THE STABILITY OF THE POLYHALIDES

BY

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CHAPTER 1

INTRODUCTION.

Molecular halogens or interhalogens compounds have, for many years, been known to be capable of associating with halide ions either in the solid state or in solution to form stable univalent species. The classic example of this is the enhanced solubility of iodine in an aqueous potassium iodide solution to form the triiodide anion. This was crystallised by Johnson (1) in 1877 and was the first inorganic triiodide identified. The earliest reference to a triiodide was however the strychnine triiodide of Pelletier and Caventore (2) in 1819. Filhol (3) made the first reference to an inorganic polyhalide in 1839. This was the mixed polyhalide $KICl_4$. Löwig and Roozeboom also investigated polyhalides during the nineteenth century (4,5). It is interesting that whilst Roozeboom was one of the leaders in the use of ternary phase rule investigation, his work on ammonium tribromide was not pursued in this manner.

At the close of the nineteenth century Wells, Penfield and Wheeler (6-8) began pioneering investigations into the polyhalide field. Much of the work was of a qualitative nature, dealing with the preparation of a particular compound or studying specific physical properties. This work was followed up by Abegg and Hamburger, Foote and Chalker, Parsons and Whittemore and Kremann and Schoulz over the period 1908 - 1912. They were mainly interested in the controversy over the formula of the potassium polyiodide (9-12).

Most of the preparative methods at this stage involved crystallisation from an aqueous solution. It was not realized that solvation could occur and although analysis often suggested this, conflicting reports were given based on an anhydrous polyhalide. It was not until 1931 when Grace (13) recognized the possibility of solvation that many of these earlier discrepancies were resolved.

In the period 1910 - 1930 interest in the polyhalides lapsed to some extent apart from a review of structural considerations by Clark (14) in 1923, the results of which however were inconclusive. The early 1930's saw a revival of interest in both the homogeneous and mixed polyhalides. In England, Grace, Cheesman, Duncan, Harris and coworkers and in America Briggs and coworkers began studying the former type of polyhalide by using phase rule techniques, in particular three component systems, which characterized solvates. At this time Cremer and Duncan (15 - 16) reviewed the polyhalide work up to this stage and reexamined the preparative methods, properties and reactions of this type of compound. Their main interest was in the mixed polyhalide of the type $MIBr_2$, but they did deal with $CsBr_3$ and CsI_3.

Although polyhalide ions are of three main types, namely X_n^-, XX'_n^- and $XX'X''^-$, e.g. I_3^-, ICl_4^- and $IBrCl^-$ respectively, throughout this treatment the general term polyhalide will refer to the homogeneous group X_n^- unless otherwise stated. The other two groups will be referred to as mixed polyhalides. The alkali metals are perhaps the most common cations associated with polyhalides, along with the ammonium and the quarternary ammonium ions. Most of the possible alkali polyhalides systems have been studied and it was the purpose of this investigation to complete the series of hydrated polyhalides mainly by studying the systems $NH_4Br - Br_2 - H_2O$; $LiBr - Br_2 - H_2O$ and $LiI - I_2 - H_2O$. The extent of the present knowledge with regard to these systems may be summarized as follows:

TABLE I.

	Bromides	Iodides
NH_4^+	NH_4Br_3 (5)	NH_4I_3, $NH_4I_5 \cdot H_2O$; $NH_4I_3 \cdot 3H_2O$ (19)
Li^+	-	$LiI_4 \cdot 4H_2O$
Na^+	-	$NaI_2 \cdot 3H_2O$; $NaI_4 \cdot 2H_2O$ (20,21)
K^+	$KBr_6 \cdot 1\frac{1}{2}H_2O$ (22)	KI_3H_2O; KI_7H_2O (23,13)
Rb^+	$RbBr_3$ (7)	RbI_3 (24)
Cs^+	$CsBr_3$ (25)	CsI_3; CsI_4 (15,26)

The authors mentioned in the table represent the major contributions on the formation and identification of the polyhalides and do not include more detailed studies of these compounds.

Up until the present investigations a rigorous study has been made of the majority of the systems with the exception of ammonium, lithium, sodium and rubidium bromides and lithium iodide. With the exception of rubidium these investigations have now been completed, rubidium having been omitted as there are no grounds for expecting other than the reported tribromide of this compound when it is considered in the light of known compounds of the other alkali metal ions.

It will be noticed that the table includes only polybromides and iodides. Chlorine will not form polychlorides in this series although tetra ethyl ammonium trichloride (31) and tetraethyl phosphonium trichloride (17) have been reported. Similarly fluorine does not form a simple trihalide, with the possible exception of the HF_2^- ion as in KHF_2 which may be considered either as a mixed polyhalide, hydrogen being regarded as a halogen, or as a simple trihalide, there being no other halogen than fluorine in the anion. Chlorine and fluorine will however form mixed polyhalides and interhalogens. Hydrogen polyhalides also have not been isolated although Magnuson and Wolfenden (27) claim to have detected HI_3 from spectrophotometric evidence. The only free acid isolated from aqueous solution is that of the mixed polyhalide ICl_4^- namely $HICl_4.4H_2O$ (28). The triiodide analogue has been isolated from benzonitrile solution i.e. $HI_3.4C_7H_5N$ (32).

Along with the alkali metals, polyhalides are formed by the quarternary ammonium ions and related ionic species. Some of these are $N(CH_3)_4I_9$, $N(C_2H_5)(CH_3)_3I_9$, $N(C_2H_5)_4I_9$ (18, 29, 31) and $(C_6H_5)N(CH_3)_3Br_3$, $(C_6H_5)N(CH_3)_3I_3$ and $(C_6H_5)N(CH_3)_3I_5$ (30). Analogous to these are the tetra alkyl phosphonium polyhalides e.g. $P(C_2H_5)_4Br_7$, $P(C_2H_5)_4Br_3$ and $P(C_2H_5)_4Cl_3$ (17) and tetraphenyl arsonium triiodide, $(C_6H_5)_4AsI_3$, (10a).

Solvation appears to play quite an important part in stabilising polyhalides both in the homogeneous and mixed systems especially in the cases of low cationic radii, e.g. lithium, sodium and potassium. In lithium and sodium it is almost certain that the solvent molecules are associated with the cation; the position of potassium is however more open to question. It is also interesting that, in some cases where an unsolvated trihalide is formed, a higher solvated polyhalide may also be formed e.g. NH_4I_3 and $NH_4I_5.H_2O$ and RbI_3 and $RbI_7.2C_6H_6$.

Solvation of polyhalides is not restricted to hydration and a large range of stable solvates have been isolated. Some examples of these include $LiI_3.4C_7H_5N$ (benzonitrile), $NaI_3.2C_7H_5N$, $KI_3.2C_7H_5N$, $KI_3.4C_7H_5N$ (32), $KI_7.C_6H_6$ (13), $NaI_5.2C_6H_5NO_2$ (33) $RbI_7.2C_6H_6$, $RbI_9.2C_6H_6$ and $2CsI_9.3C_6H_6$ (34). These are all polyiodides, iodine having a greater tendency than the other halogens to take part in polyhalide formation.

Unsolvated polyhalides may be prepared by dry methods which are often preferable as theoretical yields may be obtained and there are no side reactions such as solvent interactions. They are usually relatively slow however. The most common dry method of preparation consists of leaving the dry powdered monohalide in a vessel with free halogen so that the vapour can be absorbed. The uptake of halogen can be followed by weighing at intervals until at the theoretical uptake, or slightly above this (due to surface adsorption), the absorption ceases. The fact that there is no uptake of halogen by halide is sufficient criterion for the absence of the corresponding unsolvated polyhalide at the appropriate temperature.

The polyhalide systemslisted on table 1 have been studied at either 0° C or 25° or both, the less stable members being investigated at 0° C whilst the more stable ones have been studied up to 25° C. The rubidium bromide system has not been subject to a rigorous investigation but the reported tribromide is considered to be the only polyhalide in comparison with ammonium and caesium tribromides.

The mixed polyhalides and the hydrogen polyhalides have not been subject to a rigorous study along the present lines. Although the analyses may be a little more complex in some of these cases it should however be possible to study these also. It is also of interest that astatine has been shown to form polyhalide anions (35) e.g. AtI_2^-, $AtICl^-$, $AtIBr^-$, $AtCl_2^-$ and $AtBr_2^-$ and consequently it may also form a series of polyhalides.

Chapter 2

General Apparatus and Presentation of Results.

Although each system studied was a complete unit in itself a certain amount of equipment was common to all sections. This included items such as quantitative glassware, thermostats, equilibrium vessels and sampling devices. The aim of this chapter is to describe this equipment so that the chapters dealing with the individual systems need only include special equipment designed for that particular system.

A survey of the methods used to present the results is also included in this chapter.

Quantitative Equipment.

Both gravimetric and volumetric procedures were used throughout the complete course of this section. The major equipment used included the balance, burettes, and for standardisations, pipettes and a standard flask.

1. Balances and weights. In the early stages of this work a Mettler B 5 balance was used. This was later changed to a Sartorius projection reading balance using a box of knob form weights down to 1 gm. from Towers. In both instances the accuracy of the weights was checked against a standard set. The details of the standardisation are set out as follows.

Table 2

(Standard Weights Made by F. Sartorius, Gottingen No. A 29. 5575)

Nominal weight (gm.)	True Weight (Standard)	True Weight (Mettler)	True Weight (Towers)
50	49.99980	49.9999	50.0003
20	19.99986	19.9998	19.9998
10	10.00003	10.0000	9.9999
10	10.00002	9.9998	10.0001
5	5.00003	4.9999	5.0000
2	1.99990	1.9999	1.9999
1	1.00000	1.0000	1.0000
1̇	1.00000	1.0000	0.9999
1̇·	1.00006	1.0001	1.0000
			Weights on Sartorius balance
0.5	0.49990	0.4999	0.5000
0.2	0.20002	0.2000	0.2001
0.1	0.09998	0.1000	0.1000
0.1̇	0.09999	0.1000	0.0999
0.05	0.05000	0.0500	0.0500
0.02	0.02001	0.0200	0.0200
0.01	0.01001	0.0100	0.0100
0.01̇	0.01000	0.0100	0.0100

The grams and multiples were usually used as tares and hence any errors were cancelled out on subtraction. For the fractional weights the errors were sufficiently small in magnitude to allow the nominal values to be used. In most samples taken the mass varied from about 0.1 grams up to about 0.5 grams and here also most of the errors were eliminated on subtraction. Where possible the same actual masses were used for both parts of the weighing procedure.

The major volumetric glassware used was E-mil green line apparatus with works certificates. The apparatus in most common use is tabulated below:

2.Burettes

The three burettes used were 52/5033, a 25 ml burette used for ammonium thiosulphate; 52/5043, an automatic 25 ml burette with 3 way stopcock used for sodium thiosulphate; 52/4809, an automatic 50 ml burette used for sulphuric acid.

Table 3

Graduation Mark	Actual	volume	delivered
	52/5033	52/5043	52/4809
4.00	4.00	4.00	-
9.00	-	-	8.98
12.00	11.98	12.02	-
18.00	17.99	18.04	18.00
22.00	21.99	22.03	-
25.00	24.99	25.02	-
29.80	-	-	29.78
39.00	-	-	38.96
50.00	-	-	49.94

These volumes are to the nearest 0.01 ml for the 25 ml burettes and to 0.02 ml for the 50 ml burette.

3. Pipettes

The most frequently used pipettes were a 25 ml bulb pipette 51/18957 which delivered 24.98 ml and a 10 ml bulb pipette 51/19946 which delivered 9.99 ml. These are to the nearest 0.01 ml. As the pipettes were not new they were recalibrated using distilled water at 19° C and the corrected volumes were found to be 24.98 mls and 10.00 mls respectively. Some 5, 2, and 1 ml pipettes were also recalibrated, but these were not in general use.

4. Standard Flask

A 250 ml standard flask 51/11312 was used which contained 250.05 to the nearest 0.05 ml.

With the exception of the burette 52/5043 the calibration was sufficiently accurate. Where necessary the correction was applied about the 15 - 20 ml region in the sodium thiosulphate titres. Where possible any additional glassware required was E-mil green line.

THERMOSTAT BATHS.

The problem of maintaining the required temperature assumed major proportions during the early part of this investigation. The first thermostat used consisted of a 4 gallon oil drum placed inside a 10 gallon drum, the intervening space being packed tightly with wood wool. The equilibrium bottles were placed in the drums and a supply of ice was maintained. This was found to be very unsatisfactory due to the temperature varying as much as 3 - 4° C throughout the drum. To overcome this a pump was made to circulate the water from the bottom of the drum over the ice at the top. This was made from a length of $1\frac{1}{4}$" brass pipe with a central shaft holding 6 nickel impellers. The water was drawn from the bottom, up through the tube and was forced through a hole at the top of the tube so as to circulate back over the ice. The pump was surrounded by a galvanised iron pipe with holes drilled at the bottom and covered with gauze to prevent the entry of dirt, packing etc. The pump was fastened through a wooden lid on the thermostat and driven by a pulley drive from a stirrer motor. A siphon was also fixed into the drum to facilitate the removal of the excess water each day.

Although this gave a better temperature control it was rather difficult keeping the thermostat filled with ice over periods of several months without an inadvertent rise in temperature from a pump breakdown or halt in the supply of ice,which was obtained from a local freezing plant and was crushed and stored, for several days in some instances, in a deep freeze unit. It was also found that the equilibrium bottles were inclined to leak unless considerable care is taken in adding the ice.

In an endeavour to overcome this a refrigerated thermostat was designed and built. This consisted of a second hand commercial refrigeration unit mounted on a stand below a copper tank which served as the thermostat bath proper. The tank dimensions were about 20" x 12" x 10". The tank was surrounded by a wooden case and the intervening space was well packed with wood wool and saw-dust. A packed cover was also made. This was in 2 parts, the larger serving as a removable lid while the smaller was fixed and tubes were placed through it to allow the thermometers and stirrer to be inserted in the bath liquid. The relay and stirrer speed control were also mounted here.

The thermometers passing through the lid were a Beckmann thermometer, a standard thermometer and a contact thermometer. The standard thermometer showed the absolute temperature whilst the Beckmann showed the temperature variation. The actual temperature control was via a mercury contact thermometer. Originally this was connected to a Sunvic H.V.S. relay but it was found that there was sufficient arcing in the thermometer to distil mercury up the column and hence the temperature rose. The thermometer was then made to operate a relay which in turn operated the Sunvic switch and hence the compressor. After considering several relays and ways and means of preventing "chatter", a relay was designed which had a time delay of about 10 secs. before it switched on and an instantaneous cut out. A further 2 - 3 secs. delay for the off position was caused by the Sunvic switch. This was reduced to about one second by

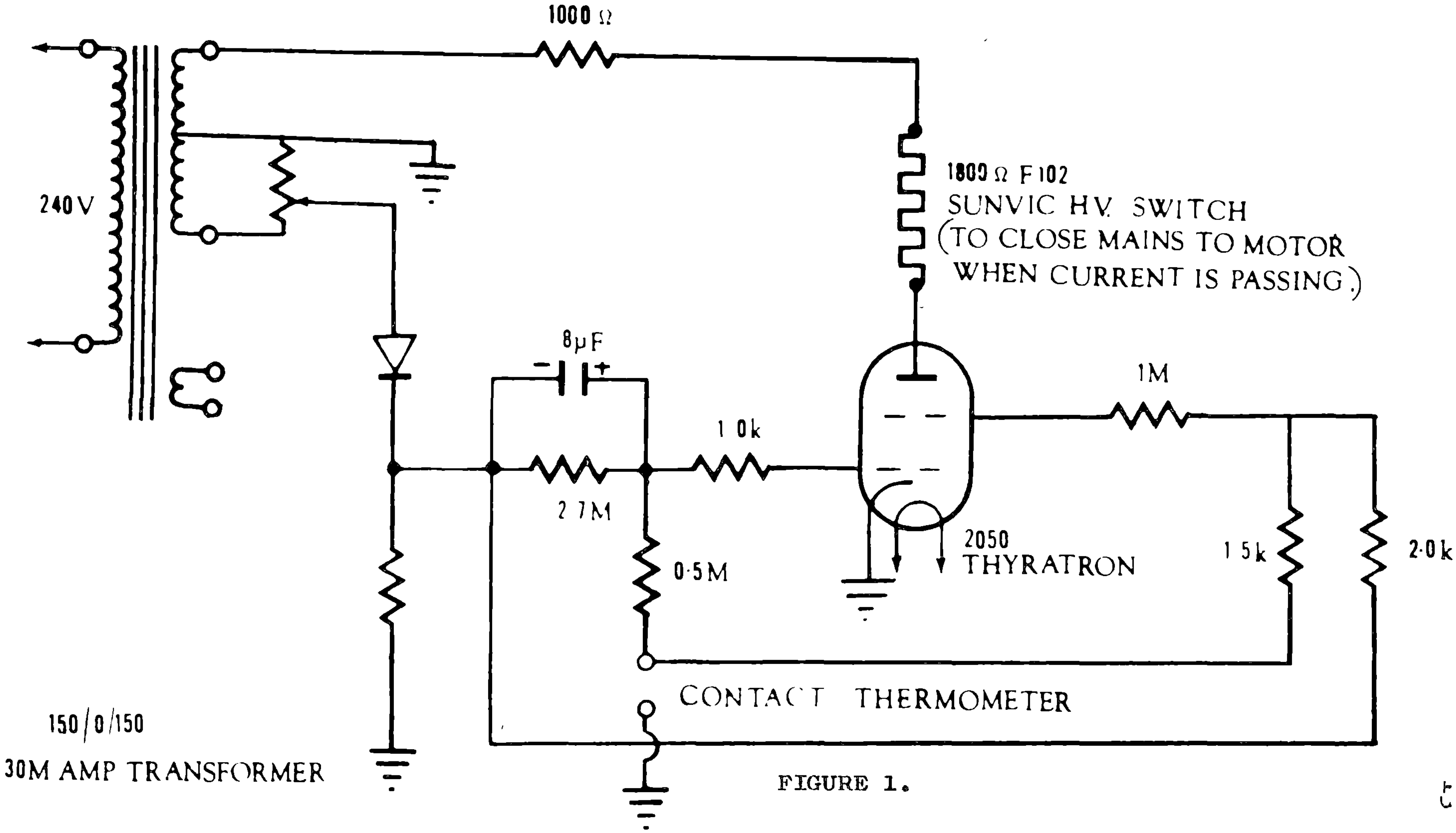

1000 Ω
240 V
1800 Ω F102
SUNVIC H.V. SWITCH
(TO CLOSE MAINS TO MOTOR WHEN CURRENT IS PASSING.)
8μF
- +
1M
1.0k
2.7M
0·5M
2050
THYRATRON
1.5k
2·0k
CONTACT THERMOMETER
150/0/150
30M AMP TRANSFORMER

FIGURE 1.

incorporating additional series resistances in the hot wire circuit. The final relay circuit is shown in figure 1.

The refrigerator bath contained about 6 gallons of water mixed with "Bluecol" radiator antifreeze.

The temperature of the bath was checked frequently and any drift was noted on the Beckman thermometer. (Initially the temperature was checked at various points throughout the bath to ensure that the stirring was adequate.) At 0^{o} C the temperature could be maintained to within $\pm$ 0.02^{o} C. The relay cycle on the average was about 20 seconds on and 1.5 minutes off. This thermostat functioned continuously requiring only routine maintenance such as replacement of stirrer motor brushes, renewal of thyratrons (about 12 months) and replacement of one Sunvic switch. Overload protection was also found to be essential on the compressor motor as occasionally the compressor stalled for one or two cycles. This was thought to be due to the entry of some liquid refrigerant into the cylinder head.

After several weeks use the thermostat switch was observed to behave in an irregular manner. This appeared to be due to water condensing in the base of the stem of the contact thermometer. It was dried out under vacuum and a plastic bag containing silica gel was fastenened over the top. This was found to alleviate the irregularity. As the relay only required a small current to "fire" there was apparently sufficient leakage over the moist surfaces to permit this.

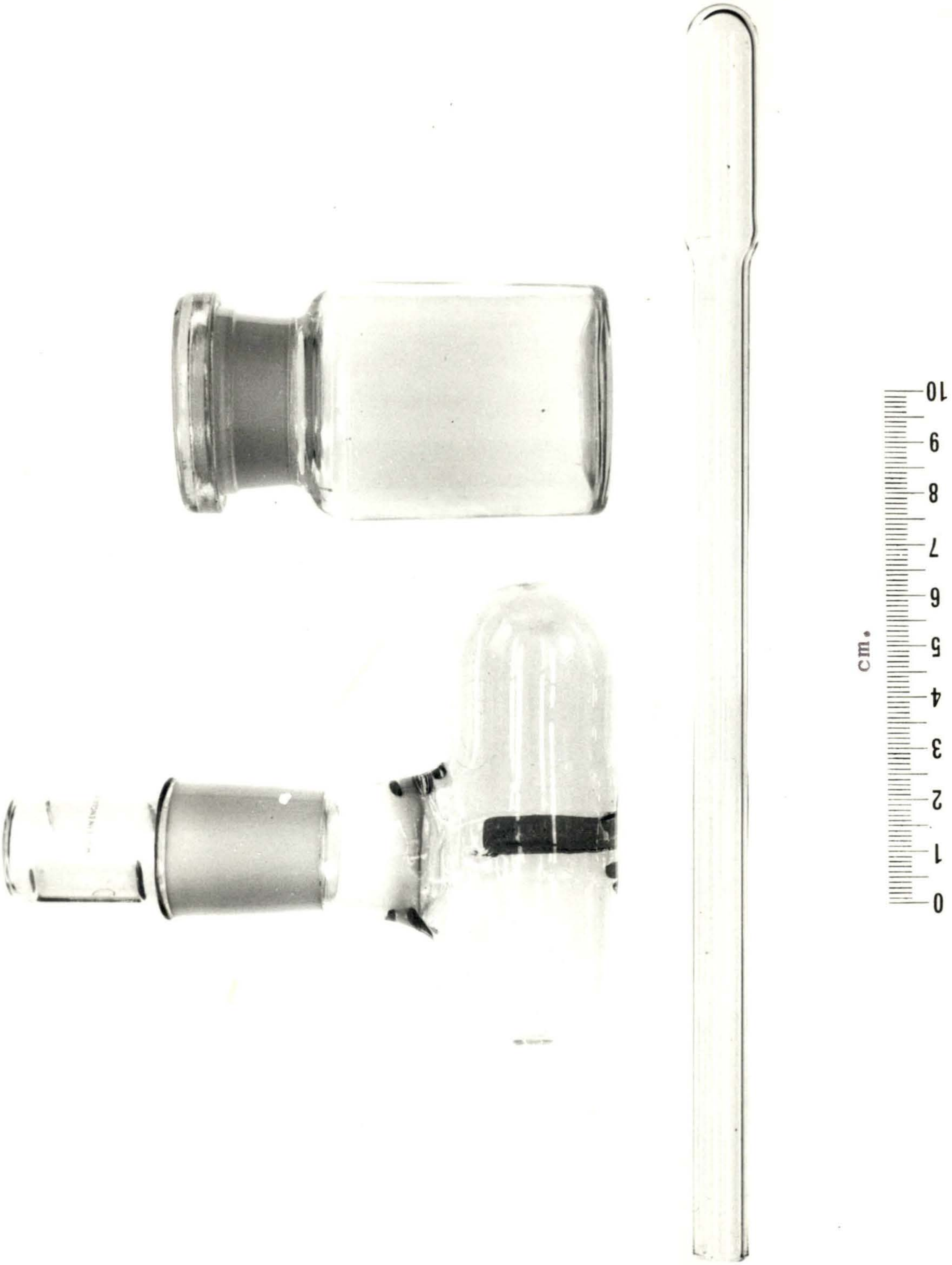

cm.
0
1
2
3
4
5
6
7
8
9
10

PLATE 1.

THERMOMETRY.

The absolute temperature was actually -0.4° C as read from a standard thermometer. This was thermometer N.P.L. 7271/58 and was calibrated for immersion to the reading. At 0.00° C it was calibrated as 0.00° C ± 0.02° C. Graduation was from -1° to 51° C and 99° to 101° C in 0.1° C steps.

EQUILIBRIUM BOTTLES.

Equilibrium bottles were designed which would best suit the system under investigation. The three main types used are shown in Plate 1.

For the ammonium bromide system the 2-oz wide neck jars were used. About a dozen bottles were chosen from a quantity of these to obtain those with the best fitting stoppers. This was done by adding bromine and weighing. They were then allowed to stand for 10 days and re-weighed. Those which lost less than about 500 mgm. bromine were taken for further grinding and polishing. These were ground in as tightly as possible with coarse and fine grinding compound. Of these twelve, about six were found to be quite tight to liquid and vapour. As a test bromine was added to the bottles. They were weighed and then allowed to stand over a period of several days. The stoppers were also tested by adding bromine to the bottle and inverting in potassium iodide solution. As added protection from any leakage of bath liquid a piece of polythene film was placed over the cap and fastened with a "Fowlers" ring and then the bottle was placed inside a larger screw top jar. Tin cans were also tried as outer containers. Although they were painted to prevent rust they were not as satisfactory as the screw top jars. Thermal equilibrium was quite readily obtained even though an air space partly surrounded the jars. In the case of the lithium bromide system the hydrated lithium bromide could not be obtained quite as "dry" as the ammonium bromide so a new type of bottle was designed for this system. It was also used in the latter stages of the ammonium bromide system. This bottle is shown in plate 1. The sintered disk (porosity No, 1) is used to allow solid to collect in the short end of the tube on tilting. The mother liquor drains into the larger end. The drained solid is then sampled and later the bottle is levelled to allow liquid to be withdrawn. The disk is placed so that the sampling equipment may be introduced on either side.

In order to prevent the entry of bath liquor by capillarity through the B24 cone a toy balloon was rolled over the top and down the neck of the bottle.

Lithium iodide-iodine-water gave a comparatively oily liquid, which was deliquescent and hence the above type bottles were found to be unsatisfactory. In this system it was considered preferable to use a sealed tube so that there was no possibility of the entry of moisture or leakage from the bottle. This did mean however that when the tube was re-sealed after sampling it sometimes had to be treated as a new tube due to the loss of iodine around the neck on sealing, and to a

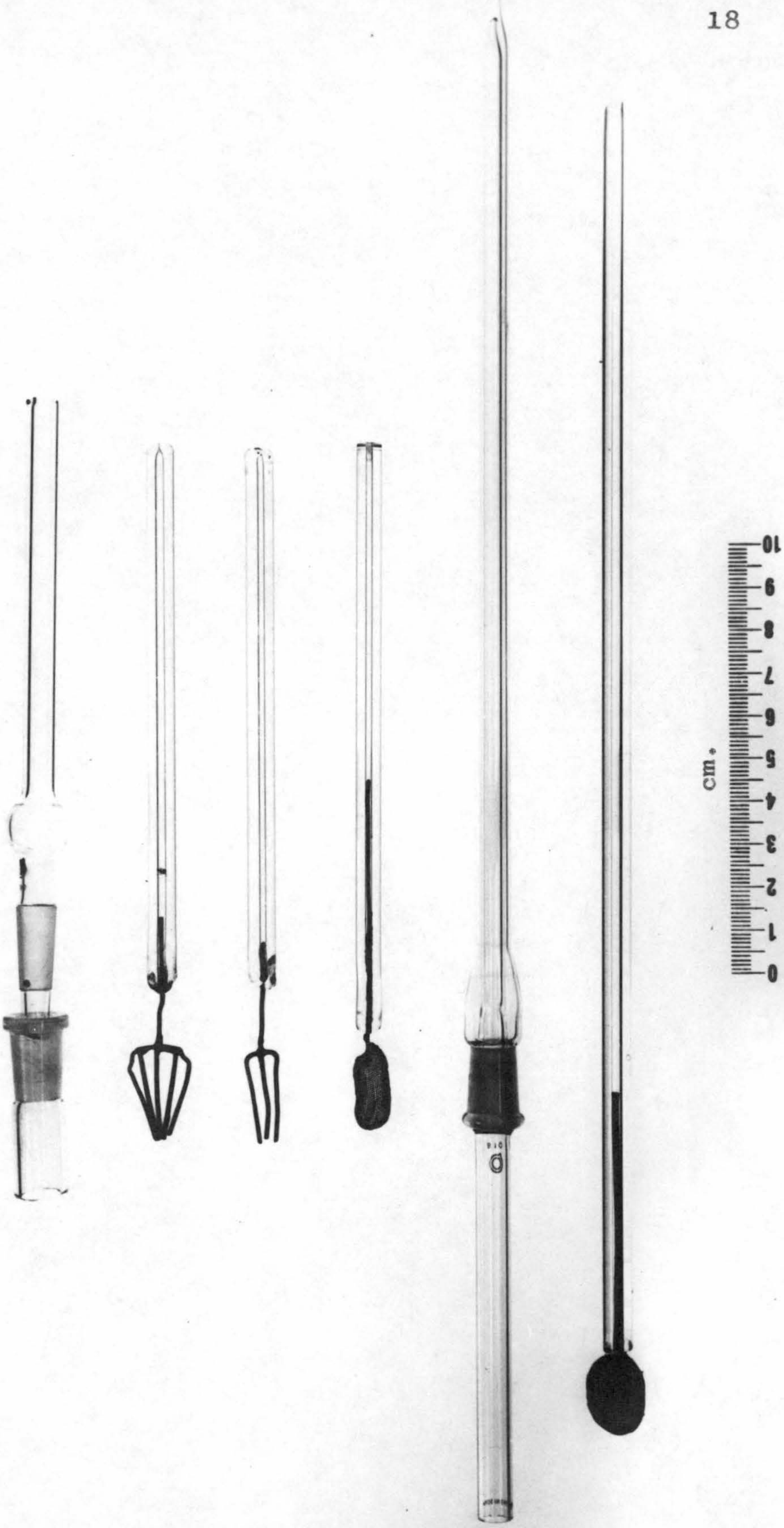

cm.
0
1
2
3
4
5
6
7
8
9
10

PLATE 2.

lesser extent due to the entry of a small amount of moisture from the blow-torch. The first tubes were made with conical bases to allow the wet solid to collect more compactly in the bottom. Later however rounded bases were used and three glass beads were added to each tube to assist in the attainment of equilibrium on shaking. Wherever possible the solid was allowed to collect in the neck of these tubes to drain before sampling, although in most cases it was sampled from the mother liquor. Some lithium bromide was also made up in this type of tube.

SAMPLING EQUIPMENT

In all cases samples of both liquid and solid phases were taken. The technique and equipment was similar although the actual dimensions depended on the type of equilibrium bottle in use.

For the smaller jars and diaphragm type tube the solid was sampled by means of a small platinum fork (plate 2). The liquid was sampled with a short pipette with a B10 cone drawn to a tip. A B10 socket passed over the tip of the pipette and a plug of glass wool was incorporated in this piece of tubing to act as a filter.

In the case of the sealed tubes a platinum spade was made from wire and gauze. A longer pipette was fitted with a sleeve containing the glass wool filter. The sleeve was made to fit down the neck of the tubes.

The sampling equipment was kept in stoppered tubes which could be placed in the thermostat baths prior to sampling so that the thermal equilibrium would not be upset during the sampling process. This is particularly important in the case of the liquid analysis.

PRESENTATION OF RESULTS.

The graphical representation of all the variables in a ternary system can become complex unless some are kept constant e.g. temperature and pressure. The most useful geometrical representation involves the use of triangular coordinates for the composition while temperature or pressure are represented perpendicular to the plane of the triangular diagram giving a triangular prism. The pure components are represented by the apices of the triangle, each side gives the binary composition and the interior the ternary composition.

In general the most practicable triangle is the equilateral triangle as it is symmetrical with respect to the three components. Any triangle may be used provided each side is divided into the same number of units.

Several different techniques have been devised to determine solid liquid equilibria in ternary systems with a view to elucidate the composition of the pure solid phase. One of the earliest methods used consisted of partial drying between filter paper, Refinements of the drying technique include the suspension of the solid on a sintered glass disc above the mother liquor to permit drainage by passing a dry gas, which causes no change in composition, through the crystals on the filter plate. These methods have a limited application dependent on the properties of the mother liquor and the solid itself.

More generally applicable methods are as follows:-

1. Possibly the most basic method used is the wet residue method of Schreinemakers (37). In an equilibrium mixture it is usually relatively easy to obtain a sample of the saturated mother liquor free from solid but it is virtually impossible to obtain the solid phase free from the adhering mother liquor. Schreinemakers showed that the composition of the pure solid must lie along the line joining the composition of the saturated mother liquor and the moist solid. By analysing a series of related solutions and wet residues and plotting the straight lines a point of intersection is obtained which corresponds to the pure solid. Theoretically all the lines must intersect in one point but in practice a number of adjacent points are usually obtained. Assuming a simple stoichiometric composition it is usually easy to choose the probable point of intersection. In some cases the lines may be found to intersect at a point indicating a liquid and not a solid phase in which case an invariant has been reached.

2. A method similar to that of Schreinemakers is due to Hill and Ricci (38, 39). In an equilibrium mixture the saturated solution, wet residue pure solid and total composition of the system all lie along the same straight line. This method requires an accurate knowledge of the total composition so that it is only necessary to analyse the saturated mother

liquor. These two points are plotted and the extrapolation carried out as in the wet residue method. The distance from the solution point to the total composition is less than the corresponding solution wet residue distance and hence any errors are amplified on extrapolation. This is offset in some cases by the errors due to evaporation or deliquescence on transferring a wet residue to the analytical apparatus. Three disadvantages of this method are

(a) If the system takes a long time to reach equilibrium there may be a possibility of leakage or evaporation in which case the accurate total composition will not be known.

(b) Samples cannot be withdrawn at intervals to see whether or not equilibrium has been attained.

(c) Due to the nature of the individual components it may be difficult to determine accurately the total composition when preparing the sample. This may however be overcome by changing the conditions e.g. raising the temperature, to obtain one phase on which to determine the total composition.

This method does have a distinct advantage in viscous systems where the equilibrium is slowly attained and the mother liquor adheres strongly to the solid.

3. In order to determine the amount of mother liquor adhering to the wet residue a fourth inert component may be added to the system. This

technique has been used by Unwar-Ullah (40) in the investigation of chlorine hydrate and BrCl hydrate. A dilute solution of copper sulphate of known concentration was used in the preparation of the hydrate. The amount of copper sulphate adhering to the wet residue was estimated to determine the amount of adherent mother liquor. In this particular case however the free halogen content of the mother liquor was apparently ignored in calculating the dry solid composition.

On paper this method is to be recommended. It lends itself to mathematical rather than graphical treatment and it does not require a number of solids in equilibrium with a number of different solutions. This is a distinct advantage when dealing with short solubility arcs. Against this there is always the possibility that the inert component may have some unpredictable effect on the equilibrium and it could be preferentially absorbed onto the solid or included in the crystal lattice.

4. Briggs (10) used a method of thermal analysis in which the saturated solution composition alone is determined. The isothermal tie lines diverge away from the pure solid composition, their length increasing with decreasing temperature. By determining the composition of the saturated solution at various temperatures a series of points are obtained along the tie line which lead to a more accurate extrapolation. This is a useful technique in systems which are temperature sensitive provided that the position of the invariant does not change so as to seriously decrease the length of the solubility arc.

A variety of other methods of lesser importance have been devised for presenting equilibrium ternary systems. One of the more important of these is the Jänecke projection (41). This method uses rectangular coordinates and is of particular use where the solubility of one component is low and where an enlargement of that particular part of the system is desirable (42). This problem was of no consequence in this investigation.

Throughout this section the Schreinemakers method is used, the results being plotted on an equilateral trilinear diagram on a weight percent bases. This was found more useful than the mole percent basis used occasionally.

Having obtained the equilibrium diagram it is then necessary to decide which point best represents the intersection of the tie lines. In the majority of cases it is sufficient to take the nearest simple integral stoichiometric composition. There are instances however where this is not satisfactory, a case in question being bromine hydrate, and consequently an algebraic method was developed to obtain the best point of intersection of the experimental tie lines.

As a first approach the equation to the line through each set of analytical points, corresponding to saturated solution and wet solid, was derived. It was then required to find an X and Y which would best fit this cluster of lines. The most feasible criterion of X and Y seemed to be the point which gave the minimum value of the sum of the square of the perpendiculars from X and Y onto each of the tie lines. This was a relatively simple process and seemingly adequate results were obtained.

One of the first objections to this method was that all lines were given equal weight whilst it seemed that points separated by a long distance would in fact show a smaller error on extrapolation than would two points close together assuming that analytical errors were comparable in each case. Weighting factors were then introduced to compensate for this, the weight depending on the ratio of the distances between the two analytical points and the distance between one of them and the point of intersection of the line. It was however found that in practice the introduction of a weighting factor did not make any significant difference to the point of intersection.

On further consultation with the mathematics department, after submitting this procedure for verification, a more refined technique, based on the same fundamental principles, was evolved. This took into account that we are here using trilinear and not rectangular coordinates, hence we have $z = 1-(x+y)$ i.e. z is not an independent variable. This method involved choosing an arbitrary point U,V close to the required X,Y and quantities dX and dY, which are corrections to be applied to U and V, were calculated. Provided dX and dY are small, the values of X and Y are thereby reached. If however they are not small, then these X and Y are taken as U and V for a further calculation of another dX and dY. This can be repeated until the values of the corrections are sufficiently small to render further repetition needless. In general, however, it was found that the value of dX and dY were sufficiently small at one computation.

Another variant of this procedure which should lead to a similar result would be to calculate the equations to each line and from these the individual points of intersection of each pair of lines could be obtained. The mean of intersections would then give a similar, best point of intersection. This method was not pursued further as it seemed more complex and perhaps not as fundamentally exact as the derived procedure. This can be judged to some extent when it is realized that for 9 lines we have only 9 perpendiculars but there would be 36 individual points of intersection.

FUNDAMENTAL CONSTANTS.

Solubility data where possible have been taken from Seidell (43) Solubility of Inorganic and Organic compounds. In all other cases where physical or chemical constants have been used they are obtained from the Handbook of Chemistry and Physics 29th edition (44) 1957 - 58. The atomic weights used here are the International atomic weights as at 1956 based on O^{16}.

Chapter 3

AMMONIUM BROMIDE - BROMINE - WATER

INTRODUCTION.

Although the system $NH_4Br-Br_2-H_2O$ has not been investigated in any detail the existence of ammonium tribromide was demonstrated in 1881 by Roozeboom (5). He isolated this compound by dissolving bromine in a saturated aqueous solution of ammonium bromide and evaporating over sulphuric acid. He obtained crystals of the colour of potassium dichromate. These were found to be readily soluble in water to give a solution smelling strongly of bromine. He also found that the ammonium tribromide was stable in the presence of free bromine but readily decomposed to ammonium bromide and bromine in an open vessel.

Roozeboom also postulated the existence of a pentabromide which he was unable to isolate. He based his hypothesis on the fact that when two moles of bromine was added to one mole of ammonium bromide in a saturated solution, the bromine all dissolved. The composition he obtained would however be in the all liquid portion of the equilibrium diagram.

Chattaway (45) also prepared ammonium tribromide by the cautious addition of concentrated ammonia to excess bromine in a freezing mixture. He also prepared it by absorbing bromine on dry powdered ammonium bromide. He tested its chemical stability be sealing some in an ampoule and heating to 180° - 200° C and then storing for four years. At the end of that period he reheated to the same temperature and later opened the ampoule and found that there had been no decomposition to nitrogen or hydrobromic acid. He also measured some dissociation pressures for ammonium tri-bromide.

In keeping with the other sections of this investigation the ternary system ammonium bromide-bromine-water was investigated at 0° C and at atmospheric pressure. This would vary slightly from day to day but this variation was not considered to be of any great consequence.

Although bromine hydrate forms part of this sytem it will not be discussed in any great detail here except where any results obtained are considered to have any bearing on the remainder of the system in particular any discrepancies in the analytical procedure. The analyses for the whole system will however be tabulated whilst the more detailed discussion of the hydrate will remain for a later chapter.

EXPERIMENTAL

PREPARATION OF REAGENTS / MATERIALS

The reagents used for this investigation were purified wherever this was considered necessary. This applied in particular to the ammonium bromide, bromine and water used to prepare each bottle.

The ammonium bromide used was May and Bakers' B.P. grade. This was re-crystallised twice from water and dried. The drying was carried out by firstly heating to about 60° C in a vacuum oven and then storing over $CaCl_2$ in a vacuum desiccator. Analysis for ammonia by the Kjeldahl method gave the purity at 100.1%.

Bromine was B.D.H. laboratory reagent grade. Before use fresh ampoules were opened and treated by a modification of the method of Scott (46). This entailed treating the bromine three times with sodium hydroxide (100 mls bromine to 10 mls 1M NaOH) to remove any free hydrobromic or other acids. The bromine was then distilled from a Claisen flask and the constant boiling distillate was re-fractionated from potassium bromide through a column packed with Raschig rings. The fraction boiling at 58.7° - 58.8° C was collected. The potassium bromide is to remove any free chlorine which may still be present in the bromine.

The water used to prepare the samples was twice distilled.

The only other reagents used were the analytical reagents. In all cases the analytical reagent grade was used. Borax used for standardis-sation was firstly re-crystallised from water. Stock solutions of reagents were maintained to allow at least a month for "ageing" before standardization.

Preparation and Equilibration of Mixtures.

In the case of ammonium bromide it was possible to make a reasonably accurate total composition. This was advantageous in that the total composition should lie along the tie line from saturated solution to wet solid. For most of the ammonium bromide system the wide neck jars with ground-in stoppers were used. Each component was weighed in, in the order ammonium bromide, water and the bromine. The bromine was usually run in from a burette. By adding the bromine to the system as the last component it was possible to know the quantity of bromine with certainty. If it were added earlier some would be lost on opening the bottle to add the other components.

After making up the bottles, the stoppers were pressed in firmly and covered. They were then shaken vigorously and warmed, if necessary, to take all the ammonium bromide into solution. It was found that this facilitated the attainment of equilibrium. The bottles were then chilled in the thermostat. In some instances supersaturation was experienced and to induce crystallisation the bottles were placed in a deep-freeze unit for a few minutes. "Seeding" was also carried out in some instances, the disadvantages of this being that the true total composition was no longer known.

The majority of the ammonium bromide bottles were equilibrated in the ice thermostat. They were shaken daily but as mentioned in the preceding section it was not until the pump was introduced into this thermostat that any semblance of real equilibrium was attained.

By withdrawing samples of liquid daily from two test bottles it was found that equilibrium was established within about 4 days. So as to eliminate any possible errors on this account the mixtures were left for at least two weeks before sampling. In many instances samples were withdrawn over a period of 1 - 2 months without any appreciable variation in results except in those instances where there had been an obvious loss of bromine or entry of water from the thermostat.

Analytical Methods.

In analysing the samples withdrawn for this sytem a known sample weight was obtained and the percentages of ammonia and free bromine were determined. The sample was added to a potassium iodide solution, the bromine liberating the equivalent amount of iodine. This was titrated with sodium thiosulphate and the whole sample was then steam distilled in the presence of sodium hydroxide to determine the ammonia.

The wet solid samples were withdrawn by means of a platinum fork. For the saturated solution sample the short filter pipette was used (plate 2). The sampling pipette and fork were kept in a stoppered test tube which was chilled in the thermostat prior to sampling. The fork was also wiped immediately preceding sampling to remove the condensed moisture. The assembled pipette was not in the atmosphere long enough for appreciable condensation within the pipette and when necessary the outside was given a wipe before sampling.

The samples, when withdrawn were rapidly transferred to weighed flasks containing 5 mls of 20% potassium iodide solution. At first 100 ml Erlenmeyer flasks with rubber stoppers were used. It was noticed that iodine was being absorbed by the rubber so these were replaced with 150 ml Florence flasks with B34 ground stoppers. These were found to be more suitable as there could be no loss of iodine and also the wide neck permitted the rapid transfer of samples. Samples of solid and liquid were taken in duplicate.

After re-weighing to determine the quantity of sample withdrawn, the solution was titrated in the flask with M/4 sodium thiosulphate.

The sodium thiosulphate was used from a 3 litre Winchester using an automatic burette with 3 way stopcock. The brown Winchester was wrapped in paper as added protection from direct sunlight. A titration bench was built with back fluorescent lighting and white tile base so that the need for any indicator in the iodine titration was eliminated. This was thought advisable in view of the later treatment of the sample. The sodium thiosulphate was standardised frequently against A.R. potassium iodate.

At the completion of the thiosulphate titration the sample was transferred quantitatively to a Parnos-Wagner ammonia distillation unit. Excess strong sodium hydroxide was added and the mixture steam distilled for about 12 minutes. At the end of this time the condenser was washed down and the distillate checked for alkali with litmus. In preference to absorbing in excess standard sulphuric acid, the ammonia was absorbed in 50 mls of 1% boric acid. This is sufficiently acid to absorb the ammonia without loss but has no marked influence on the subsequent titration with M/4 sulphuric acid. The sulphuric acid was also used from a 3 litre stock using an automatic burette. Standardisation of the sulphuric acid was made with re-crystallised borax (Standard Laboratories A.R. Grade). The re-crystallisation was carried out according to Vogel (47).

A calculation of the expected pH at the end point, based on a pKa for boric acid of 5, showed that the equivalence point would be

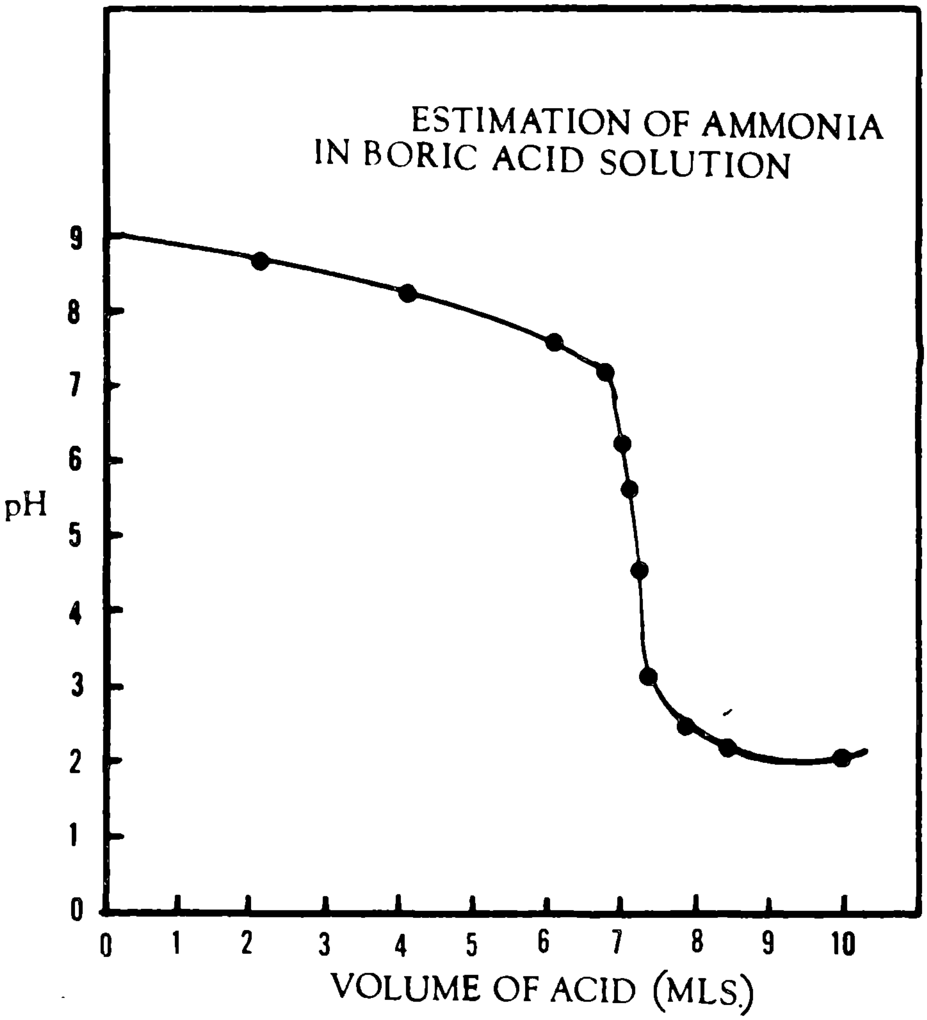

ESTIMATION OF AMMONIA
IN BORIC ACID SOLUTION
pH
0
1
2
3
4
5
6
7
8
9
0
1
2
3
4
5
6
7
8
9
10
VOLUME OF ACID (MLS.)

FIGURE 2.

in the region pH 4 - 5. This was confirmed in practice by following a typical titration with a pH meter and plotting the change of pH with the addition of acid. The meter was first calibrated against buffers of pH 4.00 and 7.00. The plot of pH versus volume of acid is shown in figure 2, the equivalence point falling over the range pH 7.0 to 2.5 i.e. at about 4.7.

Of the suitable indicators, methyl orange(pKa 3.7) and methyl red (pKa 5.1) are the most common. The end points for either of these indicators are not however always sharp and distinct for visual observation. A mixed indicator system using methyl red and methylene blue gave a much more distinct end point,the change being from a green to blue in the required pH range. The screened indicator system described by Hickman and Linstead (48) was also used. The change in colour being about pH4. This is a mixture of methyl orange and xylene cyanol F F. Titrations were also performed using the pH meter in the presence of these indicators, to determine whether or not the agreement was satisfactory. Crosschecking between the two indicators gave concordant results. The first was used in the earlier analyses. A change was later made to the second system as the end point was a little more clearly defined and also this indicator contained methyl orange which was used in the initial standardisation of the acid with borax.

Hickman and Linstead recommend a blue gas filled bulb as the source of illumination during titration. Titrations were carried out using natural light, a 100 watt blue gas-filled tungsten lamp and a 20 watt fluorescent lamp. Titres obtained were 9.62 and 9.60 ml respectively with the artificial lighting, and 9.65 with the natural light. The latter lighting was however inadequate in the laboratory. It is of interest to note that methyl orange alone with fluorescent lighting gave 9.70 - 9.75 ml showing that this indicator is undesirable in this titration. For the direct standardisation of the acid the end-point was however clearer. The titration difference between the two forms of artificial lighting was relatively small so a bench was set up using the fluorescent light. This was found to be the most even and best suited for the determination of the iodine in the absence of an indicator as previously outlined. Instrumental detection of the endpoint was considered to be an unnecessary refinement.

From the known weight of the sample and the titres for the ammonia and iodine, the percentages of ammonium bromide and bromine were calculated, the water being obtained by difference. Several runs on the analytical equipment were carried out in the early stages of the investigation using synthetic mixtures of known composition to test whether or not quantitative results were obtained. This also included blank tests on the reagents. All reagents were tested, separately and mixed, for ammonia by the steam distillation followed by absorption in boric acid. The latter test consisted of a mixture of potassium iodide, potassium bromide and iodine which was titrated with the sodium thiosulphate and then steam distilled in the presence of alkali. The effect of the boric acid on standardisation of the sulphuric was checked by dissolving the borax in both water and boric acid solution before titrating. No appreciable difference in titre was observed. Some early results were found to be low in ammonia and not totally reproducible. This was traced to a small pinhole in the distillation unit and when rectified this discrepancy was eliminated. From the results of these preliminary experiments it was decided that the proposed procedure could give reproducible quantitative results.

After plotting the results as tabulated later it was found that there was a discrepancy of about 2% in the ammonium bromide precentage in bromine hydrate. This seemed to be too consistent an d of too large a magnitude to be classed as experimental error. so the whole analytical procedure was reviewed.

The following points were checked for any possible source of error:-

(a) The actual end point in the titration of the ammonia in boric acid, althought being sharp to 1 drop of acid, was not a sharp change for the methyl red-methylene blue indicator from green to blue, there being a transitory greyish colour. At this stage the screened indicator was used as the colour change was easier to detect. On identical standard samples however the titres were the same with the two indicators. As a double check the effect of being 0.1 ml out in a typical titre was calculated. This changed the result by about 0.1% in the wet solid analysis which was not sufficient to cause the error found. Although there was still a transitory colour change with the screened indicator the first appearance of the violet was taken as the end-point both for standardisation and the sample.

(b) Any discrepancy in the ammonia determination is magnified 5 fold on converting this result to ammonium bromide. If during the distillation some sodium hydroxide was inadvertently carried over as spray, this would also increase the apparent ammonia precentage. This was tested by filling the distillation vessel with the strong alkali and passing steam for some time. The distillate was collected in the usual flask, but this contained boric acid and phenolphthalein. Other runs were also performed collecting the distillate in distilled water plus phenolphthalein. In neither of these instances was any alkali detected by the indicator. As an added precaution however a second splash bulb was fixed to the outlet to the condenser on the Parnos Wagner vessel.

(c) The standard reagents were intercompared to see that they were standard with respect to each other. To do this the sulphuric acid was standardised against borax and the sodium thiosulphate against potassium iodate as usual. The sulphuric acid was then standardised against the thiosulphate using an excess of potassium iodate and iodide. The acid was found to be 0.0953 M by this method whilst the borax gave a value of 0.0953_5 M the thiosulphate being 0.4038 M. For the iodine standardisations "Thyodene" indicator was usually used as the end-point was easier to detect and was shown not to differ from the end-point obtained by titration without an indicator. Several different sources of borax for the acid standardisation were also intercompared for the most consistent results. The three batches used were a new bottle of A.R. grade from B.D.H., a bottle of A.R. grade from Standard laboratories, and this latter product re-crystallised. The most consistent results were obtained with the third alternative, this being the standard used during the inter-comparison with the iodate and in subsequent standardistaions. The respective duplicate strengths obtained for a test acid were 0.286, 0.272; 0.270, 0.277 and 0.275, 0.276 M respectively.

(d) As well as testing the major reagents for the presence of ammonia or other steam volatile alkali, all solutions, which could perhaps come in contact with the test bottles, were checked. The main liquid tested here was the thermostat bath liquid which could possibly leak into the bottles. The bath liquid as such was tested as well as the "Bluecol" antifreeze. Neither showed the presence of any volatile base. The distilled water used in the analysis and preparation of the bottles was also tested and gave a negative result.

(e) The boric acid absorption was also tested as a possible source of error although it was considered extremely unlikely to be so as any possible error due to loss of ammonia by the weak acid would give a low result and not a high figure as observed. Several runs were, however, performed absorbing the ammonia by the conventional method of using excess standard sulphuric acid. Sodium hydroxide for the back titration was standardised against the sulphuric acid. This method was found to be far less satisfactory than the boric acid method as the end-point in the titration, using methyl orange, was not as sharp as that obtained with the mixed indicator. The fact that another standard solution had to be used was considered undesirable and a possible additional source of error, particularly in the case of sodium hydroxide which is so prone to changes in strength due to e.g. carbonation from the atmosphere and attack on the storage glassware especially the burette.

(f) Any loss of bromine during sampling would show up as a higher percentage ammonium bromide. This would be expected to be a random variation to some extent and should cause discrepancies in duplicate analyses particularly in the case of wet solids. This would only have a major effect on tie lines running right to left in the diagram, the loss of water being more likely to have the same effect with the lines running in the opposite direction. Bromine is not likely to be lost from the liquid analyses as the sample is virtually drawn up into a closed system and if it is released just above the potassium iodide solution level there is unlikely to be a significant loss. The wet solid could, however, lose some bromine on transfer. A closed sampling device was considered, this to be in the forms of a small bucket which could be drawn up into a tube before withdrawing from the bottle and then releasing this into the titration flask. This seemed to be an unnecessary complication and by holding the titration vessel very close to the equilibrium bottle only a fraction of a second was required to transfer the sample in which case losses should be negligible particularly when the fork is at the same temperature as the sample being removed and the distance to carry the sample is only a matter of a few inches. The equilibrium bottles were also placed in an ice bath during sampling to maintain their temperature. In the case of the T shaped tubes, and in later systems, the long necked tubes, the equilibrium flask was sometimes sampled directly from the thermostat.

(g) Undesirable side reactions were also investigated. The first of these was the possible formation of bromate. Bromine as bromate would not necessarily be determined by the present analytical scheme. Reduction of the sample by acid sulphite would convert bromine and bromate to bromide. In the absence of bromate, a total bromide estimation should correspond to the bromine plus bromide estimated separately.

The reactions used were the following

$$Na_2SO_3 + Br_2 + H_2O \longrightarrow Na_2SO_4 + 2HBr$$

$$Na_2SO_3 + BrO_3^- + 4H^+ \longrightarrow Na_2SO_4 + Br^- + 2H_2O$$

On the addition of a little acid the excess sulphite is decomposed and also the bromate will give the bromide. Assuming up to about 1 gram of bromine per sample, 10 mls of a 10% sulphite was used to convert the bromine to bromide. The equilibrated samples were run into the sulphite solution as well as into the potassium iodide solution as before. In the case of the sulphite they were then made up to 250 mls in a volumetric flask and 25 ml samples were withdrawn for titration. The samples were taken immediately after making up to volume in the flask. The 25 ml portions were then acidified with 5 mls 6M nitric acid and titrated by the Volhard silver nitrate method. Due to the presence of free SO_2 and acid in the solution it was not possible to use the Mohr potassium chromate method without boiling out the SO_2. Adsorption indicators were also not very satisfactory under these conditions. The silver nitrate used was approximately 0.1M being standardised against AR sodium chloride. The ammonium thiocyanate was standardised against this silver nitrate and was also about 0.1M. Twenty five ml portions of silver nitrate were used.

The results obtained showed that there could not have been any appreciable bromate formation. Some typical results obtained on a bottle which was consistently high by the KI method analysed at a total bromine and bromide 77.0% whilst the separate bromine and bromide yielded 76.9%. Another yielded 76.2% and 76.4% respectively. These slight difference were shown to have no significant effect on the lines and hence there was no apparent discrepancy due to this effect.

Another possible side reaction is the formation of NBr_3 or partly substituted ammonias. This was considered before the overall investigation began, because of the explosive nature of NBr_3. This is only formed in alkaline solutions at temperatures of about -95^{o} C. In these reaction mixtures the solution would be acidic, the only possible source of alkali being the glass bottles. This would be negligible, even over one to two months, especially when the bottles have been "aged" with bromine whilst testing the lids. Even if NBr_3 were formed in solution, alkaline hydrolysis would convert the nitrogen to ammonium or elemental nitrogen. It is therefore difficult to reconcile this with a high ammonium figure.

Chattaway (45) also showed that ammonium tribromide, which he sealed for four years in a glass ampoule, was quite stable.

From this investigation it would appear that the result obtained is a real "error" on this section of the diagram and was unlikely to be an experimental error applicable to the diagram as a whole. Other suppositions which depend on the nature of the bromine hydrate will be dealt with in the section on this compound.

RESULTS.

The results obtained for the analysis are set out in the following table and are shown plotted in figure 3. The analyses shown in the table 4 are the mean of at least two and sometimes up to six sets of figures. Although the wet solid analyses need not necessarily be identical they have been averaged for ease in presentation. The mean of a number of these points lying along the line must also be along this line. A detailed table is given in the appendix.

DISCUSSION.

The results clearly indicate that ammonium tribromide is the only stable ammonium polybromide at 0° C. This is in equilibrium with anhydrous ammonium bromide and bromine. From the swing on the invariant between ammonium tribromide and bromine it can be shown that this passes the point for ammonium pentabromide. An experiment in the preparation of the tribromide by dry methods also showed that the uptake of bromine by anhydrous ammonium bromide, in the presence of phosphorus pentoxide ceased at the theoretical value for the tribromide after about four days. Assuming

TABLE 4.

Bottle	Total Composition			Liquid Phase		Wet Solid Phase		Comments
Number	NH_4Br	Br_2	H_2O	NH_4Br	Br_2	NH_4Br	Br_2	
18	45.0	6.0	49.0	36.99	6.95	66.03	3.72	Anhydrous ammonium bromide
11a				37.08	8.73	75.18	3.29	
11	61.8	6.3	31.9	37.11	10.29	75.23	4.04	
4				37.19	12.04	69.54	5.79	
21	61.2	11.6	27.2	36.31	19.08	72.14	8.31	
7	55.5	20.2	24.3	35.04	28.13	67.51	16.09	Invariant A
8	40.0	29.0	31.0	34.65	27.76	48.30	38.29	

Bottle	Total Composition			Liquid Phase		Wet Solid Phase		Comments
Number	NH_4Br	Br_2	H_2O	NH_4Br	Br_2	NH_4Br	Br_2	
24	35.0	47.5	17.5	32.54	32.63	36.82	54.80	)
10	29.5	41.5	29.0	28.56	38.30	35.22	54.83	)
12				25.61	45.85	33.66	56.01	) Anhydrous
15	30.0	58.8	11.2	22.97	56.04	33.93	59.75	) ammonium tribromide
16	21.2	63.8	15.0	20.26	63.54	31.05	62.74	)
20	25.0	68.9	16.1	15.90	74.25	28.64	67.52	)
22	21.6	72.9	5.5	14.02	78.08	29.09	68.25	)
23	14.6	81.5	3.9	9.39	85.70	26.69	72.54	Invariant B
23a				9.02	85.98	11.63	86.42	

Bottle Number	Total Composition NH_4Br	Br_2	H_2O	Liquid Phase NH_4Br	Br_2	Wet Solid Phase NH_4Br	Br_2		Comments
34	2.0	20.5	77.5	2.74	8.79	1.85	28.79	)	
35	3.5	21.0	75.5	4.45	11.58	2.90	31.25	)	
1a				5.36	14.66	3.90	33.52	)	
9	5.0	30.0	65.0	6.91	17.66	4.32	35.88	)	Bromine
31				8.53	21.05	5.12	38.11	)	hydrate
1				9.82	27.36	7.18	36.52	)	
2a				10.35	28.66	6.63	40.12	)	
14	9.3	37.1	53.8	11.36	32.05	7.14	42.70	)	
40	10.4	40.0	49.6	12.48	33.88	7.95	42.33	)	
2				13.05	38.79	9.83	42.96	)	
19				13.81	48.77	8.26	49.20	)	
28	10.1	46.2	43.7	14.10	43.43	9.42	46.44	)	
17	10.2	58.6	31.2	13.06	59.23			)	

Bottle	Total Composition			Liquid Phase		Wet Solid Phase		Comments
Number	NH_4Br	Br_2	H_2O	NH_4Br	Br_2	NH_4Br	Br_2	
17a				13.68	62.73			Invariant C
29				12.82	67.19			Pure bromine as second phase
13a				12.88	71.88	0.85	98.94	
25				0.47	99.00			Solubility ammonium bromide in bromine.
				37.42				Solubility ammonium bromide in water
					4.00			Solubility bromine in water.

TERNARY SYSTEM $NH_4Br - Br_2 - H_2O$ at 0°C

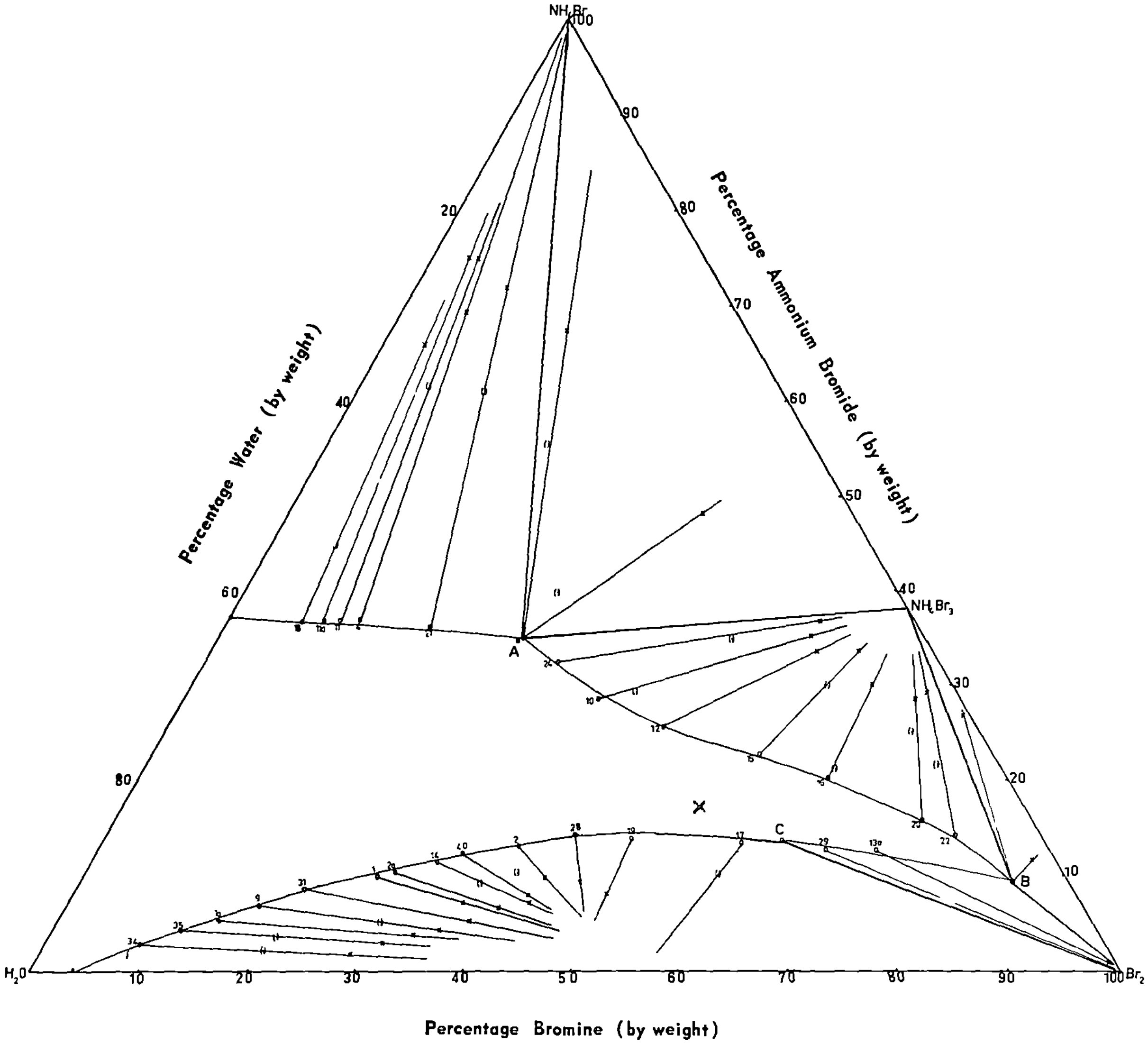


FIGURE 3.

a saturated solution at 0°C for ammonium bromide and that no solid ammonium bromide was present the addition of two mole equivalents of bromine to this would give a total composition in the all liquid region of the diagram marked x in figure 3. Also at about 20°C this would still be the case. This explains the observation of Roozeboom mentioned earlier, that two moles of bromine are soluble in a saturated ammonium bromine solution.

The results on the ammonium tribromide arc were treated by the mathematical procedure outlined in the appendix. This gave results of

	$\%NH_4Br$	$\% Br_2$
Experimental	38.44 ± 0.06	62.07 ± 0.06
Theoretical	38.00	62.00

The best point of intersection is therefore slightly outside the coordinate triangle showing a negative percentage of water. On a molar basis this corresponds to $NH_4Br_3 - 0.07\ H_2O$.

The high halogen corner of the equilibrium diagram for this and subsequent systems has been drawn assuming a zero solubility of halide and water in halogen. These solubilities were checked experimentally and were found to be insignificant on the scale used in the diagrams and have therefore been neglected. Zernicke (55) has enlarged this section of the equilibrium diagram for the potassium bromide-bromine-water system to show the typical behaviour in this segment but he also omits this in an earlier discussion of this system in the same book.

CHAPTER 4.

LITHIUM BROMIDE-BROMINE-WATER

INTRODUCTION.

The chemistry of lithium received little prominence during the development of the chemistry of the alkali metals. During this present century, however, much more interest has been taken in this element. The halides of lithium have been investigated by a number of workers, the main relevant investigations being the work of Hüttig and co-workers (49 - 52) on the lithium halide-water systems. Apart from the work of Hüttig and Schliessmann (51) these investigations have not involved polyhalides. Schliessmann (53) investigated the system anhydrous lithium bromide, bromine over the temperature range -30° C to +35° C and found that the results were similar to those obtained on pure bromine i.e. the two components existed as separate unreactive entities. This over-ruled the possibility of an anhydrous polybromide. He did not, however, investigate the possibility of a hydrated polybromide.

This section of the overall work is to investigate the system lithium bromide-bromine-water at 0° C with a view to isolating any hydrated polybromide which may exist.

EXPERIMENTAL.

Preparation of reagents.

The only common reagent used here which has not been mentioned earlier is lithium bromide. The bromine and water purification has already been described. The lithium bromide was B.D.H. laboratory reagent grade. This was partially hydrated and was analysed both by the gravimetric silver bromide method and by fuming with nitric and sulphuric acids and weighing as lithium sulphate. The purity was found to be 82.8% which corresponds to an approximate formula of $LiBr.H_2O$. The stable bromide at room temperature is the dihydrate. The monohydrate was used in the make up of all the bottles, the water in the halide being taken into account during the preparation.

As a gravimetric method of analysis was used, no other reagents were used except for an occasional test reagent etc.

Preparation and equilibration of mixtures

The lithium bromide system was equilibrated in the stoppered tube with the sintered disc (Plate 1). This was found to be the most convenient type, allowing the solid to be collected on the plate and on tilting it could drain for several hours before sampling. This permitted relatively dry samples to be obtained.

The total composition was not determined with any great accuracy due to the deliquescent nature of the lithium bromide which took up some atmospheric moisture during the weighing operation.

On completing the total make up the bottles were well stoppered, using standard Quickf~~u~~it cones and sockets.

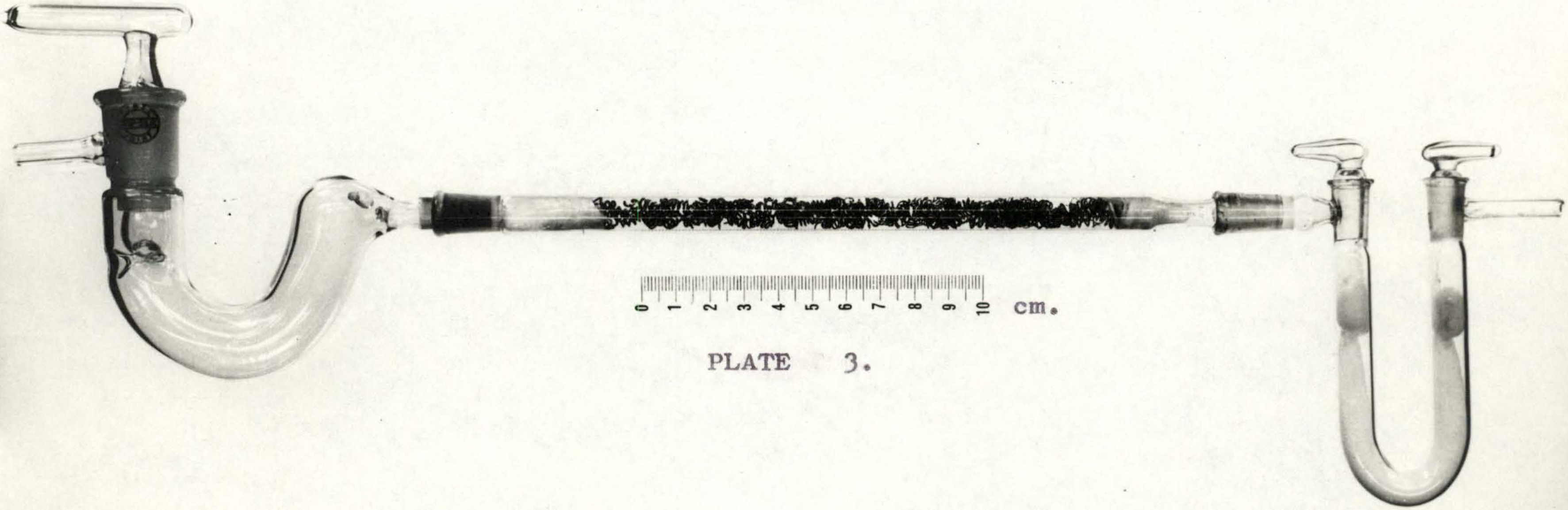

0 1 2 3 4 5 6 7 8 9 10 cm.

PLATE 3.

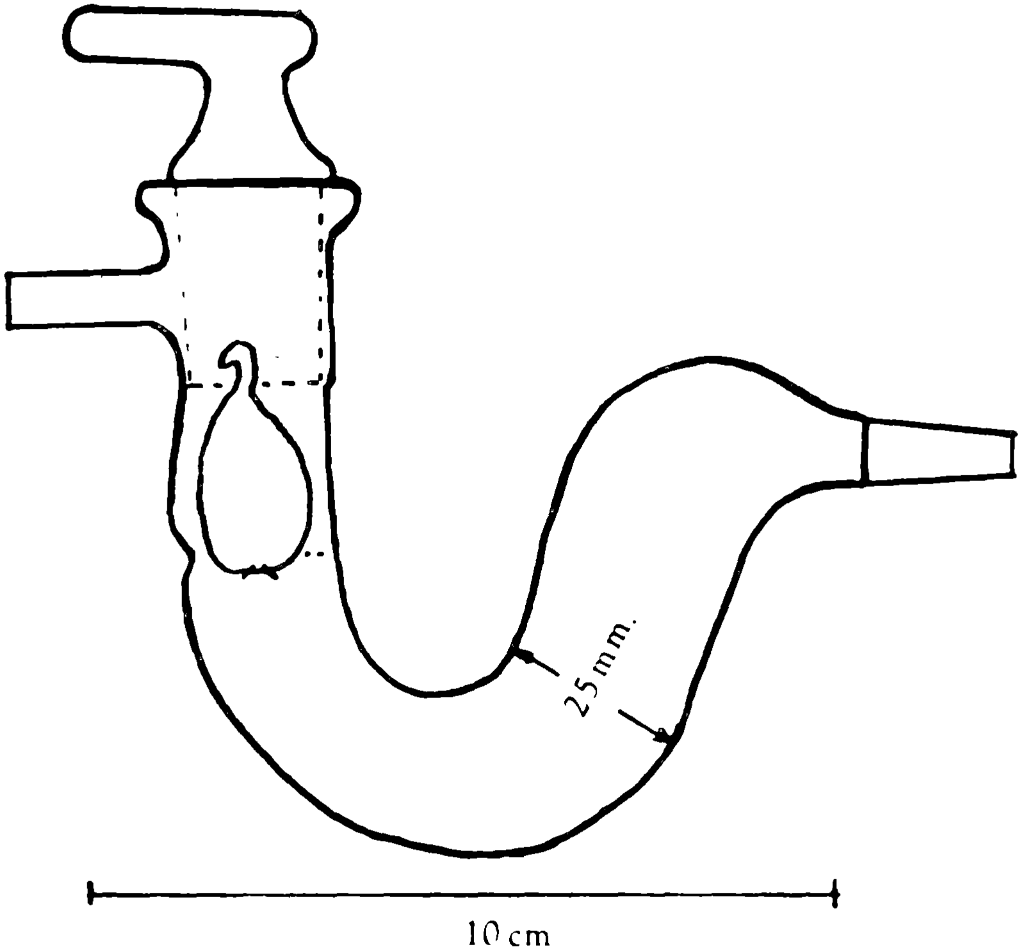


FIGURE 4.

A toy balloon was then stretched tightly over the top to complete the water tight seal. The bottles were floated in the refrigerated thermostat where they could be shaken from day to day to hasten the attainment of true equilibrium. As in the case of the ammonium bromide, equilibrium was set up within about four days, particularly if the bottle was warmed on making up to take all components into solution. In general they were left for at least two weeks before any strict analyses were performed.

Analytical methods.

Lithium does not lend itself to a volumetric method of analysis. One analytical method frequently cited in the literature is the flame photometric technique. This was rejected on account of the solutions used being fairly high in their lithium concentration, and also rather elaborate calibration curves would have to be drawn up to take account of all the other components that would be in the solution if the one sample were to be used to analyse for all the components.

A gravimetric method of analysis, based on that used by Grace (13) for the potassium polyiodides was used. The sample was rapidly transferred to the weighed "U" tube (figure 4). This was then connected in turn to the absorption tube packed with silver, which was in turn connected to a U tube of phosphorus pentoxide (Plate 3). A tube furnace surrounded the silver packed tube.

Air was drawn through the analytical train, after firstly passing through two drying traps containing phosphorus pentoxide and concentrated sulphuric acid respectively. The latter also served as a bubbler to determine the rate of passage of the air over the sample. A further phosphorus pentoxide trap was placed between the analytical train and the vacuum pump to prevent any back diffusion of moisture.

On gentle heating the bromine is then released to be absorbed by the silver and the water passes over into the pentoxide leaving the anhydrous halide in the first tube.

The sample, in the first instance, was placed in a weighed porcelain boat and pushed into a straight tube with the appropriate ground glass connections either end. The tube was wound with a heating tape but it was found that the temperature could not be controlled in a very satisfactory manner. A low Bunsen flame was also tried but the heat transfer to the actual boat could not be controlled, with the result that the bromine came off too rapidly and could not be stopped. This caused the pressure to build up inside with possible loss of water back through the train and also a definite loss of lithium bromide by spattering. The U tube finally used was found to be ideal as the sample could be weighed directly into it and the rate of heating could be controlled as it was more direct. A micro Bunsen flame was used in the initial heating. A cap was made to fit over the end of the U tube to prevent any uptake of moisture on cooling and weighing the tube at the completion of the analyses. The pear shaped bulb in the neck of the tube is to prevent any back diffusion of bromine or water vapour.

The halogen absorption tube is packed with pieces of silver foil cut finely with scissors. Some silver ribbon was also used whilst available. This was placed inside a furnace made by winding 90 yards of nichrome wire (9 ohms/yard 285.W.G.) over a piece of asbestos paper surrounding a 10" length of 1½" i.d. galvanised pipe. This was connected to a variac autotransformer to control the temperature at between 300° - 320° C.

The halogen absorption tube had to be packed with a material which would quantitatively absorb the bromine and at the same time the halide formed must be unaffected by the passage of water vapour. Metallic packings seemed to be the most useful and zinc, magnesium, aluminium, copper, iron and silver were considered. Silver seemed the best choice for the reasons now outlined.

(a) Zinc bromide. This is a low melting halide (394° C) which is very soluble in water, forming hydrates which decompose to the basic salt on heating. As water vapour passes through the tube this would not be satisfactory.

(b) Magnesium bromide. This also forms hydrates which decompose to the oxyhalide and basic salt on heating and liberate hydrogen bromide.

(c) Aluminium bromide. The melting point of this halide is 97.5° C and as this tube must be heated above 100° C this would be unsuitable. Hydrates are also formed which are easily oxidised in air. The bromide is also relatively volatile.

(d) Ferrous and Ferric bromides. These are volatile. The fact that ferric will decompose to ferrous on heating especially in aqueous solutions renders iron unsuitable to this treatment.

(e) Cuprous and cupric bromides. Cupric bromide forms hydrates and will decompose to the cuprous state with the liberation of bromine. This may not be serious in the presence of excess copper but the fact that the metal will itself oxidise renders it unsuitable.

(f) Silver bromide. The bromide is anhydrous and quite stable up to its melting point at 422° C. It is stable to oxidation and is insoluble in water and hence not likely to be affected by the passage of water vapour. Although it is more expensive than the other metals this is offset partly by the solubility of the bromide in ammonia or sodium thiosulphate and hence the unreacted silver can be re-covered for further use. In practice the silver bromide was shaken for some hours with a concentrated thiosulphate solution and then shaken with concentrated ammonia before drying and re-packing.

Desiccators were made for the silver absorption tubes by sealing a long neck onto a 50 ml round bottom flask. The base was filled with silica gel and the tubes were allowed to cool in these before weighing.

To prevent the loss of bromine or water as HBr, which could possibly be formed in the first U tube, each end of the silver absorption tube was packed with platinised asbestos to reconvert it to water plus bromine. This was made by absorbing some hexachloroplatinate on Gooch asbestos and igniting in a muffle furnace. The hexachloroplatinate was prepared from scrap platinum by dissolving it in aqua regia and treating the evaporated residue with hydrochloric acid.

Before a series of analyses each day the complete train was assembled and heated for about half an hour under experimental conditions to remove any absorbed moisture.

Blank runs were firstly performed on the equipment before actually adopting it. These runs were of two types. The first were straight runs with synthetic mixtures in order to determine whether the reactions were quantitative. For these runs the bromine was added in a weighed amount in sealed thin glass ampoules which could be broken after addition to the apparatus, the weight of glass being subtracted from the lithium bromide weight. The second series of runs were to determine whether the precautions taken to exclude atmospheric moisture were sufficient.

Before the sulphuric acid and phosphorus pentoxide were included, preceding the lithium bromide tube, it was found that the passage of air through the equipment caused an increase in the weight of the water absorption U tube. After including these additional traps the water percentage was still slightly high. Blank runs were carried out using AR potassium bromide in place of the lithium bromide but the water remained about 7 mgms too high. This was eventually overcome by regrinding the silver tube to U tube cones and sockets by hand as they apparently did not fit properly.

During this section of the work the actual volume of air passing through the apparatus was metered and from the relative humidity the actual weight of water vapour passing into the equipment was determined. A volume of 0.085 cubic feet of air was used at 69% humidity from the wet and dry bulb thermometers. This would contain 25.3 mgms of water. As the error obtained finally was never as great as 1 mgm the preliminary tubes were obviously quite effective in removing the moisture.

Air was used in all these analyses although Harris used nitrogen. This was not considered essential as the blank results obtained with air were quantitative. Each analysis took about 3 hours, the air giving about 1 bubble in 10 - 15 seconds at the start and gradually increasing the rate as the bromine was liberated.

The lithium bromide remaining in the U tube was tested on several occasions after weighing, for free bromine. A dilute potassium iodide solution was added but no iodine was liberated. This residue was also tested for alkalinity from possible hydrolysis of the lithium bromide. It was found to be quite stable under the reaction conditions however.

On plotting the results for this system it was found that the tie lines intersected at the point corresponding to the dihydrate of lithium bromide. Hüttig and Steudemann (52) showed however that the trihydrate was the stable phase up to 4° C. As the results consistently pointed to the dihydrate a further check was made on this section of the equilibrium diagram.

To determine whether the dihydrate was in fact in metastable equilibrium, "seeding" experiments were carried out using $LiBr.3H_2O$ as the seeding material to induce crystallisation. Partially dried lithium bromide was also used but the dihydrate crystallised consistently. Resulting from this observation a check was made to determine the actual hydrate formed at 0° C.

The technique used was basically similar to the fourth component method used in ternary system analysis. In this particular case some lithium bromide and water were equilibrated at 0° C in the presence of an inert dye. The dye used was Xylene Cyanol F.F. This was found to be preferable to methylene blue. The dye had to be water soluble and preferably obtained in a pure state. It also had to be free from interfering ions and a small concentration was required to give a reasonably intense colour which could easily be determined by an absorptiometric method. A low concentration was also needed to lessen the possibility of any inclusion of the dye in the actual crystal lattice of the halide.

The concentrations of dye and halide were determined in both the saturated liquid and wet solid phases. Assuming all the dye on the wet solid is associated with the mother liquor the dye concentration in this phase gives the amount of mother liquor to be subtracted from the total analysis. The remainder then should give the true composition of the dry solid phase.

The dye concentration was determined with a Hilger Spekker photoelectric absorptiometer. Using a water density of 1.00 a test sample was used to determine the most suitable of the 607 and 608 filters. Over the concentration range 0.02 - 0.01 gm/litre it was found that the orange 607 filter was the most useful, this giving readings of 0.24 and 0.57 respectively whilst the 608 gave readings of 0.9 and 0.95 respectively. A calibration curve was then drawn up using solutions containing from 0 - 0.2 gm/litre of Xylene Cyanol F.F. The calibration was performed with aqueous solutions, using 1cm cells. The effect of the addition of lithium bromide was tested. This only increased the density by less than 1% at the concentration anticipated in the actual analysis. The calibration curve was drawn from the following data, a smooth, almost linear curve being obtained.

TABLE 5.1

Spekker reading	0.243	0.393	0.572	0.779	1.000
Concentration (gm/l)	0.020	0.015	0.010	0.005	0.000

The analytical method followed in this instance was as follows: Firstly the wet solid and liquid were sampled by the normal methods and run into previously weighed small weighing bottles of the capped variety. These were re-weighed to determine the weights of the samples.

The samples were then transferred quantitatively to 10 ml standard flasks and made up to volume. After mixing, some of this solution was transferred to 1 cm cells for the determination of the dye concentration in both phases. Following this the liquid in the cells, as well as that in the standard flask, was transferred quantitatively to a 250 ml beaker. The bromide was then determined by precipitation as silver bromide, the precipitate being collected and weighed in sintered glass crucibles.

From the concentration of xylene cyanol and lithium bromide in the liquid phase it was possible to calculate the weight of water and lithium bromide associated with a known amount of xylene cyanol F.F. The percentage lithium bromide also gave a check on the solubility of the lithium bromide at 0° C. This was found to be about 57.4% by weight whilst the reported figure in the literature is 58%. For the wet solid phase the concentration of the xylene cyanol F.F. was first calculated. From this the equivalent amount of water and lithium bromide due to the mother liquor, was calculated. These weights were subtracted, along with the weight of the dye, from the total weight of lithium bromide, water and sample. The remaining lithium bromide and water must then be that due to the dry solid. The results indicated that the dry solid was the trihydrate although they showed some scatter in the actual figures. The figures obtained were 59.12, 63.80, 61.80 and 71.97% lithium bromide.

The theoretical figure for the trihydrate is 61.6%. The last figure 71.97% is obviously due to dihydrate (theoretical 70.8%). This was the last sample taken of the series and during this time the sampling scoop has probably warmed up to above 4^{o} C with the result that the dihydrate had become the stable phase.

On account of this change of phase at a temperature close to that being used considerable care had to be taken to ensure that the sampling equipment was at the same temperature as the equilibrium mixture. The tube containing this apparatus was kept in the deep freeze unit and about half an hour before sampling it was transferred to the thermostat. This ensured that the equipment would not be above 0^{o} C.

A further qualitative test of interest in verification of these results was that when lithium bromide was placed in contact with bromine vapour or with water and bromine vapours there was no uptake of the bromine apart from surface absorption in the former case and in the latter bromine was only absorbed by the water.

TABLE 6.

Bottle	Liquid Phase			Wet Solid Phase			Comments
Number	Li Br	Br_2	H_2O	Li Br	Br_2	H_2O	
1	56.55	1.52	41.93	63.74	0.76	35.50	Lithium bromide dihydrate
2	55.87	3.10	41.01	62.42	1.68	35.90	
3	54.18	3.68	42.14	62.92	1.86	35.73	
4	54.34	4.67	40.99	61.85	1.79	36.35	
5	50.68	11.09	38.23	58.68	6.26	35.06	
6	49.25	13.96	36.79	59.46	5.35	35.18	
7	48.54	16.01	35.42	57.45	9.19	33.36	
8	43.01	23.54	33.45	57.18	11.88	30.94	
9	40.03	28.46	31.51	51.39	17.74	30.87	
10	39.32	30.26	30.42	53.96	16.36	29.68	
11	35.91	34.44	29.64	48.70	21.80	29.50	
12	30.50	41.75	27.75	49.90	20.80	29.20	
13	28.88	44.94	26.18	47.76	25,86	26.37	

Bottle	Liquid Phase			Wet Solid Phase			Comments
Number	Li Br	Br_2	H_2O	Li Br	Br_2	H_2O	
14	25.50	51.17	23.34	45.58	29.65	24.77	**Lithium bromide dihydrate**
15	16.48	68.24	15.29	42.79	35.71	21.50	
16	9.99	78.12	11.89	47.46	31.51	21.03	
17	5.82	86.91	7.27	52.04	32.73	15.23	Invariant Ⓐ
	6.12	86.38	7.50				
18	6.80	18.75	74.45	3.14	37.85	59.01	Bromine hydrate
19	7.95	22.80	69.25	2.80	40.49	56.71	
20	8.63	24.70	66.67	2.85	42.01	55.14	

Bottle	Liquid Phase			Wet Solid Phase			Comments
Number	Li Br	Br_2	H_2O	Li Br	Br_2	H_2O	
21	9.15	25.75	65.10				Invariant B
22	10.9	37.1	52.0				Bromine
23	11.0	33.5	55.5				
	58.00		42.00				Solubility of lithium bromide in water
		4.00	96.00				Solubility of bromine in water.

TERNARY SYSTEM LiBr – Br_2 – H_2O at 0°C

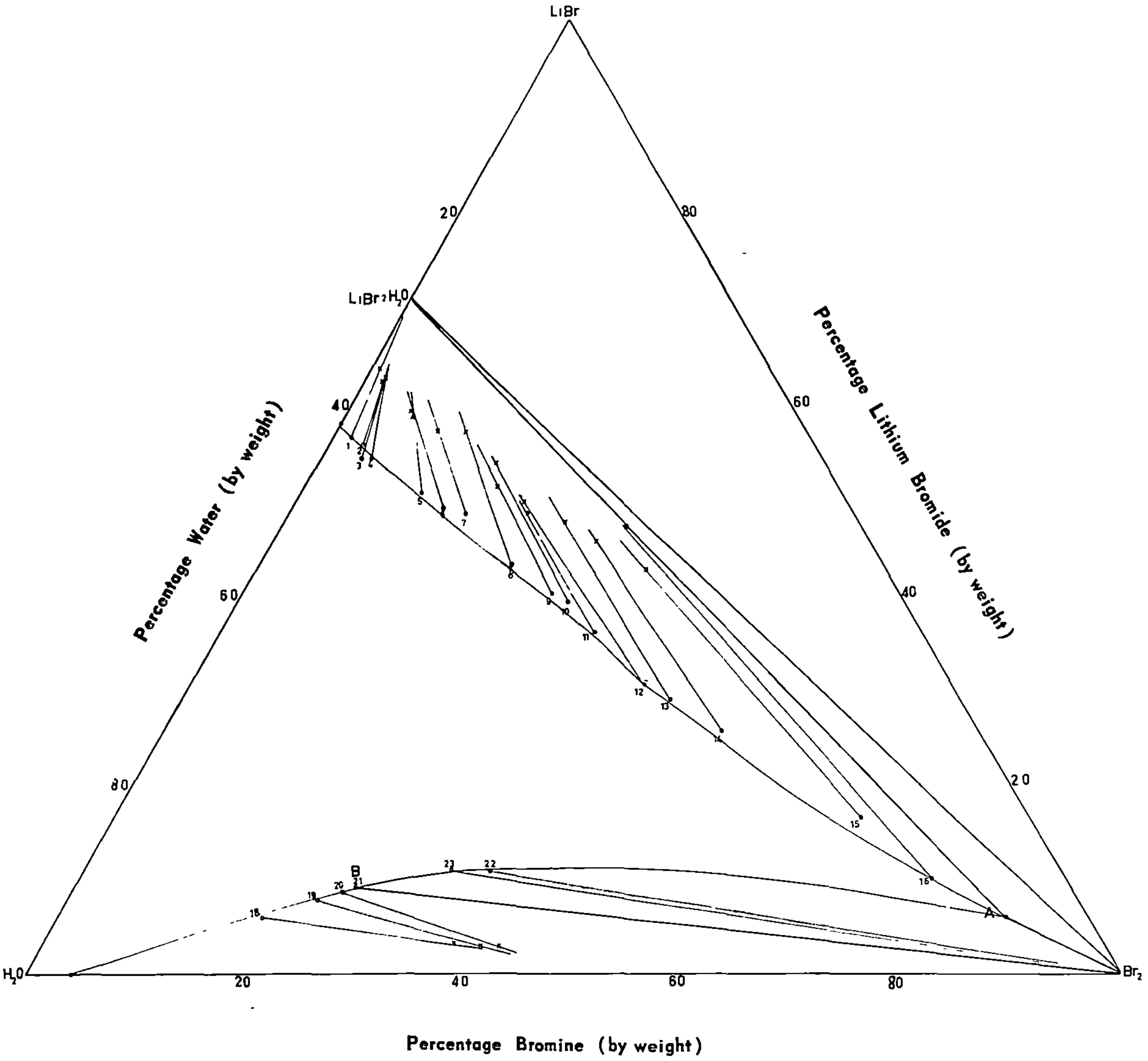


FIGURE 5.

RESULTS AND DISCUSSION.

The analytical results are listed in table 6 and are shown in figure 5.

The results obtained are in agreement with the result of Hüttig and Schliessmann (51) in that no anhydrous polybromide is formed. They also show that there is no stable hydrated polyhalide at this temperature. The possibility of a tetrahydrate was looked for in particular due to the tendency of the lithium ion to coordinate with four molecules of water, but there was no evidence of this occurring.

The formation of the dihydrate as the only solid phase was of interest due to the fact that normally the trihydrate is the stable solid at this temperature. This was verified in the absence of bromine, but the addition of bromine to give a solution with 0.76% bromine gives the dihydrate as the stable solid phase. The invariant between dihydrate and trihydrate would have therefore to be very close to the binary boundary between water and anhydrous lithium bromide. As it was obviously not going to yield any result of real interest in this investigation this invariant was not determined. It would have taken considerable time to obtain this with any certainty, particularly in obtaining the required total composition with a limited amount of material.

There is a considerable scatter as far as the tie line intersections are concerned in this system. This is mainly due to the length of the extrapolation especially towards the invariant to pure bromine. This scatter is of no great consequence as the lines are not in the vicinity of any other possible polyhalide. Had this been the case further refinements of the technique would have been essential.

The result is in accord with the other alkali halides in that anhydrous polybromides are formed by caesium, rubidium and ammonium. Hydrates are formed by potassium whilst sodium and lithium form no polybromide and also hydrogen would be expected to exhibit similar behaviour.

The possibility of forming a polyhalide at much lower temperatures cannot however be completely overruled as the investigations of Hüttig and Steudemann show that a pentahydrate of lithium bromide forms below -53°C and possibly the size of the $(Li.5H_2O)^+$ ion may be sufficient to permit polybromide formation. It is of interest that $LiI.3H_2O$ is the next solid phase in equilibrium with $LiI_4.4H_2O$ whilst $LiBr.3H_2O$ is not associated with a polybromide. As the polyiodides are usually more stable than polybromides the larger pentahydrated lithium bromide may lead to a stable polybromide. This presupposes as stable pentahydrate although the most stable hydrate seems to be the tetrahedral $Li4H_2O^+$.

CHAPTER 5

SODIUM BROMIDE-BROMINE-WATER.

INTRODUCTION.

Harris (22) during the investigation of the hydrated potassium polybromide touched briefly on the system sodium bromide, bromine, water. The only comment in his paper however was that the highest invariant at 0° C between the three components had been prepared and this was stable to the addition of bromine and hydrated sodium bromide. He gave no indication of the actual composition at this point. This section was included solely to determine this invariant by way of completing the information on this system.

The only other information available on this system is a brief treatment by Bell and Buckley (56). They investigated the solubility of bromine in sodium bromide solutions at 25° C. Recalculation of their results to a weight percent basis gave the solubility arc which would have a second liquid phase saturated with water. At 0° C this would also include bromine hydrate.

EXPERIMENTAL.

Preparation of reagents.

The only new reagent required for this section was sodium bromide which was May & Baker A.R. grade anhydrous reagent. The bromine and water, as in the previous sectionswas used. The sodium bromide was not re analysed as a fresh bottle was taken for this section of the investigation.

Analytical method.

After equilibration in both the capped bottle and sintered disc type equilibrium vessels, the wet solid and liquid samples were analysed after the same method used for the lithium bromide.

A variation of the method, which was also relevant to the lithium bromide system was also attempted. This was in order to eliminate the silver packed tube which was the weak point of the analytical train. Care had always to be taken to ensure that the suction was sufficiently slow to allow all the bromine to be absorbed by the silver. In some of the earlier runs the bromine was seen in the phosphorus pentoxide tubes at the end of the train and could not be recovered.

The first variation was to place a wash bottle containing a 10% solution of potassium iodide after the phosphorus pentoxide guard tube adjacent to the water absorbing tube. The purpose of this was to retain the bromine, which would otherwise be lost, by liberating the equivalent quantity of iodine which could be titrated with thiosulphate.

This then led to the complete elimination of the silver absorption tube and connecting the train in the order: sample tube, water tube, phosphorus pentoxide guard tube and potassium iodide solution. The air was drawn through more rapidly but the method was discarded due to the uncertainty whether or not all the bromine had passed through the phosphorus pentoxide tubes. Also with more rapid aspiration it is possible that even some of the iodine could be lost from the iodide solution and it was considered impracticable to include an additional gas scrubbing stage. It was considered that there were no real advantages in changing the analytical scheme.

RESULTS.

The results obtained for this system are summarised in the following table. Each of the liquid analyses for invariants are the mean of duplicate results.

TABLE 7.

Liquid phase		Wet solid phase		Comments
NaBr	Br_2	NaBr	Br_2	
13.26	73.43	29.80	56.22	Invariant between NaBr.
13.20	74.30			$2H_2O$ and bromine
13.23	73.86			Mean figure for invariant
6.47	12.87	2.46	36.70	Bromine
7.13	14.66	2.70	37.80	hydrate
10.37	28.95	3.17	46.35	
11.65	28.30			Invariant between bromine
10.37	28.95			hydrate & bromine
11.01	28.62			Mean value for invariant

DISCUSSION

Although potassium bromide forms a hydrated polybromide it is not surprising that a polybromide is not formed at this temperature by sodium especially as lithium also will not form a polybromide. The polyiodides are formed but the heavier halogen forms polyhalides much more readily than the lighter bromine. As with lithium bromide it could quite well be that a polybromide is formed at lower temperatures. At 0°C sodium bromide dihydrate is the stable phase. A pentahydrate is however formed at temperatures below - 24.0° C (36).

CHAPTER 6

LITHIUM IODIDE - IODINE - WATER.

INTRODUCTION.

Grace (57) in his investigation of the alkali polyiodides postulated from a brief qualitative investigation that a polyiodide of lithium melting about 10° C probably existed. He proposed that this would probably be $LiI_3.4H_2O$, analogous to $NaI_3.2H_2O$ and in fact he considered this as a further piece of evidence in favour of the above formula for the sodium polyiodide. This formula for the sodium polyiodide was later shown to be incorrect by Briggs (20), Cheesman (21) and co-workers. Abbegg and Hamburger (9) also confirmed the absence of a lithium polyiodide at 25° C.

In the case of lithium iodide the trihydrate is the stable phase from -91.0° C to 70.5° C (51) and the tie lines on this section of the diagram were found to intersect at this point.

EXPERIMENTAL.

Preparation of reagents.

Both a volumetric and gravimetric analysis was performed on each sample entailing the use of several reagents which were required in a pure state, particularly in regard to any solid, non volatile residue.

The water used in the make up of the equilibrium mixtures was the twice distilled water described earlier. In all other solutions freshly distilled water was used and in the case of the ammonium thiosulphate this was boiled out prior to making up the stock solution.

In the initial experiments the lithium iodide was Kahlbaum reagent. This contained some free iodine and was stored over sodium hydroxide in a desiccator. Analysis gave 77% LiI. The main part of the work was carried out using BDH laboratory reagent. This was free from free iodine and was analysed at 80% purity. This corresponds to a formula approximating to the dihydrate (theoretical 79%).

Iodine was purified from May and Baker resublimed iodine. The purification consisted of a sublimation in the presence of phosphorus pentoxide. Several methods of carrying out the sublimation were attempted, the most satisfactory being sublimation in a desiccator. A 6" desiccator was cleaned and the top section was wrapped with a 1 amp Electrothermal heating tape. In place of the perforated plate a glass triangle was made which supported a porcelain basin containing a mixture of iodine and phosphorus pentoxide. The desiccator was heated and the lid was covered with cloth to prevent the sublimate collecting here. The bottom section remained uncovered and on heating overnight an adequate supply of the pure iodine was maintained. A very light greyish residue remained in the basin with the phosphorus pentoxide. The iodine was kept in a dark bottle with a tight fitting glass stopper.

This process completely removed any non-volatile residue and analysis by titration with thiosulphate gave 100% purity.

The volumetric estimation of the iodine was performed by titration with ammonium thiosulphate. This was BDH reagent. The solid reagent was stored in a desiccator over caustic alkali as, on opening, there was a very pronounced odour of hydrogen sulphide. This reagent was considered unsuitable for use in the automatic type burette on account of its relative instability when stored for long periods. Stock 0.1 M solutions of about 3 litres were prepared at least 6 - 8 weeks before required.

The solutions were then filtered into a glass stoppered bottle containing about 600 mls. This smaller stock was standardised about once or twice a fortnight depending on the rate of use. Samples of 50 mls were also taken each time this bottle was filled to determine the non-volatile residue so that a correction could be made for this. Standardisation of the thiosulphate was by A.R. potassium iodate.

Equilibrium samples taken for analysis were dropped into a 5% ammonium iodide solution to render the iodine more soluble for titration. This reagent was from May and Baker and contained a considerable quantity of free iodine and insoluble residue. It was recrystallised from water but it still contained free iodine. This was removed by firstly shaking with ether before recrystallisation and then washing with ether after recrystallisation.

Sulphuric and nitric acids were used during the analyses. These were concentrated AR Ajax reagents.

Ammonium chloride was also used in small amounts. This was used as the solid A.R. reagents and was not further purified.

PREPARATION AND EQUILIBRATION OF BOTTLES.

In the preliminary investigations on this system the stoppered tubes with sintered disc and also some of the stoppered jars were used. The solutions were relatively viscous and oily compared to the bromine systems and it was found to be very difficult to stop all leakage and especially the uptake of water from the bath liquid and atmosphere, the lithium iodide being extremely deliquescent. This was only overcome by the use of the sealed, long necked tubes. The use of these tubes also necessitated the modification of the sampling equipment to the long spade and pipette. It was rather difficult to make up the equilibrium mixtures with any degree of certainty. This was mainly on account of the nature of the lithium iodide. The reagent as supplied was in a lump form. On grinding in a pestle and mortar it was much more susceptible to atmospheric moisture so this operation had to be carried out rapidly and was mainly just to break up the lumps into pieces that would fit down the neck of the equilibrium bottle rather than to powder the reagent. As the lithium iodide contained 20% water by weight only a small amount of water had to be added to each tube. In most cases the equilibrium mixtures were made up to a total of about 15 grams. The water added to these was usually of the order of 1 ml and in many cases this caused the mixture to become all liquid.

On account of the effect of these small quantities of water it was imperative that the lithium iodide should be added as quickly as possible to prevent any uptake of atmospheric moisture. For preparing the bottles the neck was flared to make a funnel so that the materials were added more easily. The bottles were also heated in the oven for about 2 days before use to remove all traces of moisture. A dry box may have been useful here but as the uptake of moisture was of no real consequence, it was not considered essential to construct one.

A 2 Kg. beam balance with a sensitivity of 20 mgm. per division was used in the preparation of the mixtures. Firstly the lithium iodide was weighed into the tube which was stored upright on the pan by placing the bulb through a hole in a rubber bung. The equivalent amount of powdered iodine was then weighed in on top of the lithium iodide. This was preferable to the reverse procedure as the iodine covered the lithium iodide hence reducing the possibility of moisture reaching the halide. Iodine vapour was also absorbed onto the iodide and had it been necessary to remove some of the iodide a small amount of iodine would have been also lost. The converse was not the case however and if too much iodine was added it could be removed, with care, without losing any of the lithium iodide. The water was pipetted into the tube, the tip of the pipette being kept as far down the neck as possible, without picking up any of the solid reagents. This was tokeep the wetted portion of the equilibrium tube below the portion to be sealed off so that none of the water is lost on sealing.

The bottles when made up to the required composition, were then warmed gently to complete solution of the reagents and three glass beads (about 3 mm diameter) were added to the bottle. These were found to greatly facilitate the attainment of equilibrium. The earlier series of experiments were carried out without these beads and it was found desirable to leave the bottles for at least 4 - 6 weeks before analysis, but when the beads were added the mixtures came to equilibrium after about 3 weeks. As far as possible no analyseswere carried out on any mixture until it had been equilibrating for about 6 weeks and in some instances bottles were kept in the thermostat over a period of 3 months before analysis. In these latter cases a large part of this period was over vacations and hence the bottles were only given an occasional shake instead of the normal daily shake. Bottles were usually retained in the thermostat and some have been re-analysed after periods of up to 12 months.

A few of the earliest bottles were not heated to take all the solids into solutions and it was found to be very difficult to obtain true equilibrium. When a complete solution was made a true equilibrium was more readily obtained. In some instances difficulty was experienced with supersaturation but usually this was overcome by placing the bottle in the deep freeze for a few hours and then allowing it to come back to 0° C in the thermostat. The thermal capacity of the thermostat was sufficiently large to permit this type of procedure without noticeably affecting the temperature of the bath.

An accurate determination of the total composition of the equilibrium tubes could have been made by taking a sample whilst it was all liquid. This was not considered to be sufficiently important however to risk changing the composition by contamination and more particularly by getting liquid up aroumd the neck of the tube where iodine and water would be lost on sealing leaving some anhydrous lithium iodide in the neck. The bottles were only shaken gently during the [illegible] solution process least some of the reagents should splash up the neck. This sometimes meant there were a few droplet of water and often films of water still on the neck before sealing.

Identification of the bottles presented a minor problem. Rubber bands around the neck were initially used but it was found that after several months some of these became lost. A glass writing ink was also useful for up to about a month and the glass had to be perfectly dry before writing. The most satisfactory identification used was a cardboard label tied to a rubber band which was fastened around the neck.

A waxed thread had to be used as the bath liquid ran along string and saturated the labels. The label could then be used for rapid identification and for keeping a record of all details of the analysis etc. for reference purposes.

ANALYTICAL METHODS.

As in the ammonium bromide system the water is determined for this system by difference. The basis of the analytical scheme used here consisted of taking a known weight of sample, titrating with ammonium thiosulphate to estimate the iodine and then fuming to dryness with sulphuric acid to estimate the lithium as sulphate. This method was considered preferable to the absorption train method, which would have been applicable here, as all four samples (duplicate solid and liquid) could be taken at the one time and the tube could immediately be resealed, otherwise several sets of the analytical train would have been required. Another alternative method would have been that used by Briggs in the cæsium iodide system (26) where the free iodine was determined by drawing air through the sample and distilling it into a series of bottles containing potassium iodide solution. These were then titrated. The iodide was then decomposed with phosphoric acid and hydrogen peroxide to liberate the combined iodine which was determined in the same manner. Although in this method the heaviest ionic species is being determined the method was avoided mainly on accountof the distillation technique which could easily lead to losses of iodine due to some either being removed [illegible] from the potassium iodide solution by the air current or some remaining in the distillation flask. It is also possible that some of the lithium iodide may be decomposed either by heat or by oxidation giving a high figure for the iodine and a low iodide figure.

It is of interest that although ammonium thiosulphate is considered to be unstable and hence unsuitable for many purposes as a reagent it was found that this is not in fact the case. A freshly prepared solution was found to change in strength over an initial period of a week or so but a stock solution which had been allowed to stand at least a month ~~or longer~~ was relatively stable. In practice the stock solution was prepared about two months before use. The stock was of 3 litre batches and this was transferred, with filtration to remove some precipitated sulphur, to a 600 ml bottle as required. The 600 ml batch usually lasted for about a month but one batch which was used over a period of 2½ months was found to change in strength by only about 0.6% i.e. a solution 0.1 M only changed by 0.0006 units.

On account of the low melting point of the polyiodide it was essential that the equilibrium temperature should not be disturbed particularly in this part of the system. In the preliminary experiment the sampling equipment was kept in a deep freeze unit prior to sampling and the equilibrium bottle was placed in a 2 litre beaker of ice and water during sampling. It was found however that there were discrepancies in the liquid analyses which were traced in the main part to the sampling equipment being at a different temperature to the sample. In all subsequent experiments the sampling equipment was placed in the thermo~~n~~stat before use and the equilibrium bottle was kept in the thermostat during sampling. After sampling the equilibrium bottle was kept in an ice salt mixture until it could be resealed and returned to the thermostat. The sampling equipment after use was rinsed in a cylinder of Kl solution, to remove the iodine. Rinsing the water was difficult as the iodine adhered to the glass in small crystals.

The samples of solid and liquid were taken in duplicate and each was dropped into a tall, capped weighing bottle containing about 10 mls of 5% ammonium iodide. The latter reagent was to keep the iodine in solution for the titration. A small amount of free iodine was present in the ammonium iodide but a blank titration was less than 0.05 ml of 0.1 M thiosulphate so a blank correction was not made. This was checked periodically. In the major part of the work there was no non-volatile residue from the ammonium iodide but a later batch using a new reagent, had a residue amounting to 0.2 mgm/10 ml sample. This correction was deducted from the weight of lithium sulphate.

After reweighing the weighing bottle to determine the weight of the sample, the iodine was titrated with the 0.1 M thiosulphate from the 25 ml "green line" burette. The titration was carried out in the weighing bottle. No indicator was used. The ammonium thiosulphate contained a non-volatile solid residue and correction had to be made for this. Part of this residue was shown to be an iron contamination which was removed by fuming with ammonium chloride. The remaining residue was usually of the order of 0.25 mgm/ml of thiosulphate and a correction was made on the weight of lithium sulphate for this.

The final stage of the analysis consisted of transferring the titrated sample quantitatively to a 250 ml beaker and evaporating the dryness on a steam bath with about 1 ml of concentrated nitric acid to remove all the iodide as iodine. The residue was then transferred to a previously ignited weighed silica crucible and after adding about six drops of concentrated sulphuric acid it was again evaporated on the steam bath to remove water before fuming on the hot plate. The beaker was also returned to the steam bath to dry to make certain all the residue had been transferred. It was rinsed again at this stage.

The low heat of the hot plate was first used to remove remaining moisture and also the sulphur from the tetrathionate and any remaining elemental iodine. On increasing the heat the nitrates decompose and the ammonium salts begin to volatilise. After all the apparent decomposition reaction had ceased the full heat was used to completely remove the ammonium salts.

The remaining residue was usually a salmon pink to pale brown colour due to the iron. This was mostly removed by adding about half a gram of ammonium chloride to each crucible and fuming. This treatment was then followed by refuming with 2 drops of sulphuric acid, followed by ignition over Bunsen and Meker burners.

After cooling and weighing the residues were again fumed with 2 drops of sulphuric acid and ignited over the burners until constant weight was obtained.

The major causes of error in this method are from the residues in the reagents and the possibility of any loss of the lithium sulphate by spattering especially during the decomposition of the nitrates and final removal of moisture. The possible entry of air borne contaminants during evaporation stages also had to be guarded against.

Several series of tests were carried out on this section of the analysis to determine the most accurate and straight forward methods.

The first concern was to determine which reagents contained residues. As already mentioned it was found that the ammonium thiosulphate was the main source of residue although some was found in the ammonium iodide. The other reagents were all found to be free of residue.

The evaporation and fuming was tested by several methods. It was found preferable to leave the treatment with sulphuric acid until the steam evaporated residue was transferred to the crucibles. Heating on the hot plate alone was found to be insufficient to attain constant weight hence the final heating was carried out over burners. The crucibles after heating, were cooled in a desiccator cabinet for about 1½ hours before reweighing. As far as possible this period of cooling was used throughout as it was found that for example, standing overnight gave a slightly different weight than if the crucible had only stood for a few hours. Constant weight was deemed to have been reached when the weights agreed to within 0.5 mgms. This was usually at the second weighing and was very rarely at more than three weighings.

QUALITATIVE TESTS.

A series of qualitative experiments were carried out as checks on the stable phases obtained from the system. Before the temperature effect of the sampling equipment was fully realised the tetra iodide solubility arc seemed to extend to such a point that it became difficult to visualise how the hydrated lithium iodide could be the next stable solid phase. The only alternatives were another hydrated

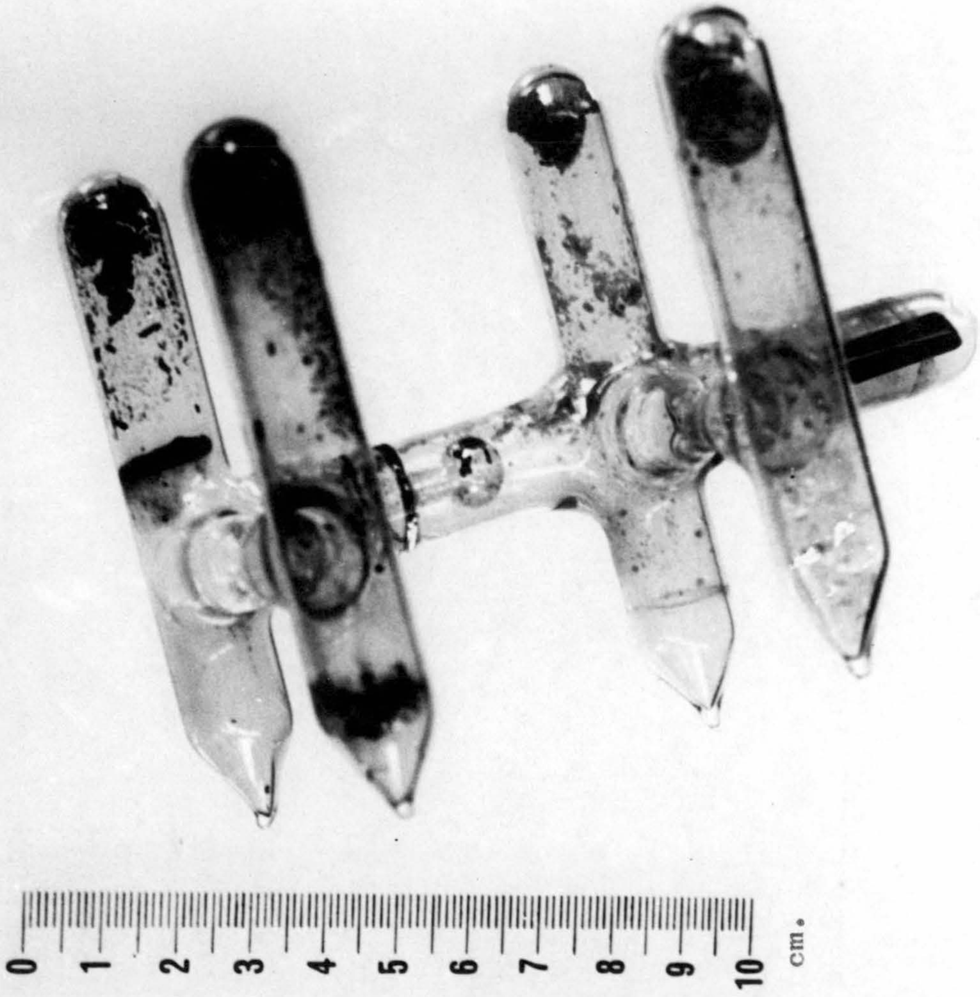

0
1
2
3
4
5
6
7
8
9
10
cm.

FIGURE 6.

polyiodide, possible the di-iodide as in the sodium iodide-iodine-water system or the anhydrous halide as in the ammonium iodide-iodine-water system. Even after the true invariant between the hydrated polyiodide and the halide had been determined the triangle covering the area of the diagram containing these two solids in equilibrium seemed so narrow that the possibility of a further stable solid was not over-ruled.

In order to show whether or not anhydrous lithium polyiodide would form an additional solid phase a sample of anhydrous lithium iodide was allowed to come into equilibrium with iodine. This was done using apparatus shown in fig. 6. Phosphorus pentoxide was placed in two limbs of the apparatus adjacent to iodine and lithium iodide respectively. A glass diaphragm separated these two sections. The apparatus was evacuated and sealed. It was then placed in an oven for two days in order to dry out the lithium iodide, and also to remove traces of moisture from the iodine. After this period the phosphorus pentoxide tubes were removed and the diaphragm was broken by means of the breaker. The tube was then returned to the oven so that the iodine would sublime onto the halide. There was no combination between the two either at this temperature (about 50° C) or at about 0° C when the tube was placed in the refrigerator. This showed that there was not anhydrous polyiodide in the system. On opening the tube and adding a drop of water to the halide the iodine was immediately taken up by the lithium iodide (indicating a hydrated polyiodide.)

To determine whether anhydrous lithium iodide could be in equilibrium with the hydrated polyiodide a sample of the reagent iodide was partially dehydrated by heating in an H shaped tuber under vacuum adjacent to phosphorus pentoxide. After drying the powdered reagent was placed in a weighing bottle with a mixing rod and then placed in a desiccator adjacent to some iodine. If the equilibrium under test existed iodine should be absorbed until a composition is reached corresponding to the intersection of the line between anhydrous lithium iodide and hydrated tetra iodide. Apart from initial surface adsorption a slight random uptake was observed over three weeks at about 0° C. After a week it became obvious that this random increase (about 10 mgm each day) was due to moisture entering the bottle on opening the desiccator and putting the cap back on the weighing bottle. It was found for example that this increase in weight was still about 10 mgms even ~~over~~ over the weekend or on allowing the system to stand for 3-4 days. There was obviously no uptake of iodine however.

A third set of similar investigations involved the use of some lithium iodide trihydrate which was obtained both by recrystallising some lithium iodide and from a drained sample from an equilibrium bottle. Two samples of each were taken and placed in a desiccator with iodine. To one pair a few drops of water were also added whilst to the other pair a phosphorus pentoxide tube was included. It was found that iodine was taken up by the moist sample but there was no reaction in the dried system. This excluded the possibility of a lower hydrate of lithium iodide being in equilibrium with iodine.

MELTING POINT OF LITHIUM TETRA IODIDE TETRAHYDRATE.

One of the equilibrium bottles, which gave an exceptionally good analysis for the hydrated polyiodide, and also contained about 1-2 grams of solid, was carefully inverted for about six weeks to allow the solid to collect in the bottom and drain. The tube was then opened and some of the solid was carefully transferred to a thin glass tube of about 2mm diameter. This had to be done rapidly and witha minimum of handling as the melting point was below room temperature.

The tube was attached to the bulb of a thermometer and immersed in a bath of cold paraffin oil. This was allowed to warm up under atmospheric conditions with constant agitation, until the solid was observed to melt. This was over the range 11.5° - 12.5° C and is in agreement with the prediction of Grace that it would melt about 10° C.

RESULTS.

The analytical results are summarised in table 8 and are shown graphically in figures 7 and 8. The first figure shows the complete diagram

TABLE 8.

Bottle	Liquid Phase		Wet Solid Phase			Comments
Number	LiI	I_2	LiI	I_2		
1	56.82	6.00	64.08	3.21	)	
2	49.97	17.80	64.21	5.64	)	
3	46.73	23.31	62.19	9.18	)	
4	41.09	33.50	62.37	10.89	)	
5	34.71	42.72	44.72	31.41	)	Lithium iodide
6	31.56	48.64	53.11	23.11	)	trihydrate
	29.48	52.16	26.58	58.82	)	
	29.58	52.19	25.51	60.08	)	
	29.77	52.21	20.06	57.27	)	Invariant A
			30.83	53.69	)	
	30.12	52.01	40.25	40.13	)	

Bottle	Liquid Phase		Wet Solid Phase		Comments
Number	LiI	I_2	LiI	I_2	
9	29.40	52.16	24.60	61.35	
10	28.90	52.85	23.76	62.70	
11	28.43	52.88	24.21	61.48	
12	27.38	53.79	23.57	62.58	
13	26.07	55.36	23.25	62.91	$LiI_4 \cdot 4H_2O$
14	25.57	55.73	22.64	64.37	
15	24.12	57.48	22.76	63.25	
16	23.20	58.75	22.80	62.00	
17	22.04	60.14	22.26	62.48	
	21.49	62.02	21.51	66.05	
	21.22	62.01	14.39	76.44	
	21.13	62.03	11.85	79.97	Invariant B

Bottle Number	Liquid Phase		Wet Solid Phase		Comments
	LiI	I_2	LiI	I_2	
18	11.12	15.25	1.60	86.92	
19	13.05	18.82	1.61	86.79	
20	13.89	19.56	1.75	92.28	
21	15.94	26.31	2.37	87.39	
22	18.01	29.05	4.40	87.40	Iodine
23	20.87	40.23	6.08	82.35	
24	22.01	47.00	8.20	80.61	
25	21.82	49.13	6.73	84.50	
26	21.61	56.09	6.02	88.33	
27	22.20	58.21	8.59	83.69	

TERNARY SYSTEM LiI – I_2 – H_2O at 0°C

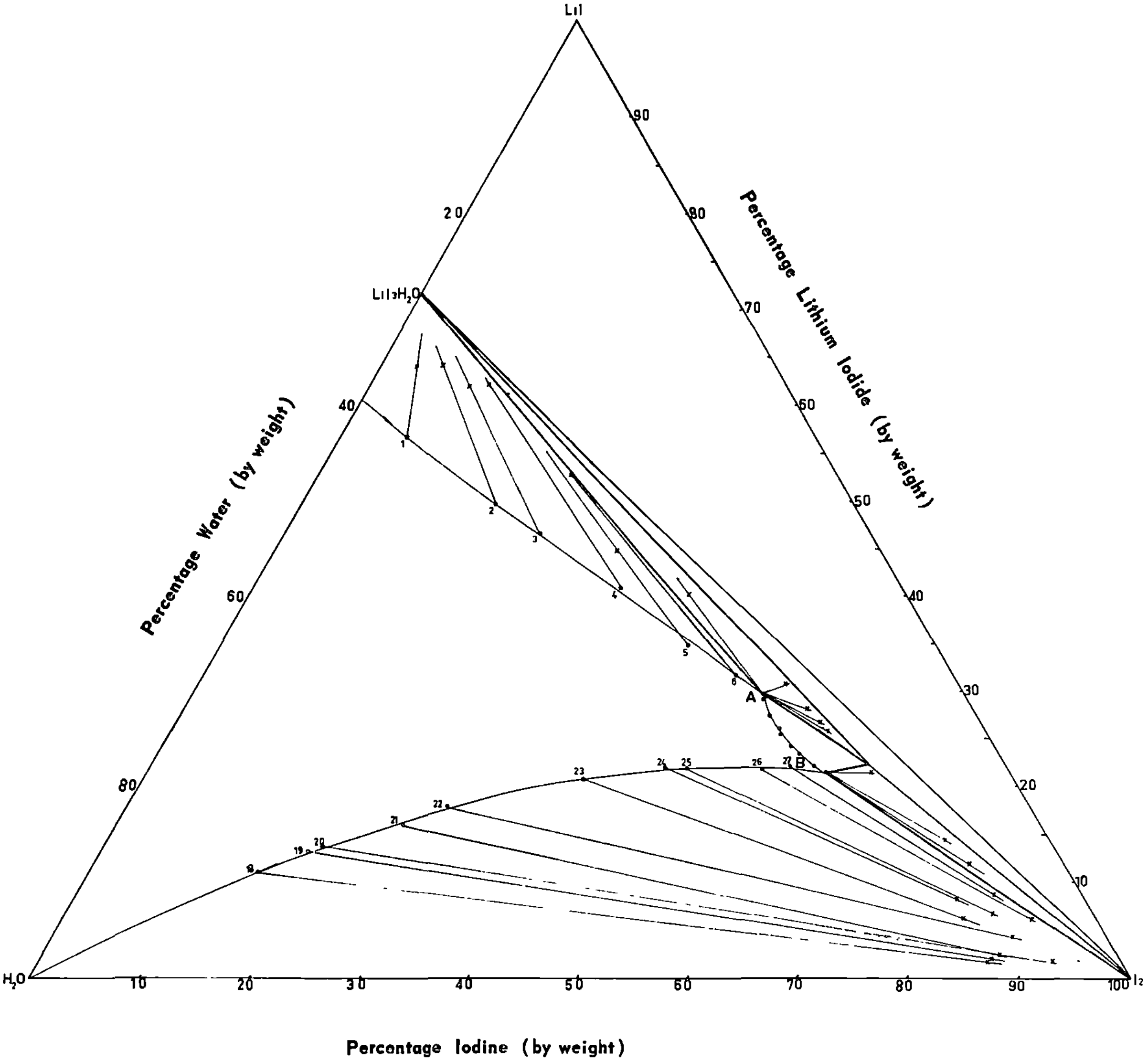


FIGURE 7.

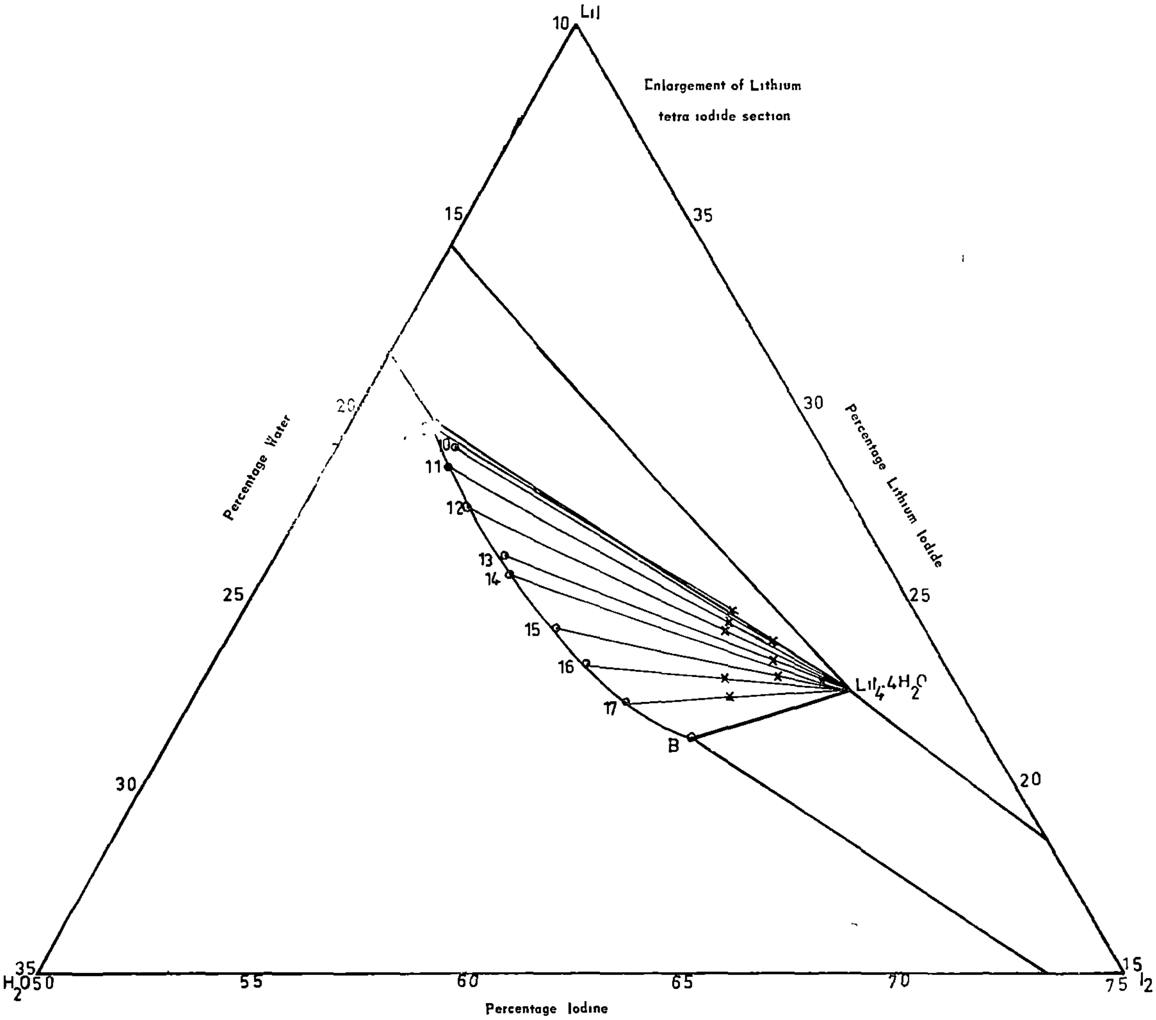

LiI
10
Enlargement of Lithium tetra iodide section
15
35
20
30
Percentage Water
Percentage Lithium Iodide
10
11
12
13
14
15
16
17
B
$LiI_4 \cdot 4H_2O$
25
25
30
20
35
15
H_2O 50
55
60
65
70
75 I_2
Percentage Iodine

FIGURE 8.

whilst the second one is an enlargement of the hydrated polyiodide section of the diagram. The tie lines are not included in this section on the complete diagram as the area is too small to show clearly the lie of these lines.

The best point of intersection of the tie lines in the hydrated tetra iodide region has been calculated by the mathematical technique described in the appendix. The complete calculation for these lines is also shown. This point was found to correspond to a figure of (22.31 ± 0.23%) lithium iodide and (65.48 ± 0.09%) iodine. The theoretical figures are 22.82% and 64.90% respectively.

A typical set of experimental results are set out to show the magnitude of the quantities measured. The following figures are for bottle 12.

	Liquid Sample		Solid Sample	
	1	2	1	2
Weight of sample (gm)	0.5922	0.4786	0.0793	0.1033
Titre (ml) $(NH_4)_2S_2O_3$	23.74	19.21	3.70	4.90
Correction for thiosulphate residue	0.0066	0.0054	0.0012	0.0015
Average weight of Li_2SO_4	0.0730	0.0594	0.0089	0.0115
Corrected weight	0.0664	0.0540	0.0077	0.0100
% I_2	53.77	53.82	62.54	63.63
% LiI *	27.47	27.29	23.57	23.57

* A correction of 0.0002 gm was also subtracted from the weight of Li_2SO_4 residue for the solid residue in the ammonium iodide.

DISCUSSION.

This section of the overall investigation has led to the isolation and identification of a new polyhalide. Although this had been suspected before it had not been completely investigated and identified.

The polyiodide was obtained inthe form of fine short needles which were the colour of an iodine iodide solution. On standing on filter paper they appeared to decompose readily to lithium iodide and iodine the lithium iodide dissolving on the moist paper.

The fact that this polyhalide is a tetrahydrate was not surprising as other tetrahydrates of the lithium ion are known. The hydrated lithium ion is also remarkably stable. The lithium ion itself would be too small to enter into polyhalide formation but the tetrahydrated co-ordination sphere makes the ionic size sufficiently large to take up halogen.

The tetraiodide formation differs from that anticipated by Grace who thought it would be $LiI_3 \cdot 4H_2O$. It is in accord however with other alkali polyiodides in that sodium and caesium form a tetraiodide.

There is considerable literature on the nature of ionic hydration and in particular, cationic hydration. This problem has been studied from many angles and widely differing results have been obtained. Bockris (58) gives an average value of 4 for the hydration of the lithium ion. Other evidence, based largely on viscosity measurements, shows that in the case of the lithium ion the coordinated solvent is held in very strong combination with the small highly charged ion. Discussions of these effects are treated in detail in Discussion of the Faraday Society (59) dealing with Interaction in Ionic Solutions. In essence it would appear feasible to treat the hydrated lithium ion as an ionic unit of sufficient size to undergo polyhalide formation. It is also of interest that the magnesium ion closely resembles lithium in this hydration effect and also that this ion will form the compound $Mg(ICl_4)_2 \cdot 4H_2O$

The overall nature of the diagram with the narrow triangular areas representing the different components explains why it was often difficult, particularly around the region of the first invariant, to make up bottles to give adequate proportions of solid and liquid. The width of these bands correspond to about 1-3% change in the water concentration and where the iodide was so deliquescent it is possible that the small errors introduced in the water concentrations could make a large difference in the position in which the total composition fell. The low melting point of the polyiodide is also in agreement with the observed fluctuation in the solubility arc with relatively small changes of temperature during sampling.

The series of experiments to determine which phases were stable, and could exist in equilibrium, yielded some interesting results. On account of the narrow triangular regions involved it seemed unlikely that, apart from iodine, the only solid phases were the tetra iodide and hydrated lithium iodide. The existence of a triiodide or even diiodide seemed likely but neither of these could be isolated. The experiment involving $LiI.3H_2O$ and iodine in the presence of both P_2O_5 and a trace of water was interesting in that it showed that iodine could be in stable equilibrium with the hydrate but not a lower hydrate or anhydrous iodide. This was slightly unexpected in view of the way in which iodine vapour was absorbed by the iodide from the reagent bottle. Presumably however, as this reagent already contained about 20% moisture, and is extremely deliquescent, the surface moisture is sufficient to permit this adsorption to be very marked.

Solutions were also prepared to cover the $LiI_4.4H_2O$ region of the diagram, as well as the NaI_2 and NaI_4 regions in this system. Magnetic susceptibilities were measured by Dr. P. W. Smith and the result for CsI_4 was confirmed in that these materials are all diamagnetic and cannot be simple ions but are probably of the form $2Li(H_2O)_4^+I_8^{2-}$.

CHAPTER 7

BROMINE HYDRATE.

INTRODUCTION.

There exists a considerable and conflicting literature on the composition of bromine hydrate. The earliest references to the hydrate were by Alexejeff (60) and Roozeboom (61) who proposed a decahydrate. A variety of different formulae have been proposed based on e.g. phase equilibrium and thermodynamic methods.

The figures reported range from a hexahydrate proposed by Bouzat (62) from heats of formation of the gas hydrates, to the decahydrate of Alexejeff, Roozeboom and Harris (54, 25). In the latter work the hydrate was approached from both the water and bromine rich sides using the potassium bromide and caesium bromide systems.

Intermediate figures have also been given. These include $Br_2 7H_2O$ by Zernicke (63) and an octahydrate by Giran (64) and d'Ans and Hoffer (65). A more elaborate treatment by Mulders (66) led to a figure of $Br_2 8.4H_2O$.

These results have been discussed by Zernicke in his paper as to possible sources of error. His own results however appear open to some criticism, in that he has apparently taken separate samples for the analysis of each component in his equilibrium mixture. Although this should not cause any error as far as the liquid analyses are concerned, it could have considerable bearing on the wet solid analyses which need not necessarily be identical unless dried to a homogeneous consistency.

Most of the workers up until this stage assumed that the formula of the hydrate would be in terms of simple integral numbers of molecules. More recent studies on the nature of clathrate compounds, and , in this case, X-ray examination of the gas hydrates, have shown that this assumption is erroneous. This is reviewed by Cramer (67) and Powell (68).

Major discussions along these lines have been put forward by M. von Stackelberg and coworkers and Clausen. A series of papers have been published by both of these authors on the general problem of the number of voids in an ice lattice which may or may not be filled depending in the size of the gas molecules.

Stackelberg and Muller (69) at first proposed two distinct structures for the gas hydrates. The one associated with bromine hydrate was thought to have a unit cell of forty eight water molecules and eight voids giving a formula of $Br_2 6H_2O$. Their structures were cubic.

Clausen (70) followed with a structure based on the body centred cube. Each unit cell contained forty six water molecules and contained six medium sized voids, which were fourteen-faced holes, and two small voids. For molecules filling only the medium sized voids this gave a ratio of 46/6 or 7 2/3 water molecules per gas molecule. He suggested that this case would include bromine.

This was later confirmed by Stackelberg and Muller (71). It was also in agreement with their experimental evidence which gave the analytical figure $Br_2 7.9 \pm 0.5H_2O$ from heat of formation data (72).

This result may be contrasted with their figure for chlorine hydrate which was Cl_2 6.0 H_2O which they assumed corresponded to 96% filling of the holes. Later work by Pauling and Marsh (73) using X-ray methods, but under about four atmospheres pressure, gave the result $6Cl_2\overset{46}{}H_2O$ or Cl_2 7 2/3 H_2O.

Another alternative proposition is given by Allen and Jeffrey (76) who have completed an X-ray investigation of bromine hydrate and conclude that it is tetragonal and not cubic, having a formula of Br_2 8.6 H_2O. By analogy with e.g. the tetra n butyl ammonium salt hydrates, which show a variety of crystal structures in the host lattice, they propose that there may also be a variety of structures of an ice lattice which will accommodate varying amounts of bromine hence giving different values for the hydrate.

Statistical mechanics has also been brought to bear on this general subject although nothing conclusive, on the specific examples in question here have been evolved. The most useful work in this field has been that of Barrer and Stuart (70) who considered the unit cell under discussion here, with the differing sizes of cavity. By comparing theoretical and experimental thermodynamic data and from dissociation pressures they were able to propose formulae and equilibrium conditions for a variety of gas hydrates.

EXPERIMENTAL AND CONCLUSIONS.

Initially it was proposed to attack the bromine hydrate problem using the ammonium bromide, bromine, water system. It was hoped that this would lead to an unambiguous result on account of there being a reasonable solubility arc, also reliable analytical figures could be readily obtained. The most consistent point of intersection in the ammonium bromide system was the point corresponding to 54.5% bromine, 2% ammonium bromide and 43.5% water.

Although this percentage of ammonium bromide is low it is outside the limit of experimental error and some explanation of this irregularity was necessary after the various possible sources of error had been investigated with no avail. This has been described in chapter 3.

On a molar ratio basis the formula given by the above percentage corresponds to $Br_2 7H_2O$ 0.06 NH_4Br and extrapolation away from NH_4Br, assuming this to be present as such, was close to the theoretical value for the heptahydrate. Although the diagram shows that neither anhydrous ammonium bromide or tribromide exist in true equilibrium with the bromine hydrate, it is perhaps more likely that any ammonium bromide would be present as the polybromide in the presence of a relatively high concentration of halogen. Calculation involving the subtraction of the stoichiometric quantity of bromine led to the formula Br_2 7.55 H_2O 0.06 NH_4Br_3. This may be taken as evidence in favour of the formula proposed by Stackelberg namely Br_2 7.67 H_2O.

In the corresponding sodium bromide system only three points were obtained on the hydrate of bromine. The mean point of intersection with the base line was at 54% bromine (actual figures 52.0%, 55.0%, 54.5%). This also corresponds roughly to the point Br_2 7 2/3 H_2O which contains 53.6% bromine. In the case of lithium bromide the bromine hydrate section of the figure was not treated in any detail but the three points here indicated a more probable figure of Br_2 10 H_2O.

It has been mentioned that the potassium bromide-bromine-water system has been studied both by Zernicke and Harris in connection with the formulation of bromine hydrate. The mathematical treatment described in the appendix has been applied to the results of both these workers. The overall result from Harris' figures gave the values $47.05 \pm 0.02\%$ Br_2 and $52.96 \pm 0.01\%$ H_2O whilst Zernickes figures gave $54.30 \pm 0.08\%$ Br_2 and $45.40 \pm 0.05\%$ H_2O. The results of each of these workers could be treated as two separate sets, one at the water rich end of the diagram and the other at the bromine rich end. Although this meant a statistical method was being applied to sets of four results, it was useful to show that each worker did in fact have unique results. The figures obtained were as follows, the first figures for each worker being those at the water rich end of the system.

	Bromine	Water
Harris 1	47.20 ± 0.04	52.85 ± 0.03
Harris 2	46.80 ± 0.02	53.03 ± 0.01
Zernicke 1	53.39 ± 0.77	46.15 ± 0.67
Zernicke 2	54.53 ± 0.23	45.32 ± 0.06

It is noteworthy that the solubility arc for the solubility of bromine in aqueous potassium bromide was the same in both sets of results even though the solid phases were different.

A brief investigation of the potassium bromide system also yielded the same solubility arc but the best intersection was approximately 50% bromine which did not give any proof one way or the other but merely added to the existing confusion. As this was not considered to be a major part of the present investigation, and could perhaps be an entire investigation on its own, it was not treated in any further detail.

From the figures that have been obtained, and in the light of the existing knowledge based on crystal structure it would perhaps appear most probable that the formula Br_2 7 2/3 H_2O would be the formula for this compound. It is interesting to note the difference in results obtained for chlorine hydrate at atmospheric pressure and at four atmospheres. This could quite well mean that conditions under which the hydrate is formed will have considerable bearing on the actual result obtained and perhaps the figure Br_2 10 H_2O is obtained under specific conditions which entail the partial filling of the voids in the ice lattice. At high pressures it may perhaps be possible that the bromine molecule could be forced into the smaller voids giving formulae up to Br_2 $5\frac{3}{4}$ H_2O or $8Br_2$ 46 H_2O.

It is also apparent that the solid contains more bromine as the initial bromine concentration increases. This is particularly the case with Zernickes results. This observation is in accord with the idea that hydrate which is formed is a function of the initial conditions and hence the number of voids in the ice lattice which are filled. Bromine hydrate as described to date is therefore not in true stable thermodynamic equilibrium with the bromine rich mother liquor.

In compounds, it is well known that the crystallization of e.g. quinol from methanol under a pressure of xenon causes the crystals to retain xenon in the crystal "cages". The solid can be dried at room temperature and pressure without losing the xenon which can however be liberated on redissolving the quinol. Once formed these crystals are stable in the sense that although true equilibrium has not been attained, the rate of change, e.g. loss of xenon, is immeasurably slow.

Similarly in the gas hydrate system already investigated it is found that the presence of an indifferent gas (or hilfsgase) stabilises the hydrate thus bromine hydrate decomposes at 6.2° under its own vapour pressure but is stable to 20° under 150 atm. of hydrogen (77).

In view of these variable factors it seems probable that in the crystals of $Br_2 \, x \, H_2O$, the value of x may depend on any of the following factors, namely the concentration of bromine at the time of crystallization, the temperature or degree of supercooling at crystallization or the pressure over the equilibrium mixture. These are factors involved in the technique of obtaining the hydrate and would vary with the experimenter.

It would appear that the determination of the formula of bromine hydrate could involve quite a large scale investigation. There are several ways of approaching this problem. Following the present investigation it should be possible to pick a suitable 3 component system to give the hydrate. Both ammonium and potassium bromides have reasonably long solubility arcs and should be adaptable to the full scale investigation. Caesium bromide as used by Harris has the added advantage that the composition can be approached from both sides of the diagram, i.e. an arc also extends back from the bromine rich segment of the diagram. A careful investigation of the possible techniques for initiating crystallization would be required and the effect of pressure or bromine concentration would also be of interest.

Alkaline earth bromides may also be useful in this investigation.

As well as the 3 component systems a complete investigation of the binary system Br_2/H_2O under different constraints would possibly yield some interesting information. The use of an inert indicator to determine the residual mother liquor on partially or almost completely dried solid may be useful in this type of investigation. This is in effect the role played by the alkali bromide in the 3 component systems but there is a greater possibility in these systems that there may be some undesirable factors involved such as competition with the bromine, for the water sites, by the alkali halide molecules. Stackelberg proposes several indirect methods of studying these hydrates namely Schreinemakers methods, thermal analysis, comparison of X-ray and pycnometric densities and change of volume of unbound water on freezing (72). Linked with this are the more direct methods e.g. determination of the heat of formation of the hydrates.

The melting point of the hydrate appears to be in the region 5° to 6° C. It would probably be very useful in this case to allow solutions of the required composition to cool slowly from room temperature down to about 0° C. The main problem here would most likely be supersaturation, but with constant agitation and seeding at regular intervals a product may be obtained which would more likely be at equilibrium with the mother liquor. It is however possible that the nature of the seed crystal and the initial solid deposited would tend to influence the hydrate obtained. To overcome this a type of fractional crystallization approach with decreasing temperature may be more satisfactory, A closed system would be essential in this case to prevent the loss of bromine.

A further possible approach is suggested by Barrer and Stuart, where they quote a critical pressure of formation of the hydrate and give a value of 42 mm. at 0^{o} C for bromine. They also state that true equilibrium can only be reached in the 3 phase region clathrate, ice and gaseous reactants. It is also noteworthy that they also propose the occlusion of air in the clathrate phase to give a mixed hydrate. It was in fact observed that on allowing a sample of hydrate to warm up slowly a considerable quantity of gas is usually evolved, this could then be air occluded in the solid phase and it may therefore be necessary to prevent this as far as possible.

Any of these methods may still give solids which are not in true equilibrium states i.e. once a particular solid is formed it ceases to be a reversible system slowly approaching equilibrium. This sort of behaviour is exemplified by the xenon compound of quinol described by Powell. In the bromine hydrate systems, solutions have been cooled to a supersaturated condition and then the crystalline material has been allowed to stand for a few weeks to reach "equilibrium". The actual hydrate produced could then be a function of the conditions at the moment of crystallization and hence be independent of the equilibrium state. It is perhaps significant that the X-ray analyses have apparently been on samples prepared from a binary system i.e. by cooling bromine and water in appropriate proportions. In a solid of this type, where we are considering the inclusion of molecular species in a crystal lattice it may be highly undesirable to have components present other than bromine and water.

Chapter 8

SOLVENT EFFECTS AND ABSORPTION SPECTRA

INTRODUCTION.

It has been shown that solvation and in particular hydration, plays an important part in the stabilisation of the polyhalides of the smaller alkali cations. Removal of solvent causes decomposition into the halide ion plus halogen. The water molecules are almost certainly associated with the cation in the hydrated compounds. It would then seem reasonable to expect other polar solvents to stabilise the polyhalide anion by a similar mechanism. Dawson (78) investigated nitromethane, nitropentane, o,m nitro toluenes, o nitro anisole, trichloronitromethane and nitrobenzene and was able to isolate some crystalline solvated polyiodides. He was also able to show an increase in the mutual solubility of halide and halogen on mixing which was also indicative of polyhalide formation. Martin (32) showed the same phenomenon in benzonitrile.

It was thought useful to extend the range of solvents, in the aromatic and aliphatic series and to see if any non polar solvents would form polyhalides. It has been shown by Grace, for example, that benzene will form a solvated polyhalide (34).

In addition to this the nature of the polyhalide ion in solution has not been studied in much detail. X-ray studies on solid unsolvated polyiodides have shown that the higher members of the series e.g. I_7^-, I_9^-, are made up of aggregates of I_3^- ions and I_2 molecules, the bonds being slightly different than normal I-I bonds (79,80). It is possible that these weak bonds would be broken in solution into the fundamental I_3^- and I_2 units.

Spectrophotometric studies on the $I_3^- \rightleftharpoons I^- + I_2$ equilibrium in dilute solution have indicated that the higher polyiodides do not exist in solutions containing univalent cations. The tetramethylammonium and potassium tri-iodides have been investigated in ethylene dichloride and aqueous solutions respectively (123,105) the spectra showing maxima corresponding to both I_3^- and I_2. As the I_2 concentration increases the I_2 peak increases in intensity but little change is seen in the I_3^- peak. Conductometric studies on the other hand, in acetonitrile were interpreted to indicate that I_5^- exists in solution above 10^{-2} M (106). The conductometric work is at a higher concentration than the spectrophotometric work and it would seem appropriate to attempt spectrophotometric work at a variety of concentrations and I_2: I^- ratios.

Although not entirely relevant to solution spectra, as part of the spectral studies, it is also useful to consider the vibrational spectra of the triodide ions.

In all cases the potassium iodide/iodine mixtures have been used for spectrophotometric work and sodium iodide has also been used in solubility studies. Conclusions based on these systems should be typical of the polyhalides of the univalent cations. A recent report, along similar lines, by Gorelov and Serebrennikov (119)indicates that cations in higher valency states will form higher polyiodides in aqueous solution. They show absorption maxima corresponding to a 1:1 complex between I^- & I_2 for the alkali metal and ammonium ions, 1:2 for beryllium, magnesium, calcium, strontium and barium, 1:3 for a variety of rare earth metal ions and aluminium and 1:9 for the hexammine cobalt III ion.

EXPERIMENTAL AND RESULTS

The experimental work is in four main sections and these are perhaps best treated separately.

a) The effect of I_2 on the solubility of I^- was tested for a number of solvents. As part of this investigation the sodium polyiodide in nitrobenzene was prepared and analysed to confirm the proposed formula given by Dawson.

b) The absorption spectra of I^-, I_2 and mixtures of I_2 and I^- were taken in a number of solvents to demonstrate the formation of a polyiodide, confirming the results in the previous section.

c) The effect on the absorption, on changing the concentration of I_2 and KI in aqueous solution was determined.

d) The infra-red absorption of the triiodide ion was investigated.

(a) Solubility Studies

The formation of polyhalides in solution can be demonstrated qualitatively by determining whether there is any increase in the solubility of the halide in the presence of halogen (78,32). This technique has also been used in conjunction with solvent extraction studies in studying the extraction of caesium from aqueous solutions as a polyiodide in nitrobenzene (107).

The solvents investigated were nitromethane, nitropropane, nitrobenzene, acetonitrile, benzonitrile, otoluonitrile, benzene, dioxane, toluene, cyclohexane, n hexane, chlorobenzene, iodobenzene, thiophene, formamide, dimethyl formamide and dimethyl sulphoxide.

The halides used were sodium and potassium iodides. These are virtually insoluble in all the above solvents. Two solutions were saturated with respect to iodide and iodine and the saturation concentrations at room temperature were determined. A third solution was then saturated with respect to both iodide and iodine and the mother liquor was analysed. In the former cases standard sodium thiosulphate and silver nitrate analyses were used. In the latter case weighed samples of mother liquor were taken, using a filter pipette as described in earlier chapters. The iodine was then determined by adding excess water and titrating with sodium thiosulphate. For the iodide the samples were allowed to evaporate to dryness to remove the solvent, water being added in the case of the more steam volatile solvents. The iodine was also removed by further gentle heating and the iodide residue was then weighed.

As anticipated the solvents were in two classes. The nonpolar or weakly polar solvents, namely benzene, toluene, chlorobenzene, iodobenzene, dioxan, n hexane and cyclohexane, showed little or no increase in the solubility of iodide or iodine. The polar solvents however showed an appreciable increase in the solubility of the two components. Although benzene showed no marked solvent effect a small quantity of needle like crystals were obtained on evaporation. Cyclohexane also gave dark shiny crystals on evaporation but these were found to be elemental iodine.

Of the polar solvents thiophene, formamide, dimethyl formamide and dimethyl sulphoxide were unsuitable for this type of study as they can react chemically with iodine, especially under these conditions of high iodine concentrations.

Dawsons Sodium Polyiodide

As part of this project the sodium polyiodide which can be crystallised from nitrobenzene was prepared and analysed, as Dawson had not rigorously checked its composition. It was dried by draining on a porous plate in a desiccator over iodine and nitrobenzene. Phosphorus pentoxide was found to remove the solvent leaving powdered [illegible] sodium iodide and iodine. The dried material melted at 43°C. Analysis by titration of a weighed sample with ammonium thiosulphate, followed by evaporation and treatment with nitric and sulphuric acids to form sodium sulphate gave analytical results as follows:

	% Na I	$\%I_2$
Found	16.4, 16.6	55.5,56.0,55.2
Calculated	16.6	56.0

The calculated values are given for NaI_5, $2C_6H_5NO_2$.

(b) Absorption Spectra in Organic Solvents

Although solubility measurements of the type described give an indication as to whether or not a polyiodide is formed in a particular solvent it is perhaps more conclusive to measure the absorption spectra of these solutions.

In this connection the bands to be investigated are the I_3^- bands at 34,800 and 28,400cm $^{-1}$ and the I_2band at 21,800 cm^{-1}.

A 5ml sample of each of the above solvents was saturated with respect to potassium iodide. To a second similar sample, iodine was added to give a solution of approximately 10^{-4}M concentration. The absorption spectra were taken of 2 ml aliquots diluted 1:1 with solvent.

A third spectrum was taken of a solution prepared by taking equal volumes of the original iodide and iodine solutions.

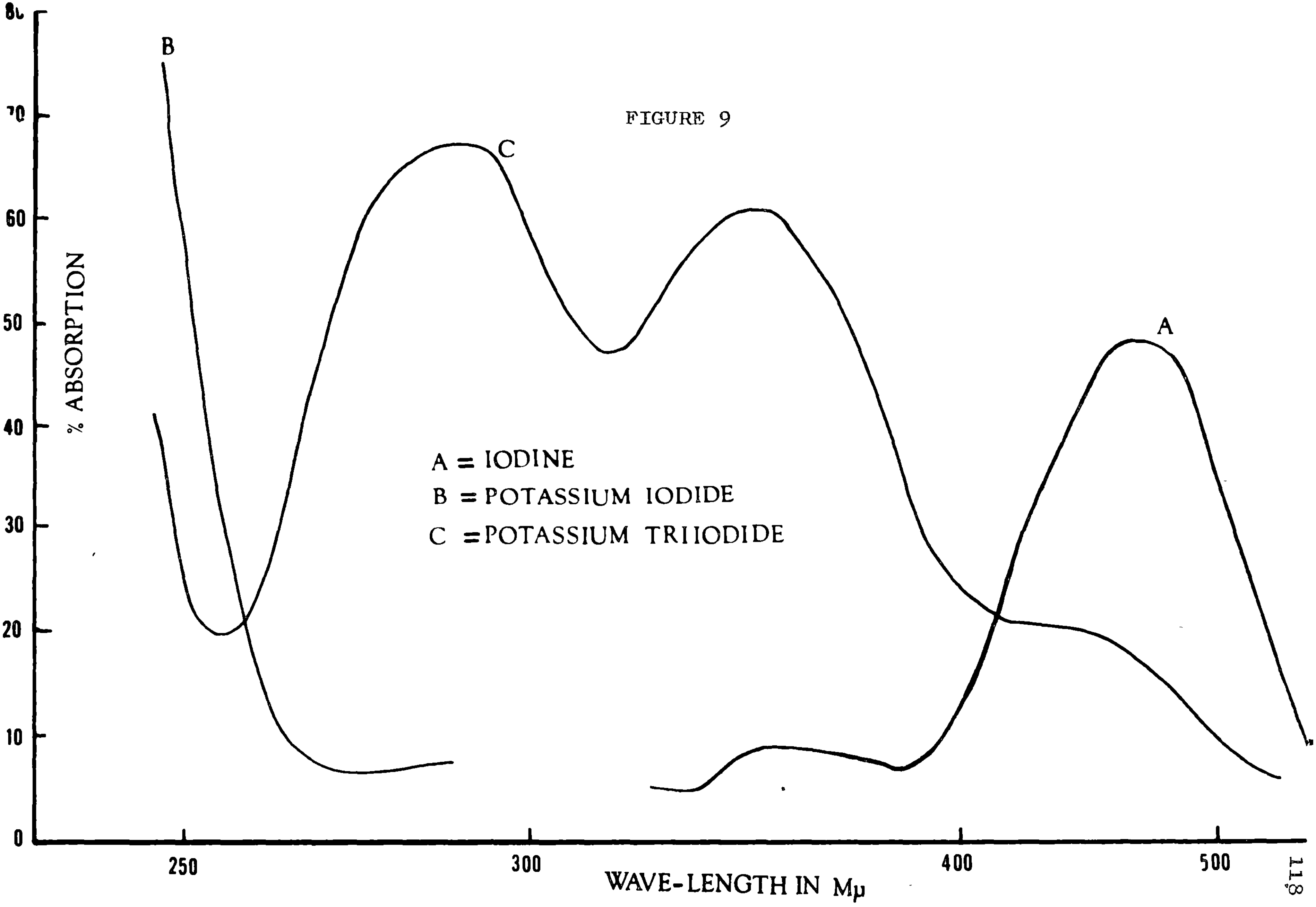


FIGURE 9

% ABSORPTION
80
70
60
50
40
30
20
10
0
250
300
400
500
WAVE-LENGTH IN Mμ
A
B
C
A = IODINE
B = POTASSIUM IODIDE
C = POTASSIUM TRIIODIDE

Measurements were made in 1cm suprasil cells on a Unicam SP700 recording spectrophotometer over the range 40,000 - 20,000 cm^{-1} i.e. 2500-5000°A. This borders on the strong iodide absorption at about 38,000 cm^{-1} and covers the polyiodide peaks at 34,800 and 28,400 cm^{-1} and the iodine peak at 21,800 cm^{-1}. Some of the solvents e.g. iodobenzene also absorbed strongly in this region. In these cases the samples were diluted with a hydrocarbon solvent e.g. cyclohexane. The spectra obtained are typified by those shown in figure 39, for aqueous solutions of potassium iodide, iodine and KI. In all cases of polar solvents the polyiodide peaks were observed. The non-polar solvents, which give the characteristic violet solutions, showed only the iodine peak. Benzene and dioxane showed an additional band at about 34,000cm^{-1} but this is due to the 1:1 charge transfer complex between the solvent and iodine. The polar solvents show the iodine band until the iodide is added. This does not disappear completely but the intensity is markedly reduced.

(d) Polyiodides In Aqueous Solution

The purpose of the preceding two sections has been to demonstrate that polyiodides exist in solution as such i.e. they are not completely dissociated into iodide and iodine. The complexity of the anion has not been determined by any of these investigations. As mentioned in the introduction some spectrophotometric work along these lines has been done, showing that the triodide ion is the stable species in solution containing a univalent cation. Similar investigations with higher valency cations have shown that higher polyiodides may exist under these conditions. Solubility and partition studies on aqueous rare earth metals iodide, iodine solutions (108,109) also indicate that polyiodides exist in these cases.

Prior to the publication, in translation, of the work of Gorelov and Serebrennikov (119) a series of experiments were performed, in dilute solution, to determine the nature of the absorption peaks in the polyhalide solutions. A stock potassium iodide solution (10^{-2}M) was prepared and iodine was added to 10ml portions of this to make solutions approximately I_3^-, I_5^-, & I_7^- & I_9^-. A saturated iodine solution was also prepared. The iodine would not dissolve completely in the I_9^- solution and analysis showed this to approximate to a stoichiometry of $I_{8.3}^-$ These solutions were diluted to about 10^{-4}M.

The type of spectrum obtained is shown in figure 11. Increase of the iodine concentration significantly increased the iodine absorption but not the I_3^- peaks as demonstrated by the Russian workers. Polyvalent cations were not included in this treatment. In order to demonstrate more clearly that the iodine peak was more pronounced in the polyiodide solutions of stoichiometry higher than I_3^- the spectra were re run using the I_3^- solution as reference. In these cases the 22,000 cm^{-1} iodine absorption was very marked.

Although the spectra of the dilute solutions showed that I_3^- was apparently the only stable polyiodide in these solutions it did not prove the non-existence of the higher polyiodides at all concentrations. It was preferable to take the spectra of the mother liquor from which the higher polyiodides could crystallise as dilution would tend to facilitate the dissociation reaction.

The potassium polyiodide ternary diagram of Grace was taken to ascertain the desirable regions to obtain spectra. It was found that by taking a value of 48% I_2 by weight and 17-24% KI in 1% steps, the solid polyiodide region could be traversed and the I_2: KI ratios were such that the extremes were outside the region of formation of the KI_3 & KI_7 hydrates.

These solutions were shaken in stoppered weighing bottles and sampled at the end of one week. The mother liquors were dark opaque liquids and could not be placed in the conventional cells. Variable path length cells were also unsuitable due to the absorption of the iodine into the teflon washers. A special holder for two suprasil discs was constructed. These discs were 25 mm diameter. The holder fitted into the instrument window retaining ring and had an annular slot to hold the discs. A small drop of mother liquor was taken and pressed between the plates until a very thin film (approximately 10 microns) was formed. The two windows were held together by surface tension and no further clamping was necessary. Air was used in the reference beam. Spectra were run on all the solutions. The same peaks as before were observed although the iodine peak was more in evidence in the samples approximating a KI_3 composition.

Since these peaks lie on the borderline between the quartz and glass regions several series of runs were made using microscope cover slips as cells. These were light and were taped onto the instrument window retaining rings. By this method the low iodine samples could be used in the reference beam for the spectra of the higher concentration solutions.

Only qualitative results could be obtained by this technique as it is extremely difficult to produce films of equal thickness, and in the case of the cover slips it was impossible to get an even thickness over the full cell area due to distortion of the thin glass plates. Sufficient information was obtained however to show that even in these solutions only I_3^- & I_2 peaks could be observed.

Vibrational Spectra

X-ray crystallographic studies of the polyiodides show that in general the iodine-iodine bonds are not all equivalent. Infra-red and Raman studies may then also be used to gain some information on the bonding in the polyhalide. In theory this could be done both in the solid and in solution but practical difficulties would possibly make solution spectra difficult. Stammreich and coworkers have studied ICl_2^-, $BrCl_2^-$, Br_3^- and ICl_4^-, by infra-red and Raman methods and conclude that the results are in accord with a molecular orbital description of the bonding using p orbitals (110). This will be discussed in detail in the next chapter.

The spectra of the above ions were taken in the solid state as nujol mulls and in nitrobenzene solution. Acetonitrile and chlorbenzene were transparent in the appropriate spectral region but the former was too volatile and the polyhalides were insoluble in the latter. The tribromide was the tetrabutyl ammonium compound. The triiodide ion was not studied although mention was made of this in a study of the spectra of diatomic interhalogens and the halogens. A band at 112.3 cm^{-1} in pyridine solution was assigned to I_3^-.

Iodine shows a Raman active absorption at 213cm^{-1}.If it were assumed that I_3^- consists of an iodine molecule associated, by a weak polar interaction, with an iodide ion then it might be expected that a polyiodide absorption would be observed at about this frequency. Some spectra on CsI_3 in nujol were run on a Beckman IR7 spectrometer between 200-600cm^{-1}. Polythene films and KRS5 plates were used for cells. No significant absorption was observed. The frequency range could not be extended below 200 cm^{-1}. Pressed discs may have been more useful in this case but facilities were not available to make these.

As it was not possible to actually observe spectra it was of interest to attempt to predict spectra and in particular to predict any changes in spectra as the configuration of the anion is changed. To do this it is first of all necessary to obtain stretching force constants K1, K2 and the interaction force constant K3. Badgers' rule (111) can be used to estimate K1 and K2, using the relationship $K^{1/3} = \frac{C_{ij}^{\ 1/3}}{(r_e - d_{ij})}$,where r_e is the equilibrium internuclar distance in Å, K is the force constant in megadyne/cm and C_{ij}, d_{ij} are constants related to the position of atoms i and j in the periodic table. For both i and j in the fourth row, as is the case of iodine atoms, then $(C_{ij})^{1/3} = 0.49$ and $d_{ij} = 1.76$ Å. Calculations can be made for the cases of CsI_3 and $As\phi_4I_3$ where the interatomic distances are 2.83Å and 3.04Å for CsI_3 and 2.90Å for each bond in $AS\phi_4I_3$. i.e. tetraphenyl arsonium triiodide. The values obtained are

K1 (2.83Å) = 0.960 md/A°

K2 (3.04Å) = 0.561 "

K1,K2(2.90Å) = 0.794 "

The interaction force constant K3 has to be assumed. Stammreich has published values of 0.36 for ICI_2^-, 0.26 for $BrCl_2^-$ 0.32 for Br_3^-. A value of 0.3 md/Å was therefore used in these calculations as there was no justification for going beyond one significant figure and these figures are all of the order of 0.3 md/Å.

It is then possible to solve the F,G matrix (112,116).

$$\left| F - G^{-1}\lambda \right| = 0$$

where $\lambda = 4\pi^2\nu^2$, ν being the frequency (cm^{-1}) and

$$F = \begin{vmatrix} K1 + K3 & K3 \\ K3 & K2 \end{vmatrix} \text{ and } G = \begin{vmatrix} 2u & -u \\ -u & 2u \end{vmatrix}$$

where u is the reciprocal mass of the iodine atom for the symmetric and asymmetric stretches.

The predicted frequencies are then

CsI_3	157 cm^{-1}	127 cm^{-1}
$AS\phi_4I_3$	166 cm^{-1}	122 cm^{-1}

It is obvious from these figures that the spectra would be well outside the range of the IR7. These values seem reasonable when considering the figure of 110 cm^{-1} assigned by Stammreich to I_3^-. Spectra of I_2 bonded by charge transfer are also reported in the region of 180 - 200 cm^{-1}

for benzene, pyridine and trimethylamine (112). An I-I force constant, for a 2.83 Å bond, of 0.952 md/Å was proposed in the latter case.

It would have been useful to have had a more reliable figure for the interaction force constant. A private communication with Stammreich indicated that although the totally symmetric frequency is about 110 cm^{-1} it would be meaningless to calculate an interaction force constant at present, from the Raman active mode. Some preliminary spectroscopic work by his group would indicate that intermolecular forces are important as the observed frequencies are strongly dependent on the cation and the nature of the solvent.

Conclusion:

The role of solvent in polyhalide formation is interesting on account of the variety of observed effects. The most obvious role is in solvation of the smaller cations. In these cases presumably the ionic radius of the cation is too small or, as a consequence of this, the surface charge density is too great to permit a stable unsolvated polyhalide to form.

Solvation of ions, especially cation, by polar solvents is well known. It is not surprising that the non-polar solvents are not associated with stable polyhalides as they are unable to form a solvation sheath around the cation. Polyhalide ions could also be strongly polarised by the solvents acting as Lewis bases. This would account for the fact that the polyhalides are much more soluble and are stronger electrolytes than the simple halides.

Benzene solvated polyiodides are probably partly formed by this sort of mechanism. Benzene is well known for its interaction with iodine to form a 1:1 complex, the benzene acting as a Lewis base and donating electrons to the iodine. The polar entity which is produced would then be capable of inducing polyiodide formation. The stability of the solid benzene polyiodides could also arise from the space filling of holes in the polyiodide lattice by benzene molecules. The benzene is weakly held as these compounds have low melting points and a relatively high vapour pressure of benzene (approximately 50 mm. at 25°C compared with 100 mm for pure benzene at 26°C)

Stable polyhalides have only been reported from aqueous or aromatic solvent solution. The polar aliphatics with a comparable number of carbon atoms do however show spectral evidence for the triiodide ion being formed in solution. The non polar or weakly polar solvents on the other hand show no spectral evidence for polyiodides. It is interesting that toluene or cyclohexane will not behave in a similar manner to benzene which would indicate more than just a space filling property causing the latter to form polyiodides.

The behaviour of the solvent opens up an interesting field for structural investigations to determine the type of solvation. Substituted cyclohexanes, especially nitro and nitrilo substituents would give information on whether the puckered ring is likely to affect polyhalide stability. This would also be interesting when compared with the case of o nitro toluene which forms a solid polyiodide whilst toluene itself will not.

A mixed solvent system e.g. benzene/nitrobenzene would also be interesting in determining whether a polyhalide solvated with a "large" solvent molecule is able to incorporate a "space filler" in its lattice. Mixed solvents would however bring in analytical difficulties.

The observation of Martin (26) that no polyiodides in benzonitrile are formed by Rb^+, Cs^+, NH_4^+ whilst they are formed with H^+, Li^+, Na^+ and K^+ would support the idea that the smaller cations must solvate to form a polyhalide whilst the larger cations are already of sufficient magnitude. The benzene solvated polyiodides of Rb and Cs do not invalidate this argument as the polyiodides in these cases are hepta and ennea iodides which would require larger cations.

In solution it would appear that the polyhalides of the univalent cations are readily dissociated into the simple triiodide and iodine. Other methods of testing this point would be the application of infra-red analysis around the 100-200 cm^{-1}, region where any interactions between I^- and I_2 and I_3^- and I_2 etc. should be detected if they are of any significance. Similarly the application of N.M.R. may be a powerful tool in this regard although it is likely that the iodide signal would be too broad to detect any shifts due to polyiodides (117).

In the case of stable solids, x-ray analysis would give considerable useful information on the role of the solvent. Unfortunately nothing has been done along these lines, probably because of the nature of the solid that is produced.

CHAPTER 9

ELECTRONIC STRUCTURE AND GEOMETRY OF THE TRIIODIDE ION.

INTRODUCTION.

In Chapter 1 reference was made to the large variety of polyhalide anions which have been described in the literature. From a study of these it is possible to draw the qualitative conclusion that the stability of a polyhalide compound depends on the relative sizes of the cation and anion, the stability increasing with increasing cation size. Solvation also has a stabilising influence on those compounds which can incorporate solvent, possibly as cationic solvation, into their crystal lattice. In order to gain a more quantitative understanding of the polyhalides it is of interest to investigate the nature of the actual bonding in these anions.

There is a considerable amount of discussion in the literature on the bonding in the polyhalides and interhalogens. This has been reviewed and extended by Havinga and coworkers (79-81). To summarize this briefly there are three possible approaches which may be used. The first, and simplest, proposal was the electrostatic interaction between a halide anion and one or more halogen molecules (81-83). This model gives an asymmetric anion and it is difficult to explain a symmetric triiodide ion or an interhalogen compound on this approach. Difficulties arise with some of the mixed polyhalides.

An alternative is that the halogens, other than fluorine make use of hybrid orbitals composed of s, p and d orbitals of the valence shell to form more than one bond around a halogen atom. Objections have been raised against the use of high energy d orbitals (81, 96) in e.g. ICl_4^- where a square planar configuration could arise from p^2d^2 hybrids on the central iodine or sp^3d^2 hybrids, the trans positions being taken up by lone pairs. The use of d orbitals is also unlikely on considering the results of nuclear quadrupole coupling experiments (87) and Raman spectra (85) of the chloroiodides.

The third alternative is that the bonding involves the p orbitals of the valence shell in such a way that a row of three atoms share four valence electrons (81, 86, 87, 88). The three atoms of a triiodide ion are thus thought to be bonded by four valence electrons spread over the 5p σ orbitals of the three iodine atoms. Using this as a working hypothesis Havinga used a simple Hückel molecular orbital approach to interpret the structures of a number of polyhalide ions and interhalogens. This amounts to regarding the triiodide ion as a resonance hybrid of I^-.......I - I and I - I ......I^-, the overall structure being symmetrical with the two end iodines bearing formal charges of $-\frac{1}{2}$, i.e. $^{-\frac{1}{2}}\text{I} — \overset{0}{\text{I}} — \text{I}^{-\frac{1}{2}}$. A similar view has been discussed for the analogous system XeF_2 (89), Xenon being isoelectronic with the iodide ion.

The main objection to this approach is that the one obtains, in the case of triiodide, a centrosymmetric ion, whereas it has been shown, from X-ray analysis, that the anion in NH_4I_3 and CsI_3 is asymmetric but $As\emptyset_4I_3$ is symmetric, where $\emptyset$ is the phenyl radical. Havinga then went on to suggest that the asymmetry is due to an asymmetric electrostatic field about the anion in the crystal. In order to demonstrate this he considered a triiodide ion with a unit positive charge 4Å from one end and along the internuclear axis and was able to show that the bond orders were in accord with the observed geometry. Havinga was unable to relate bond orders and bond lengths in a quantitative manner but he was able to show a qualitative agreement. He was also unable to correct for the total electrostatic field in the crystal although his model system was a useful approximation for qualitative interpretation. By calculating the total electronic energies for the observed configurations of the ions and comparing this with alternative geometries and the energies of an isolated ion and halogen molecule he was also able to show that the observed structures were of the lowest energy.

Slater (104) and Mooney-Slater (100) have approached this problem from a slightly different view-point. They considered the triiodide ion as an association of iodide and iodine and were able to postulate, by analogy with H_3, that the energy of the triiodide ion shows two minima when the distance D_{13}, defined as the separation of the terminal iodine atoms, is greater than a critical value D_c, and only one minimum when D_{13} is less that D_c. The minima are symmetrical about the centre of the system. This means that for any D_{13} less than D_c there is then only one position for the central iodine and for D_{13} greater than D_c there are two possible positions. It is then proposed that D_{13} is greater than D_c in CsI_3 and less than or equal to D_c in $As\phi_4I_3$. It is difficult however to decide whether the "typical" configurations should be the symmetric or asymmetric form. This approach will only predict possible geometries based on an interatomic distance $D_{1,3}$ and does not consider electrostatic potential effects from the atoms in the crystal.

The aim of the work in this chapter was to extend the treatment of the triiodide ion. To do this a variable electronegativity self-consistent field (VESCF) approach was used to study the triiodide ion under the following conditions

(a) in vacuum i.e. no external electrostatic fields

(b) in both symmetric and asymmetric fields due to neighbouring cations

(c) in the actual crystal fields observed in CsI_3 and $As\phi_4I_3$

It was then hoped that it may be possible to predict the actual geometries of I_3^- ions by direct minimization of energy and to draw conclusions about the stability of the anion.

The triiodide ion is the only ion considered in these calculations as it is the only one where adequate X-ray data is available for both a symmetric and an asymmetric ion. It is also the basis unit in the other polyiodides and results obtained with this ion can readily be extended to other polyhalides.

METHOD

The method used and results obtained will be outlined in this chapter, detailed calculations will be given for a typical system in an appendix.

As a first approach the calculations of Havinga were checked to confirm his results using the simple Hückel treatment.

The VESCF method, used in the further studies of this ion, has been described in detail in the literature (90 - 94). The effective nuclear charge $Z\mu$ for the atomic orbital χ_μ is regarded as a function of the electron density at atom μ and thus various basic integrals, all dependent on $Z\mu$ become functions of the electron distribution. In this regard the VESCF method differs from the other self consistent field methods where constant values are taken. It is then possible to use an iterative procedure until self-consistent values are obtained for the bond order matrix and $Z\mu$.

Although the VESCF method has been applied mainly to π bond systems it can also be used to describe σ bonding, using the same type of expressions for the various integrals etc. This has been done for a number of A_2Y_4 systems e.g. N_2O_4, $C_2O_4^=$ (95).

The VESCF matrix elements are obtained from the expressions

$$F_{\mu\mu} = -I_\mu + \tfrac{1}{2}P_\mu\gamma_\mu + \sum_{\nu\neq\mu}(P_\nu - X_\nu)\gamma_{\mu\nu}$$

and $F_{\mu\nu} = \beta_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\gamma_{\mu\nu}$
where μ and ν refer to any two atoms in the ion.

I_μ is the valence state ionization potential of the iodine atom and refers to the process $I(S^2P^5)V_1 \rightarrow I^+(S^2P^4)V_0$.

I_μ may be regarded as a function of Z_μ, the effective nuclear charge, as the greater the total electronic charge around an atom the easier it will be to ionize an electron from it. The ground state ionization potentials for the isoelectronic series I, Xe^+, Cs^{++} are used to obtain a quadratic relationship between I_μ and Z_μ as described in the appendix, Z_μ for the iodine atom as obtained from Slater's Rules, is 7·60 e.v. (113).

Although Slater's rules are likely to be less reliable for orbitals of such a relatively high principal quantum number as iodine, then for say carbon, these calculations use the variation of Z_μ with net charge on the atom under consideration. The coefficient for the variation of Z_μ per valence electron is then the important quantity and this is virtually independent of the absolute value of Z_μ

The resulting plot is almost linear but can be more accurately expressed by the quadratic

$$I_\mu = 0{\cdot}133\ Z_\mu^2 + 5{\cdot}9397\ Z_\mu - 42{\cdot}368$$

P_μ is the σ electron density on atom μ and $P_{\mu\nu}$ is the σ electron bond order for the $\mu\nu$ bond.

X_ν is the core charge at atom ν with respect to σ electrons and is one for each iodine atom, $-(P_\nu - X_\nu)$ therefore represents the electronic charge on atom μ.

Neutral atom potentials are also neglected in this treatment (93, p. 555 method B) (i.e. the fields of the uncharged atoms).

The monocentric coulomb repulsion integral γ_μ, which is also dependent on Z_μ, is given by a Paoloni type formula (92) using the ionization potential (I) and electron affinity (A) of the neutral atom.

i.e. $I - A = k \times Z_\mu$ where $I = 10{\cdot}455$ e.v. and

$k = 0.923$ $A = 3{\cdot}44$ e.v.

From this $\gamma_\mu = 0{\cdot}923\ Z_\mu$

The two centre coulomb repulsion integral $\gamma_{\mu\nu}$ is given by the Mataga-Nishimoto formula (93, p.555 method J) where

$\gamma_{\mu\nu} = \dfrac{-14{\cdot}4}{r_{\mu\nu} + a_{\mu\nu}}$ ($r_{\mu\nu}$ is the interatomic distance in Å and $a_{\mu\nu}$ is constant, being fixed by the average of the monocentric coulomb repulsion integrals i.e. $\frac{1}{2}(\gamma_\mu + \gamma_\nu) = \dfrac{14{\cdot}4}{a_{\mu\nu}}$).

$\beta_{\mu\nu}$ is the core resonance integral. A variety of methods have been proposed, in the case of carbon and a few other atoms to estimate the variation of $\beta_{\mu\nu}$ with bond length (96) but no tabular data is available for atoms of high atomic number such as iodine. Since the bonds in CsI_3 are not of equal length it was essential to make some estimate of $\beta_{\mu\nu}$ for a variety of values of $r_{\mu\nu}$, the interatomic distance.

The published potential energy curve for the iodine molecule was used to obtain energies for the various appropriate interatomic distances (97). If the binding energy of this molecule is derived from the interaction of the $5p\sigma$ valence electrons then we have

$$E(r) = -2I_{\mu} + \frac{1}{2}\gamma_{\mu} - \frac{3}{2}\gamma_{\mu\nu} + 2\beta_{\mu\nu} + \frac{14{\cdot}4}{r_{\mu\nu}}$$

where $E_{(r)}$ is the potential energy in e.v. for an interatomic distance $r_{\mu\nu}$ Å, and all other quantities are as previously described. The evaluation of all the quantities other than $\beta_{\mu\nu}$ is possible and hence the value of this can be obtained.

The geometry of the triiodide ion is available from x-ray diffraction data for three crystals. These are CsI$_3$ (98), NH$_4$I$_3$ which was studied by Mooney in 1935 (99) and $(C_6H_5)_4AsI_3$ which was also studied by Mooney (100). The earlier NH$_4$I$_3$ paper is less reliable than the other two as estimates of errors are not known and the structure was based on an early investigation of CsI$_3$ by Bozorth and Pauling (101). Geometries as given in references 98 + 100 will therefore be used.

As a starting point in the VESCF calculations the bond order matrix as derived from a Havinga first approximation, has been used. This will be detailed in the appendix.

Although model systems, based on the known geometries of the triiodide ion, gave useful information on the variation of bond order with bond length for variable β, it was of prime interest to determine the effect of varying the external electrostatic field. This is included as part of the core field in the VESCF calculations. In the first place calculations, analogous to those of Havinga, were performed i.e. a cation was placed at one end of a triiodide ion and the effect of varying the cation to anion distance was determined. In addition to this a cation was placed at each end of the symmetric triiodide to see if there was any significant difference between this and the case of the anion in "vacuuo". Havinga studied bond order relationships in the absence of external fields and in the field of neighbouring cations at arbitrary distances from the anion, the treatment was then further extended so as to be more in line with the fields actually encountered in the crystals.

A net charge Qk for the kth external ion produces a coulomb potential for an electron in atomic orbital X_μ of $-14{\cdot}4\ Qk/R\mu k$ e.v.; $R\mu k$ being the relevant internuclear distance in Å. The surrounding ions thus produce a change in the core coulomb integral.

$$F_{\mu\mu} = -14{\cdot}4 \sum_{k} Qk/R\mu k \text{ e.v.}$$

It was found however that one had to be careful about how far one went from the central iodine atoms as the potential is inclined to fluctuate with the distance. To overcome this it is better to attempt to calculate the actual field as experienced by the separate iodine atoms in the actual crystal. Calculations of this type for the whole crystal are inclined to be lengthy for if we consider a unit charge and we require convergence to about 0·1 e.v. we need to include all the atoms in a sphere of about 100 Å radius.

Ewald (102) has however given a method for carrying out this type of summation so that convergence is attained more rapidly. In this method the potential ψ_i at atom i due to atoms l is given by

$$\psi_i = (4\pi/\Delta)\sum_G S(G)G^{-2}e^{-G^2/4\eta} - 2q_i(\eta/\pi)^{\frac{1}{2}} + \sum_l \frac{q_l}{r_l}F(\eta^{\frac{1}{2}}r_l)$$

where q_i and q_l are the charges on atoms i and l; r_l is the distance from atom l to the reference atom i. $F(\eta^{\frac{1}{2}}r_l)$ is an error function given by $F(x) = (2/\pi^{\frac{1}{2}})\int_x^{\infty} e^{-s^2}\,ds$. The constant η is chosen such that both summations converge rapidly and the final potential is independent of η. G is 2π times the vector from the origin to a lattice point in the reciprocal lattice of the crystal and $G^2 = 4\pi^2\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)$ where h, k, l are the Miller indices and a, b, c are the cell parameters in Å. S(G) is the structure factor, $S(G) = \sum_t q_t e^{-iG\cdot r_t}$, r_t being the reciprocal lattice vector, and q_t the charge on atom t.

Caesium triiodide is orthorhombic of symmetry Pmcn or C_{2v}^{16h} and has four molecules per unit cell. The structure factor then is of the form

$$S(G) = \sum_t q_t \cos 2\pi\left(\frac{hx}{a} + \frac{ky}{b} - \frac{h+k-l}{4}\right)\cos 2\pi\left(\frac{h+k-l}{4} + \frac{lz}{c}\right)$$

The details of one of these calculations will be included in the appendix. In practice the structure factor term is a constant at each iodine atom and consequently need not be considered in the VESCF treatment. This term was therefore omitted in the final calculations.

To calculate the total valence-electron energy of the triiodide ion as a function of the position of the nuclei the relationship given by Pople (103) was used. This is expressed as

$$E = \frac{1}{2} \sum_{\mu,\nu} P_{\mu\nu} \left(H_{\mu\nu} + F_{\mu\nu}\right) + \sum_{\mu<\nu} \frac{14.4}{r_{\mu\nu}}$$

where E is the total valence electron energy and the quantities $P_{\mu\nu}$, $F_{\mu\nu}$, $r_{\mu\nu}$ have been defined elsewhere.

whilst for $\nu \neq \mu$, $H_{\mu\nu} = \beta_{\mu\nu}$ and for

$$\nu = \mu, \quad H_{\mu\nu} = \alpha_{\mu\nu} = -I_{\mu} + \sum_{\nu\neq\mu} X_{\nu} \gamma_{\mu\nu}$$

The core charge X_{ν} is one for each iodine atom.

This is the same expression as was used in the calculation of β from the Morse curve.

Results and Discussion

From quite a large series of V.E.S.C.F. calculations on the triiodide ion for a variety of geometries and electrostatic fields, the main points to be discussed are the following:

a) The effect of the lattice field on the anion, as shown by a comparison of the results for the free ion and the ion in the crystal and the possibility of representing the ion in the crystal by a model consisting of cations placed along the interatomic axis of a linear anion.

b) The feasibility of using V.E.S.C.F. bond orders to establish a useful bond order: bond length relationship to predict and interpret observed geometries for other compounds containing an I - I bond.

c) The relationship between total energies and the observed geometries in the crystal.
d) Other implications of the total energies with respect to the properties of the triiodide anion and other polyatomic ions in crystals.

The results of the V.E.S.C.F. calculations on model systems consisting of a linear triiodide with cations at varying distances from the ends and using integral β values are listed in table 14 , in the appendix 2. These showed the desirability of using the calculated β values throughout the present studies as there was a small, but significant, dependance, of the final results, on the value of β.

Having established this, the effect of the external electrostatic field on the triiodide anion was determined by firstly considering the asymmetric anion in the influence of a zero field, in the influence of cations at 4,6,8 and 10Å from one end, in the field of the nearest neighbour ions of the crystal and in the actual crystal field. Following this a similar abbreviated series of calculations were carried out for the symmetric ion namely in zero field with cations at 4Å from each end and in the crystal. In addition to these, calculations were carried out to duplicate the crystal field by a simple model consisting of two cations at each end of the anion.

The results are listed in Table 9.

In this table the electronic charges at each iodine (Q_1, Q_2 and Q_3) and the bond orders P_{12}, P_{23}, are listed for a variety of fields for the two observed geometries. In the case of the asymmetric I_3^-, P_{12} refers to the 3.04 Å bond i.e. atom 1 has the higher negative charge.

3.04Å 2.83Å TABLE 9.

I_1 ——— I_2 ——— I_3

	A	B	C	D
Q_1	-0.451	-0.648	-0.560	-0.520
Q_2	-0.160	-0.112	-0.138	-0.148
Q_3	-0.389	-0.239	-0.302	-0.332
P_{12}	0.671	0.559	0.616	0.649
P_{23}	0.716	0.822	0.776	0.754

	E	F	G	H
Q_1	-0.499	-0.573	-0.910	-0.907
Q_2	-0.153	-0.153	0.709	0.711
Q_3	-0.349	-0.274	-0.800	-0.804
P_{12}	0.652	0.601	0.393	0.399
P_{23}	0.743	0.784	0.585	0.579

2.90Å 2.90Å

I_1 ——— I_2 ——— I_3

	I	J	K	L
Q_1	-0.421	-0.472	-0.823	-0.823
Q_2	-0.159	-0.056	0.646	0.647
Q_3	-0.800	-0.472	-0.823	-0.823
P_{12}	0.698	0.706	0.539	0.539
P_{23}	0.698	0.706	0.539	0.539

Column A refers to a zero external field
Column B " " a cation 4 Å from I_1
Column C " " a cation 6 Å " I_1
Column D " " a cation 8 Å " I_1
Column E " " a cation 10 Å " I_1
Column F " " the nearest neighbour field (100)
Column G " " calculated total field
Column I " " zero external field
Column J " " cations 4Å from each end
Column K " " calculated total field
Column H & L refer to cations placed so as to duplicate the crystal fields.

There are several important points to be noted from this table. Firstly it can be seen that the simple model as used by Havinga does not adequately describe the triiodide anion in a crystal. The fields, as used by Havinga, still gives a slight negative charge to the central iodine, but the crystal field leads to a positive charge on this atom. Havinga had no way of estimating the potential at the anion due to the crystal and could only assume that a value of 4Å was reasonable where this distance represents the sum of the ionic radii of the caesium and iodide ions.

The potential energy of an electron 4Å from a positive ion was related to the I - I binding energy in iodine (36K cal/mole) so that a correction could be made to the Coulomb integral. This series of results indicate however that the field effect is much greater than this and is in fact duplicated, in the case of the symmetric anion, by a cation at 1.08Å from each end of the ion and, in the case of the asymmetric anion, by a cation at about 0.98Å from I_1 and 1.05Å from I_3. It is also interesting, in the latter case, that it is necessary to consider cations at either end and not just one end, as was done by Havinga, especially aince in the crystal I_1 is surrounded by four near neighbour cations whilst the other two iodines have only two near neighbour cations. It is not however sufficient to consider just the nearest neighbours as is shown by column F for CsI_3. In this case the nearest neighbours as shown in Figure 10 were used to calculate the external fields.

The results in columns H and L also confirm the observation that the structure factor term may be omitted in the crystal field calculations. The diagonal F matrix

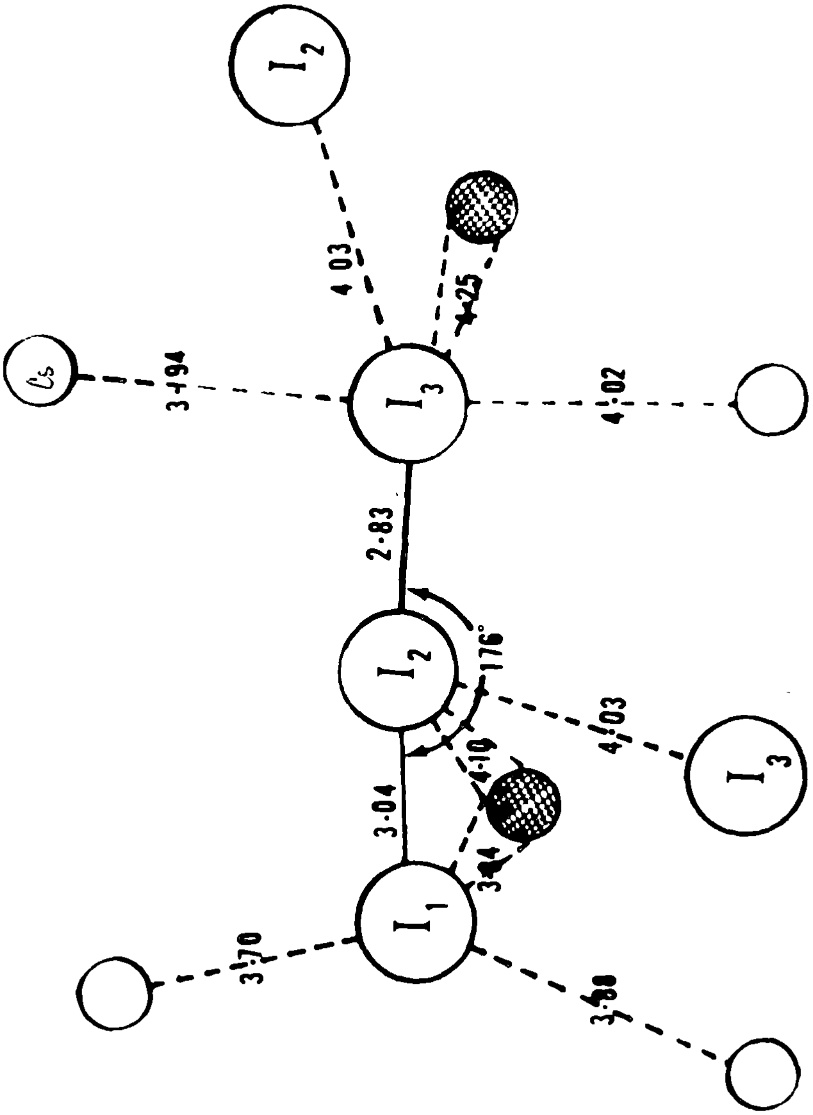

I_2
4·03
4·25
C_s
3·94
I_3
4·02
2·83
I_2
176°
4·03
I_3
3·04
4·10
3·44
I_1
3·70
3·88

FIGURE 10.

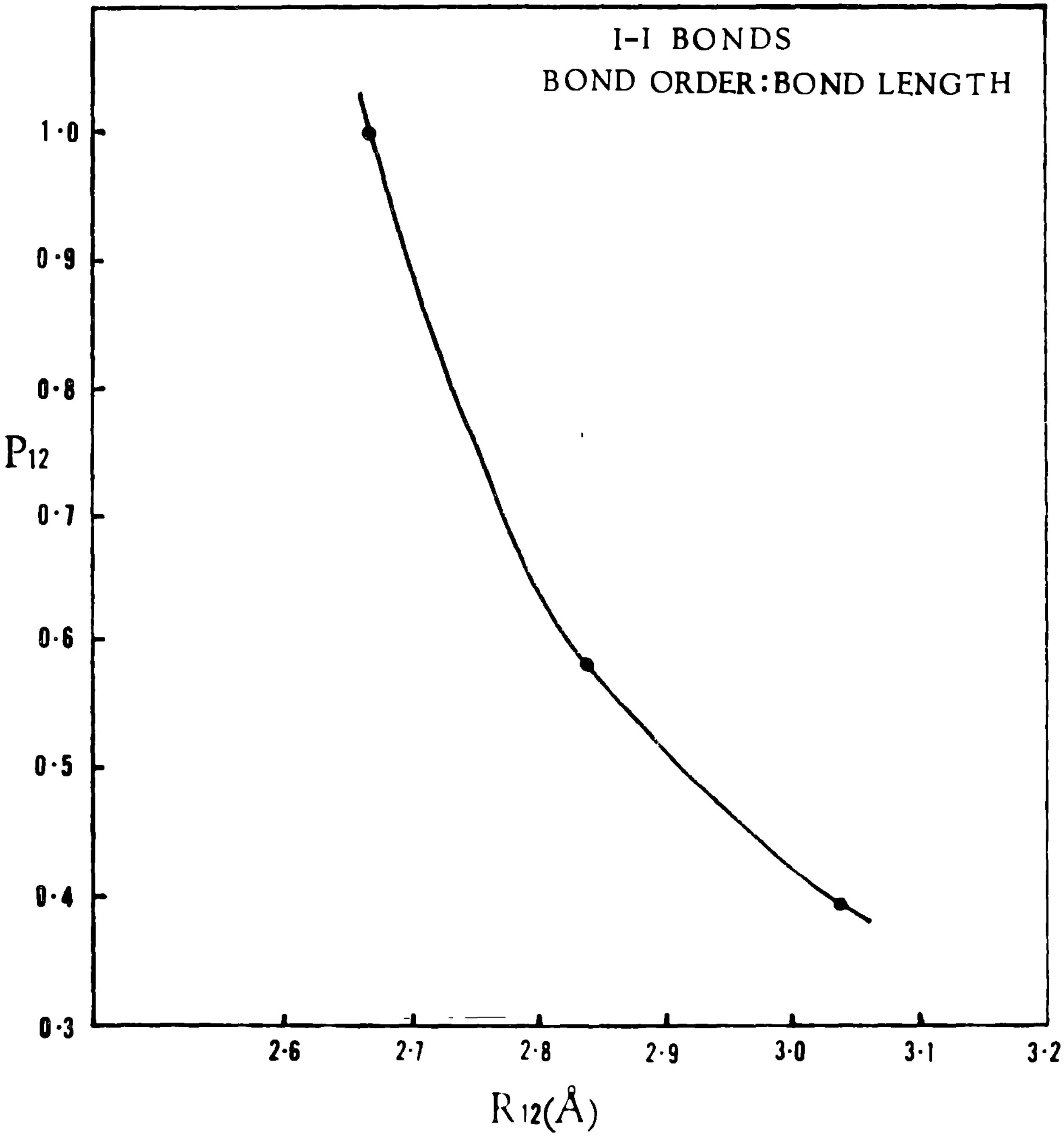

I-I BONDS
BOND ORDER:BOND LENGTH
P_{12}
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
2·6
2·7
2·8
2·9
3·0
3·1
3·2
R_{12}(Å)

FIGURE 11.

elements in H and L differ from the corresponding terms in G & K respectively by a constant, hence the omission of a constant factor, included in each element, does not affect the final result.

One aim of molecular orbital calculations is to derive a quantitative relationship between bond orders and bond lengths. This has been done for carbon-carbon bonds for a large number of compounds and it is possible to predict bond lengths from bond orders with reasonable accuracy (113). A similar relationship for iodine-iodine bonds is shown in figure 11. The points on the graph correspond to the I - I bond in iodine, caesium triiodide (two values) and tetraphenyl arsonium triiodide. This graph is also interesting in that the points for the two crystals fall on a smooth curve indicating that the molecular orbital treatment, with correction for the two different crystal fields, gives satisfactory results in this situation. The points are also within about 0.02Å of the mean curve, which is whithin the accuracy of the experimental bond length determinations.

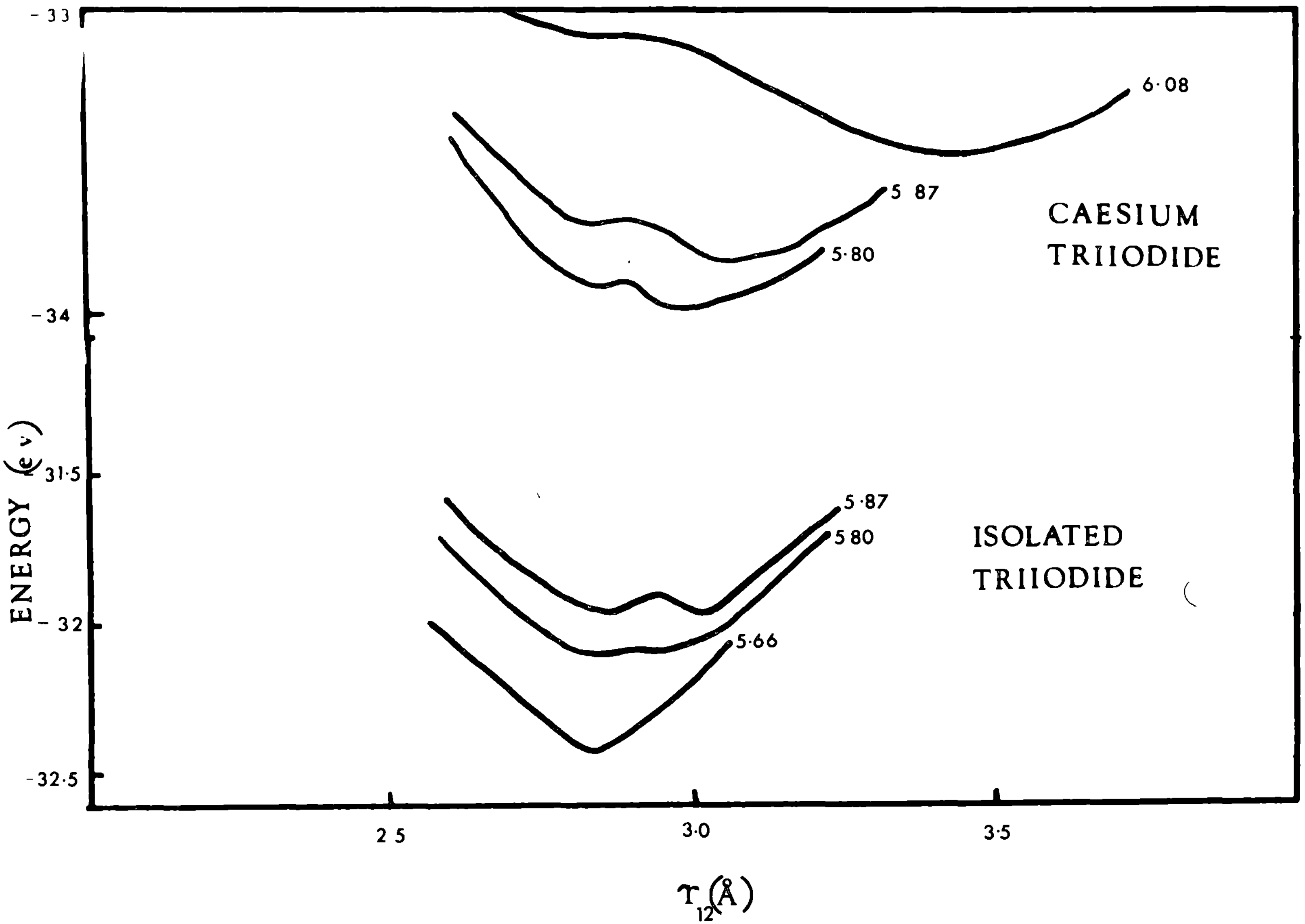
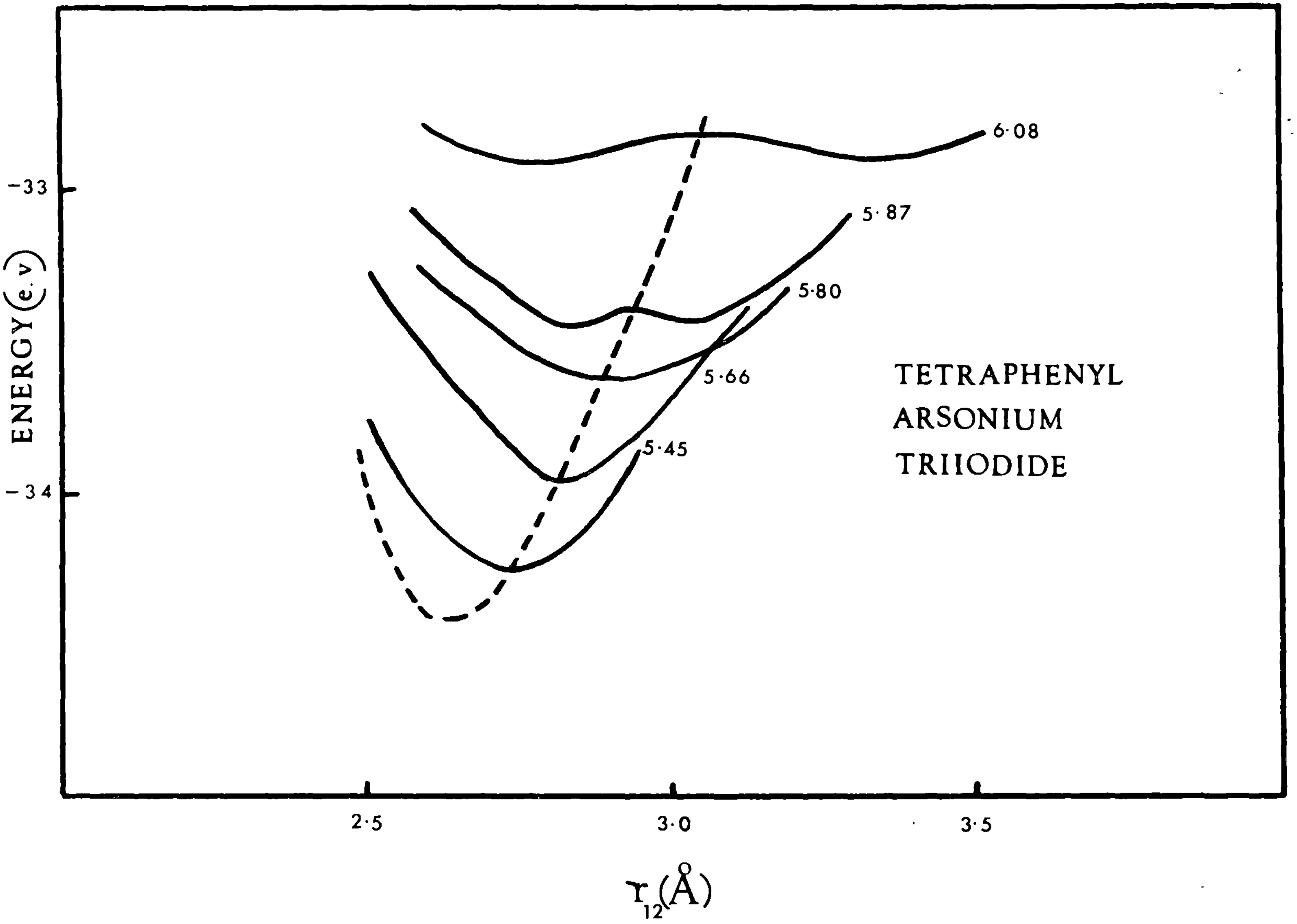

-33
-34
-31·5
-32
-32·5
ENERGY (e v)
2 5
3·0
3·5
r_{12}(Å)
6·08
5 87
5·80
CAESIUM TRIIODIDE
5 ·87
5 80
5·66
ISOLATED TRIIODIDE

FIGURE 12.



ENERGY (e.v)
−33
−34
2·5
3·0
3·5
r_{12}(Å)
6·08
5·87
5·80
5·66
5·45
TETRAPHENYL
ARSONIUM
TRIIODIDE

FIGURE 13.

By considering the total valence electron energies for a number of configurations of I_3^- it was possible to obtain a family of curves similar to those given by Slater (104) for H_3. There were three cases to be considered. These were:-

a) the triiodide ion in vaccuo

b) the triiodide ion in the symmetric crystal field.

c) the triiodide ion in the asymmetric crystal field.

For each of these a family of curves was obtained by taking the appropriate field and a variety of terminal iodine interatomic distances (r_{13}). For each fixed r_{13} the position of the central iodine was altered so that a relationship was obtained between r_{12} and the total energy.

The results of these calculations are listed in table 10 and are shown graphically in figures 12 & 13.

TABLE 10.

Total Valence Electron Energies.

1. Zero external field.

r_{13}Å	r_{12}Å		E (ev)
5.87	2.62,	3.25	-31.625
	2.935		-31.898
	3.04,	2.83	-31.940
5.80	2.62,	3.18	-31.787
	2.90		-32.082
	2.935,	2.865	-32.088
	3.04,	2.76	-32.037
5.66	2.83		-32.415
	2.90,	2.76	-32.342
	2.935,	2.725	-32.286
	3.04,	2.62	-32.107

2. Tetraphenyl arsonium triiodide.

r_{13}Å	r_{12}Å		E (ev)
6.08	2.62,	3.46	-32.818
	2.83,	3.25	-32.890
	2.90,	3.18	-32.849
	3.04,		-32.842

r_{13} Å	r_{12} Å	E (ev)
5.87	2.62, 3.25	-33.143
	2.90, 2.97	-33.420
	2.935	-33.386
	3.04 2.83	-33.446
5.80	2.62, 3.18	-33.312
	2.90	-33.602
	2.935, 2.865	-33.610
	3.04, 2.76	-33.565
5.66	2.515, 3.145	-33.332
	2.83	-33.991
	2.90, 2.76	-33.909
	2.935, 2.725	-33.848
	3.04, 2.62	-33.656
5.45	2.725	-34.266
	2.83, 2.62	-34.165
	2.935, 2.515	-33.813
5.2	2.6	-34.393
4.8	2.4	-33.997

3. Caesium triiodide

r_{13} Å	r_{12} Å	E(ev)
6.08	2.62	-32.937
	2.83	-33.088
	2.90	-33.087
	3.04	-33.167
	3.18	-33.281
	3.25	-33.386
	3.46	-33.480
	3.68	-33.338
5.87	2.62	-33.350
	2.725	-33.545
	2.83	-33.709_7
	2.87	-33.706
	2.935	-33.709_6
	3.04	-33.838
	3.145	-33.796
	3.25	-33.712
5.80	2.62	-33.504
	2.76	-33.820
	2.865	-33.912

r_{12}Å	E(ev)
2.90	-33.926
2.935	-33.958
3.04	-33.975
3.18	-33.811

These curves are similar to those given by Slater for the symmetric field cases. The curve for $r_{13} = 5.80$Å shows that at this interatomic distance the double minimum in the energy curve has been reduced to a single minimum and the value of r_{12} at this minimum corresponds to the observed geometry. It is interesting however that the families of curves for both the symmetric crystal field and zero field are almost identical in form although they differ in the absolute value of energy, the former being at the lower energy. It is also interesting that the total energy is still decreasing below the critical distance for r_{13} down to $r_{13} = 5.83$Å, after which it increases. This is probably due, in part to neglecting electron exchange repulsion forces between closed shells on different ions. The size of the triiodide that can be tolerated by the lattice may be a compromise between these repulsions and the internal triiodide ion energy. The repulsion term which has been included is a core repulsion term for the nuclei and would not become significant until much smaller values of r_{12} are reached.

The curves for the asymmetric field are perhaps more interesting. These show that the stable configuration is an asymmetric ion and the observed r_{12} of 3.04Å corresponds to the minimum on the curve for r_{13} = 5.87Å It is not however obvious in this case why r_{13} should by 5.86Å as observed and not e.g. 5.80Å as in the symmetric ion. In the latter the energy "barrier" is less noticeable and it would appear that this field would favour an overall r_{13} of 5.80Å and r_{12} of about 2.90Å. The shape of the curve for r_{13} = 6.08Å indicates that the stable configuration, in this case, is an iodide ion and iodine molecule. The energy decreases until r_{23} is about 2.60Å which approximates the normal I - I bond length (2.67Å). At r_{23} distances less than this energy begins to increase again. In all these calculations where the crystal field has been included, no correction has been made for the effect of shifting all the corresponding central iodine atoms in the remainder of the crystal. This would be a lengthy task as it would be necessary to carry out the interative Ewald and V.E.S.C.F. procedure for each configuration. This correction is not however likely to be very significant as the cation and end iodine atoms are remaining fixed and the major part of the electrostatic field is due to these atoms. A more significant variation in the electrostatic field would probably be observed on changing the r_{13}

interatomic distance. This alteration has also been neglected in these calculations.

From the results of these calculations it can be said that the molecular orbital treatment using 5pσ orbitals is adequate in understanding the geometry of the triiodide ion. It is also interesting that the use of the Morse curve, to obtain values of $\beta_{\mu\nu}$, gives satisfactory results for a variety of bond lengths. This is, perhaps, one of the best possible methods for obtaining these integrals within the general framework of the V.E.S.C.F. method.

These calculations also open up a large field of study on the properties of polyhalides and other polyatomic ions or molecules. In the first instance it should be possible to extend this type of calculation to the higher polyhalides and interhalogens to explain the observed geometries. It should also be possible, by considering a series of asymmetric polyhalides of varying stability, to obtain an estimate of the forces required in the crystal to convert e.g. I_3^- into I^- and I_2 as the stable configuration. One of the main points of interest would be to compare the crystal fields in solvated polyhalides with the unsolvated analogue e.g. $NH_4I_3\ H_2O$ and NH_4I_3. This would be extremely useful in interpreting the role of the solvent, or large cation, in the stabilisation of the polyhalide ion. A considerable amount of structural data would be required before anything very conclusive could be done along these lines at present.

This type of treatment is not confined to the polyhalides however and possibly more useful information may be obtained by considering other similar systems with polyatomic anions. Such compounds would include e.g. azides, carbonates, nitrates and oxalates. The same principle of stabilisation of the anion by a large cation is well known in these series of compounds and more structural data is available on some of these.

The observation of the central maximum also opens up the possibility of some interesting spectroscopic work on the polyiodides. This may also apply to other polyhalide or e.g. azides. The calculated height of the central maximum is about 100 - 200 cm^{-1} and if the two outer iodines are virtually stationary during the asymmetric stretch vibration of the triiodide, the central iodine behaves as if it occupies a broad flat minimum. Some interesting infrared absorptions will also be present if the first vibrational level is below this maximum so that inversion splittings will be observed (126).

These two compounds would be expected to show very different infra red spectra in this case as the inversion splitting would be expected in higher vibrational levels in the asymmetric ion than in the symmetric ion. It would also be interesting to re-examine the nuclear quadrupole coupling data in the light of these crystal effects. The work done on ICl_4^- and ICl_2^- indicated that there is little effect on these supposedly symmetric ions, except in the case of the hydrates. Additional x-ray structural data would be needed so that these field effects can be properly established.

In conjunction with additional x-ray work a careful study of the electron density projections around each iodine would be useful, especially in relation to central iodine. It may be expected that an asymmetric ion would show comparable distributions at each iodine as is shown in CsI_3. The symmetric ion may however show that the position of the central iodine is not as clearly defined as the terminal iodine positions. The published data on $As\phi_4I_3$ does not indicate whether this is the case or not.

CHAPTER 10

CONCLUSION

Remarks have been made at the end of each chapter regarding the conclusions relevant to the chapter. It is useful however to collate the main points and summarise these in a general discussion.

At the beginning of this investigation it was known, from a qualitative argument, that the stability of a polyhalide ion was regulated by the relative sizes of the cation and anion. Thus chlorine will not form polyhalides of the type under consideration whilst iodine forms a large number and bromine forms a few. On the other hand lithium and sodium are the only alkali metals not forming polybromides down to 0°C yet all the alkali metals will form polyiodides. In the cases where the cation is relatively small a polyhalide will form only if there is a possibility of solvation so we have anhydrous caesium triiodide but only a hydrated potassium triiodide and both hydrated and anhydrous ammonium triiodide. We also have higher polyiodides than the triiodide withlarge cations e.g. the alkyl substituted ammonium cations.

The major experimental part of this investigation has been directed at completely defining the alkali polyhalide systems and has led to the identification of the tetrahydrated lithium tetraiodide. It has also been shown that no new polybromides are formed, down to 0°C by lithium, sodium and ammonium bromides. In conjunction with these studies it has also been shown that the lithium polyiodide and the two sodium polyiodides are diamagnetic and hence the simple formulae are not acceptable. It is most probable that their structures would be analogous to the caesium tetraiodide, where two triiodide ions are linked via an iodine molecule to form an I_8^{2-} ion.

To further extend this aspect of the overall treatment it would be interesting to gain more information on the hydrogen polyhalides. The existence of $HICl_4$ (28) and the presence of HI_3 in solution (27,32) have been demonstrated. If one assumes a formula $(H_9O_4)^+$ for the hydrogen ion, i.e. $H_3\overset{+}{O}$ surrounded by 3 water molecules, then it would seem feasible that such a cation may form a polyiodide, possibly of the type I_8^{2-}. A low temperature investigation of the system $HI - I_2 - H_2O$ would be useful if it can be demonstrated that a solid will form at a workable temperature and that sufficiently long solubility arcs are obtained. The nature of the HI would impose some experimental difficulties in this system, where side reactions and volatility of components, could lead to erroneous results. It should however be possible to estimate e.g. free iodine and total iodine in a system of this type, water being estimated by difference.

Extension to other simple systems seems unlikely as it appears that the existence of solid homogeneous polyhalides is exceptional amongst inorganic ions other than the alkali metals and complexes of the tetraphenyl arsonium and substituted ammonium types. Some work has been done along these lines e.g. the system BaI - I_2 - H_2O has been studied and no polyiodide is produced (122). Likewise Sn,As,Sb and Bi iodides do not form polyiodides (124). Thallium forms a compound TlI_3 which was thought to be a thallous polyiodide but this has been disputed (125). Polyvalent metal ions do however show the properties of polyhalide formation in solution (119). In the "mixed" polyhalide ions ICl_4^- will form a compound with magnesium, but even in this large group of compounds the divalent cations are exceptional in polyhalide formation, with the exception of some metal ammine polyhalides. (127).

An uncertain factor in the stablisation of the polyhalide ions is still the actual role of the solvent. It has been amply demonstrated that solvent must be present in the crystal in the case of the smaller cations, before a stable polyhalide is possible. It would seem to be an obvious corollary that this solvent must be associated in some way with the cation. Cationic solvation is well known in, for example, Li^+, Na^+ solution where thermodynamic, transport and other studies have shown that these ions can disrupt the structure of the water by ordering the nearest neighbour molecules. Larger molecules do not do this to the same extent. Ammonium is an intermediate case where it has been shown that the tetrahedral arrangement of hydrogen atoms around the N does not influence the solvent structure. A clear picture of the position of potassium is not gained on this basis as it does not form a hydrate as readily as the smaller alkali metal ions. It is a borderline case and it may be that there are other weaker effects which may be predominant here.

Polar solvents other than water would be expected to show a similar behaviour and these may be more efficient in the formation of higher polyhalides due to their own larger "bulk". Benzene would seem in the first instance, to be an exception but polarisation effects still cannot be ignored when there is ample evidence that benzene will form a polar complex with iodine and this could well be sufficient to permit its incorporation into a polyhalide crystal. It would be interesting to compare structural data on the benzene solvated potassium polyiodide and a polar aromatic analogue, e.g. benzonitrile, to see whether the organic molecule is included in the crystal in the same spatial arrangement.

Molecular orbital calculations give an adequate explanation of the observed geometries of the polyiodide ion, except for the slight deviations of the bond angles from 90° and 180°. By considering the electrostatic potentials surrounding these ions in a crystal it is also possible to show why some ions are centrosymmetric, as would be expected in the isolated ion, and some are slightly asymmetric. Total valence electron energy calculations also show that the observed geometries correspond approximately to the convergence of the double energy minimum into a single minimum. The molecular orbital calculations have also shown the possibility of further interesting infra red spectral investigations into the nature of the potential barrier in symmetric and asymmetric anions. They also open up the possibility of extending this type of calculation to a large number of other crystals, containing polyatomic anions, other than polyhalides.

It would be useful to do this to verify whether or not the structural principles derived for triiodide are,in general, applicable to other systems.

In going from ammonium iodide and caesium iodide to the triiodides, there is a change in crystal structure from the sodium chloride and caesium chloride structures to an orthorhombic crystal. It may also be significant here that ammonium iodide can exist in the caesium chloride structure at reduced temperatures. This structural change may only be to accomodate the larger anion, or it could also be related to the strength of the perturbing electrostatic field. The crystal field is probably an important factor in determining the stability of the anion. A symmetric field would seem to have little effect on the anion but the asymmetric field favours one resonance structure. It would be interesting to know if the crystal field is symmetric in a case like hydrated potassium triiodide, as it may be expected that an anhydrous KI_3 would be asymmetric, by analogy with NH_4I_3 and CsI_3. It would also be interesting to obtain a similar family of energy curves for a hypothetical anhydrous KI_3 to determine whether or not the crystal field is such that the only stable structures correspond to an iodide ion and an iodine molecule. A knowledge of the symmetry of the field in polyhalides solvated with organic molecules would also be interesting in cases like sodium and potassium polyhalides.

Until more structural data is available it is difficult to make any definite conclusions with regard to these effects but results to date are encouraging. It is possible, by suitable extensions of these theories, that more quantitative statements can be made about the stability of the polyhalides, than just saying that the stability is dependent on the effective size of the cation.

More detailed solution spectral studies in the visible and ultra violet would also be useful in understanding the nature of the stable polyiodide ion. In solution the electrostatic field effects should be reduced and should be symmetric. It may be possible, from spectra, to draw conclusions as to the nature of the anion in this phase and to make interesting comparisons with the anion in the solid. By a choice of suitable solvents, infra red studies may also be useful in this regard.

APPENDIX 1.

ALGEBRAIC EXTRAPOLATIONS.

INTRODUCTION.

In chapter 2 reference was made to a variety of methods used to present the results obtained in a ternary system. This appendix is to outline the events leading up to the development of a general algebraic treatment of results and to detail the derivation of this treatment and including a worked example.

The method of indirect analysis of solid phases was put forward by Schreinemakers (37) for the analysis of ternary systems involving at least one solid and one liquid phase. At the time it was proposed there were few grounds for doubting that the composition of solid compounds could be expressed in terms of fairly small integral numbers of molecules, and a simple graphical treatment of experimental data generally sufficed to indicate the required composition. More recently, since the concept of "simple" molecular ratios has become less rigid, the method has been less favourably regarded. Thus, Stackelberg (72), in discussing the composition of the halogen hydrates, for which he proposed compositions based on structural considerations, dismissed conclusions based on Schreinemaker's method as "inaccurate".

It is clear from geometrical considerations that each single tie-line observed in applying Schreinemakers's method is liable to magnify random error of analysis; but when a cluster of converging

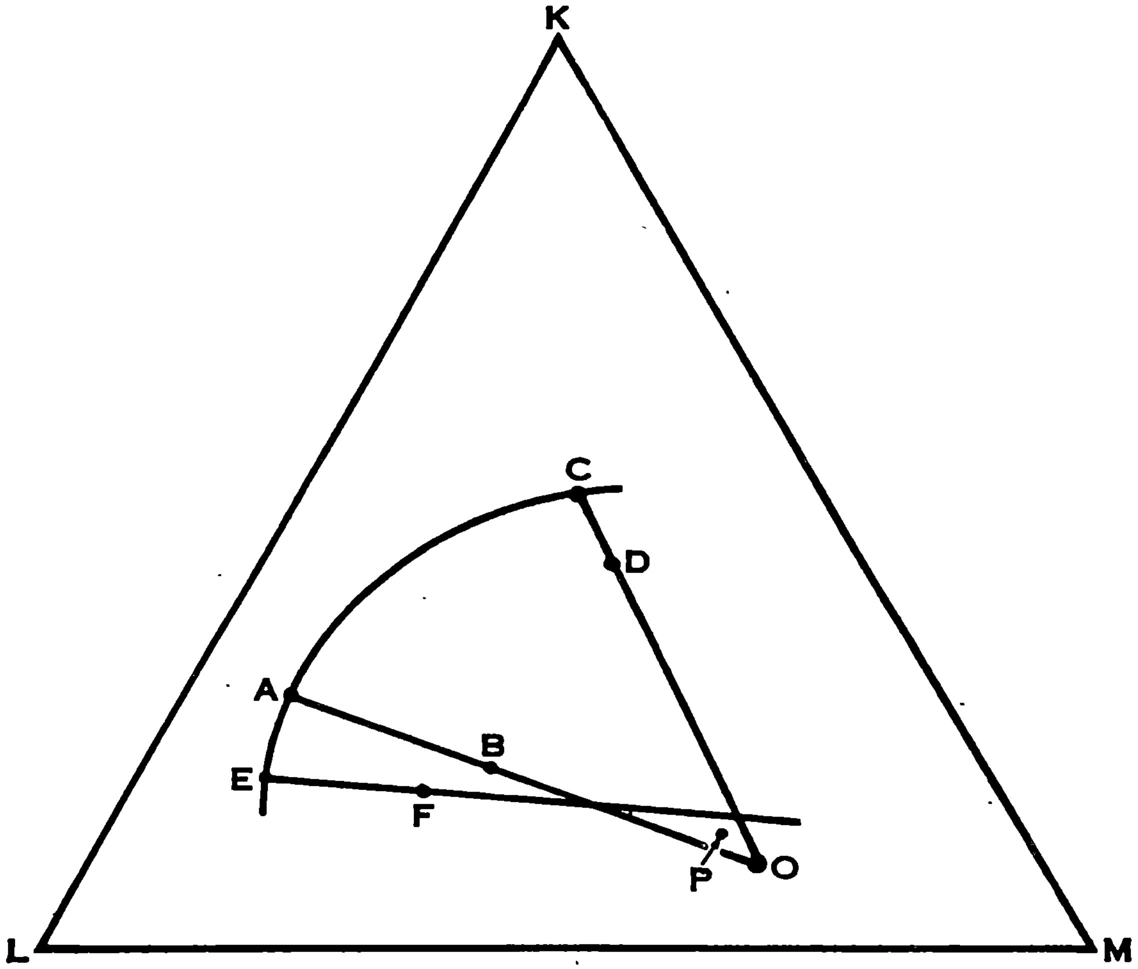

K
C
D
A
B
E
F
P
O
L
M

FIGURE 14.

tie-lines is observed it should be possible to estimate their "best" intersection with some degree of certainty even without the guidance of the simple ratio rule.

More refined algebraic procedures have been proposed whereby an algebraic extrapolation is used or the equations to pairs of tie-lines are solved for (X,Y), the point of intersection (38,120,121). In Figure 14 a, AB and CD represent two tie-lines running from solutions A,C through corresponding wet solids or original mixture B,D; for two such lines there is a unique point of intersection O. If, however, a third pair of observations gives a line EF which does not pass through O, the problem is to choose a point such as P(X,Y) which represents the most probable composition for the solid phase common to all three; the problem may be extended to any greater number of such tie-lines.

A relatively simple approach was at first attempted in which the equations to the lines AB, CD etc. were derived and hence the sum of the squares of the perpendiculars $\Sigma(p^2)$ from the point P was obtained. This sum was in terms of X and Y. The minimising conditions for this sum are that

$$\frac{d\Sigma(p^2)}{dX} = \frac{d\Sigma(p^2)}{dY} = 0$$

This led to the equations

$$X\Sigma\left(\frac{l^2}{l^2+m^2}\right) + Y\Sigma\left(\frac{lm}{l^2+m^2}\right) - \Sigma\left(\frac{l}{l^2+m^2}\right) = 0$$

and

$$Y\Sigma\left(\frac{m^2}{l^2+m^2}\right) + X\Sigma\left(\frac{lm}{l^2+m^2}\right) - \Sigma\left(\frac{m}{l^2+m^2}\right) = 0$$

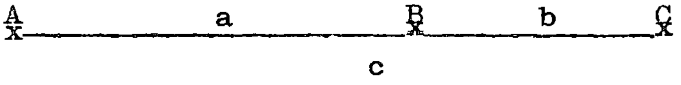
where

$$l = \frac{y_2 - y_1}{x_1y_2 - x_2y_1} \qquad \text{and } m = \frac{x_1 - x_2}{x_1y_2 - x_2y_1}$$

These equations are then solved for X and Y.

This procedure did, however, completely ignore any weighting which should perhaps be applied to the lines. Obviously, the greater the distance between the analyses for saturated solution and wet solid, the more accurate will be the extrapolation. Weighting factors were therefore applied, these being related to the ratios of the segments of the tie line.

In the straight line ABC if the distances between the points A,B and C are a,b,c as shown, then the ratios a/c or b/c may be used to give an



estimate of the relative weighting which should be applied to the line in the above procedure. The ratios $(a/b)^2$ and $(a/c)^2$ were calculated and applied to the data obtained for NH_4Br_3. The results are tabulated below:

	$\%NH_4Br$	$\%Br_2$
Theoretical	38.00	62.00
Not weighted	38.47	62.41
a/b	38.41	62.16
$(a/b)^2$	38.33	62.04
$(a/c)^2$	38.43	62.18

In this example the weighting factor does not make any significant difference to the result obtained, although the ratio $(a/b)^2$ is closer to the theoretical figure in both $\%NH_4Br$ and $\%Br_2$.

The validity of these methods were discussed with a number of mathematicians at this stage. As a result of correspondonce with Dr. D.J. Finney, Reader in Statistics Aberdeen via Dr. E.C. Wood and discussions with Dr. W.E. Knolle at the Hobart Technical College a more general and more refined procedure was developed.

In practice we are given a number of sets (1,.....n) of experimental points, each set lying (apart from experimental error) on a single tie-line, and each set intersecting at a single point (X,Y) representing the composition of the solid phase. We then require the best estimates of X,Y and the slopes m_p(p = 1,......n) of various tie-lines. As "best" estimates we choose the values which minimize the sum of the squares of the distances of the points from the appropriate tie-lines. This leads to a set of non-linear equations for m_p, X, and Y which are most conveniently solved by iteration. Approximate values for m_p, X, and Y are chosen and a Taylor expansion is made in the differences dm_p, dX, and dY of the best m_p, X, and Y and the approximate values, retaining only first-order terms. The resulting linear equations are then solved for dm_p, dX and dY. This procedure can then be repeated if required, a single iteration being sufficient in most cases.

As a first approximation each set of points is fitted separately to a straight line (by minimizing the sum of the squares of distance of the points from the line) and then the best point of intersection is estimated by finding a point such that the sum of the squares of its distance from the various fitted tie-lines is a minimum. New values for the slopes of the tie-line are then determined on the assumption that the tie-lines pass through the selected point and the resulting values are then used as starting values in the iterative process described above.

PROCEDURE

In the most general case we are given n sets of points, where n is the number of equilibrium systems and hence the number of lines which must intersect. To each n we have N_p points corresponding to analytical points or initial composition. These are represented by

$$(x_{p(1)}, y_{p(1)}), (x_{p(2)}, y_{p(2)}) \ldots (x_{p(N_p)}, y_{p(N_p)}),$$

$$p = 1,2,3,\ldots\ldots n;\ N_p \geqslant 2.$$

In practice N_p is usually taken as two; i.e. two points are taken on each line, these being two of the analytical compositions of wet solid and saturated solution or alternatively the initial total composition.

PROCEDURE contd.

The distance of a point (a,b) from the straight line $y - Y = m(x - X)$ is given by

$$\frac{y-b-m(X-a)}{\sqrt{m^2+m+1}}$$

in the triangular system.

The sum of the distances squared of the points (x_{pq}, y_{pq}) from the corresponding straight lines is given by

$$S = \sum_{p=1}^{n} \sum_{q=1}^{Np} \frac{\left[Y-y_{pq} - m_p(X-x_{pq})\right]^2}{m_p^2 + m_p + 1} \qquad q = 1, 2, \ldots Np.$$

To find the quantities $m_p (p = 1, 2, 3, \ldots n)$, X and Y for which S has a minimum we use the equations $\frac{dS}{dm_p} = 0$ $(p = 1, 2, 3 \ldots n)$; $dS/dX = 0$ and $dS/dY = 0$.

For simplification of the expressions the following notations are used:

$$Y_{pq} = Y - y_{pq}; \quad X_{pq} = X - x_{pq}; \quad k_p = \frac{1}{m_p^2 + m_p + 1}$$

$$\text{Then} \quad S = \sum_{p,q} \frac{(Y_{pq} - m_p X_{pq})^2}{m_p^2 + m_p + 1}$$

$$\frac{dS}{dm_p} = \sum_q \left[\frac{(2m_p X_{pq}^2 - 2X_{pq} Y_{pq})}{m_p^2 + m_p + 1} \right.$$

$$- \frac{(Y_{pq} - m_p X_{pq})^2 (2m_p + 1)}{(m_p^2 + m_p + 1)^2} \Bigg] = 0$$

$q = 1, 2, 3 \; ..... \; Np; \quad p = 1, 2, 3 \; ..... \; n.$

Multiplying by $(m_p^2 + m_p + 1)^2$ and rearranging the terms

$$(1) \quad m_p^2 \sum_q (X_{pq}^2 + 2X_{pq} Y_{pq}) + 2m_p \sum_q (X_{pq}^2 - Y_{pq}^2)$$

$$- \sum_q (2X_{pq} Y_{pq} + Y_{pq}^2) = 0$$

Also $\quad - 1/2 \; dS/dX = \sum_{p,q} k_p \left[Y_{pq} m_p - X_{pq} m_p^2 \right] = 0$

$$(2) \text{ i.e. } \sum_p m_p^2 k_p \sum_q x_{pq} - \sum_p m_p k_p \sum_q y_{pq}$$

$$- \sum_p m_p^2 k_p Np \, X + \sum_p m_p k_p Np \, Y = 0$$

and $\quad 1/2 \; dS/dY = \sum_{p,q} k_p \left[Y_{pq} - m_p X_{pq} \right]$

$$(3) \text{ i.e. } \sum_p m_p k_p \sum_q x_{pq} - \sum_p k_p \sum_q y_{pq} - \sum_p m_p k_p Np \, X$$

$$+ \sum_p k_p Np \, Y = 0$$

To solve equations (1), (2) and (3) for X and Y the point (U,Y) is taken very close to the best point of intersection and the corrections $dX = X-U$ and $dY = Y - V$ are determined.

The best straight line passing through the set of points (x_{pq}, y_{pq}) $q = 1, 2 \ldots\ldots Np)$ is the straight line through the points

$$\frac{\sum_q x_{pq}}{Np}, \quad \frac{\sum_q y_{pq}}{Np} \quad \text{and} \quad \frac{\sum_q x_{pq}^2}{\sum_q x_{pq}}, \quad \frac{\sum_q x_{pq} \cdot y_{pq}}{\sum_q x_{pq}}$$

Let (u_{p_1}, v_{p_1}) and (u_{p_2}, v_{p_2}) be two points on this straight line. The equation to the straight line through these points is given by $y = M_p x + C_p$

where

$$M_p = \frac{v_{p_2} - v_{p_1}}{u_{p_2} - u_{p_1}} \quad \text{and} \quad C_p = \frac{v_{p_1} u_{p_2} - v_{p_2} u_{p_1}}{u_{p_2} - u_{p_1}}$$

The distance squared of the point (U, V) from the straight line $y = M_p x + C_p$ is given by

$$K_p \left[V - M_p U - C_p\right]^2 \quad \text{where} \quad K_p = \frac{1}{M_p^2 + M_p + 1}$$

The sum of the squares $R = \sum_p K_p \left[V - M_p U - C_p\right]^2$

and this is minimised.

Hence $-1/2 \; dR/dV = -\sum_p K_p M_p \left[V - M_p U - C_p\right] = 0$

i.e. (4) $\left(\sum_p M_p^2 K_p\right) U - \left(\sum_p M_p K_p\right) V + \sum_p M_p K_p C_p = 0$

Also $-1/2 \; dR/dV = -\sum_p K_p \left[V - M_p U - C_p\right] = 0$

i.e. (5) $(\sum_p M_p K_p)U - (\sum_p K_p)V + \sum_p K_p C_p = 0$

Equations (4) and (5) are then solved for U and V.

Approximate values $\bar{m}_p$ are determined for the m_p from the equations:

$$(1') \quad \bar{m}_p^2 \sum_q (U_{pq}^2 + 2U_{pq} V_{pq}) + 2\bar{m}_p \sum_q (U_{pq}^2 - V_{pq}^2) - \sum_q (2U_{pq} V_{pq} + V_{pq}^2) = 0$$

$$p = 1, 2, 3, \ldots n$$

where $U_{pq} = U - x_{pq}$ and $V_{pq} = V - y_{pq}$

The root of the quadratic equation (1') nearest to M_p is taken for $\bar{m}_p$.

To determine the small corrections dX and dY and $dm_p = m_p - \bar{m}_p$ $(p = 1, 2, \ldots n)$ Taylor's theorem is applied to the equations (1), (2) and (3). This leads to the following linear equations in dX, dY and dm_p:

$$(6) \quad \left[\bar{m}_p \sum_q (U_{pq}^2 + U_{pq}V_{pq}) + \sum_q (U_{pq}^2 - V_{pq}^2)\right] dm_p$$

$$+ \left[\bar{m}_p^2 \sum_q (U_{pq} + V_{pq}) + 2\bar{m}_p \sum_q U_{pq} - \sum_q V_{pq}\right] dX$$

$$+ \left[\bar{m}_p^2 \sum_q U_{pq} - 2\bar{m}_p \sum_q V_{pq} - \sum_q (U_{pq} + V_{pq})\right] dY = 0$$

$$p = 1, 2, 3, \ldots n.$$

$$(7)\quad \sum_p \bar{m}_p^2 \bar{k}_p \sum_q U_{pq} - \sum_p \bar{m}_p k_p \sum_q V_{pq} + \sum_p \Big[(\bar{m}_p^2 + 2\bar{m}_p) k_p^2$$

$$\sum_q U_{pq} + (\bar{m}_p^2 - 1)\bar{k}_p^2 \sum_q V_{pq} \Big] dm_p + \sum_p (\bar{m}_p^2 \bar{k}_p Np) dX$$

$$- \Big(\sum_p \bar{m}_p \bar{k}_p Np \Big) dY = 0 \qquad \text{where } \bar{k}_p = \frac{1}{\bar{m}_p^2 + \bar{m}_p + 1}$$

$$(8)\quad \sum_p \bar{m}_p \bar{k}_p \sum_q U_{pq} - \sum_p \bar{k}_p \sum_q V_{pq} + \sum_p \Big[-(\bar{m}_p^2 - 1)\bar{k}_p^2 \sum_q U_{pq}$$

$$+ (2\bar{m}_p + 1)\bar{k}_p^2 \sum_q V_{pq} \Big] dm_p + \Big(\sum_p \bar{m}_p \bar{k}_p Np \Big) dX$$

$$- \Big(\sum_p \bar{k}_p Np \Big) dY = 0$$

The dm_p from equations (7) and (8) is eliminated by using (6) and these are then solved for dX and dY.

Having found U, V, dX and dY, the best point of intersection (X,Y) is determined provided dX and dY are small:

$$X = U + dX; \qquad Y = V + dY$$

otherwise the procedure may be repeated using the corrected values as U and V.

To estimate the standard deviations of X and Y the numbers $m_p (p = 1, 2, \ldots n)$ are determined. A close approximation is found by making the expression

$$T_p = \sum_q \left[Y_{pq} - m_p X_{pq}\right]^2 \quad \text{a minimum,} \qquad p = 1, 2, \ldots n.$$

Hence

$$m_p = \frac{\sum_q X_{pq} Y_{pq}}{\sum_q X_{pq}^2}$$

The standard deviation S_{yp} of the y_{pq} is given by

$$S_{yp} = \sqrt{\frac{T_p}{Np - 1}}$$

The standard deviation Sm_p of the m_p is given by

$$Sm_p = \frac{S_{yp}}{\sqrt{\sum_q X_{pq}^2}} \qquad \text{hence}$$

$$Sm_p = \sqrt{\frac{\sum_q (Y_{pq} - m_p X_{pq})^2}{\sum_q X_{pq}^2 (Np - 1)}}$$

Equations (7) and (8) are used to express dX and dY in terms of the dm_p $(p = 1, 2, \ldots . n)$.

The following notations are used

$$A_p = (m_p^2 + 2m_p)\, k_p^2 \sum_q X_{pq} + (m_p^2 - 1)\, k_p^2 \sum_q Y_{pq}$$

$$B_p = -(m_p^2 - 1)\, k_p^2 \sum_q X_{pq} + (2m_p + 1)\, k_p^2 \sum_q Y_{pq}$$

$$f = \sum_p m_p^2 k_p N_p \qquad g = \sum_p m_p k_p N_p \qquad h = \sum_p k_p N_p$$

Equations (7) and (8) then reduce to

$$(7') \qquad \sum_p A_p dm_p + f dX - g dY = 0$$

$$(8') \qquad \sum_p B_p dm_p + g dX - h dY = 0$$

$$dX = \frac{\sum_p (hA_p - gB_p) dm_p}{g^2 - fh} \qquad dY = \frac{\sum_p (gA_p - fB_p) dm_p}{g^2 - fh}$$

Hence the standard deviation S_X and S_Y of X and Y are given by

$$S_X = \sqrt{\frac{\sum_p (hA_p - gB_p)^2 Sm_p^2}{(g^2 - fh)^2}} \quad \text{and} \quad S_Y = \sqrt{\frac{\sum_p (gA_p - fB_p)^2 Sm_p^2}{(g^2 - fh)^2}}$$

The corresponding coefficients of the equations (7) and (8) may be used as close approximations of the numbers A_p, B_p, f, g and h in the evaluation of S_X and S_Y.

For the system lithium iodide-iodine-water the results obtained for the saturated solution and wet solid analyses are set out under the columns x_1, y_1, x_2, y_2 where x refers to the percentage lithium iodide and y the percentage iodine by weight, and subscripts 1 and 2 refer to solution and wet solid respectively.

For the data given $n = 9$; $n_1 = n_2 = n_3 \ldots = n_9 = 2$ i.e. each set contains only 2 points hence $u_{pq} = x_{pq}$ and $v_{pq} = y_{pq}$. The symbols (N,p) are used to denote the pth number in the Nth column. The following general notations are used:

$$[N \times M] = \sum_p (N,p) \times (M,p), \quad [N^2] = \sum_p (N,p)^2 \quad \text{and}$$

$$[N] = \sum_p (N,p)$$

To facilitate the setting out and details of procedure the tables of figures along with any calculations are set out on the large pages whilst the procedure for obtaining the columns will be set out on a separate page adjacent to each section.

$(5,p) = (3,p) - (1,p)$

$(6,p) = (4,p) - (2,p)$

$(7,p) = (2,p)(3,p) - (1,p)(4,p)$

$(8,p) = (6,p)/(5,p)$

$(9,p) = (7,p)/(5,p)$

$(10,p) = (8,p)^2$

$(11,p) = (10,p) + (8,p) + 1$

$(12,p) = 1/(11,p)$

$(13,p) = (8,p)(11,p)$

$(14,p) = (10,p)/(11,p)$

Code No.	p	x_{p_1} (1,p)	y_{p_1} (2,p)	x_{p_2} (3,p)	y_{p_2} (4,p)	(5,p)	(6,p)	(7,p)	M_p (8,p)	C_p (9,p)	(10,p)	(11,p)	(12,p)
9	1	29.40	52.16	24.60	61.35	-4.80	9.19	-520.5540	-1.9146	108.4488	3.6657	2.7511	0.3635
10	2	28.90	52.85	23.76	62.70	-5.14	9.85	-556.3140	-1.9163	108.2323	3.6722	2.7559	0.3629
11	3	28.43	52.88	24.21	61.48	-4.22	8.60	-467.6516	-2.0379	110.8179	4.1530	3.1151	0.3210
12	4	27.38	53.79	23.57	62.58	-3.81	8.79	-445.6101	-2.3071	116.9580	5.3227	4.0156	0.2490
13	5	26.07	55.36	23.25	62.91	-2.82	7.55	-352.9437	-2.6773	125.1573	7.1679	5.4906	0.1821
14	6	25.57	55.73	22.64	64.37	-2.93	8.64	-384.2137	-2.9488	131.1310	8.6954	6.7466	0.1482
15	7	24.12	57.48	22.76	63.25	-1.36	5.77	-217.3452	-4.2426	159.8126	17.9997	14.7571	0.0678
16	8	23.20	58.75	22.80	62.00	-0.40	3.25	- 98.9000	-8.1250	247.2500	66.0156	58.8906	0.0170
17	9	22.04	60.14	22.26	62.48	+0.22	2.34	- 38.3428	10.6364	-174.2855	113.1330	124.7694	0.0080
													1.7195

p	(13,p)	(14,p)
1	-0.6959	1.3324
2	-0.6953	1.3325
3	-0.6542	1.3332
4	-0.5745	1.3255
5	-0.4876	1.3055
6	-0.4371	1.2889
7	-0.2875	1.2197
8	-0.1380	1.1210
9	+0.0852	0.9067
Σ	-3.8649	11.1654

$[9 \times 13] = -503.6727$ $\qquad$ $[9 \times 12] = 199.2627$

$$U = \frac{[12][9 \times 13] - [13][9 \times 12]}{[13]^2 - [12][14]} = \frac{-95.9348}{-4.2615} = 22.51$$

$$V = \frac{[13][9 \times 13] - [14][9 \times 12]}{[13]^2 - [12][14]} = \frac{-278.2031}{-4.2615} = 65.28$$

$(15,p) = U - (1,p)$

$(16,p) = V - (2,p)$

$(17,p) = U - (3,p)$

$(18,p) = V - (4,p)$

$(19,p) = (15,p)(16,p)$
$\qquad + (17,p)(18,p)$

$(20,p) = (15,p)^2 + (17,p)^2$

$(21,p) = (16,p)^2 + (18,p)^2$

$(22,p) = 2(19,p) + (20,p)$

$(23,p) = (21,p) - (20,p)$

$(24,p) = (23,p)/(22,p)$

$(25,p) = (24,p)^2 + (24,p) + 1$

$(26,p) = \pm\sqrt{(25,p)}$ Sign chosen
so that $(27,p) \approx (8,p)$

$(27,p) = (24,p) + (26,p)$

$(28,p) = (27,p)^2$

$(29,p) = (27,p) + (28,p) + 1$

$(30,p) = 1/(29,p)$

$(31,p) = (27,p)/(29,p)$

$(32,p) = (28,p)/(29,p)$

$(33,p) = 2(27,p)$

$(34,p) = (27,p)(22,p) - (23,p)$

$(35,p) = (15,p) + (17,p)$

$(36,p) = (16,p) + (18,p)$

$(37,p) = (35,p) + (36,p)$

$(38,p) = (28,p)(37,p)$
$\qquad + (33,p)(35,p) - (36,p)$

$(39,p) = (28,p)(35,p)$
$\qquad - (33,p)(36,p) - (37,p)$

$(40,p) = -(38,p)/(34,p)$

$(41,p) = -(39,p)(34,p)$

$(42,p) = \underline{(32,p) + 2(31,p)}$
$\qquad / (29,p)$

$(43,p) = (31,p)^2 - (30,p)^2$

$(44,p) = (42,p) - (43,p)$

$(45,p) = (35,p)(42,p)$
$\qquad + (36,p)(43,p)$

$(46,p) = -(35,p)(43,p)$
$\qquad + (36,p)(44,p)$

p	U_{p_1} (15,p)	V_{p_1} (16,p)	U_{p_2} (17,p)	V_{p_2} (18,p)	(19,p)	(20,p)	(21,p)	(22,p)	(23,p)	(24,p)	(25,p)
1	-6.89	13.12	-2.09	3.93	-98.6105	51.8402	187.5793	-145.3808	135.7391	-0.9337	0.9381
2	-6.39	12.43	-1.25	2.58	-82.6527	42.3946	161.1613	-122.9108	118.7667	-0.9663	0.9647
3	-5.92	12.40	-1.70	3.80	-79.8680	37.9364	168.2000	-121.7996	130.2636	-1.0695	1.0743
4	-4.87	11.49	-1.06	2.70	-58.8183	24.8405	139.3101	- 92.7961	114.4696	-1.2336	1.2882
5	-3.56	9.92	-0.74	2.37	-37.0690	13.2212	104.0233	- 60.9168	90.8021	-1.4906	1.7313
6	-3.06	9.55	-0.13	0.91	-29.3413	9.3805	92.0306	- 49.3021	82.6501	-1.6764	2.1339
7	-1.61	7.80	-0.25	2.03	-13.0655	2.6546	64.9609	- 23.4764	62.3063	-2.6540	5.3897
8	-0.69	6.53	-0.29	3.28	- 5.4569	0.5602	53.3993	- 10.3536	52.8391	-5.1035	21.9422
9	+0.47	5.14	+0.25	2.80	+ 3.1158	0.2834	34.2596	+ 6.5150	33.9762	+5.2151	33.4124

p	(26,p)	m_p (27,p)	(28,p)	(29,p)	k_p (30,p)	$m_p\ k_p$ (31,p)	$m_p^2\ k_p$ (32,p)	(33,p)	(34,p)
1	-0.9686	- 1.9023	3.6187	2.7164	0.3681	-0.7003	1.3322	- 3.8046	140.8188
2	-0.9836	- 1.9499	3.8021	2.8522	0.3506	-0.6836	1.3330	- 3.8998	120.8971
3	-1.0365	- 2.1060	4.4352	3.3292	0.3004	-0.6326	1.3322	- 4.2120	126.2464
4	-1.1350	- 2.3686	5.6103	4.2417	0.2358	-0.5584	1.3227	- 4.7372	105.3272
5	-1.3158	- 2.8064	7.8759	6.0695	0.1648	-0.4624	1.2976	- 5.6128	80.1548
6	-1.4608	- 3.1372	9.8420	7.7048	0.1298	-0.4072	1.2774	- 6.2744	72.0204
7	-2.3216	- 4.9756	24.7566	20.7810	0.0481	-0.2394	1.1913	- 9.9512	54.5029
8	-4.6842	- 9.7877	95.7991	87.0114	0.0115	-0.1125	1.1010	-19.5754	48.4988
9	+5.7803	+10.9954	120.8988	132.8942	0.0075	+0.0827	0.9097	+21.9908	37.6608
Σ					1.6166	-3.7137	11.0971		
2Σ					3.2332	-7.4274	22.1942		

						a_p	b_p			
p	(35,p)	(36,p)	(37,p)	(38,p)	(39,p)	(40,p)	(41,p)	(42,p)	(43,p)	(44,p)
1	-8.98	17.05	8.07	46.3025	24.3043	-0.328809	-0.172593	-0.0252	0.3549	-0.3801
2	-7.64	15.01	7.37	42.8059	22.1180	-0.354069	-0.182949	-0.0120	0.3441	-0.3561
3	-7.62	16.20	8.58	53.9495	25.8582	-0.427335	-0.204823	0.0201	0.3099	-0.2898
4	-5.93	14.19	8.26	60.2427	25.6918	-0.571958	-0.243924	0.0485	0.2562	-0.2041
5	-4.30	12.29	7.99	74.7735	27.1249	-0.932822	-0.338406	0.0614	0.1970	-0.1356
6	-3.19	10.46	7.27	81.1067	26.9642	-1.126163	-0.374397	0.0601	0.1490	-0.0889
7	-1.86	9.83	7.97	205.9893	43.8030	-3.779419	-0.803682	0.0343	0.0550	-0.0207
8	-0.98	9.81	8.83	855.2799	89.3216	-17.635073	-1.841728	0.0101	0.0125	-0.0024
9	+0.72	7.94	8.66	1054.9346	-96.2198	-28.011476	+2.554906	0.0081	0.0068	+0.0013

p	(45,p)	(46,p)
1	6.2773	-3.2937
2	5.2566	-2.7161
3	4.8672	-2.3333
4	3.3479	-1.3769
5	2.1571	-0.8194
6	1.3668	-0.4546
7	0.4769	-0.1012
8	0.1127	-0.0113
9	0.0598	+0.0054

$d_1 = [32 \times 35] - [31 \times 36] = -52.4367 + 53.1153 = 0.6786$

$g_1 = [31 \times 35] - [30 \times 36] = 23.5455 - 23.7794 = -0.2339$

$d_2 = [40 \times 45] + 2[32] = -16.9345 + 22.1942 = 5.2597$

$d_3 = [41 \times 45] - 2[31] = -5.5384 + 7.4274 = 1.8890$

$g_2 = [40 \times 46] + 2[31] = 5.5361 - 7.4274 = -1.8913$

$g_3 = [41 \times 46] - 2[30] = 2.4432 - 2.2332 = 0.2100$

$$d_X = \frac{d_3g_1 - d_1g_3}{d_2g_3 - d_3g_2} = \frac{-0.5843}{4.6772} = -0.125$$

$$d_Y = \frac{d_1g_2 - d_2g_1}{d_2g_3 - d_3g_2} = \frac{-0.0532}{4.6772} = -0.011$$

$U = 22.51 \quad \therefore \quad X = 22.38$

$V = 65.28 \quad \therefore \quad Y = 65.27$

$(47,p) = X - (1,p)$

$(48,p) = Y - (2,p)$

$(49,p) = X - (3,p)$

$(50,p) = Y - (4,p)$

$(51,p) = (47,p)(48,p) + (49,p)(50,p)$

$(52,p) = (47,p)^2 + (49,p)^2$

$(53,p) = (51,p)/(52,p)$

$(54,p) = (48,p) - (53,p)(47,p)$

$(55,p) = (50,p) - (53,p)(49,p)$

$(56,p) = (54,p)^2 + (55,p)^2/ (52,p)$

$(57,p) = \sqrt{(56,p)}$

There are several check points on the calculation, these are listed as follows:

$(30,p) \approx (12,p)$

$(31,p) \approx (13,p)$

$(32,p) \approx (14,p)$

$d_3 = - g_2$

	X_{p_1}	Y_{p_1}	X_{p_2}	Y_{p_2}			m_p				Sm_p
p	(47,p)	(48,p)	(49,p)	(50,p)	(51,p)	(52,p)	(53,p)	(54,p)	(55,p)	(56,p)	(57,p)
1	-7.02	13.11	-2.22	3.92	-100.7346	54.2088	-1.8583	0.0647	-0.2054	0.000855	0.0292
2	-6.52	12.42	-1.38	2.57	- 84.5250	44.4148	-1.9031	0.0118	-0.0563	0.000075	0.0087
3	-6.05	12.39	-1.83	3.79	- 81.8952	39.9514	-2.0499	-0.0119	+0.0387	0.000041	0.0064
4	-5.00	11.48	-1.19	2.69	- 60.6011	26.4161	-2.2941	+0.0095	-0.0400	0.000064	0.0080
5	-3.69	9.91	-0.87	2.36	- 38.6211	14.3730	-2.6871	-0.0054	+0.0222	0.000036	0.0060
6	-3.19	9.54	-0.26	0.90	- 30.6666	10.2437	-2.9937	-0.0099	+0.1216	0.001453	0.0381
7	-1.74	7.79	-0.38	2.01	- 14.3184	3.1720	-4.5140	-0.0644	0.2947	0.028687	0.0932
8	-0.82	6.52	-0.42	3.27	- 6.7198	0.8488	-7.9168	+0.0282	-0.0551	0.004514	0.1694
9	+0.34	5.13	+0.12	2.79	+ 2.0790	0.1300	+15.9923	-0.3074	0.8709	6.561243	2.5615

p	(58,p)	(59,p)	(60,p)	(61,p)
1	-10.4452	26.4770	-0.3050	0.7731
2	-8.4345	21.2388	-0.0734	0.1848
3	-6.4609	15.6351	-0.0413	0.1001
4	-2.7503	5.6930	-0.0220	0.0455
5	-1.2689	2.0672	-0.0076	0.0124
6	-0.3242	-0.0623	-0.0124	-0.0024
7	+0.3134	-1.2961	+0.0292	-0.1208
8	+0.1678	-0.5863	+0.0284	-0.0993
9	+0.0934	-0.5640	+0.2392	-1.4447

$f = 2[32] = 22.1942$

$g = 2[31] = -7.4274$

$h = 2[30] = 2.2332$

$|g^2 - fh| = 5.6022$

$[60]^2 = 1.5969$

$[61]^2 = 2.7557$

$$S_X = \frac{[60]^2}{|g^2 - fh|} = \frac{1.5969}{5.6022} = \frac{1.2637}{5.6022} = 0.23$$

$$S_Y = \frac{[61]^2}{|g^2 - fh|} = \frac{2.7557}{5.6022} = \frac{1.6600}{5.6022} = 0.30$$

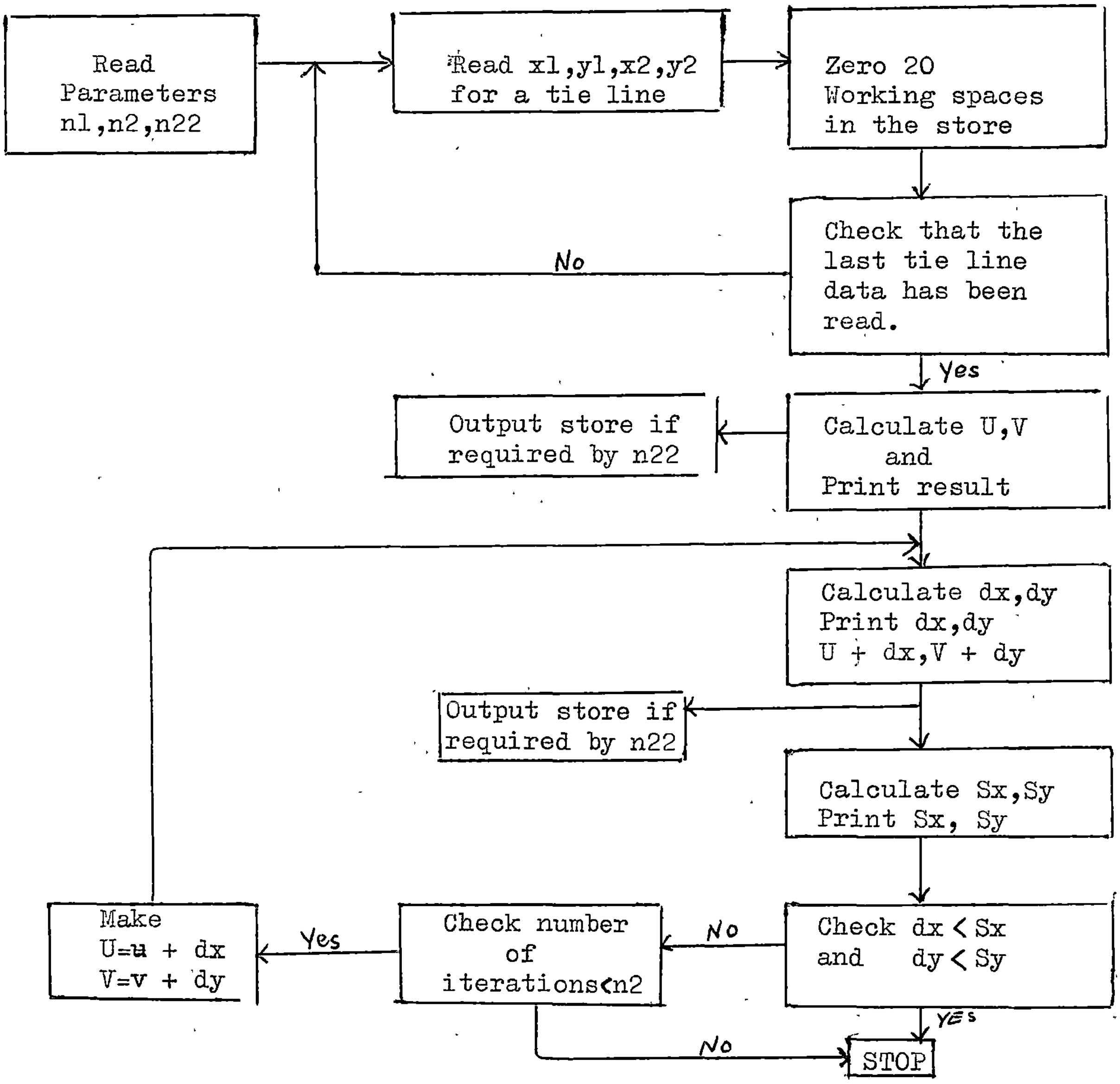
$\therefore\ X = 22.38 \pm 0.23$

$\ Y = 65.27 \pm 0.30$

Although this procedure is lengthy and subject to operator errors on a desk calculator, it is readily programmed for an electronic computer. This was done for the Ferranti Sirius computer using Sirius autocode. The program includes the same basic steps as already outlined, but since it is many times faster and more accurate, additional iterations can be included. As a criterion for iteration it was decided to compare the values obtained for dX and dY with Sx and Sy. If either dX or dY was greater than Sx or Sy respectively, then the iterative process was repeated. An arbitrary parameter was also included to limit the number of iterations.

A simplified flow diagram for the program is shown in figure 15. The program procedure differs slightly to the desk method in that each tie line is calculated up to the arithmetic operations at the end of each of the three parts of the procedure. The section dealing with dX and dY also has some additional internal steps so that the sign of the square root is chosen correctly (see 25,p in detailed outline). A check is also made on the sign of (24,p) before the root is taken. If this did happen to be negative its sign is changed and a point out makes note that this has been done.

This computer will treat the lithium iodide data in about five minutes, One necessary precaution to be taken in compiling data is to ensure that, when a line is parallel to one side of the coordinate triangle, an infinite slope is not introduced. This can usually be overcome by suitably selecting the data, either by interchanging the x and y values to give a zero slope, or by using the percentage of the third component.


Read Parameters n1,n2,n22
Read x1,y1,x2,y2 for a tie line
Zero 20 Working spaces in the store
Check that the last tie line data has been read.
No
Yes
Output store if required by n22
Calculate U,V and Print result
Calculate dx,dy Print dx,dy U + dx,V + dy
Output store if required by n22
Calculate Sx,Sy Print Sx, Sy
Check dx < Sx and dy < Sy
No
Check number of iterations<n2
Yes
Make U=u + dx V=v + dy
No
YES
STOP

Input Data

Title to Problem

n1 = no of tie lines
n2 = max number of iterations
n22 = store output control
Table of x1,y1,x2,y2, values for each tie line.

FIGURE 15.

It may be noted that the results obtained by the desk calculator differ slightly to those obtained by computer. This is undoubtedly due to either operator errors, or round off errors on the desk machine.

All the systems studied including Harris' and Zernicke's results, have been calculated by both methods. A number of other published systems related to the polyhalides have been recalculated by the computer and a few unrelated systems with longer tables of data have also been satisfactorily checked.

APPENDIX 2

CALCULATIONS ON THE TRIIODIDE ION

INTRODUCTION

Chapter 9 outlined the various types of calculations that were made on the triiodide ion. The more significant results were also discussed. This appendix is to give a detailed treatment of some typical calculations to show the procedure adopted.

The various steps taken in order were

(i) Havinga's Hückel method calculations were checked

(ii) A VESCF procedure was applied to the triiodide ion

(iii) Values of β were calculated

(iv) A coordinate diagram for CsI_3 and $As\phi_4I_3$ was prepared.

(v) The electrostatic potential at the iodine atoms of the anion in CsI_3 and $As\phi_4I_3$ was calculated by the Ewald method.

(vi) The total energy of the triiodide anion in the crystalline solid was also calculated

Calculations

1. Hückel calculations

The basic theory of molecular orbital calculations by the Hückel method will not be detailed here as it is adequately discussed in Streitwieser (96) and Havinga's thesis (81).

Taking the case of I_3^- with a cation 4 Å from one end Havinga assumed that this would make the coulomb integral for the iodine atom nearest the cation more negative by $0{\cdot}1\,\beta$ where β is the interaction integral.

If we start with the model

$$\underset{\text{cation}}{\times}\;\text{———}\overset{}{4\text{Å}}\text{———}\;\overset{-\frac{1}{2}}{I_1}\;\text{———}\;\overset{0}{I_2}\;\text{———}\;\overset{-\frac{1}{2}}{I_3}$$

where we have a charge of $-\frac{1}{2}$ on I_1 and I_3 and zero on I_2 and using Havinga's first approximation the coulomb integrals will be expressed by $(\alpha - 0{\cdot}1\beta + 0{\cdot}1\beta)$ for I_1, α for I_2, $(\alpha - 0{\cdot}1\beta)$ for I_3.

We can then calculate the energy levels E from the secular determinant

$$\begin{vmatrix} \alpha-E & \beta & 0 \\ \beta & \alpha-E & \beta \\ 0 & \beta & (\alpha-E)-0{\cdot}1\beta \end{vmatrix} = 0$$

Dividing each then by β and making $\frac{\alpha-E}{\beta} = x$ we obtain the equation

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x-0{\cdot}1 \end{vmatrix} = 0$$

Hence $x^3 - 0{\cdot}1x^2 - 2x + 0{\cdot}1 = 0$.

The roots of this equation can be calculated as

$x = -1{\cdot}3903,\ 0{\cdot}04994$ and $1{\cdot}441$

The third root need not be calculated as there are only four electrons to distribute between the three energy levels, hence only the two of lowest energy will be used.

To calculate the bond orders and electron densities we need the coefficients c_1, c_2 and c_3 for the equations

$$c_1x + c_2 = 0$$

$$c_1 + c_2x + c_3 = 0$$

$$c_2 + c_3(x-0{\cdot}1) = 0$$

and as a check

$$c_1^2 + c_2^2 + c_3^2 = 1$$

For $x = -1{\cdot}3903$	For $x = 0{\cdot}04994$
$c_1^2 = 0{\cdot}2629$	$c_1^2 = 0{\cdot}5006$
$c_2^2 = 0{\cdot}5082$	$c_2^2 = 0{\cdot}00124_9$
$c_3^2 = 0{\cdot}2288_5$	$c_3^2 = 0{\cdot}4981$
$c_1c_2 = 0{\cdot}3655_5$	$c_1c_2 = -0{\cdot}02500$
$c_2c_3 = 0{\cdot}3410$	$c_2c_3 = 0{\cdot}02494$
$c_1c_3 = 0{\cdot}2453$	$c_1c_3 = -0{\cdot}4994$

The charge density

$$P_\mu = \sum_i n_i c_{i\mu}^2$$

where $c_{i\mu}$ is the coefficient of atom μ in the i^{th} molecular orbital which is occupied by the n_i electrons. The sum is over all i. The bond order

$$\underset{\mu\neq\nu}{P_{\mu\nu}} = \sum_i n_i c_{i\mu} c_{i\nu}$$

where ν designates an atom other than μ.

From these equations we obtain

$P_1 = 1{\cdot}5271$; $P_2 = 1{\cdot}0189$; $P_3 = 1{\cdot}4540$

$P_{12}=0{\cdot}6811$; $P_{23}= 0{\cdot}7319$; $P_{13}=-0{\cdot}5087$

Since the core charge (X_μ) on each carbon atom on removing the 4 electrons under consideration is +1 the nett charge density is $(1 - P_\mu)$

The triiodide ion would then be represented as follows

$$\begin{array}{ccccc} -0\cdot527 & & -0\cdot019 & & -0\cdot454 \\ I_1 & \overline{0\cdot681} & I_2 & \overline{0\cdot732} & I_3 \end{array}$$

2) Calculation of β

If we consider the iodine molecule as having a covalent bond formed from two $5p\sigma$ electrons, the ground state energy E(r) for an interatomic distance r can be expressed by the sum

$$E_{(r)} = 2\alpha_{core} + 2\beta_{core} = \tfrac{1}{2}\gamma_{\mu} + \tfrac{1}{2}\gamma_{\mu\nu} \mp \frac{14\cdot4}{r_{\mu\nu}}$$

This is an expanded form of the energy relationship given by Pople (103) which has already been mentioned in considering the total energies of the triiodide ions. If

$$\alpha_{\mu} = -I_{\mu} + X_{\nu}\gamma_{\mu\nu}$$

and $X_{\nu} = 1$ then

$$E_{(r)} = -2I_{\mu} = 2\beta + \tfrac{1}{2}\gamma_{\mu} - \tfrac{3}{2}\gamma_{\mu\nu} + \frac{14\cdot4}{r_{\mu\nu}}$$

All these quantities have previously been defined.

The ground state dissociation energy

$$D_e = D_o + \text{zero point energy}$$

where D_o is the dissociation energy from the v = 0 vibrational state. This is expressed by the monocentric terms in the summation hence

$$D_e = (-2I_{\mu} \ast \tfrac{1}{2}\gamma_{\mu})$$

The difference between the dissociation energy D_e and the energy $U_{(r)}$ at an interatomic distance r is then the sum of the two centre terms i.e. as $r_{\mu\nu}$ goes to infinity $D_e = U_{(r)}$. It can then be shown that

$$D_e - U_{(r)} = \tfrac{3}{2}\gamma_{\mu\nu} - 2\beta - \frac{14\cdot4}{r_{\mu\nu}}$$

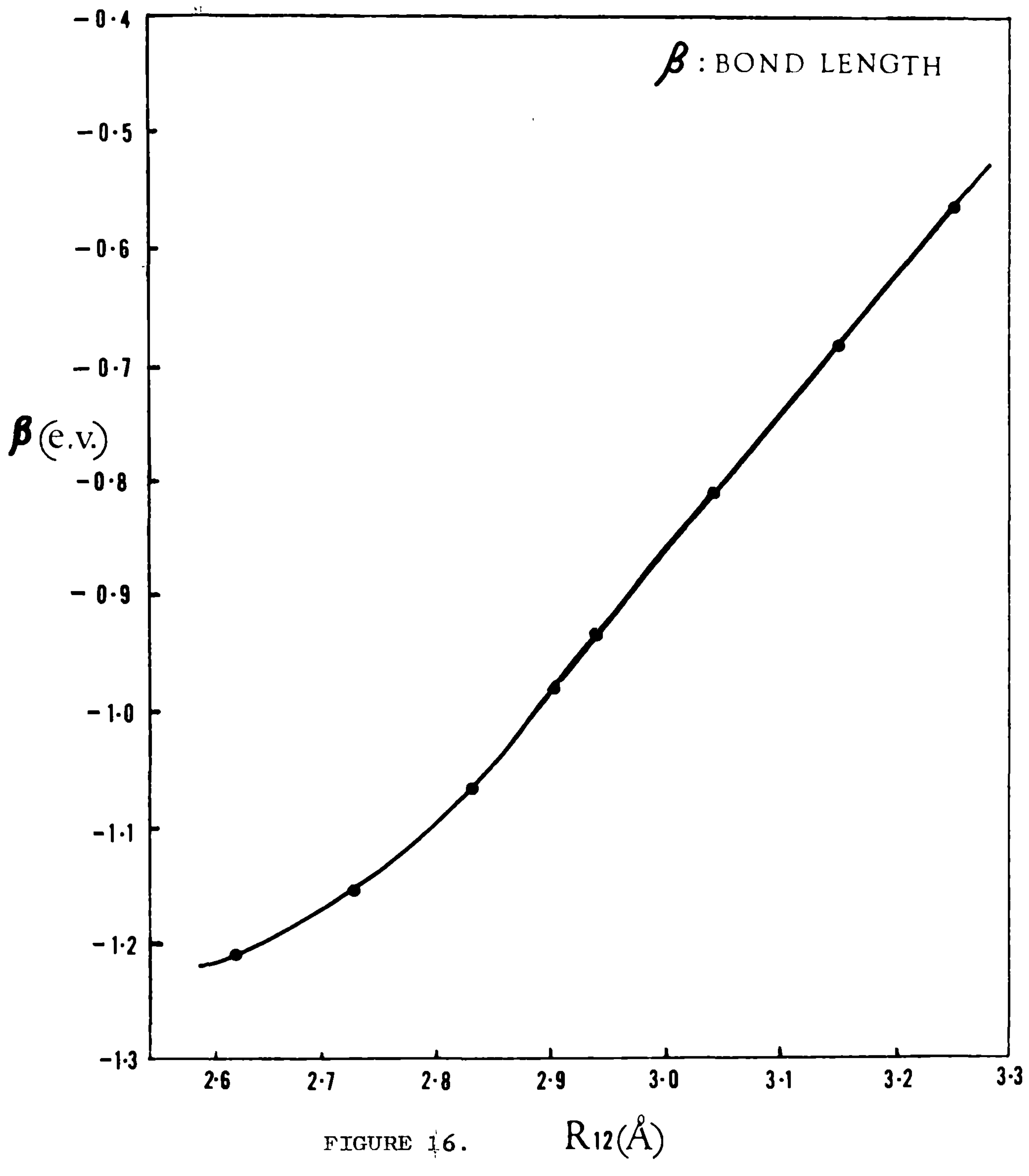

β : BOND LENGTH
β (e.v.)
−0·4
−0·5
−0·6
−0·7
−0·8
−0·9
−1·0
−1·1
−1·2
−1·3
2·6
2·7
2·8
2·9
3·0
3·1
3·2
3·3
R12(Å)

FIGURE 16.

The quantities d_e and $U_{(r)}$ are obtained from the potential energy curve for the iodine molecule (97) and $\gamma_{\mu\nu}$ can be evaluated as is described in the following section dealing with a typical VESCF calculation.

The following table lists the values of $U_{(r)}$ $D_e - U_{(r)}$ and β for a variety of interatomic distances. The dissociation energy D_e is the sum of the zero point energy of 102·1 cm^{-1} and D_o of 12452·5 cm^{-1}.

Table 11.

$r_{\mu\nu}$(Å)	$U_{(r)}$ cm^{-1}	$D_e-U_{(r)}$ e.v.	$+\beta$ ev
2·620	102	1·5438	−1·209
2·725	150	1·5379	−1·151
2·83	850	1·4511	−1·064
2·90	1670	1·3495	−0·977
2·935	2179	1·2864	−0·931
3·04	3460	1·1276	−0·812
3·145	5000	0·9366	−0·680
3·25	6340	0·7705	−0·564

The variation of β with r is shown in fig. 16

3) V.E.S.C F. Calculations

The theoretical basis of the VESCF method has been outlined in chapter 9. This approach allows an iterative treatment until self consistent figures are obtained for the bond order matrix and effective nuclear charges. Values for $F_{\mu\mu}$ and $F_{\mu\nu}$ must first be calculated so that the determinant

$$\begin{vmatrix} F_{11}-E & F_{12} & F_{13} \\ F_{21} & F_{22}-E & F_{23} \\ F_{31} & F_{32} & F_{33}-E \end{vmatrix} = 0$$

may be solved for E. The calculation of bond order and charge densities is then the same as in the Hückel method.

There are several steps in the calculation of $F_{\mu\mu}$ and $F_{\mu\nu}$ which should be outlined in detail. The expressions used to obtain $F_{\mu\mu}$ and $F_{\mu\nu}$ are

$$F_{\mu\mu} = -I_\mu + \tfrac{1}{2}P_\mu\gamma_\mu + \sum_{\nu\neq\mu} (P_\nu - X_\nu)\,\gamma_{\mu\nu} \qquad (1)$$

$$F_{\mu\nu} = \beta_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\gamma_{\mu\nu} \qquad (2)$$

where μ and ν refer to any two atoms in the ion. Of the other symbols, P_μ, $P_{\mu\nu}$ and X_ν have been described in the Hückel treatment.

The valence state ionization potential I_μ and the coulomb repulsion integrals γ_μ, $\gamma_{\mu\nu}$ are dependent on the effective nuclear charge Z_μ. This is obtained from Slater's Rules (113). Z_μ is the difference between the atomic number and a screening constant. The screening constant for iodine is the sum of

(i) 0·35 for each 5s and 5p electron

(ii) 0·85 for the 4s, 4p, 4d electrons

(iii) 1·0 for all other electrons

This gives a value of 7·6 for I^+.

The monocentric coulomb repulsion integral γ_μ is given by the relationship $\gamma_\mu = I_\mu - A_\mu$ where I_μ and A_μ are the valence state ionisation potential and electron affinity respectively. As this is dependent on the effective nuclear charge it is possible to evaluate the relationship $\gamma_\mu = k \times Z_\mu$ where k can be evaluated from the experimental ionisation potential and electron affinity for iodine. The value for k, as outlined in chapter nine is 0.923.

The quantity $\gamma_{\mu\nu}$ is obtained from the values of γ_μ and γ_ν by the Mataga - Nishimoto formula,

$$\gamma_{\mu\nu} = - \frac{14.4}{r_{\mu\nu} + a_{\mu\nu}}$$

where $a_{\mu\nu}$ is a constant given by the formula $\frac{1}{2}(\gamma_\mu \quad \gamma_\nu) = \frac{14.4}{a_{\mu\nu}}$ and $r_{\mu\nu}$ is the interatomic distance in Å. The only remaining term to be evaluated is I_μ , the valence state ionisation potential. As we will be dealing with fractional charges it is necessary to derive a relationship which will permit this to be evaluated in terms of Z_μ . By taking the ionisation potentials for the isoelectronic series I, Xe^+, Cs^{++} we have the same screening constant and an increase of one, in the valence shell core charge. This leads to values of 7.60, 8.60 and 9.60 for Z_μ . For the actual case of iodine however the core charge is remaining constant whilst Z_μ is varying with the fractional charge. It is then necessary to scale down the I_μ to correspond to the appropriate core charge of 7. The ionisation potentials, as derived from Moores' tables (114) are therefore multiplied by 7/7,7/8

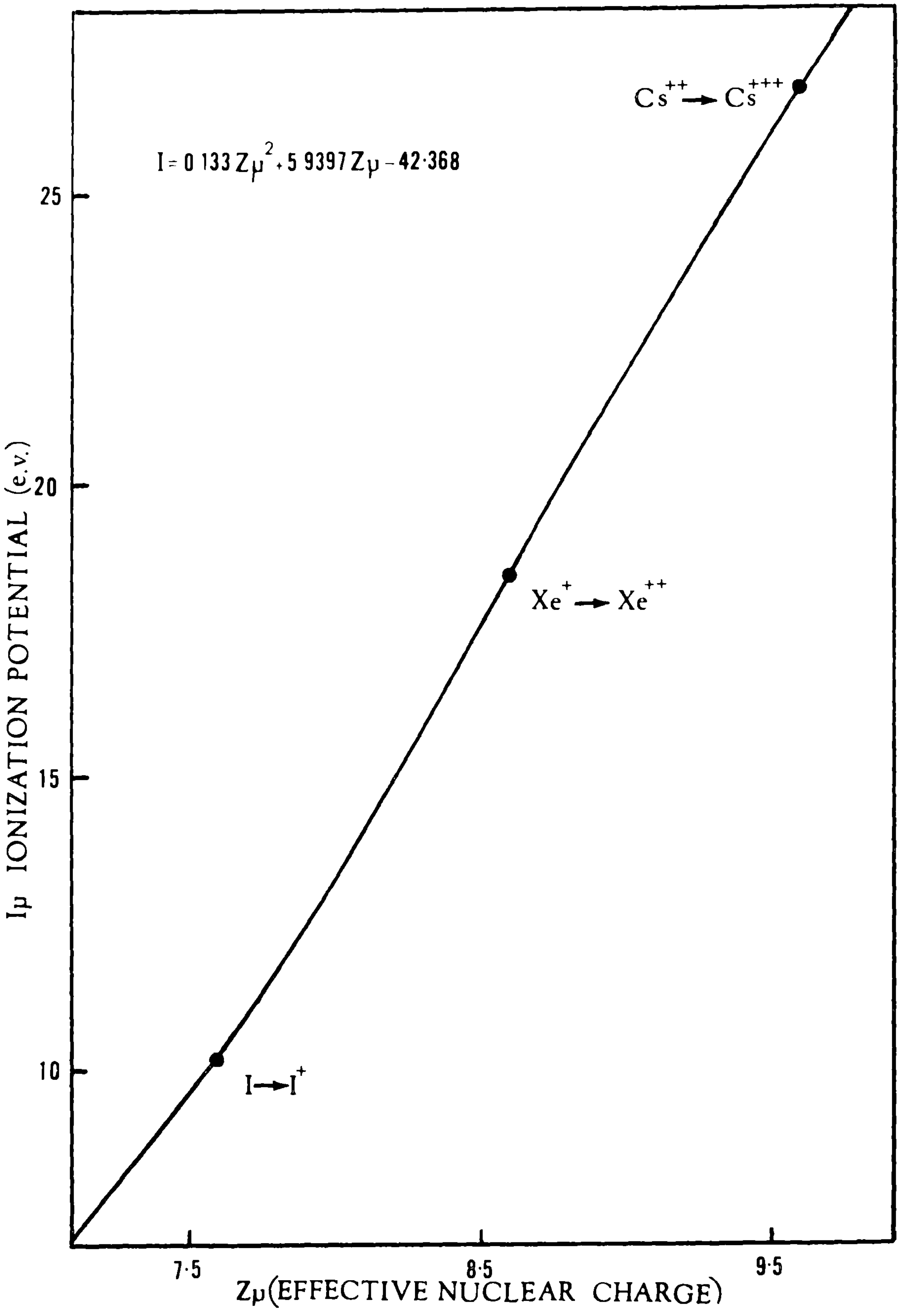

Cs^{++} → Cs^{+++}
I = 0 133 Zμ^2 + 5 9397 Zμ − 42·368
25
20
15
10
Iμ IONIZATION POTENTIAL (e.v.)
Xe^{+} → Xe^{++}
I → I^{+}
7·5
8·5
9·5
Zμ(EFFECTIVE NUCLEAR CHARGE)

FIGURE 17.

and 7/9 respectively. The ionisation potentials, before scaling are 10.455, 21.2 and 34.6 ev for I, Xe^{+} and Cs^{++}. This is an approximation as there are terms in the ionisation potential expression which would not be properly adjusted by this scaling. The potential energy, which is the largest term in this expression, is adjusted so that this is a desirable approximation.

Although only three points are obtained for a plot of scaled ionisation potential versus Z_{μ} , it is possible to fit these to a quadratic relationship by a least aquares method (115) and the expression

$$I_{\mu} = 0.133\ Z_{\mu}^{2} + 5.9397\ Z_{\mu} - 42.368 \qquad \text{(a)}$$

is obtained, figure 17.

As an example of the V.E.S.C.F. procedure, the case of the triiodide ion in Cs I_3 will be taken. This will also be considered under the influence of a cation 4 Å from one end, along the internuclear axis,

$$+ \_\_\_\_ 4\text{Å} \_\_\_\_ I_1 \_\_\_\_ 2.84\text{Å} \_\_\_\_ I_2 \_\_\_\_ 3.04\text{Å} \_\_\_\_ I_3$$

the geometry being as shown. The angle between I_1 and I_3 will be taken as 180°. The core resonance integral β will be given a value of -6 e.v. for $\beta_{12} = \beta_{23}$ and zero for β_{13} It is necessary to assume electron densities and bond orders at each atom in order to calculate the effective nuclear charges. The Havinga first approximation results, as detailed in the part one of this chapter, are a convenient starting point. The external electrostatic field is included as part of the diagonal $F_{\mu\mu}$ elements of the F matrix.

The electron densities to be used are $P_1 = 1.527$ $P_2 = 1.619$, $P_3 = 1.454$.

$Z_1 = 7.6 + 0.93 (X_1 - P_1)$ where $X_1 = 1.0$

$Z_1 = 7.414$.

From the quadratic relationship (a) $I_1 = 8.93$ e.v.

$\gamma_1 = 0.923 Z_1 = 6.8431$

Similarly $Z_2 = 7.593$; $I_2 = 10.38$; $\gamma_2 = 7.0083$

and $Z_3 = 7.439$; $I_3 = 9.15$; $\gamma_3 = 6.8662$

$$a_{12} = \frac{2 \times 14.40}{\gamma_1 + \gamma_2} = \frac{28.80}{13.8514} = 2.0792$$

$$\gamma_{12} = \frac{14.40}{a_{12} + r_{12}} = \frac{14.40}{2.0792 + 3.04} = 2.8129$$

Similarly $a_{23} = 2.0758$ $\gamma_{23} = 2.8129$

and $a_{13} = 2.1008$ $\gamma_{13} = 1.8066$

Also from the Havinga result $P_{12} = 0.681$, $P_{23} = 0.732$, $P_{13} = - 0.509$ The cation electrostatic potential is given by $-\frac{14.4}{r_\mu}$ where r_μ is the distance from atom μ to the cation. These values are $- 3.6, -2.045, -1.459$ e.v. for atoms 1, 2 and 3 respectively.

All the necessary terms are now evaluated to calculate the F matrix elements $F_{\mu\mu}$ and $F_{\mu\nu}$ using the equations 1 and 2, the appropriate electrostatic potential term being added to equation 1.

For atom 1, $F_{11} = -I_1 + \frac{1}{2} P_1\gamma_1 - [(1-P_{12})\gamma_{12} + (1-P_{13})\gamma_{13}] - \frac{14.4}{r_1} = -6.4078$

Similarly $F_{22} = -6.5289$ e.v. and $F_{33} = -4.5805$ e.v.

Also $F_{12} = \beta_{12} - \frac{1}{2} P_{12}\, \gamma_{12} = -7.0267$ e.v.

and $F_{23} = -6.9980$ e.v. and $F_{13} = 0.4607$ e.v.

The energy levels can then be obtained from the secular determinant

$$\begin{vmatrix} (-6.4078 - E) & -7.0267 & 0.4607 \\ -7.0267 & (-6.5289 - E) & -6.9980 \\ 0.4607 & -6.9980 & (-4.5805 - E) \end{vmatrix} = 0$$

The roots of this equation are E = -15.768, -5.956, 4.206 e.v.

The coefficients C_1, C_2 and C_3 can then be calculated in a manner similar to that used in the Hückel treatment. These are set out in the following table.

TABLE 12.

E (e.v.)	C_1	C_2	C_3
4.206	0.473	-0.677	0.564
-5.956	0.706	-0.091_4	-0.702
-15.768	0.527	0.730	0.435

The coefficients of the two lowest energy levels can be used to obtain the values of $P_1, P_2, P_3, P_{12}, P_{23}$, and P_{13} as outlined in the Hückel method and these values can be used in another iteration. The following table lists the values P_1, P_2, and P_3 for a number of such iterations.

TABLE 13.

Iteration	P_1	P_2	P_3
1	1.527	1.019	1.454
2	1.552	1.082	1.364
3	1.549	1.053	1.390
4	1.631	1.130	1.239
5	1.575	1.064	1.361
6	1.619	1.112	1.269
$6'$	1.600	1.093	1.308
7	1.598	1.082	1.321

It can be seen from the first six sets of figures that the values are oscillating about a mean, in a manner analogous to the damping of a balance. The "balance" relationship can then be applied to facilitate convergence i.e.

mean = $\dfrac{n_1 + 2n_2 + n_3}{4}$ where n_1, n_2 and n_3 are successive values. The figures $6'$ represent the mean of the preceding three sets of readings and one further iteration on this is found sufficient for this problem. Similar calculations were made for $\beta = -4, -6$ and -8 e.v. The same procedure was also used for a symmetric triiodide ion.

A computer program became available for V.E.S.C.F. calculations at this stage and these results could be checked and the number of model systems could be increased.

On the average about 10 iterations are performed by the computer for each system.

A summary of the model systems treated is given in the following table.

TABLE 14.

V.E.S.C.F. Calculations on Model Systems.

Symmetric triiodide.

		$P_1 = P_3$	P_2	$P_{12} = P_{23}$
Zero field	- 2	1.4398	1.1205	0.7020
	- 4	1.4587	1.0825	0.7047
	- 6	1.4686	1.0628	0.7057
	- 8	1.4747	1.0507	0.7062
Cation 4Å from each end	- 2	1.4791	1.0419	0.7065
	- 4	1.4857	1.0287	0.7068
	- 6	1.4891	1.0218	0.7069
	- 8	1.4912	1.0176	0.7070

TABLE 14 (contd.)

Asymmetric triiodide.

		P_1	P_2	P_3	P_{12}	P_{23}
Zero field	-2	1.4438	1.1216	1.4345	0.6990	0.7047
	-4	1.4616	1.0834	1.4550	0.7025	0.7068
	-6	1.4708	1.0635	1.4657	0.7040	0.7074
	-8	1.4765	1.0512	1.4723	0.7048	0.7076
Cation 4Å	-2	1.6009	1.0912	1.3079	0.6022	0.7931
	-4	1.5767	1.0633	1.3600	0.6297	0.7743
	-6	1.5615	1.0479	1.3906	0.6461	0.7617
	-8	1.5512	1.0384	1.4104	0.6569	0.7530
Cation 6Å	-2	1.5312	1.1073	1.3614	0.6469	0.7550
	-4	1.5256	1.0738	1.4004	0.6627	0.7452
	-6	1.5213	1.0561	1.4226	0.6722	0.7382
	-8	1.5179	1.0452	1.4369	0.6785	0.7333
Cation 8Å	-2	1.4996	1.1137	1.3866	0.6659	0.7373
	-4	1.5026	1.0781	1.4193	0.6772	0.7317
	-6	1.5031	1.0594	1.4376	0.6837	0.7273
	-8	1.5029	1.0478	1.4492	0.6879	0.7242
Cation 10Å	-2	1.4826	1.1168	1.4006	0.6760	0.7276
	-4	1.4902	1.0801	1.4297	0.6848	0.7243
	-6	1.4933	1.0609	1.4458	0.6898	0.7214
	-8	1.4949	1.0492	1.4560	0.6930	0.7192

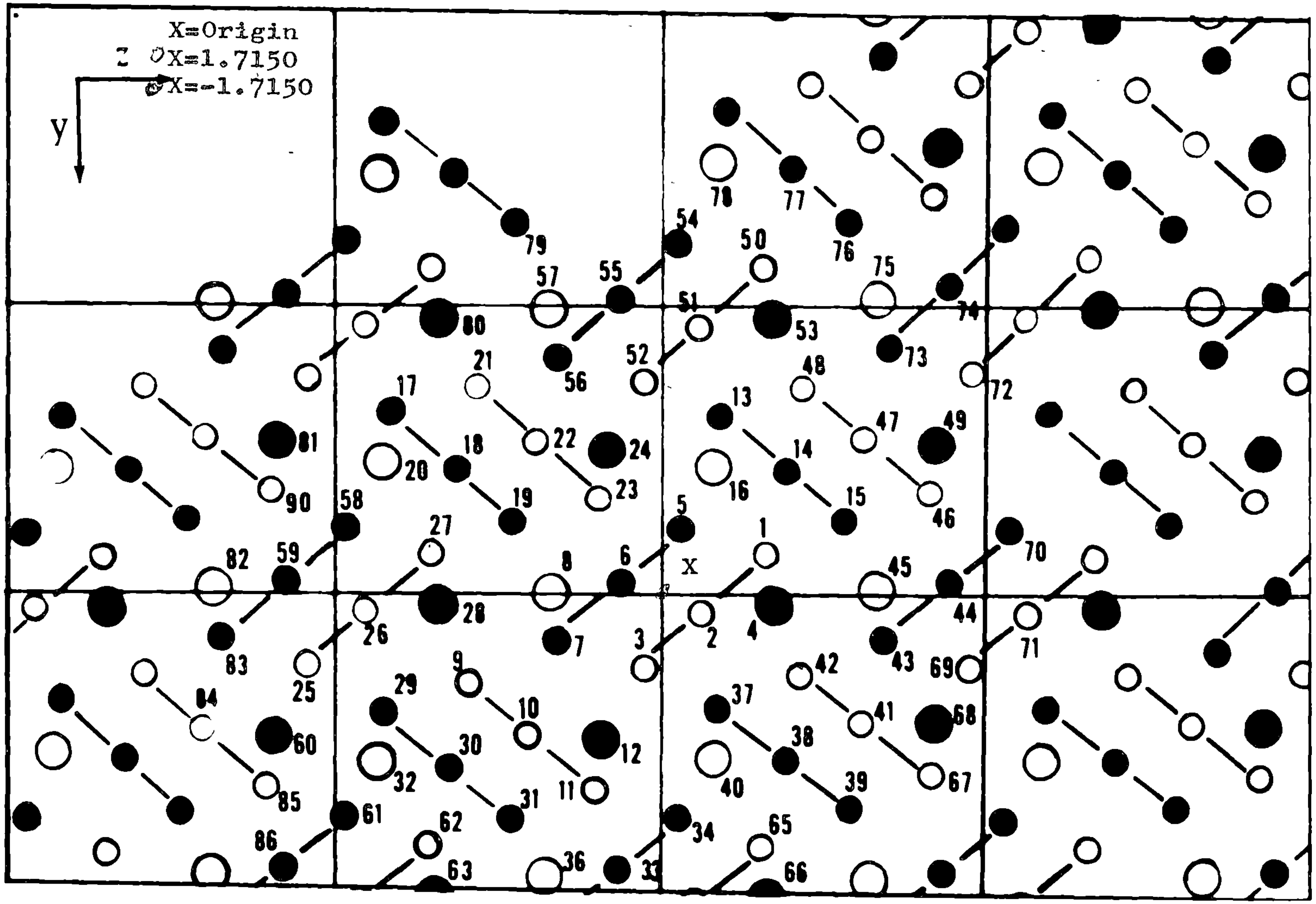

X=Origin
○X=1.7150
●X=-1.7150
y
X

FIGURE 18.

4) Coordinates of Atoms in CsI_3 and $As\phi_4I_3$.

As part of the calculation of the electrostatic field at a reference triiodide ion in the caesium triiodide and tetraphenyl arsonium triiodide crystals it was necessary to calculate the coordinates of the atoms which were likely to be included in the summation for this field. The term involving the distances of these atoms from the reference iodine atoms is $\sum_{l} q_l/r_l \; F(\eta^{\frac{1}{2}} r_l)$ where η is a constant, r_l is the distance (Å) from the reference iodine atom to a neighbouring atom l and $F(\eta^{\frac{1}{2}} r_l)$ is an error function of the type $F(x) = 2/\pi^{\frac{1}{2}} \int_0^x e^{-s^2} ds$ Since $\eta^{\frac{1}{2}}$ was given a value of 0.35 and $F(3.5) \sim 0$, the coordinates of all the atoms within about a 10Å radius of the reference anion were required.

Caesium triiodide has an orthorhombic structure with a space group Pmcn (98). The unit cell dimensions are

a = 6.86 Å, b = 9.98Å, C = 11.09 Å

and the projection on the (100) plane is shown in figure 18. The coordinates of the four molecules in the unit cell are given by the four sets of coordinates $\pm (x,y,z)$; $\pm (x - a/2, y - b/2, - z + c/2)$. Taking the origin at the point indicated in the figure the coordinates of atoms 20 - 23 are given by Tasman and Boswijk as -

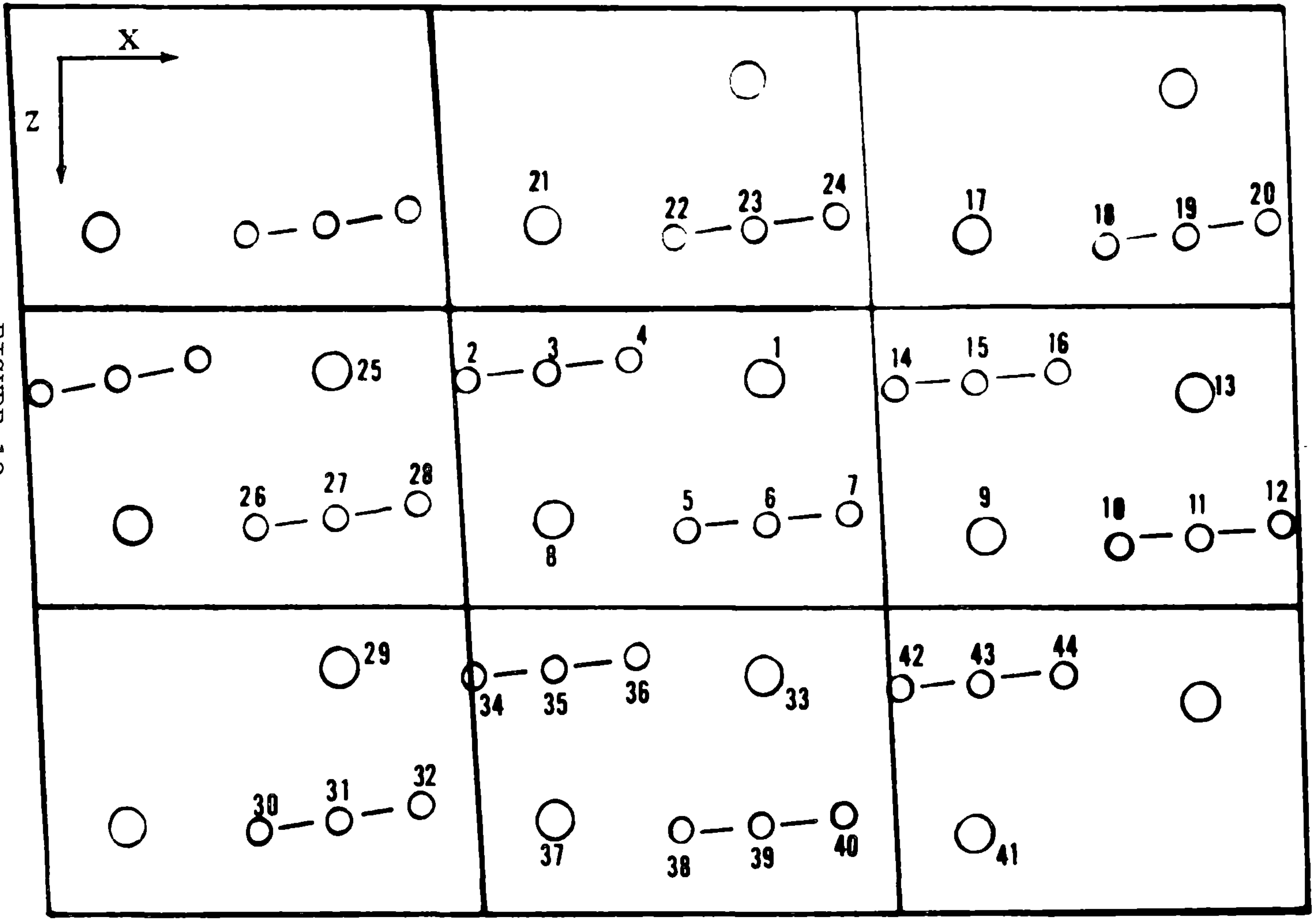

X
Z

FIGURE 19.

Atom	x	y	z (Å)
20	1.7150	-4.6307	-9.1592
21	1.7150	-7.3523	-6.3180
22	1.7150	-5.4890	-4.1898
23	1.7150	-3.5908	-1.8199

From these figures it is possible to obtain the coordinates of the 90 atoms numbered in figure 18 by making the relevant unit cell displacements in the y and z directions. Atoms above and below the two planes indicated in the figure are also included in the summation.

The tetraphenyl arsonium triiodide unit cell is monoclinic with a space group P2/n. The unit cell dimensions are

$a = 15.34$ Å, $b = 7.63$ Å, $c = 10.63$ Å, $\beta = 93.4^{\circ}$

and there are two molecules per unit cell. The projection on (010) is shown in figure 19. In this case the coordinates of atoms 1 - 4 are listed as follows

Atom	x	y	z (Å)
1	11.5050	0.0000	7.9725
2	0.9511	1.2971	7.4729
3	3.8350	1.2055	7.9725
4	6.7189	1.2971	8.4721

From thses the coordinates of atoms 5 - 44 can be obtained.

5) Crystal electrostatic potential calculations.

In each of the crystals under consideration the potential was calculated at the iodine atoms numbered 5, 6, and 7 in the preceding figures. The Ewald formula gives the potential ψ_i at atom i in a crystal as the sum

$$\psi_i = 4\pi/\Delta \sum_{G}' S(G)G^{-2}\, e^{-G^2/4\eta} - 2q_i(\eta/\pi)^{\frac{1}{2}} + \sum_{l}' q_l/r_l\, F(\eta^{\frac{1}{2}}\, r_l)$$

where all these symbols have been defined in chapter nine.

Of these three terms in this expression the second i.e. $2\, q_i(\eta/\pi)^{\frac{1}{2}}$ does not involve a summation and is therefore readily evaluated.

The constant η has to be chosen such that the first and last terms are suitably convergent. A value of $\eta^{\frac{1}{2}} = 0.35$ gives 75 terms to be summed in the first or structure factor term and 62 terms per iodine atom in the last or error function term. Changing the constant $\eta^{1/2}$ to 0.45 the corresponding numbers were 149 and 27. The value of 0.35 was therefore used throughout, except for a check on the method with both values to establish that the result was the same in each case.

The structure factor term is a constant for each iodine atom as it is a function of the unit cell. It is therefore not required for the V.E.S.C.F. procedure as a constant added to the potential at each atom will not affect the differences between the diagonal F matrix elements ($F_{\mu\mu}$)

and consequently the bond order matrix is unchanged. This term was only evaluated in the earlier calculations for caesium triiodide to establish its magnitude, and as part of the check on the choice of η

Starting from assumed values of the electron distribution in the triiodide ion an iterative process was used until a convergent result was obtained for these charges. This involves an Ewald summation for an electrostatic field, followed by a V.E.S.C.F. calculation for the new electron densities, at each iteration. It was desirable to use a computer for the Ewald calculation as well as the V.E.S.C.F. calculations. A series of simplified programmes were written which could do this in about an hour of machine time. The V.E.S.C.F. program was already available.

The various programs used were as follows:-

a) Alteration of charges on each iodine atom
b) Calculation of $\eta^{\frac{1}{2}} r_l$ and q_l/r_l
c) Calculation of $F(\eta^{\frac{1}{2}} r_l)$ and summation $\sum_l q_l/r_l \, F(\eta^{\frac{1}{2}} r_l)$
d) Calculation of $G^{-2} e^{-G^2/4\eta}$
e) Calculation of $S(G) \, G^{-2} e^{-G^2/4\eta}$ and summation.

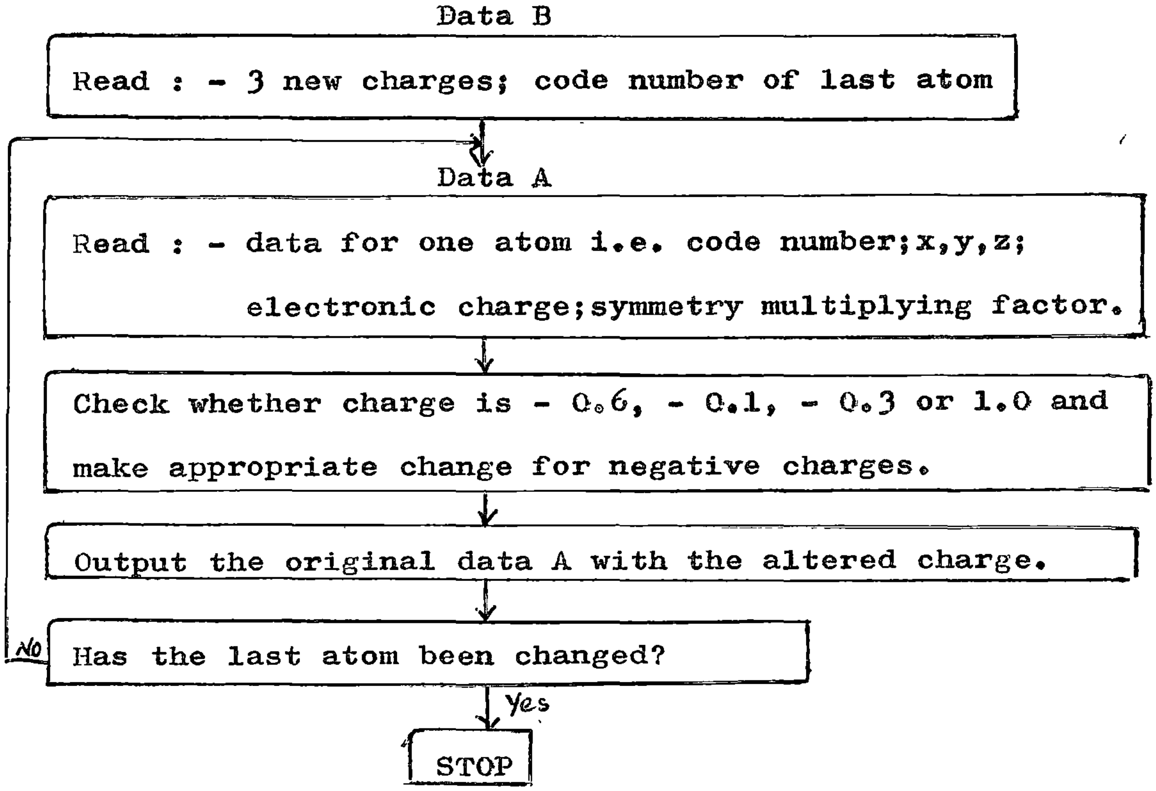
These programs are all written in Sirius autocode for use on the Ferranti Sirius computer. The basic steps in each of these programs will be outlined diagramatically.

a) Alteration of charges on each iodine atom

The basic coordinate data has six figures per atom and is of the form atom code number; x,y,z coordinates Å; electronic charge; and multiplying factor of two or one, depending on whether a similar atom is in an equivalent position on the opposite side of the reference atom plane or not. For Cs I_3 the factor is two for atoms in x planes other than that of the reference atom and one for atoms in this plane. For $As\phi_4I_3$ the factor is one for all planes. In the basic data charges of - 0.6, - 0.1 and - 0.3 are assigned to the iodine atoms in caesium triiodide i.e.

$$\overset{-\,0.6}{I_1}\overset{3.04\text{Å}}{\rule{3cm}{0.4pt}}\overset{-\,0.1}{I_2}\overset{2.83\text{Å}}{\rule{3cm}{0.4pt}}\overset{-\,0.3}{I_3}$$

These charges must be altered at each iteration.

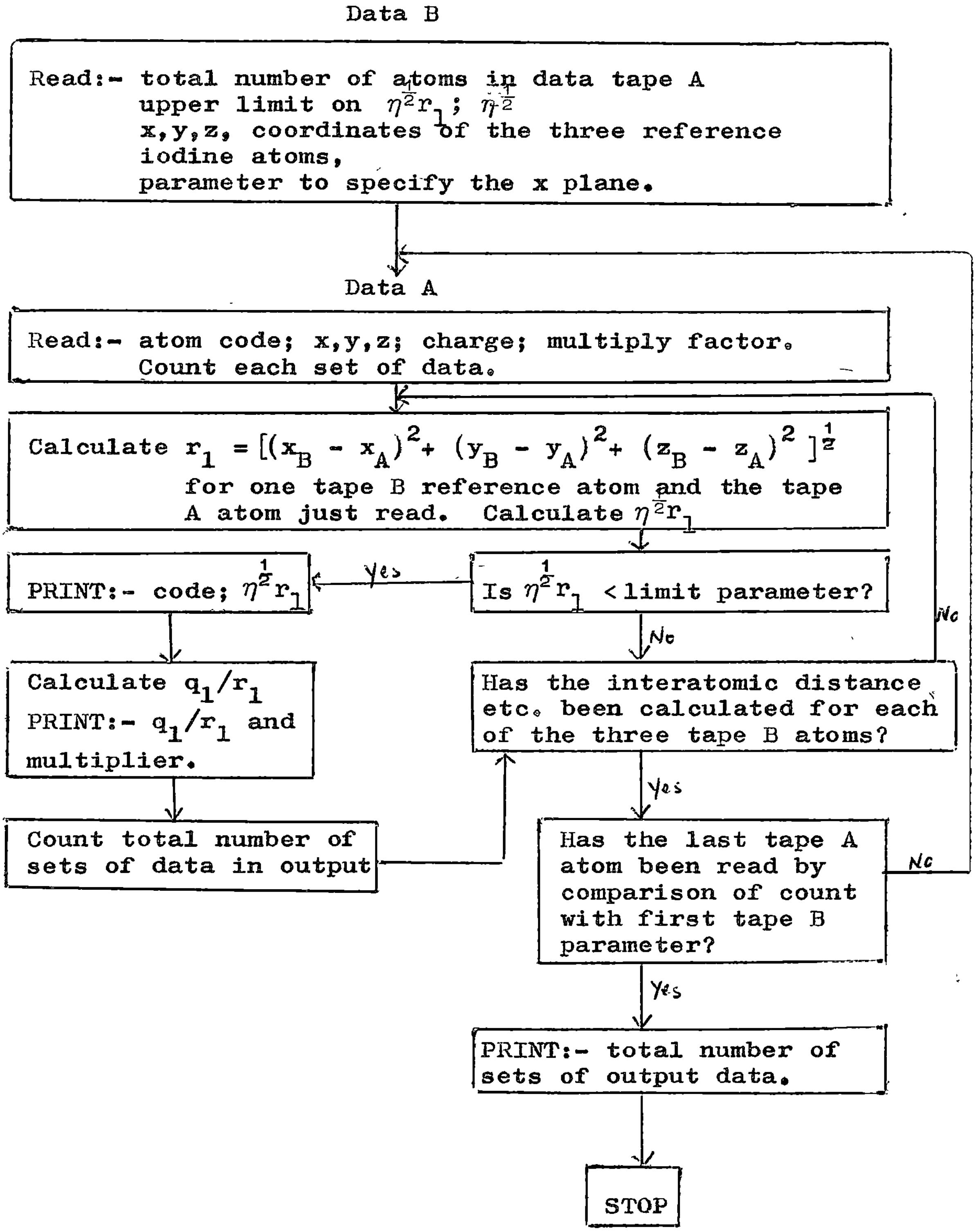

Data B
Read : - 3 new charges; code number of last atom
Data A
Read : - data for one atom i.e. code number; x,y,z; electronic charge; symmetry multiplying factor.
Check whether charge is - 0.6, - 0.1, - 0.3 or 1.0 and make appropriate change for negative charges.
Output the original data A with the altered charge.
No
Has the last atom been changed?
Yes
STOP

The output from this program is then used as input tape A in the calculation of q_1/r_1 and

b) Calculation of q_1/r_1 and $\eta^{\frac{1}{2}} r_1$

In this calculation the coordinates of the three reference atoms are input as tape B along with the value of $\eta^{\frac{1}{2}}$ and also an upper limit on the value of $\eta^{\frac{1}{2}} r_1$ as the error function tends to zero as $\eta^{\frac{1}{2}} r_1$ tends to infinity. A value of 3.5 makes the error function $\sim 1 \times 10^{-6}$. The total number of atoms from the preceding tape A are also included. An x parameter, which adds an appropriate constant to the x coordinates of the atoms in tape A, is also included. This parameter then causes the tape A data to become the data for another plane of atoms. A separate set of tape A data is also required for the three iodine atoms directly above the reference atoms.

The output atom code is modified in this program so that, for example, atoms 4 from tape A would be changed to 104 for the quantities referred to the first reference atom, 204 for the second and 304 for the third.


Data B
Read:- total number of atoms in data tape A
upper limit on $\eta^{\frac{1}{2}}r_1$; $\eta^{\frac{1}{2}}$
x, y, z, coordinates of the three reference iodine atoms,
parameter to specify the x plane.
Data A
Read:- atom code; x,y,z; charge; multiply factor.
Count each set of data.
Calculate $r_1 = [(x_B - x_A)^2 + (y_B - y_A)^2 + (z_B - z_A)^2]^{\frac{1}{2}}$ for one tape B reference atom and the tape A atom just read. Calculate $\eta^{\frac{1}{2}}r_1$
Is $\eta^{\frac{1}{2}}r_1$ < limit parameter?
Yes
PRINT:- code; $\eta^{\frac{1}{2}}r_1$
Calculate q_1/r_1
PRINT:- q_1/r_1 and multiplier.
Count total number of sets of data in output
No
Has the interatomic distance etc. been calculated for each of the three tape B atoms?
No
Yes
Has the last tape A atom been read by comparison of count with first tape B parameter?
No
Yes
PRINT:- total number of sets of output data.
STOP

c) Calculation of $\sum_{1} q_1/r_1 \; F(\eta^{\frac{1}{2}} r_1)$

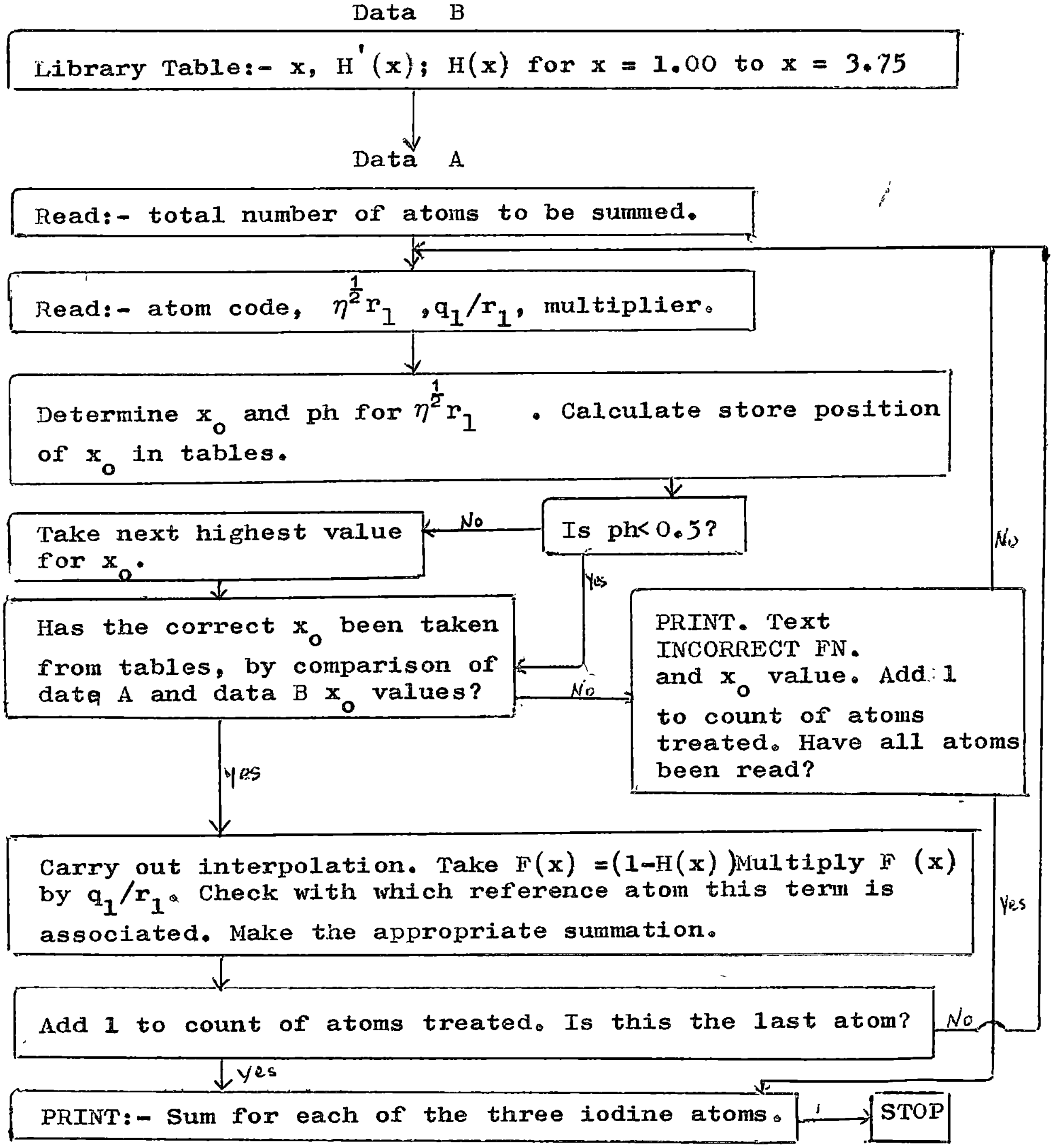
This program takes the information for the previous output, in particular q_1/r_1 and $\eta^{\frac{1}{2}} r_1$, and, by reference to an input table, the error function is obtained. This is multiplied by q_1/r_1 and then summed for the appropriate reference iodine atom. The error function

$$H\ (x) = 2/\pi^{\frac{1}{2}} \int_0^x e^{-s^2}\, ds$$

is tabulated to fifteen decimal places and for increments in x of 0.0001 from 0 to 1.0 and at intervals of 0.001 from 1.0 to 5.6 (118). The required function F (x) is the derivative from x to ∞ and is given by $(1 - H(x)\ )$. A library tape was prepared with the error function tabulated at intervals of 0.01 in x from x = 1.00 to x = 3.75. The derivative $H'\ (x) = 2/\pi^{\frac{1}{2}}\ e^{-x^2}$ was also generated, by the computer, on this tape for each x. This range of x was taken as values of $\eta^{\frac{1}{2}} r_1$ or x, were not encountered less than 1.00 and an arbitrary upper limit on $\eta^{\frac{1}{2}} r_1$ was put at 3.5 in the preceding computation. Values of $\eta^{\frac{1}{2}} r_1$ are obtained to greater accuracy than 0.01 and an interpolation can be used to obtain a more accurate value of the error function between successive tabulated x values. The interpolation formula was

$$H\ (x_o + ph) = H\ (x_o) + ph\ H'(x_o) - p^2h^2\ H'(x_o)\ [x_o - 1/3\ ph\ (2\ x_o^2 - 1) + 1/6\ p^2h^2\ x_o\ (2\ x_o^2 - 3),\ ]\ ,$$

where $H(x_o + ph)$ is the required value for the function, ph indicating the difference between the given x and x_o, the nearest tabulated value of x. For values of x greater than 2.5 the terms in $p^4 h^4$ are omitted.



Data B

Library Table:- x, $H'(x)$; $H(x)$ for $x = 1.00$ to $x = 3.75$

Data A

Read:- total number of atoms to be summed.

Read:- atom code, $\eta^{\frac{1}{2}} r_1$, q_1/r_1, multiplier.

Determine x_o and ph for $\eta^{\frac{1}{2}} r_1$. Calculate store position of x_o in tables.

Is ph< 0.5?

Take next highest value for x_o.

Has the correct x_o been taken from tables, by comparison of data A and data B x_o values?

PRINT. Text INCORRECT FN. and x_o value. Add 1 to count of atoms treated. Have all atoms been read?

Carry out interpolation. Take $F(x) = (1 - H(x))$ Multiply F (x) by q_1/r_1. Check with which reference atom this term is associated. Make the appropriate summation.

Add 1 to count of atoms treated. Is this the last atom?

PRINT:- Sum for each of the three iodine atoms.

STOP

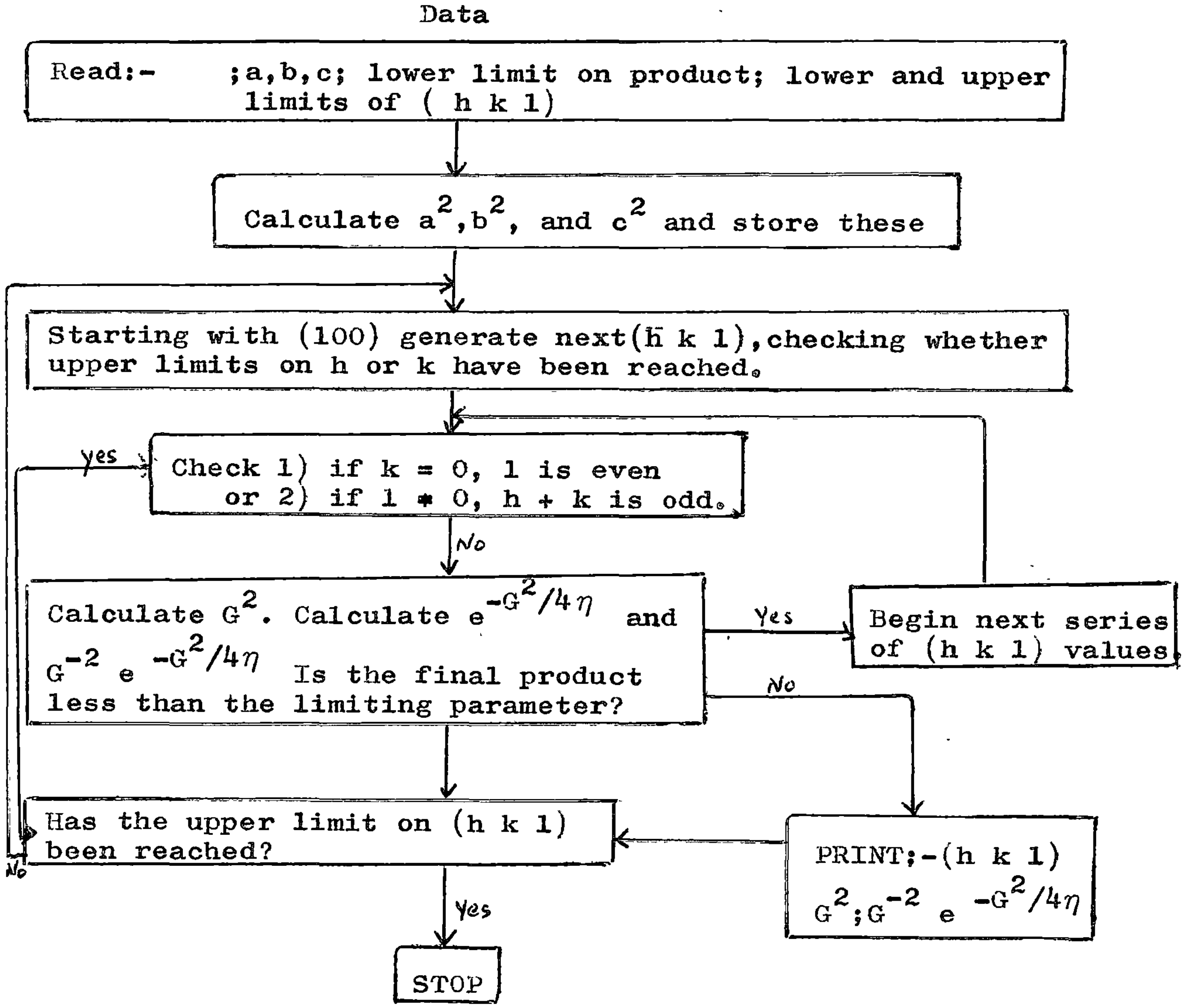
The preceding programs were the ones in most common use. The remaining structure factor was also calculated for caesium triiodide.

The structure factor term consists of two main parts, $S(G)$ and $G^{-2}\ e^{-G^2/4\eta}$. G is 2π times the vector from the origin to a lattice point in the reciprocal lattice i.e.
$G^2 = 4\pi^2\ (h^2/a^2 + k^2/b^2 + l^2/c^2)$,
where h,k,l are the Miller indices and have values ranging from $-\infty$ to $+\infty$, and a,b,c are the unit cell parameters.K

For the orthorhombic caesium triiodide the actual structure factor $S(G)$ is zero for (h 0 l) for l odd and (h k 0) for h + k odd. The first program was to calculate the non zero combinations of h,k and l for h,k, and l from (0 0 0) up to any arbitrary value. In this case (9 9 9) was taken as the upper limit. Since the indices are as square terms it was only necessary to calculate the positive combinations of (h k l). The combinations of (h k l) are taken in the order

(0 0 0);(1 0 0);(2 0 0);.... (0 1 0);(1 1 0);(2 1 0); ....
(0 2 0);(1 2 0);(2 2 0);.... (0 0 1);(1 0 1);(2 0 1); ....
(0 1 1);(1 1 1);.... etc.

The G^2 term is necessarily increasing with h k l in a particular series but the term $G^2\ e^{-G^2/4\eta}$ is decreasing. A lower limit can be placed on this as it is to be multiplied by the product of a constant multiplied by two cosine terms, the constant being of the order of 1 - 10. In the practice it was this parameter which was responsible for transfers to the next series of (h k 1) values and not the parameters giving the upper limits on h and k.


Data
Read:- ;a,b,c; lower limit on product; lower and upper limits of (h k 1)
Calculate a^2, b^2, and c^2 and store these
Starting with (100) generate next(h k 1), checking whether upper limits on h or k have been reached.
Yes
Check 1) if k = 0, 1 is even or 2) if 1 ≠ 0, h + k is odd.
No
Calculate G^2. Calculate $e^{-G^2/4\eta}$ and $G^{-2}\,e^{-G^2/4\eta}$ Is the final product less than the limiting parameter?
Yes
Begin next series of (h k 1) values
No
Has the upper limit on (h k 1) been reached?
No
PRINT;-(h k 1) G^2; $G^{-2}\,e^{-G^2/4\eta}$
Yes
STOP

Having obtained a series of values of (h k l) which will give non zero structure factor terms it was then necessary to calculate the terms of the type $q_t\ e^{iG.r_t}$ for all combinations of (h k l) and then multiply these by ($G^{-2}\ e^{-G^2/4\eta}$). The vector r_t from the origin to the t^th^ atom is given by

$$r_t = (x a + y b + z c.)$$

The vector G from the origin to a lattice point in the reciprocal lattice is given by

$$G = 2\pi (h a^* + k b^* + l c^*)$$

where a^*, b^*, c^*, are the primitive translations of the reciprocal lattice. Hence

$$G.r_t = 2\pi (h x + k y + l z)$$

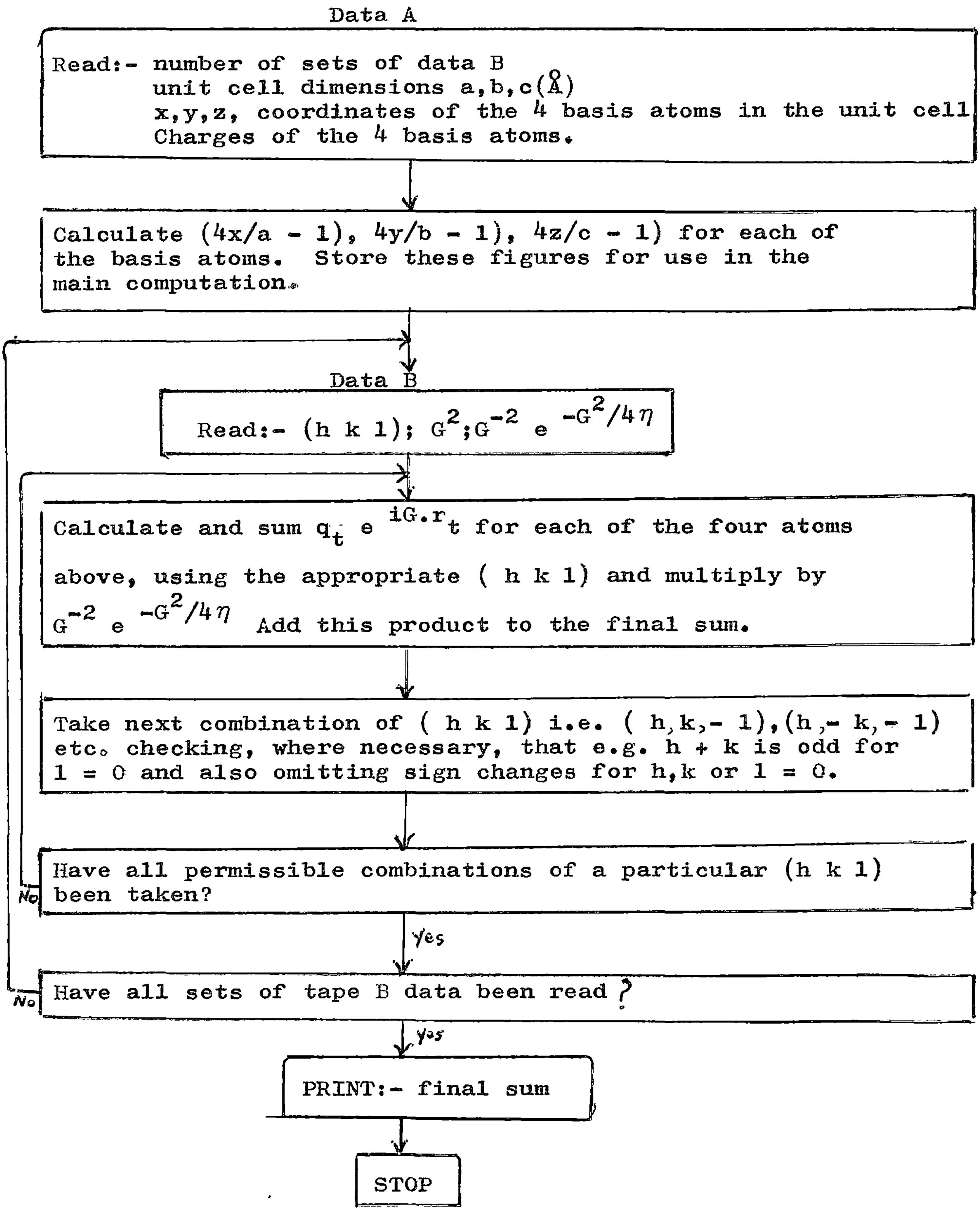
and $e^{iG.r_t}$. will be of the general form cos h x + i sin h x.

Since the coordinates of the atoms in the unit cell are ± (x,y,z,), ± (x - a/2,y - b/2,- z + c/2) the structure factor is given by

$2 \cos 2\pi (h x/a + ky/b + lz/c) + \cos 2\pi(h/a(x - a/2) + k/b(y - b/2) + l/c(- z + c/2))$. The sine terms will cancel since all the atoms are in pairs on either side of the origin as a centre of inversion. Expressing this sum as a product, the structure factor becomes

$$4 \cos 2\pi (hx/a + ky/b + \frac{l - h - k}{4}) \cos 2\pi(lz/c + \frac{h + k - l}{4})$$

From this it can be seen that if l = 0 and h + k is odd the second part of this product is zero. Also since



Data A

Read:- number of sets of data B
unit cell dimensions a,b,c(Å)
x,y,z, coordinates of the 4 basis atoms in the unit cell
Charges of the 4 basis atoms.

Calculate ($4x/a - 1$), $4y/b - 1$), $4z/c - 1$) for each of the basis atoms. Store these figures for use in the main computation.

Data B

Read:- (h k l); G^2;G^{-2} $e^{-G^2/4\eta}$

Calculate and sum $q_t\ e^{iG.r_t}$ for each of the four atoms above, using the appropriate (h k l) and multiply by $G^{-2}\ e^{-G^2/4\eta}$ Add this product to the final sum.

Take next combination of (h k l) i.e. (h, k, - l),(h, - k, - l) etc. checking, where necessary, that e.g. h + k is odd for l = 0 and also omitting sign changes for h,k or l = 0.

Have all permissible combinations of a particular (h k l) been taken?

Have all sets of tape B data been read ?

PRINT:- final sum

STOP

$x/o = 1/4, 3/4$ etc. $k = 0$, the first part of the product is of the form $\cos 2\pi\ (nh/2 + 1/4)$ hence for any h and for l odd this is also zero. For Computation it is convenient to write this expression as

$$4[\cos \pi/2\ \ h\ (4x/a - 1) + k\ (4y/b - 1) + 1]$$
$$[\cos \pi/2\ \ l\ (4z/c - 1 + h + k]$$

The terms $(4x/a - 1)$, $(4y/b - 1)$, $(4z/c - 1)$ are calculated for each of the four basis atoms and the sum $S(G) = \sum_t q_t e^{iG.r_t}$ is calculated for a particular value of (h k l). This is then multiplied by the appropriate value of $G^{-2}\ e^{-G^2/4\eta}$ from the previous program and the final product is summed.

This completes the various steps in the Ewald summation. Although there are a large number of short programs it was convenient to do the calculation in this manner as it was relatively simple to use an output from one program as the input for the succeeding program.

The results obtained at each iteration are listed in table.

TABLE 15.

Electron densities Q_1, Q_2 and Q_3 at each iodine atom in the triiodide anion, at each iteration.

ITERATION	Q_1	Q_2	Q_3
a) Caesium triiodide			
1	-0.6	-0.1	-0.3
2	-0.73	-0.078	-0.347
3	-0.819	0.226	-0.407
4	-0.867	0.349	-0.482
5	-0.888	0.449	-0.561
6	-0.901	0.599	-0.699
7	-0.904	0.650	-0.746
8	-0.907	0.686	-0.779
9	-0.909	0.709	-0.799
b) Tetraphenyl arsonium triiodide			
1	-0.7	0.4	-0.7
2	-0.743	0.485	-0.743
3	-0.774	0.548	-0.774
4	-0.797	0.594	-0.797
5	-0.813	0.626	-0.813
6	-0.823	0.646	-0.823

4) Calculation of Total Valence Electronic Energies.

Although the calculation of total electronic energies is relatively straight forward a computer program was also written to do this as there were a considerable number to be calculated.

The Pople relationship used was

$$E = \tfrac{1}{2} \sum_{\mu,\nu} P_{\mu\nu} (H_{\mu\nu} + F_{\mu\nu}) + \sum_{\mu<\nu} \frac{14.4}{r_{\mu\nu}}$$

These terms have all been defined in Chapter 9. The term $H_{\mu\nu}$ is given by

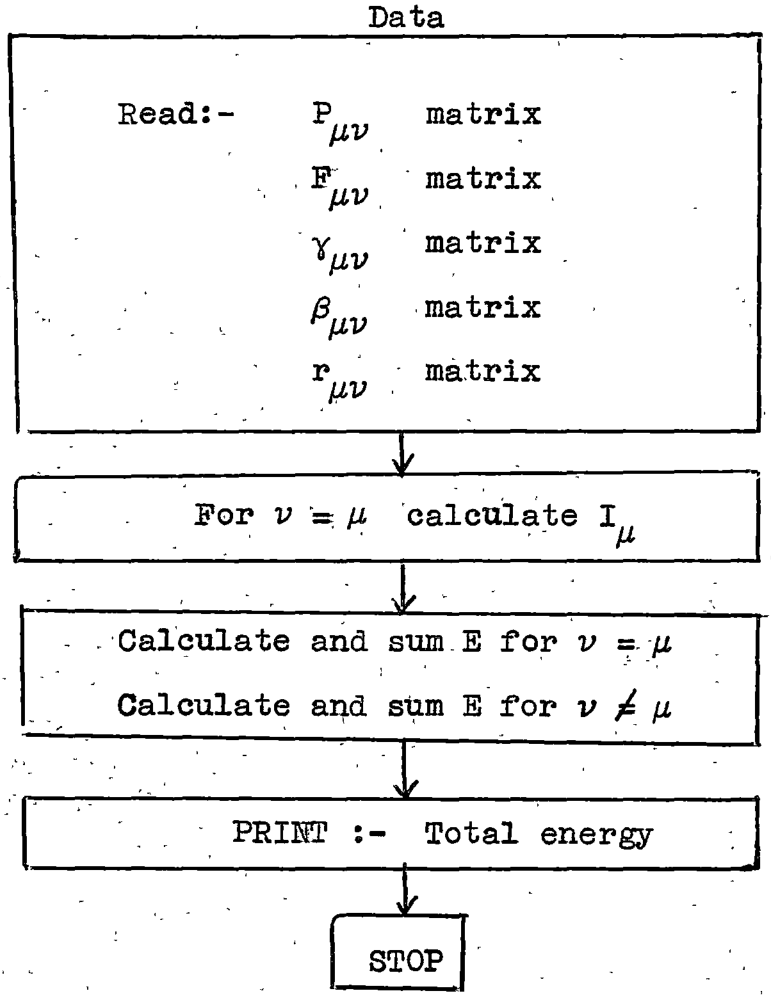
$$H_{\mu\mu} = -I_{\mu} + \sum_{\nu\neq\mu} X_{\nu}\, \gamma_{\mu\nu}$$

and $$H_{\mu\nu} = \beta_{\mu\nu}$$

The V.E.S.C.F. procedure either uses or calculates each of these quantities as described. The output from this program gives $F_{\mu\nu}$, $\gamma_{\mu\nu}$ and $P_{\mu\nu}$ at the last iteration. From $P_{\mu\nu}$ the ionisation potential could be calculated from the quadratic relationship

$$I_{\mu} = 0.133\, Z_{\mu}^{2} + 5.9397\, Z_{\mu} - 42.368$$

$\beta_{\mu\nu}$ and $r_{\mu\nu}$ are input for the V.E.S.C.F.


Data
Read:- $P_{\mu\nu}$ matrix
$F_{\mu\nu}$ matrix
$\gamma_{\mu\nu}$ matrix
$\beta_{\mu\nu}$ matrix
$r_{\mu\nu}$ matrix
For $\nu = \mu$ calculate I_μ
Calculate and sum E for $\nu = \mu$
Calculate and sum E for $\nu \neq \mu$
PRINT :- Total energy
STOP

APPENDIX 3.

The following tables list the detailed analytical figures for the ammonium bromide, lithium bromide and lithium iodide systems. All figures are percentages by weight. The tables and figures in chapters 3,4 and 6 are derived from these tables.

Bottle	Liquid		Solid	
Number	NH_4Br	Br_2	NH_4Br	Br_2
18	37.07	7.03	64.77	3.84
	36.91	6.87	67.29	3.60
11a	37.09	8.82	75.23	3.25
	37.07	8.64	75.13	3.33
11	36.72	10.30	75.60	3.97
	36.99	10.18	75.09	4.02
	37.49	10.35	75.00	4.14
	37.23	10.34		
4	36.82	12.03	69.43	5.91
	37.55	12.06	69.65	5.67
21	36.15	19.02	70.77	8.78
	36.13	19.12	73.51	7.85
	36.49	19.10		
	36.49	19.02		
7	35.04	28.14	67.86	15.61
	35.04	28.12	67.16	16.90
			67.52	15.75
8	35.13	27.84	48.45	38.14
	34.16	27.69	48.16	38.44
24	32.28	32.50	36.93	54.76
	32.81	32.77	36.72	54.85
10	28.58	38.28	54.21	35.1
	28.54	38.32	54.40	35.44
			54.91	35.12
15	22.86	56.27	58.79	33.45
	22.84	56.16	60.28	33.69
	23.21	55.69	60.00	34.22
			59.69	34.38
			59.99	33.93
16	20.36	63.45	62.80	31.18
	20.31	63.49	62.68	30.92
	20.11	63.67		
20	15.81	74.32	28.62	67.39
	15.98	74.18	28.67	67.80

Bottle	Liquid		Solid	
Number	NH_4Br	Br_2	NH_4Br	Br_2
22	13.98	78.31	29.79	67.71
	14.06	78.10	29.11	67.79
	14.05	77.83	29.59	68.79
			28.05	68.88
			28.91	68.11
23	9.41	85.88	26.59	71.80
	9.38	85.52	26.45	73.12
			26.94	72.54
23a	9.03	86.00	11.63	86.42
	9.02	85.96		
34	2.80	8.72	1.74	31.84
	2.77	8.77	1.89	28.78
	2.81	8.86	1.93	27.46
	2.79	8.65	1.72	29.58
	2.83	8.86	1.90	27.61
	2.77	8.87	1.92	27.50
35	4.44	11.56	2.94	31.05
	4.46	11.59	2.88	31.41
1a	5.91	14.63	4.26	32.37
	4.81	14.70	3.75	34.39
			3.79	33.80
9	6.93	17.75	4.34	35.65
	6.92	17.69	4.24	36.33
	6.90	17.56	4.37	35.65
	6.88	17.64		
31	8.53	21.43	5.11	37.12
	8.57	20.89	5.38	37.55
	8.48	21.84	5.08	38.75
			4.93	38.84
			5.10	38.27
1	9.77	27.39	7.18	36.52
	9.88	27.33		

Bottle	Liquid		Solid	
Number	NH_4Br	Br_2	NH_4Br	Br_2
14	11.58	31.78	7.11	42.18
	11.44	31.82	7.20	41.95
	11.29	32.33	6.93	41.82
	11.12	32.28	7.32	42.86
			7.14	42.09
40	12.48	33.87	8.03	42.34
	12.48	33.89	8.01	42.19
			7.82	42.47
2	13.02	33.82	10.43	43.98
	13.08	33.76	9.23	41.94
19	13.89	48.86	8.53	48.99
	13.74	48.69	8.01	49.41
28	14.07	43.39	9.36	46.53
	14.14	43.48	9.48	46.35
17	13.06	59.23		
17a	13.68	62.73		
29	12.86	67.10		
	12.79	67.29		
13a	12.41	71.97	1. 4	98.64
	12.91	71.79	0.29	99.25
25	0.47	99.00		
2a	10.23	28.67	6.43	39.75
	10.47	28.65	6.81	38.93
			6.66	41.69

Bottle Number	LiBr	Br_2	H_2O	LiBr	Br_2	H_2O
1	56.40	1.36	42.25	63.49	0.72	35.79
	56.71	1.68	41.62	63.99	0.80	35.21
2	55.94	3.13	40.93	62.01	1.60	36.39
	55.81	3.08	41.10	62.83	1.76	35.41
3	54.19	3.59	42.31	62.42	1.58	36.00
	54.16	3.86	41.97	63.42	2.14	34.44
4	54.32	4.68	41.00	61.85	1.79	36.35
	54.36	4.66	40.98			
5	50.71	11.04	38.25	58.62	6.49	34.89
	50.66	11.13	38.21	58.74	6.03	35.23
6	49.38	13.90	36.72	59.57	6.30	34.13
	49.13	14.01	36.86	59.35	6.40	34.25
7	48.43	16.00	35.59	57.24	9.21	33.55
	48.64	16.01	35.25	57.66	9.17	33.17
8	42.97	23.52	33.51	57.08	11.96	30.96
	43.06	23.56	33.38	57.26	11.80	30.94
9	39.97	28.16	31.87	50.82	18.23	30.95
	40.09	28.76	31.15	51.96	17.25	30.79
10	39.81	29.78	30.41	54.12	16.00	29.88
	38.84	30.75	30.42	53.80	16.72	29.48
11	35.91	34.44	29.64	48.97	21.45	29.58
				48.43	22.15	29.42
12	30.51	41.70	29.79	50.25	20.50	29.55
	30.50	41.80	29.70	49.55	21.10	29.35
13	28.80	44.92	26.28	47.99	25.61	26.39
	28.95	44.97	26.08	47.53	26.11	26.36
14	25.30	51.23	23.47	45.61	29.50	24.89
	25.70	51.10	23.20	45.55	29.80	24.65
15	16.46	68.27	15.27	42.58	35.70	21.72
	16.50	68.21	15.29	43.00	35.72	21.28
16	9.99	78.11	11.89	47.46	31.51	21.03
	9.98	78.12	11.90			

Bottle	Liquid			Solid		
Number	LiBr	Br_2	H_2O	LiBr	Br_2	H_2O
17	5.78	86.81	7.41	52.04	32.73	15.23
	5.86	86.01	8.13			
	6.06	86.01	7.93			
	6.07	86.29	7.64			
	6.43	86.63	6.94			
	5.91	86.59	7.50			
18	6.57	18.64	74.79	3.14	38.13	58.73
	7.03	18.86	74.11	3.15	37.57	59.28
19	7.95	22.80	69.25	2.89	40.37	56.74
				2.71	40.61	56.68
20	8.60	24.63	66.77	2.75	41.95	55.30
	8.66	24.77	66.57	2.95	42.07	54.98
21	9.00	25.70	65.30			
	9.30	25.80	64.90			
22	10.6	37.2	52.2			
	11.20	37.0	51.8			
23	11.0	33.5	55.5			

Bottle Number	Liquid Phase LiI	Liquid Phase I_2	Solid Phase LiI	Solid Phase I_2
1	57.07	6.13	63.98	3.28
	56.57	5.87	64.19	3.14
2	49.90	17.60	64.60	5.48
	50.04	18.00	63.82	5.80
3	46.75	23.15	62.58	8.73
	46.71	23.48	61.80	9.63
4	40.99	33.33	62.52	10.49
	41.19	33.66	62.22	11.29
5	34.71	42.72	44.72	31.41
6O	31.96	48.64	53.53	22.25
	31.16	48.65	52.69	23.96
	29.40	52.06	26.58	58.82
	29.56	52.26	26.58	58.82
	29.56	52.16	25.52	60.38
	29.61	52.21	25.50	59.78
	29.75	52.21	27.99	57.25
	29.78	52.20	28.13	57.29
			30.86	53.79
			30.30	53.59
	30.12	52.01	40.01	40.46
			40.49	39.80
9	29.40	52.16	24.60	61.35
10	28.87	52.87	23.71	62.72
	28.92	52.84	23.80	62.67
11	28.58	52.85	24.49	61.05
	28.28	52.91	23.93	61.91
12	27.29	53.82	23.57	62.54
	27.47	53.77	23.57	62.63
13	26.01	55.68	23.34	62.69
	26.13	55.04	23.16	63.13
14	25.57	55.86	22.58	64.67
	25.76	55.73	22.79	64.07

Bottle	Liquid Phase		Solid Phase	
Number	LiI	I_2	LiI	I_2
14	25.38	55.60		
15	24.16	57.58	22.77	63.23
	24.08	57.37	22.75	63.27
16	23.20	58.75	62.00	22.80
17	22.02	60.15	62.25	22.26
	22.05	60.13	62.70	22.27
	21.49	62.02	21.42	66.49
	21.50	62.01	21.60	65.61
	21.20	62.00	14.18	76.79
	21.24	62.03	14.60	76.09
	21.13	62.00	11.70	80.00
	21.13	62.05	12.00	79.94
18	11.13	15.23	1.60	86.90
	11.11	15.27	1.60	86.95
19	13.15	18.80	1.60	86.79
	12.95	18.84	1.63	86.79
20	13.73	19.69	1.72	92.56
	14.06	19.43	1.77	92.00
21	15.92	26.30	2.51	87.50
	15.95	26.32	2.23	87.28
22	17.95	29.20	4.18	88.09
	18.07	28.90	4.62	86.71
23	20.87	40.23	6.12	82.38
	20.86	40.23	6.04	82.32
	20.88	40.22		
24	21.85	47.01	8.29	80.47
	22.17	47.00	8.11	80.75
25	21.81	49.11	6.75	84.33
	21.82	49.14	6.71	84.67
26	22.00	55.79	6.31	88.04
	21.22	56.39	5.73	88.61
27	22.18	58.18	8.76	83.54
	22.21	58.23	8.42	83.84

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