CCLXI.—*Studies of Valency. Part X. Electrometric Titration of Vernon's α- and β-Dimethyltelluronium Bases.*

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IN a previous paper of this series (this vol., p. 307), it was shown that the isomeric bases from which the α- and β-dimethyltelluronium dihalides are derived are of the same order of strength as ammonia. The hydroxy-halides, on the other hand, although readily convertible into normal salts, are acid rather than basic in character, since they are approximately neutral towards indicators (such as methyl-orange and methyl-red) which give an end-point a little on the acid side of neutrality. This result can be interpreted most readily by saying that the kation of the hydroxy-halide $[TeMe_2OH]^+ Cl^-$ is more ready to lose a *hydrogen ion* according to scheme 1, which leaves the octet intact, than to lose a second *hydroxyl ion,* as in scheme 2, in which the octet is converted into a sextet.

1. $[TeMe_2OH]^+ \rightleftharpoons [TeMe_2O] + H^+$;
compare $[NH_4]^+ \rightleftharpoons NH_3 + H^+$.
2. $[TeMe_2OH]^+ \rightleftharpoons [TeMe_2]^{++} + OH^-$.

An anomaly was encountered, however, in the fact that, whereas the molecular conductivities of the α-base varied from 1·9 to 3·4 ($v = 16$—256), those of the β-base varied only from 33 to 37 ($v = 32$—512), in spite of the much larger absolute values of the conductivities. By way of contrast, it may be recalled that the conductivity of diethylmercury hydroxide varies from 1·2 to 1·9 and that of hydrazine from 1·7 to 5·5, in the range $v = 16$—256, whilst the conductivity of methylamine varies from 21 to 70, that of dimethylamine from 24 to 81, and that of diethylamine from 31 to 93 in the same range. An electrometric investigation was therefore undertaken in order to compare the relative strengths of the two bases by the various electrical methods now available.

Conductivity of Bases.—Since the bases cannot be purified by crystallisation from solution, it was necessary to adopt other methods for checking their purity. The high conductivity of the β-base and the small increment on dilution might have been due to the presence of (i) undecomposed halide, (ii) silver compounds derived from the silver oxide used in the preparation of the bases, or (iii) trimethyltelluronium compounds formed by a molecular rearrangement of the β-base which is known to take place under the influence of alkalis. Since the β-base had been prepared by evaporating a solution of the α-base to dryness under reduced pressure, it was unlikely that its high conductivity could be due to undecomposed halide, for this must have been present also as an impurity in the α-base; and the presence, in solutions of the β-base, of dissolved silver compounds which were not also present in the α-base was even less probable, since they would be likely to be removed during the conversion of the α- into the β-base by evaporation. The possible presence of trimethyltelluronium salts was eliminated by preparing a solution of the β-base from the β-dibromide, in just the same way as the α-base was prepared from the α-salts.

The molecular conductivities of seven solutions of the two bases are in Table I. The values are rather less concordant than those of compounds which can be purified by ordinary methods; but the equivalent conductivities of the β-base were found to be consistently greater by about 30 units than those of the α-base, and to vary over the same small range on dilution. The most trustworthy values were obtained by preparing the β-base from a β-salt instead of directly from the α-base, and their validity was confirmed by their close agreement with the conductivities of a sample which Vernon had obtained in a solid form by evaporating a solution of the base to dryness in a tube which was then sealed. The close concordance of these additional data shows that the results recorded in the previous paper were substantially correct, even although they may not be easy to explain.

TABLE I.

Molecular Conductivity ($\Lambda^{25°}$) *of Dimethyltelluronium Bases.*

		v = 16.	32.	64.	128.	256.	512.
α-Base :	Series 1	1·9	2·2	2·6	2·9	3·4	4·3†
	Series 2	3·2	3·5	3·8	4·1	4·8	6·3
	Series 3	2·7	3·1	3·5	3·9	4·8	6·0
β-Base.	From α-base : Series 1 ...		34	35	36	37	37
	*Series 2...		32	33	35	36	37
	From β-salt		30·7	31·9	33·3	34·5	35·6
	Vernon's sample		30·7	32·4	33·7	34·6	35·8

* This solution was evaporated *twice* to dryness, since a solution which had been evaporated only once gave conductivities about 2 units less than those recorded above.

† $\Lambda^{25°} = 6{\cdot}0$ at $v = 1024$.

Conductivity of Carbonates.—Since it appeared possible that some of the variations of conductivity might be due to the conversion of the bases into carbonates by absorption of atmospheric carbon dioxide, experiments were made to determine the magnitude of this effect, and the results are in Table II. The solutions of the two bases were standardised by titration in the presence of bromophenol-blue. Since the molecular conductivity of a saturated solution of carbon dioxide ($M/30{\cdot}3$) is $\Lambda^{25°} = 1{\cdot}3$ (approx.), the molecular conductivities at $M/32$ would be increased by $1{\cdot}3 \times 32/30{\cdot}3 = 1{\cdot}4$ on saturation with carbon dioxide, if no chemical combination occurred. In general, the conductivity of a base is

TABLE II.

Molecular Conductivity of Carbonates.

		v.	$\Lambda^{25°}$.
α-Base.	Original sample	32	3·22
	Saturated with CO_2 (40 mins.)	32	40·4
	Passed CO_2-free air (8 hours)	32	3·96
		64	4·2
		128	5·1
		256	6·8
		512	9·7
β-Base.	Original sample	32	31·0
	Passed CO_2-free air (4 hours)	32	31·6
	Saturated with CO_2 (40 mins.)	32	39·0
	Passed CO_2-free air (8 hours)	32	32·0

decreased by the presence of carbon dioxide, since the bicarbonate ion is much less mobile than the hydroxyl ion; but in the present instance the bases are so weak that this effect was reversed, and the conductivity was increased in each case to about 40 units. The carbonates are, however, so unstable, and their formation is so incomplete, that the maximum conductivity of the carbonated solutions was only about one-third of that of a typical binary electrolyte. Since, then, only about one-third of the base is present as carbonate, the carbon dioxide must also be held only reversibly; it was therefore removed completely by a current of purified air, the conductivities of the solutions falling again to values similar to those recorded in Table I.

$$TeMe_2(OH)_2 + CO_2 \underset{2}{\overset{1}{\rightleftharpoons}} [TeMe_2OH]^+ + HCO_3^-$$

It will be seen that the two bases are practically equal in their power of holding carbon dioxide. This result is not in agreement with the simple (but incorrect) deduction from the conductivities, that the β-base is perhaps 10 times stronger than the α-base; but it is in harmony with the results of the potentiometric titrations described below, which show that there is an intermediate stage of neutralisation within which the two bases are of nearly equal strength.

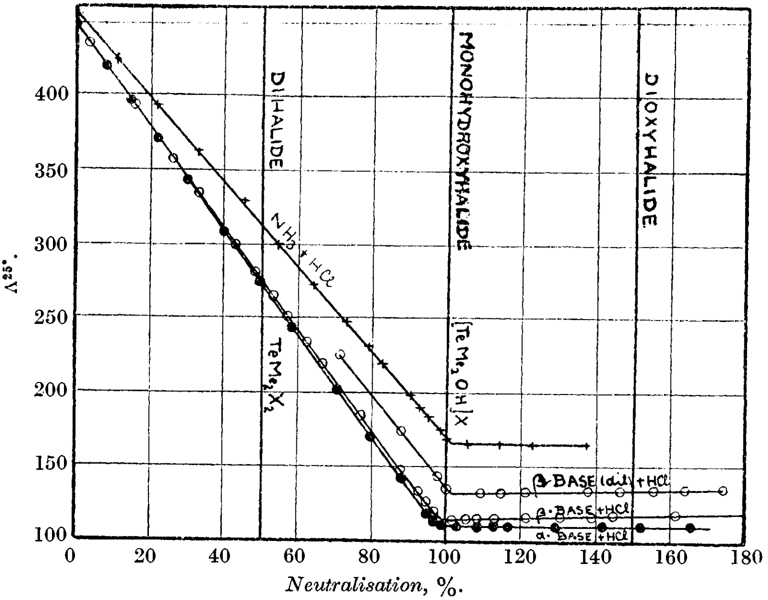
Conductivity Titrations.—In doing a conductivity titration it is usual to add a mineral acid to a solution of the base, and to observe the decrease of conductivity which takes place as the hydroxyl ions are replaced by chloride or bromide ions. In the case of the dimethyltelluronium bases this method cannot be used, since the conductivity undergoes only an insignificant increase as the feebly ionised base is converted into a more strongly ionised salt. A large decrease of conductivity was produced, however, when the α- or β-base was added to a mineral acid, since the mobile hydrogen ions of the acid were then replaced by the much more sluggish $[TeMe_2OH]^+$ ions of the hydroxy-salt.

The titration curves are reproduced in Fig. 1, together with a curve for the neutralisation of *N*/10-hydrochloric acid by *N*/10-ammonia. The addition of the α-base (about *N*/7) to *N*/10-hydrochloric acid produced a continuous decrease of equivalent conductivity up to 100% neutralisation, after which the conductivity remained almost constant, since further additions of the weak α-base did not contribute substantially to the conductivity of the solution. The neutralisation curve shows a well-defined break, corresponding to the formation of the hydroxy-halide [α-$TeMe_2OH$]Cl; but no discontinuity at all can be seen at the composition $TeMe_2Cl_2$, which would be represented by the addition of *half* a molecular proportion of the base to a molecule of the acid; and in the same way, no break was observed at points corresponding in composition to substances more basic than the hydroxy-halide.

The β-base (about $N/11$) gave a neutralisation curve of the same form as that of the α-base, with a well-defined break at the composition [β-$TeMe_2OH$]Cl, but no perceptible change of direction at the composition of the normal salt. In this case the specific conductivity was increased by adding an excess of the base, which has a substantial conductivity of its own; but no further discontinuity was observed in these more basic solutions. A duplicate determination with the β-base gave slightly higher molecular conductivities during neutralisation (perhaps because the acid was slightly stronger), but the remaining data agreed so closely with the earlier values that they could not be represented by a separate curve. On the other hand, a more dilute solution ($N/110$ approx.) gave higher equivalent conductivities throughout, the value at the neutral point being $\Lambda^{25^\circ} = 116$ (approx.) at $N/176$ as compared with 108 (approx.) at $N/29$.

Fig. 1.

Conductivity titrations.



Potentiometric Titrations with a Hydrogen Electrode.—α-Base. For these titrations, 20 c.c. of an $N/10$-solution of the α-base, which had been standardised by titration with methyl-orange as indicator, were neutralised with 0·962*N*-hydrobromic or 0·198*N*-hydrochloric acid. The results were not very trustworthy, since the α-base poisoned the hydrogen electrode, giving rise to a progressive decrease of *E.M.F.* with time. An approximate result, obtained by passing a rapid stream of purified hydrogen over the electrode, showed, however, that equivalence was reached at the composition $TeMe_2(OH)Br$, and that there was no second inflexion at the point represented by $TeMe_2Br_2$.

β-*Base.* Similar experiments with the β-base gave two inflexions, one at 100%, corresponding to the formation of the hydroxy-halide [β-$TeMe_2OH$]Cl, and the other (much less sharply defined) at about 50% neutralisation, corresponding to the formation of a basic salt containing 2 mols. of the base to 1 mol. of acid. A white precipitate appeared in every case at about 75% neutralisation, reached a maximum, and then redissolved sharply at 100% neutralisation. A small quantity of the precipitate formed during the titration of the β-base with hydrobromic acid was collected, dried, and weighed. It was dissolved in water and acidified with nitric acid,* and silver nitrate added (0·0152 gram gave 0·0039 gram AgBr: Br = 10·9. $TeMe_2Br_2,7TeMe_2O$ requires Br, 10·5%). The precipitate, although collected from a nearly neutral solution, is therefore far more basic than the crystalline dioxy-iodide which Vernon prepared from the α-base.

Potentiometric Titrations with a Glass Electrode.—More trustworthy results were obtained by using a glass electrode of the type described by Hughes (this vol., p. 491), since this electrode is not poisoned by the tellurium bases. The electrode had been in constant use for some months and gave an *E.M.F.* of 55 millivolts per p_H, as compared with 58 millivolts for a hydrogen electrode. The titrations were made at atmospheric temperature (about 16°). The curves for six titrations are reproduced in Fig. 2.

α-*Base.* A solution of the α-base was standardised by titration with bromophenol-blue as indicator, since the approximate results obtained with the hydrogen electrode showed that the end-point of the titration would be given more correctly with this indicator than with methyl-orange. An *N*/10-solution (20 c.c.) was then titrated with *N*-hydrochloric acid. The potentiometric curve was confirmed by a duplicate determination in which the strength of the base was *N*/12·5. The foot of the curve was at 8·2 instead of 8·9; but the two curves then converged, and became coincident as the neutral point was approached.

The curves have the characteristic form for a weak base, with

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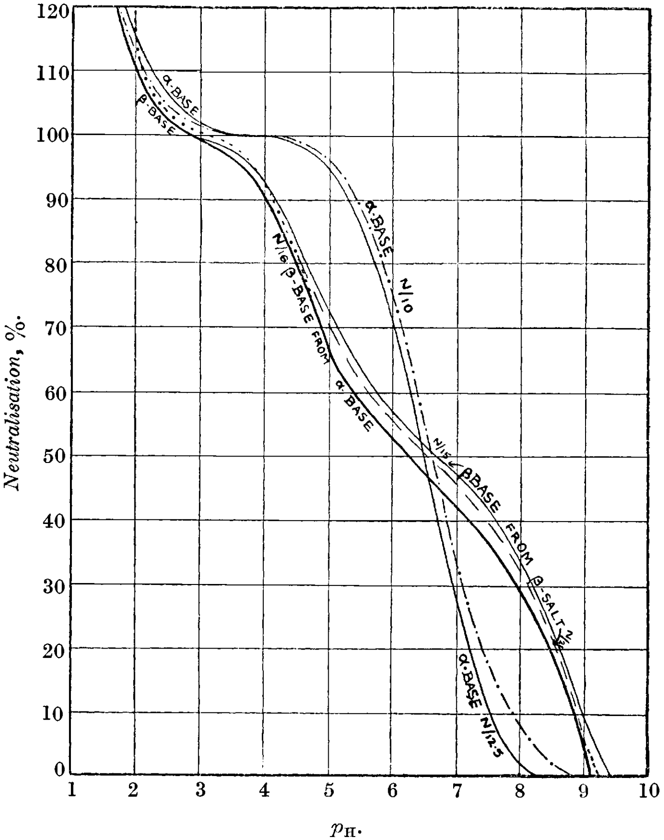
* No precipitate of dihalide was formed, such as always appears when acid is added to the α-hydroxy-salts.

a single inflexion at the composition of the hydroxy-halide [α-$TeMe_2OH$]Cl. The "equivalence point" is at $p_H = 3{\cdot}9$, and the inflexion is quite well defined, since $p_H = 4{\cdot}8$ at 98% and 3·0 at 102% neutralisation. Half-neutralisation occurs at $p_H = 6{\cdot}5$, from which it follows that $-\log K_b = 7{\cdot}5$. These results confirm the conclusion that N/10-solutions of the base can be titrated with

Fig. 2.

Potentiometric titrations.



methyl-orange ($p_H = 2{\cdot}9$—$4{\cdot}0$), but would give a more trustworthy end-point with bromophenol-blue ($p_H = 3{\cdot}0$—$4{\cdot}6$); for weaker solutions, a more acid indicator should be used.

β-*Base*. Four curves for the β-base are shown in Fig. 2. The full curve is for an N/16-solution freshly prepared from the α-base, and it agrees closely with the dotted curve for an N/32-solution of Vernon's crystalline sample of the β-base (compare p. 1998). Two solutions, $N/15{\cdot}4$ and $N/21$, prepared from the β-dibromide, were slightly more alkaline during the first half of the titration, but then the curves converged upon and became identical with the two curves for samples prepared from the α-base.

All the curves show an inflexion at the composition of the hydroxy-halide, [β-$TeMe_2OH$]Cl, together with a weaker inflexion at about 50% neutralisation; a white precipitate was also seen again between 75 and 100% neutralisation. The "equivalence point" is at $p_H = 3{\cdot}0$, but the inflexion is less well defined than in the case of the α-base, since $p_H = 3{\cdot}4$ at 98% and 2·6 at 102% neutralisation, giving a range of only 0·8 in place of 1·8 units; the end-point, even with the most suitable indicator (*e.g.*, methyl-orange), is therefore not likely to be very sharp.

The second inflexion, at 50% neutralisation, indicates that a basic salt is formed in solution at a composition corresponding to the formula $2TeMe_2O,HCl$; but, since the inflexion occurs at $p_H = 6{\cdot}5$, it follows that this basic salt is acid rather than alkaline in its reaction, and that (like the hydroxy-halide) it is therefore more ready to part with a hydrogen than with a hydroxyl ion.

The formation of this basic salt makes it impossible to deduce the strength of the base in the usual way from the p_H at half-neutralisation. Since, however, $p_H = 8{\cdot}3$ at 25% neutralisation, the strength of the β-base may be deduced from the relation $-\log K_b = \log (1 - x)/x + p_{K_w} - p_H$, where x is the degree of neutralisation, whence $-\log K_b = 6{\cdot}2$ for the free base. At 75% neutralisation, $p_H = 4{\cdot}8$ and $-\log K_b = 8{\cdot}7$ for the basic salt. The β-base is therefore stronger than the α-base in the initial stages of neutralisation, but the basic salt which is then formed is not so strong as the α-base; the weaker α-base thus gives a sharper end-point at 100% neutralisation, and yields an α-hydroxy-halide which is more nearly neutral than the isomeric β-hydroxy-halide.

Hydrolysis of Basic and Normal Salts.—From the potentiometric curves it is possible to deduce a series of theoretical values for the percentage hydrolysis of the hydroxy-salts as follows :

			Hydrolysis at	
	$-\log K_b$.	K_b.	$v = 100$.	$v = 1000$.
[α-$TeMe_2OH$]Cl to free base ...	7·5	$3{\cdot}1 \times 10^{-8}$	0·6%	2%
[β-$TeMe_2OH$]Cl to basic salt ...	8·7	2×10^{-9}	2%	7%

The normal salts, on the other hand, are shown to be almost completely hydrolysed in water; but the percentage of unhydrolysed salt can be deduced from the fact that a saturated solution of the α-di-iodide in cold water, which has a concentration of $N/235$, shows an absorption band with a maximum extinction coefficient, $\log \varepsilon = 2{\cdot}4$ at 3340 Å.U. Since a dry *alcoholic* solution of the di-iodide gives a maximum extinction coefficient, $\log \varepsilon = 3{\cdot}7$, at a slightly longer wave-length, we can (by ignoring the influence of the solvent) calculate that the *aqueous* solution contains only about 1/20 of its nominal content of iodide, or that the α-di-iodide is hydrolysed, to the extent of about 95%, to the hydroxy-iodide and hydriodic acid.

Basic Salts.—The potentiometric titrations of solutions of the β-base provide conclusive evidence of the formation of a basic salt, in which the acid and base are united in the ratio $2TeMe_2O,HCl$, to form (in Vernon's nomenclature) a "β-trioxychloride," since it could also be derived from three molecules of the base and one molecule of the normal salt. On the other hand, the potentiometric curves for the α-base agree with the conductivity titrations in giving no indications of the existence in solution of any salt but the hydroxy-halide. This result is remarkable in view of the fact that Vernon prepared from the α-base two basic salts which he formulated as follows:

(i) Di-iodotetramethylditelluronium oxide, $O(TeMe_2I)_2$.

(ii) Di-iodohexamethyltritelluronium dioxide, $TeMe_2(O{\cdot}TeMe_2I)_2$.

The "α-dioxyiodide" (ii) separates from water in large transparent plates, with about $\frac{1}{2}H_2O$ of crystallisation; but it can also be obtained in anhydrous, colourless scales, *e.g.*, from concentrated ammonia, and can be prepared quite readily in this form by grinding the solid α-di-iodide with concentrated ammonia and then recrystallising it from aqueous ammonia. The "α-monoxyiodide" (i) separates as a bright yellow powder when an aqueous solution of the "dioxy-iodide" is boiled for some minutes and then cooled quickly.

Vernon states that the melting point of the monoxyiodide "fluctuates between 112° and 125°" and that "repeated analyses have shown considerable variations in both carbon and hydrogen." Our own experiments have shown that the yellow powder, which generally melts at about 116°, is stable if dried immediately; but, if it is allowed to stand in contact with water (or even in moist air) for some hours, it changes to a colourless form, which melts at 122°. Since it appeared likely that the pure monoxyiodide would be colourless like the dioxyiodide, we thought at first that the coloured form might be an aquo-compound, but this conclusion could not be confirmed by analysis. For instance, no difference could be detected between the halogen content of the yellow and the colourless form of the salt; and no change in weight was produced when a weighed quantity of the coloured powder was transformed to the colourless form by the action of water, and then dried. The conversion of the unstable into the stable form is therefore not accompanied by any important change of composition, and may perhaps be formulated as depending on an interaction of the type $TeMe_2O + TeMe_2I_2 \rightleftharpoons I[TeMe_2{\cdot}O{\cdot}TeMe_2]I$, whereby a trace of coloured di-iodide is converted into a colourless oxyiodide. This change may perhaps be reversible in solution, but it proceeds to completion in one direction under the conditions of our experiments, and we have not yet been able to reproduce the yellow form from the stable colourless form by any direct process.

TABLE III.

Equivalent Conductivities of Basic Iodides at 25°.

	v = 128.	256.	512.	1024.	2048.
α-Monoxyiodide, $\frac{1}{2}(TeMe_2)_2OI_2$	94	98	100·5	102	105
α-Dioxyiodide, $\frac{1}{2}(TeMe_2)_3O_2I_2$	98	101	104	105	107

The equivalent conductivities of aqueous solutions of the monoxyiodide and dioxyiodide, reckoned in each case on the calculated concentration of iodine, are set out in Table III. The conductivities differ only by a small amount, which corresponds roughly with the conductivity of the extra molecule of base in the latter compound. The values for the monoxyiodide are about six units lower than those recorded (this vol., p. 314) for solutions of the α-hydroxyiodide made up by titration; but this discrepancy does not appear to have any theoretical significance. The basic salts are indeed disappointing compounds from the stoicheiometric point of view, and cannot be used with safety unless previously analysed. Thus, the yellow monoxyiodide is obviously a mixed product, and the anhydrous form of the dioxyiodide is prepared by a method which does not admit of any sharp separation from the less basic monoxyiodide. Finally, the crystalline form of the dioxyiodide contains "about half a molecule of water," which makes its chemical constitution difficult to interpret, and even throws doubt on the empirical composition of any individual sample which has not been analysed. That these doubts are well founded is shown by the fact that an equimolecular mixture of the di-iodide with the dioxyiodide gave an i-factor of 2·2 in a freezing-point determination, and equivalent conductivities ranging up to $\Lambda^{25^\circ} = 140$ at $v = 2048$ litres; which we can only interpret on the supposition that the mixture was so deficient in base that it was "extensively hydrolysed" in solution, just as Vernon reported in the case of the monoxyiodide.

Freezing Points.—In addition to individual determinations of the freezing points of the α-monoxy- and dioxy-iodides, several series of measurements were made of the freezing points of solutions of the α- and β-bases during progressive neutralisation. In the earlier series, the bases were neutralised with hydriodic acid; but, as these measurements were complicated by the separation of precipitates, they were repeated with hydrochloric acid, and only the β-base then gave a transient white precipitate. The data are set out in Tables IV and V.

TABLE IV.

Freezing Points of Aqueous Solutions of α-Base.

(*a*) 14 c.c. of *N*/9·76-α-base and *N*-HCl.

Neutralisation.	F. p.	*i*.
Water =	**2·969**	—
0%	2·756	1·11
13	2·750	1·16
25	2·757	1·15
38	2·750	1·21
51	2·748	1·25
60	2·735	1·34
67	2·729	**1·38**
76	2·718	1·47
86	2·704	1·56
95	2·683	1·70
101	2·671	**1·79**
108	2·660	1·87
124	2·630	2·09

(*b*) 14 c.c. of *N*/9·76-α-base and *N*-HCl.

Neutralisation.	F. p.	*i*.
Water =	**2·966**	—
0%	2·752	1·12
13	2·752	1·15
25	2·749	1·18
35	2·747	1·21
44	2·739	1·27
54	2·733	1·32
60	2·728	1·36
67	2·721	**1·41**
76	2·711	1·49
86	2·707	1·53
95	2·691	1·64
101	2·679	**1·73**
108	2·665	1·83
130	2·628	2·12

(*c*) 15 c.c. of *N*/10·5-α-base and *N*/1·05-HI.

Neutralisation.	F. p.	*i*.
Water =	**3·057**	—
0%	2·845	1·20(?)
14	2·859	1·14
28	2·858	1·16
42	2·857	1·19
56	2·852	1·25
63	2·848	1·29
70	2·842	1·34
* 77	2·859	1·24
88	2·851	1·30
95	2·848	1·34
102	2·845	1·37
109	2·838	1·44
116	2·825	1·51
123	2·823	1·55
130	2·815	1·62
142	2·795	1·78
† 179	2·890	1·18

(*d*) 14 c.c. of *N*/9·76-α-base and *N*/1·39-HI.

Neutralisation.	F. p.	*i*.
Water =	**2·968**	—
0%	2·774	1·015
11	2·779	1·018
23	2·782	1·021
34	2·781	1·05
46	2·775	1·11
57	2·767	1·18
64	2·763	1·21
68	2·748	1·31
* 75	2·737	1·40
86	2·730	1·47
93	2·719	1·56
† 100	2·778	1·20
107	2·785	1·17
125	2·787	1·19

* A white precipitate appeared and disappeared between these limits.

† The separation of a permanent red precipitate of the di-iodide was followed by an abrupt rise of freezing point.

The freezing-point data confirm the conclusion that the free bases are dissociated only to a small extent in solution, the *i*-factor for both bases being about 1·1. On the other hand, the freezing points indicate that the hydroxy-halides are dissociated almost completely, the *i*-factor recorded for the α-hydroxy-chloride in two

TABLE V.

Freezing Points of Aqueous Solutions of β-Base.

(*a*) 15 c.c. of $N/15{\cdot}4$-β-base and N-HCl.

	Neutralisation.	F. p.	*i*.
	Water =	**2·968**	—
	0%	2·836	1·10
	18	2·827	1·18
	36	2·813	1·31
	54	2·800	1·44
	72	2·781	1·62
*	87	2·770	1·73
	96	2·759	1·83
	105	2·748	1·95
	128	2·727	2·15

(*b*) 15 c.c. of $N/15{\cdot}4$-β-base and N-HCl.

	Neutralisation.	F. p.	*i*.
	Water =	**2·966**	—
	0%	2·829	1·14
	14	2·822	1·20
	27	2·822	1·22
	41	2·815	1·29
	50	2·810	1·33
	59	2·804	1·39
	68	2·800	1·44
*	77	2·789	1·54
	91	2·783	1·61
	100	2·769	1·74
	114	2·744	1·98
	132	2·707	2·32

(*c*) 15 c.c. of $N/15{\cdot}4$-β-base and $N/1{\cdot}39$-HI.

	Neutralisation.	F. p.	*i*.
	Water =	**3·023**	—
	0%	2·887	1·13
	15	2·882	1·18
	30	2·878	1·23
	44	2·879	1·24
	59	2·875	1·29
	67	2·874	1·31
	74	2·867	1·38
†	85	2·870	1·36
	93	2·873	1·35
	100	2·880	1·29
	108	2·865	1·43
	122	2·869	1·41

* A white precipitate appeared and disappeared between these limits.

† A brownish-pink precipitate appeared and disappeared between these limits.

duplicate determinations being 1·79 and 1·73, whilst that for the β-hydroxy-chloride rose to 1·95 and 1·98 (corrected values, 1·90 and 1·84) in solutions from which a transient slight precipitate had been cleared by the addition of 5 and 14% excess of acid respectively. The lower values recorded for the α-hydroxy-chloride may be due to a partial formation, by loss of water, of a monoxy-chloride, which would give a maximum value $i = 1{\cdot}5$ (compare footnote, this vol., p. 319).

The freezing-point depressions for the iodide solutions are rendered uncertain by the separation of insoluble basic iodides; but the values of the *i*-factor, 1·34 and 1·31, for solutions corresponding in composition with Vernon's α-dioxyiodide, are in close agreement with three values, 1·38, 1·37, and 1·34, for more dilute solutions (0·024—0·006N) of the crystalline salt, although they are rather lower than the factors 1·55 and 1·57 calculated from two determinations of molecular weight by Vernon (J., 1921, **119**, 693). These values, which have been reckoned on the concentration of the base in the solutions, are compatible with an almost complete dissociation of the α-dioxyiodide into α-hydroxy-iodide ($i = 1{\cdot}7$) and α-base ($i = 1{\cdot}1$), which would give an *i*-factor of 1·5.

Our own measurements of the freezing-point depression of a solution of the α-monoxyiodide lead to values, $M = 145$, $i = 2{\cdot}04$, which are in close agreement with the corresponding figures, $M = 143$, $i = 2{\cdot}07$, deduced from Vernon's measurements (J., 1921, **119**, 693); but, since they were made with the unstable yellow form, which is " extensively hydrolysed " by water (Vernon, *loc. cit.*), we do not regard them as trustworthy, and attach no importance to the fact that they are slightly in excess of the maximum theoretical value for complete hydrolysis of the oxyiodide, and complete ionisation of the resulting hydroxy-iodide. On the other hand, the *i*-factors for solutions prepared by adding hydriodic acid to the free base are too low, as a result of precipitation of insoluble products from the solution. The most trustworthy value, therefore, was obtained by dissolving the colourless oxyiodide (m. p. 122°) to a dilute solution, of concentration 0·0254*N*, which gave an *i*-factor 1·82, in good agreement with the values given by the soluble hydroxy-chlorides.

The *i*-factor for the β-base at 50% neutralisation is about 1·4 for each molecule of base, or 2·8 for a salt of the composition $2TeMe_2O,HCl$.

The following notes are made in reference to the products which separate from solution at different stages of neutralisation of the two bases by hydriodic acid.

α-*Base.* At 67% neutralisation (dioxyiodide) the solution first deposits the less soluble monoxyiodide, and then gives crystals of the hydrated dioxyiodide. The precipitate seen at about 80% neutralisation consists entirely of the monoxyiodide, but at 100% neutralisation the solution deposits both the monoxyiodide and the di-iodide.

β-*Base.* At 50% neutralisation (trioxyiodide) the solution slowly deposits a brown precipitate with no definite melting point; this precipitate is probably analogous to the basic bromide which is formed during the potentiometric titration of the β-base. At 67% neutralisation (dioxyiodide) the separation of the brown precipitate leaves a colourless solution from which the β-di-iodide is obtained. At 100% neutralisation, the normal product would be either a hydroxy-iodide, or a monoxyiodide formed from it by loss of water; actually, however, the solution deposits the β-di-iodide, leaving behind an alkaline solution of the base.

Summary.

(*a*) The molecular conductivity of the α-base at 25° varies from 3 to 6, and that of the β-base from 31 to 36, in the range from $v = 32—512$. The molecular conductivities are increased to about 40 (at $v = 32$) by saturation with carbon dioxide, but are reduced to normal values by passing a current of purified air through the solutions.

(*b*) Conductivity titrations of the bases show a break at the composition of the hydroxy-halide, but give no indication of the presence in the solutions either of the normal salt or of any more basic compound than the hydroxy-halide.

(*c*) Potentiometric titrations of the α-base with a glass electrode show the typical behaviour of a weak base, forming a nearly neutral hydroxy-salt; but they give no indication of the presence in solution of the dioxyiodide which Vernon prepared in a crystalline form. The curve for the β-base, on the other hand, shows an inflexion at about 50% neutralisation, corresponding with the formation of a basic salt of the composition $2TeMe_2O,HCl$, which has not been obtained in the free state.

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