISTANCE =',E14.7)
0082              WRITE(3,13)(CACID(I),CBASE(I),R(I),SP1(I),SP2(I),I=1,N)
0083           13 FORMAT(//,3X,'CONC. ACID',6X,'CONC. BASE',6X,'BASE/ACID',6X,'SP.CO
                 1ND.OBS.',4X,'SP.COND.CALC.',(/,5(1X,E14.7,1X)))
0084              WRITE(3,14)STDEV
0085           14 FORMAT(//,2X,'STD. DEV. ON SP. COND. =',F14.7,'%')
0086              RETURN
0087              END
```

## REFERENCES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