CCXXV.—*Studies of Valency. Part IX. Molecular Structure of Thallium Salts.* (a) *Thallium Tri-iodide ;* (b) *Alkyl Derivatives.*

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(*a*) *Thallium Tri-iodide* [with MRS. R. R. GOLDSTEIN].

THALLIUM tri-iodide may be formulated either as thallic iodide or as a thallous polyiodide. From analogy with other thallic salts, the first of these formulæ has been generally adopted; but, since the iodide is a black, insoluble compound, whilst thallic chloride and bromide are soluble deliquescent salts, there is ample contrast to justify a different formulation of the iodide. Thus, Wells and Penfield (*Z. anorg. Chem.*, 1894, **6**, 312) concluded that, since thallium tri-iodide is isomorphous with the tri-iodides of rubidium and cæsium, it should be formulated as the polyiodide of a univalent metal. The formation of a polyiodide by thallium would be exceptional, however, since the ease of formation of polyiodides increases with the atomic volume of the kation (Ephraim, "Inorganic Chemistry," 1926, p. 200), reaching a maximum in the case of cæsium, with atomic volume 70, whereas the atomic volume of thallium (17) lies between those of lithium (13) and sodium (23·7). Maitland and Abegg (*Z. anorg. Chem.*, 1906, **49**, 341), on the other hand, suggested that thallium tri-iodide may be tautomeric, exhibiting one or other structure according to the reagent employed. Thus the sparing solubility of the iodide is cited as characteristic of a thallous salt, whilst the capacity of forming complex ions, as in the compound $KTlI_4$, which Johnson prepared in 1878 from potassium tri-iodide and thallous iodide (J., **33**, 183), is characteristic of thallic salts.

This conflict of opinion has been resolved in the present paper with the help of spectroscopic observations, which show that the iodine in alcoholic solutions of thallium tri-iodide is not present in the form of a tri-iodide ion. Spectroscopic observations have also shown that, although thallium tri-iodide does not combine with iodine to form a pentaiodide $[TlI_2]I_3$, the complex salt $KTlI_4$ persists in solution. Several new addition compounds of thallium tri-iodide with pyridine and with the chloropyridines are also described, which retain their individuality in solution. The spectroscopic evidence, which shows that the trihalides are not ionised completely even in dilute solutions, has been corroborated by measurements of conductivities in methyl alcohol and in acetonitrile, which show that the trihalides behave only as weak binary electrolytes. Finally, it has been shown that the chemical properties of thallium tri-iodide and of its compounds with pyridine are those of a thallic salt, giving only doubtful indications of thallous ions in solution.

Chemical Properties.—Well-formed crystals of thallium tri-iodide were prepared by boiling thallous iodide and iodine in equivalent proportions with methyl alcohol in a reflux apparatus, filtering the liquid, and concentrating it by evaporation in a vacuum desiccator containing calcium chloride. When titrated with potassium iodate in presence of a high concentration of hydrochloric acid (Berry, *Analyst*, 1926, 137), 0·261 g. of the crystals gave a titre corresponding with 0·264 g. of TlI_3. Reduction by heating with excess of sodium arsenite solution gave 56·0% of TlI (TlI_3 requires 56·6%). 0·293 G. of the compound gave 0·353 g. of silver iodide, whence I = 65·1% (Calc., 65·1%).

The brown solutions of thallium tri-iodide in alcohol, acetone, acetonitrile, and nitrobenzene show the reactions of tervalent thallium but only give doubtful indications of the presence of thallous ions. Thus, when excess of alkali is added to solutions of thallium tri-iodide in methyl alcohol or in acetonitrile, a quantitative yield of thallic oxide is produced, *e.g.*, 0·5355 g. of the iodide in acetonitrile gave 0·206 g. of oxide, the calculated yield being 0·209 g. On the other hand, when potassium bromide or iodide in aqueous acetonitrile is added to a solution of thallium tri-iodide in acetonitrile, a slight turbidity is produced, which might be attributed to the separation of thallous bromide or iodide; but this disappears on the addition of an excess of the alkali halide, and no turbidity was observed when methyl alcohol was used as solvent in place of acetonitrile. Again, when potassium chromate in aqueous acetonitrile is added to a solution of thallium tri-iodide in acetonitrile, a little thallous chromate separates; but when methyl alcohol is used as a solvent a precipitate of thallic hydroxide is produced.

When aqueous potassium iodide is added to solutions of thallium tri-iodide, the colour becomes paler, and precipitation of thallic oxide is impeded. Thus, whilst sodium hydroxide gives a precipitate immediately, sodium carbonate does so only after a few moments, unless the liquid is heated. Ammonia precipitates thallic oxide, but precipitation is prevented if ammonium chloride be first added. Since these phenomena appear to be due to the formation of complex ions, experiments were made on the behaviour of aqueous potassium iodide towards thallium tri-iodide dissolved in nitrobenzene. It was found that rather less than one molecular proportion of potassium iodide was taken up by thallium tri-iodide in the nitrobenzene solution.

Reducing agents convert thallium tri-iodide into thallous iodide, but no conclusions can be drawn regarding the constitution of this compound by considering its response to reagents such as sodium arsenite and thiosulphate, since other thallic salts are reduced by them and both reagents are oxidised by tri-iodide ions.

Preparation of Derivatives of Thallium Tri-iodide with Pyridine and with Chloropyridines.—Meyer (*Z. anorg. Chem.*, 1900, **24**, 321) prepared addition compounds by adding pyridine to aqueous solutions of thallic chloride or bromide; these compounds are white, sparingly soluble substances, which are readily hydrolysed by water with separation of thallic oxide. If, however, pyridine be added to solutions of thallic chloride containing excess of hydrochloric acid, the product contains thallium and chlorine in the ratio of 1 to 4. Addition compounds of thallic iodide with pyridine were prepared by Renz (*Ber.*, 1902, **35**, 1110), who described the compound TlI_3,C_5H_5N as a " dunkel orangerothes krystallinisches Pulver " and the compound $(TlI_3)_2(C_5H_5N,HI)_3$ as a " prächtig zinnoberrothes krystallinisches Pulver." The percentages of thallium in these products were not determined, but those of the other elements were in agreement with the formulæ assigned. Our own observations are set out below.

(*a*) *Pyridinium iodide.* When pyridine is added to solutions of thallium tri-iodide, fine orange-coloured precipitates are formed. Darker-coloured compounds were obtained when the base was added to solutions prepared by dissolving thallic oxide in aqueous hydriodic acid, or to solutions of thallium tri-iodide containing excess of iodine in organic solvents, but since the ratio of thallium to iodine varied from 1/3 to 1/5, it is very doubtful if any of these preparations was pure. One specimen, which separated from acetone in fine, dark red crystals, gave, however, a ratio Tl : I = 1 : 4 exactly, with two molecular proportions of pyridine to each atom of thallium, and therefore appeared to be a definite chemical *compound.*

(i) The compound was reduced with sodium arsenite, the resulting thallous iodide collected and weighed (TlI = 40·2%), and the filtrate analysed by Volhard's method (43·6% of additional iodine), *i.e.*, Tl = 24·8%, I = 59·0%; the pyridine is therefore 16·2% (by difference). (ii) The compound was reduced by sodium arsenite, the resulting thallous iodide being determined by direct titration with potassium iodate (Found : TlI, 39·3%; *i.e.*, Tl = 24·2%). (iii) By gravimetric analysis, I = 58·0% [$(C_5H_5N)_2HTlI_4$ requires Tl, 23·4; I, 58·4; C_5H_5N, 18·2%].

(*b*) *Pyridine.* By grinding pure thallium tri-iodide with a considerable excess of pyridine, a *compound* having the composition $(C_5H_5N)_2TlI_3$ was readily prepared. After filtration from a small insoluble residue, the liquid was largely diluted with water; the orange-coloured precipitate was collected, and dried over soda–lime in a desiccator. Two such preparations were analysed (i) by titration with potassium iodate directly, and (ii) by titration with potassium iodate of the thallous iodide obtained by reduction with sodium arsenite [Found : TlI, 43·8, 44·1 ; I (extra), 33·8, 34·5 ; C_5H_5N (by diff.), 22·4, 21·4 ; I (total, as AgI), 50·7. $TlI_3(C_5H_5N)_2$ requires TlI, 44·5 ; I (extra), 34·2 ; C_5H_5N, 21·3 ; I (total), 51·3%].

This addition compound dissolves readily in many organic solvents, forming coloured solutions ; but whilst iodine is violet in chloroform or benzene, and brown in alcohol or acetone, solutions of the compound of thallium tri-iodide and pyridine have the same golden-yellow colour in methyl and ethyl alcohol, acetone, glacial acetic acid, benzene, nitrobenzene, or nitromethane. Moreover, when pyridine is added to a solution of thallium tri-iodide in acetonitrile, the dark brown colour is changed to a pale golden-yellow. The chemical reactions of the tri-iodide do not, however, appear to be modified by the presence of pyridine.

(*c*) *Dichloropyridine.* A *compound* was prepared by boiling thallium tri-iodide (3 g.) and dichloropyridine (4 g.) with methyl alcohol for 2 hours under reflux. The dark brown liquid was decanted from some undissolved thallium tri-iodide, and the compound was precipitated by dilution with water. The golden-yellow, crystalline solid was collected and dried by exposure over soda–lime in a desiccator. Analysis of two samples gave TlI, 25·0, 25·1 ; I (extra), 19·6, 19·8 ; $C_5H_3NCl_2$ (by diff.), 55·4, 55·1. $TlI_3(C_5H_3NCl_2)_5$ requires TlI, 25·0 ; I (extra), 19·2 ; $C_5H_3NCl_2$, 55·8%.

(*d*) *Trichloropyridine.* When this was boiled with thallium tri-iodide in methyl-alcoholic solution, a *compound* was isolated as before [Found : TlI_3, 37·8. $TlI_3(C_5H_2NCl_3)_5$ requires TlI_3, 39·1%].

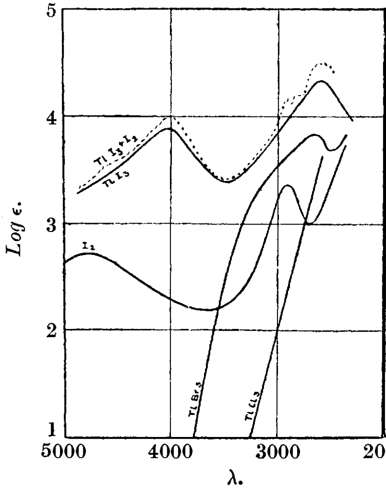
(*e*) *Tetrachloropyridine* combines only slowly with thallium tri-iodide. On addition of excess of water to the alcoholic solution, a yellow precipitate separates, but it soon decomposes with separation of thallous iodide and free iodine. The successive replacement of hydrogen by chlorine in the pyridine nucleus appears to diminish the basic properties to such an extent as to prevent the formation of stable additive compounds.

(*f*) *Pentachloropyridine* did not give an addition compound with thallium tri-iodide.

Absorption Spectra.

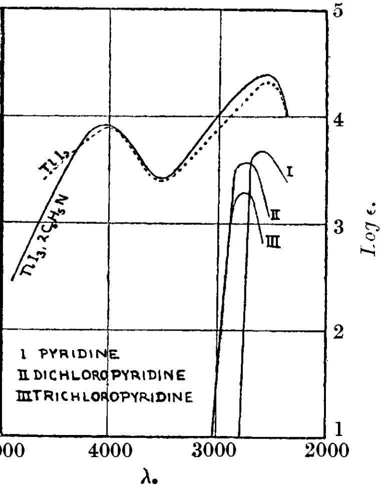
The extinction coefficients were determined in absolute methyl alcohol (free from acetone) by methods which have already been described. The iodide was dissolved directly in the solvent by vigorous stirring, but the chloride and bromide, which are very hygroscopic, were extracted with methyl alcohol from the yellow double salts, $TlCl_3,3TlCl$ and $TlBr_3,TlBr$ (Berry, *Proc. Camb. Phil. Soc.*, 1924, **22**, 363), and the thallium content was determined by analysis. The complex salt, $KTlI_4$, was prepared in blackish-brown crystals by refluxing thallium tri-iodide and potassium iodide with alcohol and allowing the solution to evaporate in a desiccator containing calcium chloride; the alcohol-wet crystals were dissolved in methyl alcohol and the thallium content of the solution was determined by analysis. The extinction coefficients have been plotted in Figs. 1, 2, and 3, and the most important data are summarised in Table I.

FIG. 1.



Molecular extinction coefficient of $TlCl_3$, $TlBr_3$, *and* TlI_3 *in methyl alcohol.*

FIG. 2.



Molecular extinction coefficients of pyridine compounds in methyl alcohol.

TABLE I.

Extinction Coefficients of Tervalent Compounds of Thallium.

Formula.	Logarithm of extinction coefficient.		
$TlCl_3$	1·0 at 3240	3·0 at 2740	
$TlCl_3(C_5H_5N)_2$	1·0 at 3200	3·0 at 2780	
	Maxima.		Step-out.
$TlBr_3$	3·85 at 2670		
TlI_3	3·9 at 4000	4·35 at 2600	
$TlI_3 + I_2$	4·0 at 4000	4·45 at 2550	4·2 at 2900 to 2700
$TlI_3 + KI$	3·9 at 4000	Not observed	4·0 at 2950 to 2750
$KTlI_4$	4·0 at 4020	4·45 at 2550	4·05 at 3000 to 2800
C_5H_5N		3·65 at 2590	
$C_5H_3NCl_2$		3·55 at 2710	
$C_5H_2NCl_3$		3·40 at 2760	
$TlI_3 + (C_5H_5N)_2$	3·9 at 4010	4·4 at 2600	
$TlI_3,(C_5H_3NCl_2)_5$	3·9 at 4000	4·4 at 2630	
$TlI_3,(C_5H_2NCl_3)_5$	3·8 at 4000	4·4 at 2630	
$HTlI_4,(C_5H_5N)_2$	4·0 at 4030	4·45 at 2580	4·0 at 3000 to 2750

The absorption spectra of $TlCl_3$, $TlBr_3$, and TlI_3 may be compared either with those of $CHCl_3$, $CHBr_3$, and CHI_3 (J., 1926, 622) or with those of KCl, KBr_3, and KI_3 (*loc. cit.*). In each series the chloride shows only a general absorption in the far ultra-violet region, whilst the bromides show at least the close proximity of an absorption band; the iodides, on the other hand, give two absorption bands, one in the more distant part of the ultra-violet spectrum, and the other with its foot extending into the visible spectrum and giving rise to visible colour. This produces a contrast between the black tri-iodide and the colourless trichloride which is sufficient to prove that the thallic salts are not mere aggregates of thallium and halogen ions, as the corresponding thallous salts appear to be. On the other hand, the fact that the two maxima in TlI_3 are separated by 1400 Å.U., whereas the maxima given by $\overset{+}{K}\overset{-}{I_3}$ and by $C_6H_4Br{\cdot}\overset{+}{N}Me_3\overset{-}{I_3}$ (unpublished measurements) are only separated by 650 and 720 Å.U., respectively, is incompatible with the view that the absorption is caused by a tri-iodide ion. The absorption curves also show that, whereas the tri-iodide ion produces a " general absorption " beyond the twin maxima, the molecular extinction coefficients of thallium tri-iodide decrease progressively at wave-lengths less than those of the two maxima. We therefore conclude that the iodine atoms are not present as a tri-iodide ion, but are joined, at least in part, by covalent bonds directly to the metal. This conclusion is obviously compatible with the view that, since the tri-iodide does not differ from the double salts $Tl_3^I(TlCl_6)$, $Tl_3^I(TlBr_6)$, and $Tl^I(TlBr_4)$ in the same pronounced way as from the simple chloride and bromide, the solid iodide may perhaps be a double salt, $Tl^{III}(TlI_6)$, of the cryolite type; but the data now recorded do not enable us to test the validity of this very plausible view.

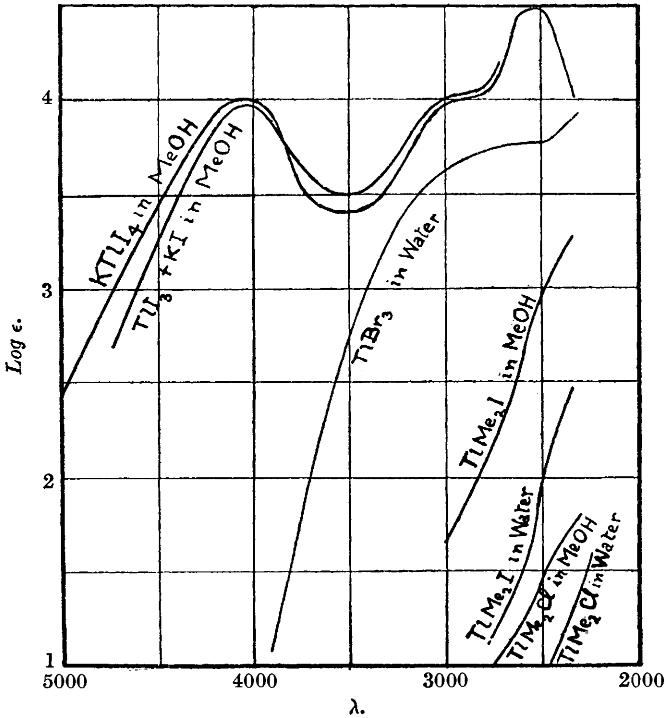
A study of the absorption spectra provides a similar solution to the similar problem presented by the tribromide. Since it gives an ultra-violet absorption band ($\log \varepsilon = 3{\cdot}85$ at 2670 Å.U.) which is not given either by thallic chloride or by potassium bromide, we can again conclude that the salt is not a mere aggregate of thallium and halogen ions; on the other hand, the bromine cannot be present as a perbromide ion, since the details of the absorption spectra differ very widely, in spite of a superficial resemblance between the maxima set out below :

$\overset{+}{K}\overset{-}{Br_3}$	Maximum	at $\log \epsilon = 3{\cdot}5$ at 2700 Å.U. in water.
$C_6H_4Br{\cdot}\overset{+}{N}Me_3\overset{-}{Br_3}$	,,	at $\log \epsilon = 3{\cdot}4$ at 2600 Å.U. in alcohol.
$TlBr_3$	,,	at $\log \epsilon = 3{\cdot}85$ at 2670 Å.U. in methyl alcohol.

Thus the two perbromides give a narrow absorption band at 2600—

2700 Å.U., but this is preceded by a well-marked step-out, which only just fails to reach a maximum, log ε = 1·8 at λ = 3800, just beyond the visible region of the spectrum. Thallium tribromide, on the other hand, gives a broad unsymmetrical maximum at 2670 Å.U., but with no sign of a step-out at 3800 Å.U., since the solutions are highly transparent in the part of the spectrum where the two perbromides only just fail to give an absorption band. The data for an *aqueous* solution of thallium tribromide, which are reproduced in Fig. 3, are almost identical with those for the solution in *methyl alcohol* in Fig. 1, but show a step-out in place of the shallow maximum.

FIG. 3.



Molecular extinction coefficients of potassium thallic iodide, etc.

In the case of the trichloride no similar question arises, since the trichloride ion appears to be still unknown; and the "general absorption" of the salt is in complete agreement with this conclusion.

In addition to the simple salts, an equimolecular mixture of thallium tri-iodide and iodine was examined, in order to ascertain whether one of the atoms of iodine could be converted into a tri-iodide ion; but the mixture gave only an additive absorption, including the two maxima of thallium tri-iodide and a step-out at 2900 Å.U. A similar step-out is found in the spectrum of the complex salt $KTlI_4$, solutions of which were prepared both by dissolving the black crystals of the salt and by mixing potassium and thallic iodides. Since potassium tri-iodide gives a band at 2900 Å.U., this step-out might be attributed to a reversible formation of potassium tri-iodide, according to the equation

$$KI + TlI_3 \rightleftharpoons KTlI_4 \rightleftharpoons KI_3 + TlI;$$

but this would not be in harmony with the conclusions of Maitland and Abegg as to the stability of the $[TlI_4]^-$ ion.

The addition compounds of thallium tri-iodide with pyridine and with the chloropyridines have lost the black colour of the tri-iodide, and show instead various shades of orange-red; the pyridinium compound, $(C_5H_5N)_2HTlI_4$, is also bright red. These changes of colour are due to alterations in the foot of an absorption band on the edge of the visible region, the width of which is greatly reduced when the tri-iodide is combined with pyridine, but they are not accompanied by any marked changes in the ultra-violet absorption of the salt.

Molecular Conductivities.

The conductivities of the trihalides were measured by methods that have already been described. Since thallium tri-iodide is insoluble in water, the solvents used were methyl alcohol and acetonitrile. The methyl alcohol was refluxed for 3 hours with sodium hydroxide, fractionated, and then treated with a mercury–aluminium couple until no further action took place. Basic impurities, such as methylamine, were eliminated by distillation from succinic acid, after which the product was dried again with a fresh mercury–aluminium couple; the alcohol was then dry enough to permit of the use of phosphoric oxide for further desiccation. The acetonitrile, from Messrs. British Drug Houses, had an initial conductivity of 35 gemmho. It was allowed to stand over solid potassium hydroxide for several hours to remove acetic acid and moisture, and was then dried with calcium chloride, distilled, shaken with a little phosphoric oxide for several hours, and left in contact with it over-night. After a final distillation the specific conductivity of the liquid had fallen to 1·9 gemmho.

Thallic chloride and bromide were extracted from the double salts, $TlCl_3,3TlCl$ and $TlBr_3,TlBr$ or $TlBr_3,3TlBr$, by prolonged contact with the solvent, and were separated from the thallous halides by filtration. Since the thallous halides dissolve to an appreciable extent in acetonitrile *in the presence of the thallic halides*, a definite source of error remains, even when the conductivities of the saturated solutions of the two thallous salts (6·037 gemmho for the chloride and 9·781 gemmho for the bromide) are deducted from the values obtained for the corresponding thallic salts. This source of error becomes inappreciable, however, when methyl alcohol is used as the solvent, and is absent in the case of the iodide, which was weighed out and dissolved directly in the solvent.

TABLE II.

(i) *Molecular Conductivities of Thallium Salts in Acetonitrile at* 25°.

(*a*) Thallium trichloride (filtered from thallous chloride).

v =	56	112	224	448	896	1792	3584
Λ^{25° =	129	139	148	154	161	161	169

(*b*) Thallium tribromide (filtered from thallous bromide).

v =	5	11	22	43	86	171	343	686	1371
Λ^{25° =	80	89	98	106	113	120	125	129	134

(*c*) Thallium tri-iodide.

v =	128	256	512	1024	2048	4096
Λ^{25° =	79	85	91	99	109	116

(*d*) Tetraethylammonium iodide (Walden).

v =	100	200	500	800	1000	2000	4000	8000	∞
Λ^{25° =	*142*	*163*	*173*	*175*	*180*	*184*	*186*	*189*	*200*

(ii) *Molecular Conductivities of Thallium Salts in Methyl Alcohol at* 25°.

(*a*) Thallium trichloride (filtered from thallous chloride).

v =	101	202	404	808	1616
Λ^{25° =	28	30	31	33	36

(*b*) Thallium tri-iodide.

v =	128	256	572	1024	2048
Λ^{25° =	17	20	24	29	39

(*c*) Dimethylthallonium iodide.

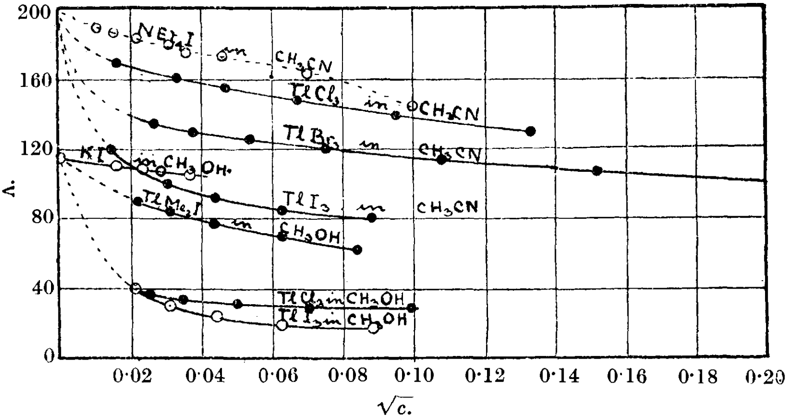
v =	141	256	512	1024	2048
Λ^{25° =	62	69·7	78	85	90·5

(*d*) Potassium iodide (Frazer and Hartley).

v =	721	1243	1724	2346	3997	∞
Λ^{25° =	*105·16*	*107·45*	*108·57*	*109·44*	*110·73*	*114·85*

The molecular conductivities of the trihalides are shown in Table II, where some other typical data are included for comparison; but the only results from which quantitative conclusions can be drawn are for the trichloride in methyl alcohol and for the tri-iodide in methyl alcohol and in acetonitrile. The conductivities in acetonitrile are several times greater than those of lithium chloride, and rather more than half as great as those of sodium or potassium iodide; but it is clear that the salts are behaving only as binary electrolytes, and that their electrolytic dissociation does not extend beyond the first halogen $TlX_3 \rightleftharpoons TlX_2^+ + X^-$. A similar statement can be made in reference to the solutions in methyl alcohol, where the conductivities of the two thallium salts at a dilution of $N/2000$ are still only about one-third as great as those of potassium iodide. The conductivity data are therefore in agreement with the absorption spectra in indicating that, even in dilute alcoholic solutions, a part of the halogen is still attached to the metal. Moreover, since the curves obtained by plotting Λ against $\sqrt{c}$, as in Fig. 4, deviate very widely from the linear relation given by potassium iodide in methyl alcohol, and the inflected line for tetraethylammonium iodide in acetonitrile, it is clear that, even when the salts are regarded only as binary electrolytes, their electrolytic dissociation is very much below that required for complete ionisation according to the formulæ of Debye and Hückel.

FIG. 4.



Molecular conductivities of thallium salts in acetonitrile and in methyl alcohol.

(*b*) *Alkyl Derivatives* [with F. L. GILBERT].

Although thallium forms many tervalent salts, the only alkyl derivatives that have been prepared up to the present are of the type $TlMe_2I$; moreover, these dialkyl halides cannot be condensed by the action of metallic sodium to molecules of the type $Me_2Tl{\cdot}TlMe_2$, comparable with the (bimolecular) lead trixylyl, $(C_8H_9)_3Pb{\cdot}Pb(C_8H_9)_3$, prepared by Krause and Smitz (*Ber.*, 1919, **52**, 2165). Since no convincing explanation has yet been given of the non-formation of tri-alkyl compounds of the type $TlMe_3$, it appeared desirable to investigate the dialkyl derivatives, in order to find out whether their ionisation is " complete," as in the case of the quaternary ammonium bases and salts, or whether it is reversible and incomplete as in the case of ammonium hydroxide and mercuric chloride.

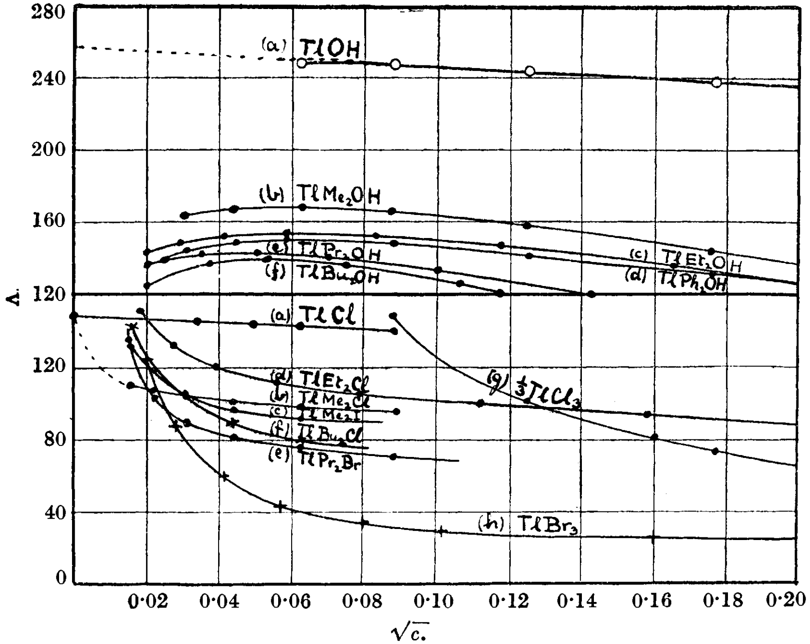
Dimethylthallonium iodide was prepared by the action of the Grignard reagent on the ether-soluble pyridine compound of thallic bromide, and the product was compared with a specimen generously placed at our disposal by Dr. Goddard, which had been prepared by a modification of the method of Meyer and Bertheim (*Ber.*, 1904, **37**, 2051). Our material had a salmon-pink tint, whilst Dr. Goddard's was tinted yellow, but in each case the colour was removed when the solutions were filtered; both specimens decomposed at 275°, although the decomposition point recorded by Goddard (J., 1921, **119**, 674) was 295°. We are also indebted to Dr. Goddard for preparations of the diethyl iodide, the dipropyl bromide and iodide, and the dibutyl bromide. These sparingly soluble salts were washed with water before being converted into the freely soluble bases, and in some cases the salts were recovered in a purified form by neutralising the base with a halogen acid.

The experimental work included measurements of the molecular conductivity of aqueous solutions of several of the dialkyl halides, and of the bases from which they were derived, but comparative observations were also made of the conductivity of thallium tribromide in water. Potentiometric observations were made of the neutralisation of the dimethyl base with *N*-sulphuric acid and of the dipropyl base with *N*-hydrochloric acid; a comparative series of potentiometric measurements was also made of the neutralisation of thallous hydroxide with *N*-sulphuric acid. Finally, the molecular extinction coefficients of dimethylthallonium chloride and iodide were measured in aqueous and methyl-alcoholic solutions, as well as those of aqueous thallic bromide, which had been examined previously in methyl alcohol.

Molecular Conductivities.

(*a*) *Dialkyl Salts.*—The molecular conductivities of aqueous solutions of dimethylthallonium chloride and iodide are set out in Table III (i), with Shukoff's data for the diethyl chloride (*Ber.*, 1905, **38**, 2691), and our own data for the dipropyl bromide (decomposes without fusion at 240°), and for a specimen of the dibutyl chloride (decomposes without fusion at 160°), which we prepared through the free base from Dr. Goddard's specimen of the bromide; the molecular conductivities have also been plotted in Fig. 5 against the square root of the concentration. Ostwald's data for thallous chloride, which give an exactly linear relation between Λ and $\sqrt{c}$, were taken as a criterion of the behaviour of a binary salt which is ionised completely even in the solid state. It is then immediately obvious that the molecular conductivity of the chloride, $TeMe_2Cl$, falls very far short of the standard for complete ionisation, although there is no clear evidence of hydrolysis, since the curve could be extrapolated quite easily to the value of Λ_∞ given by the data for thallous chloride.* On the other hand, the molecular conductivity of the iodide, $TlMe_2I$, rises so rapidly in dilute solutions that we are obliged to postulate an extensive hydrolysis of the salt, since extrapolation to zero concentration would give a value far in excess of the molecular conductivity of a binary electrolyte. Shukoff's data for diethylthallonium chloride, which were carried to much higher concentrations, show just the same phenomena of incomplete electrolytic dissociation in strong solutions and hydrolysis in weak solutions. The curve for the diethyl chloride is followed fairly closely by our own curve for the dibutyl chloride; the dipropyl bromide, on the other hand, appears to be even less completely dissociated, and more extensively hydrolysed, than the dibutyl

FIG. 5.



Molecular conductivities of thallium bases and salts in water.

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* The curve for the dimethyl chloride intersects the curves for other dialkyl halides, but its accuracy was confirmed by a duplicate series of measurements.

chloride, to which it is related in much the same way as the chloride and iodide of the dimethyl base.

(*b*) *Thallic Chloride and Bromide.*—Evidence of hydrolysis was also obtained on measuring the molecular conductivities of aqueous solutions of thallium tribromide. A solution was prepared by extracting the yellow tetrabromide, $Tl[TlBr_4]$, with water, and its concentration was estimated by gravimetric analysis. Since the thallous salt is insoluble in water, even in the presence of the thallic salt, the correction which was required for solutions in acetonitrile (p. 1756) is no longer needed. The results of the measurements are included in Table III (i), together with Meyer's data for the chloride (*Z. anorg. Chem.*, 1900, **24**, 341). Over the range from 19·4 to 1240 litres, the conductivities are independent of time, but are lower than those of a typical binary salt. At a dilution of 2480 litres, however, the increment of conductivity on doubling the volume, which had been growing progressively throughout, rose to nearly 50% in the freshly diluted solution, and a further increase of nearly 50% occurred when the solution was kept for an hour. This behaviour shows again that a part of the conductivity is due to hydrolysis, exactly as Meyer had postulated in the case of the chloride. The phenomena of incomplete electrolytic dissociation in concentrated solutions and extensive hydrolysis in dilute solutions are, indeed, even more strongly marked in thallic bromide (where the curve plotted in Fig. 5 turns suddenly vertical at $\sqrt{c} = 0{\cdot}02$) than in the alkylated salts. The curve for thallic chloride is of a similar type, but it is difficult to say whether the higher conductivity of the solutions is due to a higher degree of ionisation of the salt or merely to a more extensive hydrolysis.

It is perhaps desirable to add that the evidence cited by Meyer (*Z. anorg. Chem.*, 1900, **24**, 321; 1902, **32**, 72) to show that only two-thirds of the chlorine in thallic chloride is precipitated by silver nitrate has not been confirmed (Cushman, *Amer. Chem. J.*, 1901, **26**, 505) and cannot therefore be used as a proof that only a part of the halogen is ionisable. In our experience, there is a perceptible weakening of the opalescence when a very dilute solution of thallic chloride is mixed with silver nitrate and thallic nitrate is then added; but on keeping for some time the opalescence returns to its original strength. We also find that, just as in the case of ferric oxide, hydrochloric acid is a much better solvent for thallic hydroxide than is nitric acid, which only dissolves the oxide very slowly (Willm, *Ann. Chim. Phys.*, 1865, [4], **149**, 76). For this experiment, equal quantities of thallic hydroxide were precipitated from 1 g. each of the pyridine compound of thallic bromide; the precipitate was only partially dissolved even when heated with 50 c.c. of *N*-nitric acid, but it was dissolved at once in the cold by only 5 c.c. of *N*-hydrochloric acid; and, when a brown cloud had been produced by diluting to 2000 c.c. and adding 1 c.c. of *N*-sodium carbonate, the liquid was rendered clear again by adding only 2 c.c. of *N*-hydrochloric acid. The incomplete ionisation of thallium tribromide can, however, be demonstrated by a qualitative experiment in the same way as in the case of mercuric chloride. For this purpose, a sample of thallic oxide, which gave no coloration when digested under identical conditions with aqueous phenolphthalein, was heated in a test-tube in a water-bath with aqueous potassium bromide and phenolphthalein, whereupon a very decided alkalinity appeared after a short time. A similar alkalinity was developed in aqueous potassium chloride. This result can be explained by assuming a fixation of bromide ions by the thallium, with a consequent liberation of hydroxyl ions as shown in the reversible equation:

$$\mathrm{Tl(OH)_3} + 3\overset{+}{\mathrm{K}}\overset{-}{\mathrm{Br}} \rightleftharpoons \mathrm{TlBr_3} + 3\overset{+}{\mathrm{K}}\overset{-}{\mathrm{OH}}.$$

TABLE III.

(i) *Molecular Conductivities of Thallium Salts in Water at 25°.*

(*a*) TlCl	v =	128	256	512	∞				
(Kohlrausch)	$\Lambda^{25°}$ =	*140*	*143*	*145*	*149*				
(*b*) $TlMe_2Cl$	v =	128	256	512	1024	2048	4096		
	$\Lambda^{25°}$ =	96	98	100	103	106	111		
		97	100	102	105	108	114		
(*c*) $TlMe_2I$	v =	256	512	1024	2048	4096			
	$\Lambda^{25°}$ =	93	97½	104	118	131			
(*d*) $TlEt_2C$	v =	20	40	80	160	320	640	1280	2560
(Shukoff)	$\Lambda^{25°}$ =	*84*	*93*	*100*	*106*	*112*	*120*	*131*	*149*
(*e*) $TlPr_2Br$	v =	128	256	512	1024	2048	4096		
	$\Lambda^{25°}$ =	70	76	80	89	106	136		
(*f*) $TlBu_2Cl$	=		80	89	106	122	144		
(*g*) $TlCl_3$	v =	2	4	8	16	32	64	128	
(Meyer)	$\Lambda^{0°}$ =	*105*	*122*	*145*	*176*	*223*	*307*	*437*	
	$\Lambda^{25°}$ =	*144*	*178*	*207*					
h) $TlBr_3$	v =	19·4	38·8	77·6	155·2	310	620	1240	2480
	$\Lambda^{25°}$ =	23	25	28	33	43	78	87	124
		(No change with time………………………………………)							183 (1 hr.) 210 (3 hrs.)

(ii) *Molecular Conductivities of Thallium Bases in Water at 25°.*

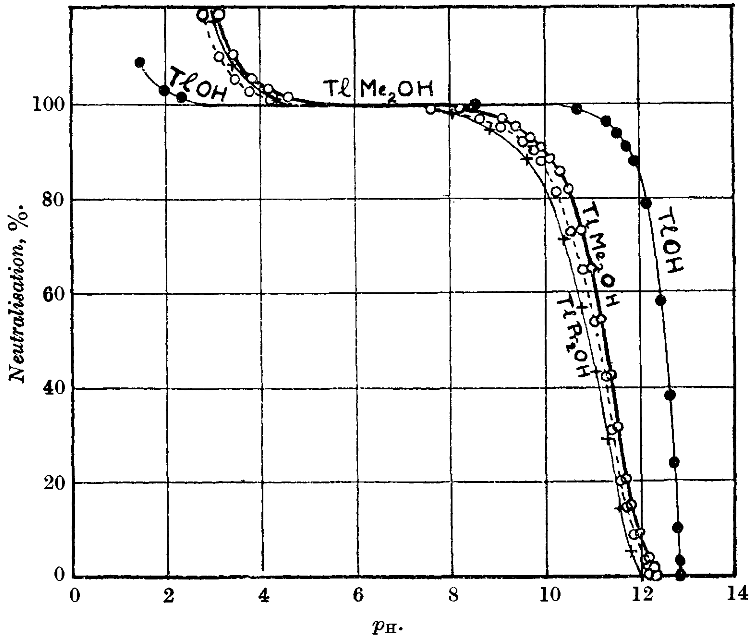
(*a*) TlOH	v =	2	4	8	16	32	64	128	256
(Ostwald)	$\Lambda^{25°}$ =	*182*	*200*	*217*	*230*	*238*	*244*	*248*	*248*
(*b*) $TlMe_2OH$	v =	8·13	16·33	32·65	65·3	130·6	261·2	522·4	1045
(Hein)	$\Lambda^{25°}$ =	*107*	*127*	*143*(?)	*157*	*165*	*169·5*	*167·6*	*164·1*
(*c*) $TlEt_2OH$	v =	9	18	36	72	144	288	576	1152
(Hein)	Λ^{25} =	*100·1*	*116·3*	*131·2*	*144·8*	*153·1*	*154·6*	*153·8*	*149·8*
(*d*) $TlPh_2OH$	v =	8	16	32·1	64·2	128·3	256·6	513·3	1026·6
(Hein)	$\Lambda^{25°}$ =	*98·7*	*113·6*	*127·1*	*139·8*	*148·4*	*151·6*	*150·3*	*145·1*
(*e*) $TlPr_2OH$	v =			50	100	200	400	800	1600
	$\Lambda^{25°}$ =			120	131	139	143	144	140
(*f*) $TlBu_2(OH)$	v =				89	178	356	712	1424
	Λ^{25} =				126	137	141	138	131

(*c*) *Dialkyl Bases.*—The evidence that the dialkylthallonium halides are extensively hydrolysed in dilute solutions indicates that these salts are derived from relatively weak bases, which are ionised only incompletely and reversibly in solution. This conclusion was established by observations of the molecular conductivities of the free bases, which are set out in Table III (ii), and are plotted against the square root of the concentration in Fig. 5. Since data were already available for the dimethyl, diethyl, and diphenyl bases (Hein and Meininger, *Z. anorg. Chem.*, 1925, **145**, 95), we have examined only the dipropyl and dibutyl compounds, which we prepared in the usual way by use of silver oxide from Dr. Goddard's specimens of the halides. As a standard of comparison we have taken Ostwald's data for thallous hydroxide (*J. pr. Chem.*, 1886, **33**, 352; 1887, **35**, 112), since this base shows the typical behaviour of a strong electrolyte. Thus, the curve showing the relation between Λ and $\sqrt{c}$ is linear from $N/2$ to $N/128$, and only begins to droop at a dilution of $N/256$, owing probably to the increasing influence of carbon dioxide in the conductivity water. The data of Hein and Meininger, then, show that, whilst the ratio Λ/Λ_∞ is about 85% for thallous hydroxide at $v = 8$, the corresponding percentages for aqueous solutions of the dimethyl, diethyl, and diphenyl bases are 41·8, 42·0, and 42·4 at $v = 8{\cdot}02$, 9·0, and 8·13, respectively. These ratios can no longer be used as a direct measure of the ionisation of the base, but, since the conductivities of the dialkyl bases at $v = 8$ are only about half as great as those of thallous hydroxide, the coefficient of ionisation of these bases cannot be greater than about 50%. This conclusion is confirmed by the data for the dipropyl and dibutyl bases, where the conductivities are even lower in the linear portion of the curves, whilst the drooping of the curves at dilutions beyond $N/128$ corresponds closely with that of the curves plotted from the data of Hein and Meininger.

Electrometric Titrations.

A preliminary titration of a $N/10$-solution of dimethylthallonium hydroxide against N-hydrochloric acid with a hydrogen electrode confirmed the conclusion that the hydroxide could not be classed with the alkalis as a " strong " base; but it did not provide a trustworthy measure of the strength of the base. A direct comparison was therefore made between $N/10$-thallous hydroxide and $N/16$-dimethylthallonium hydroxide with the help of a glass electrode, which had been in constant use for some months, and gave an *E.M.F.* of 54 millivolts per unit of p_H. The bases were titrated with N-sulphuric acid, in order to avoid the precipitation of the sparingly soluble dimethylthallonium chloride, which had been observed in the preliminary experiment; a saturated solution of potassium sulphate was used as a junction liquid to the calomel electrode. The resulting curves are shown in Fig. 6, together with a curve deduced from the readings of a hydrogen electrode immersed in the same solution. These curves show that, whilst thallous hydroxide behaves as an alkali, the dimethyl base is of a lower order of strength ($-\log K_b = 3$), and is presumably ionised only incompletely and reversibly. The accuracy of the data was confirmed by the fact that a titration with a glass electrode of the dipropyl base at a concentration of $N/14{\cdot}3$ gave a curve which followed that for the dimethyl base, with a steady deviation of about 0·2 unit on the side corresponding with the curves for weak bases.

Fig. 6.



Potentiometric titration of bases.
Full lines = glass electrode.
Broken line = hydrogen electrode.

Absorption Spectra.

All the dialkylthallonium halides that we have studied are colourless salts, but the absorption spectra of the dimethyl chloride and iodide were examined in order to ascertain if there was any characteristic absorption in the ultra-violet. The molecular extinction coefficients in water and in methyl alcohol are plotted in Fig. 3. The contrast between the two salts appeared at first to support the view, which we had deduced from the conductivity data, that the dialkyl halides are ionised only reversibly in solution; but, when the solutions of the iodide were photographed against equivalent solutions of potassium iodide, the extinction coefficients were found to be practically identical with those of the chloride, and are therefore an additive function of the absorption of the two ions. The ratio Λ/Λ_∞ at $N/100$ is about 50% in methyl alcohol and may be estimated at 65% in water (where Λ_∞ cannot be determined directly, on account of hydrolysis); the proportion of undissociated salt in the $N/50$ solutions used for the measurements of absorption was probably at least one-half in methyl alcohol and one-third in water. The additive relation cannot therefore be explained away by the electrolytic dissociation of the salt in the dilute solutions used for the spectroscopic measurements, but must be admitted to hold good also for the undissociated molecules of the salt. On the other hand, in view of the regularity with which covalent iodides, including even methyl iodide itself, give rise to very strong absorption bands in the ultra-violet region, it seems unlikely that the selective absorption of thallium tri-iodide would disappear completely in dimethylthallonium iodide, if the iodine in the latter compound were linked to the halogen by a real bond. We can therefore only conclude that, in this case, the spectroscopic data are in closer accord with Fajans's theory of aggregates of deformable ions as a cause of incomplete electrolytic dissociation, than with the view that a low conductivity always implies the formation of covalent molecules.

General Conclusions.

The chemistry of thallium presents certain peculiarities which await an explanation in terms of the electronic theory of valency. Thus, it is remarkable that *thallium,* although a third-group metal, forms a series of very stable univalent thallous salts, whilst *gold,* which might be expected (like silver) to be most stable in the form of a univalent kation, gives rise generally to tervalent auric salts. Again, the alkyl derivatives, instead of being of the types AuEt and $TlEt_3$, interleaving with $HgEt_2$ and $PbEt_4$, are of the types $AuEtBr_2$, $AuEt_2Br$ (Pope and Gibson, J., 1907, **91**, 2061) and $TlMe_2I$ (Meyer and Bertheim, *loc. cit.*). These apparent anomalies, however, find a simple interpretation in the following observations. (i) The elements Au, Hg, Tl, Pb have escaped from the domination of the *octet* rule, but are still subject to the *duplet* rule (compare *Trans. Faraday Soc.*, 1928, **24**, 31); any even-numbered aggregate of electrons, from 78 up to 86, can therefore form a stable system. As in the case of the acids (*ibid.*, p. 1), this dominance by the duplet rule is very favourable to reversible ionisation. (ii) As has long been recognised, metallic mercury, with its low boiling point and monatomic vapour, possesses some of the characteristics of an inert gas, although, as Sidgwick has pointed out (" Electronic Theory of Valency," p. 179), it contains two electrons more than are required to complete the outer shell of 18 *O*-electrons; it therefore provides, with niton, an electronic configuration of maximum stability, which the intermediate elements tend to take up in their various compounds. (iii) Mercury and thallium are related to one another in the same way as carbon and nitrogen, so that a molecule in one series becomes an ion in the other, as in the well-established case of CH_4 and $\overset{+}{N}H_4$. The significance of these considerations can be seen from the following table.

Number of electrons.	78	80	82	84	86
(*a*) Gold.	Au^+	$AuCl$	$AuCl_3$	$AuCl_4^-$	
(*b*) Mercury.	Hg^{++}	Hg Hg_2^{++}	$HgPh_2$ $HgCl_2$ Hg_2Cl_2	$HgCl_3^-$	HgI_4^{--}
(*c*) Thallium.	Tl^{+++}	Tl^+	$TlPh_2^+$ $TlMe_2^+$ $TlBr_2^+$	$TlBr_3$ $TlMe_2I$ $TlMe_2OH$	$TlCl_3^{--}$ $TlBr_4^-$
(*d*) Lead.	Pb^{++++}	Pb^{++}	$PbEt_2^{++}$	$PbEt_3^+$	$PbEt_4$

(i) 80 *Electrons.* The univalent thallous ion, with 80 electrons round the nucleus, as in the atom of elementary mercury, retains its charge just like the ion of an alkali metal, *e.g.*, in concentrated solutions of thallous salts and of thallous hydroxide, and even in crystals of thallous chloride and bromide, which are built on the same face-centred cubic lattice as cæsium chloride. The hydrolysis of dilute solutions of thallous fluoride (Kohlrausch and Steinwehr, *Sitz. Preuss. Akad. Wiss. Berlin*, 1902, **26**, 581) and of thallous oxalate (Abegg and Spencer, *Z. anorg. Chem.*, 1905, **46**, 406) has been cited as evidence of the weakness of the base, but, since the conductivity of thallous hydroxide is equal to that of the alkalis, and no hydrolysis has been detected in thallous chloride, nitrate, etc., we may suppose that it is the weakness of the acid rather than of the base which is responsible for the hydrolysis. There is therefore no evidence that the 80 electrons of the ion are converted into the system of 82 electrons which would be present in the covalent molecule, TlOH, of a reversibly-ionised base.

(ii) 81 *Electrons.* A more serious reflexion on the stability of the thallous ion is found in Drucker's suggestion (*Z. Elektrochem.*, 1922, **28**, 463) that univalent thallium forms diatomic kations, like mercury, but by a reversible process, $2Tl^+ \rightleftharpoons Tl_2^{++}$. In the case of mercury, the formation of a diatomic kation makes it possible to formulate the mercurous ion with 80 electrons round each nucleus, just as in the monatomic vapour, and thus to maintain the duplet rule; in the case of thallium, however, this process would increase the number of electrons round each nucleus from 80 to 81, and thus provide an exception to the duplet rule. This hypothesis was introduced as a device to interpret the freezing points, transport numbers, and conductivities of thallous nitrate over the range 0·04—0·14*N* (as well as certain data for thallous sulphate) on the basis of Ostwald's dilution formula, and without using the theory of strong electrolytes. It leads to a ratio $Tl_2^{++}/Tl^+ = 1/7$ at $N/10$, but is not supported by any independent evidence, and can be ruled out on the ground that, whilst the presence of pairs of mercury atoms can be inferred from the *X*-ray analysis of crystalline calomel, the same type of evidence shows equally clearly that the atoms of thallium in the thallous halides are present exclusively as single atoms or univalent ions.

(iii) 82 *and* 84 *Electrons.* The univalent dialkyl ions of the type $TlMe_2^+$ correspond to the covalent molecules, $HgPh_2$ and $HgCl_2$, of the mercury series, with 82 electrons round the nucleus. In marked contrast to the univalent thallous salts, the dialkyl halides do not obey the formulæ for strong electrolytes; the bases from which they are derived are also considerably weaker than thallous hydroxide, and can no longer be classed with the alkalis as examples of "complete ionisation." There can therefore be little doubt that the dialkyl halides, and the bases from which they are derived, as well as the corresponding trihalides and their bases, are capable of yielding non-conducting molecules, such as $TlMe_2I$, $TlMe_2OH$, and $TlBr_3$, which are of the same order of stability as their univalent ions. The spectroscopic evidence, however, indicates that the non-conducting forms of these salts may be ionic doublets, rather than covalent molecules. The existence of systems in which the thallium nucleus is surrounded by 84 electrons in molecules such as $TlMe_2Br$ and $TlBr_3$ is therefore less well-established than in the case of the mercury, where it is unlikely that the three halogens in the ion $HgBr_3^-$ are related unequally to the metal. The doubt which thus arises as to the real existence of the 84-electron system, with only 2 electrons less than the next inert gas, may furnish a clue to the reason why it has not been found possible to prepare the trialkyl derivatives of thallium, since these could not be expected to exist in a form corresponding with the ionised molecules of $\overset{+}{Tl}Me_2\overset{-}{I}$, and could therefore only be produced if the 84-electron system were stable.

(iv) 86 *Electrons.* The complex mercury salts of the type $NH_4^+[HgBr_3]^-$ sometimes assume the more stable configuration of niton by combining with a molecule of water; but they do this even more readily by taking up a second molecule of the alkali halide as in K_2HgI_4, etc. In the case of thallium, a similar tendency is seen in the conversion of the deliquescent crystals of thallic chloride and bromide into beautifully crystalline and sparingly soluble salts of the type $Tl^+[TlBr_4]^-$, where the atom of thallium inside the bracket has at last assumed the niton configuration which we find also in $PbCl_4$ and in $PbEt_4$. Another example of the niton configuration is found in the double thallous salt 2AgCl,TlCl, which crystallises from a molten mixture of the silver and thallous chlorides, and to which the structure $Ag_2^{++}[TlCl_3]^{---}$ may be assigned. In complex anions of the type $Tl_3[TlCl_6]$, however, the outer 8-electron shell of the inert gas is replaced by a 12-electron shell, just as in the 6-co-ordination compounds of cobalt and platinum.

(v) 78 *Electrons.* The formation of the 78-electron group in Au^+, Hg^{++}, Tl^{+++}, and Pb^{++++} involves the removal of two electrons from the stable mercury configuration. This becomes progressively more difficult as the charge on the ion increases, so that we cannot be sure whether the relatively high conductivity of aqueous solutions of thallic chloride is due to the ability of the salt to behave as a quaternary electrolyte or merely to hydrolysis; on the other hand, the low conductivity of the salt in non-aqueous solutions shows that, under less favourable conditions, it behaves only as a binary electrolyte, $TlCl_3 \rightleftharpoons \overset{+}{Tl}Cl_2 + \overset{-}{Cl}$ (compare $TlMe_2I \rightleftharpoons \overset{+}{Te}Me_2 + \overset{-}{I}$). The existence of thallic ions in infinitesimal quantities can, however, be inferred from potentiometric measurements.

Summary and Conclusions.

(*a*) Thallium tri-iodide has been examined in order to determine whether it should be regarded as thallic iodide, or as a thallous polyiodide. Solutions in methyl alcohol and acetonitrile form addition compounds with pyridine and chloropyridines, and complex ions with potassium iodide, and exhibit the general reactions of a thallic salt, but the reactions of thallous ions could not be detected with certainty.

(*b*) The absorption spectrum of the tri-iodide in methyl alcohol shows two maxima, but these are separated by 1400 Å.U., whereas those of potassium tri-iodide are separated only by 650 Å.U. The spectrum is therefore not that of a tri-iodide ion, nor can the compound be a simple aggregate of tervalent thallium and univalent iodide ions, since these ions are colourless and do not give rise to any absorption bands. The iodide is therefore regarded as a tervalent compound, in which a part at least of the halogen is linked directly to the metal.

(*c*) The molecular conductivities of the thallium trihalides in methyl alcohol and in acetonitrile are less than those of potassium iodide; the salts therefore behave only as binary electrolytes, in which some of the halogen is linked to the metal, even in the most dilute alcoholic solutions.

(*d*) Dimethylthallonium iodide is hydrolysed in dilute aqueous solutions and is derived from a base which is much weaker than thallous hydroxide. The molecular conductivity of thallic bromide is less than that of a binary electrolyte, except in dilute aqueous solutions where it is hydrolysed progressively.

(*e*) The properties of thallium are discussed on the basis of the hypothesis that mercury and thallium are related to one another in the same way as carbon and nitrogen.

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