CLXVII.—*The Parachor and Chemical Constitution. Part XII. Fused Metals and Salts.*

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THE earlier papers of this series have been concerned chiefly with substances which, in the liquid state, are non-conductors of electricity; the parachors of conducting liquids (metals and salts) will now be considered. These liquids exhibit many abnormalities in their physical properties and are usually classed as highly associated substances (compare Turner, "Molecular Association," Longmans, Green, and Co., Ltd., 1915, pp. 27, 59). It is clear that the presence of a high concentration of charged ions or molecules must have a profound effect upon the internal pressure of a liquid, for such charged particles possess a much larger external field of force than neutral molecules. It is therefore not surprising to find that the parachors of salts exhibit a number of anomalies and may be either greater or less than the predicted values. It will be clear from what follows that much more experimental work will have to be done before these anomalies can be accounted for satisfactorily. We are here making a preliminary survey of the field and intend to investigate more closely the types of substance in which anomalies have been encountered.

The parachor of a salt involves the constant for a polar bond. It has already been argued by one of us (Sugden, J., 1927, 1177) that this linkage should have the same effect upon the parachor as a semipolar double bond, *viz.*, $-1{\cdot}6$ units. A direct test of this hypothesis is provided by the parachors of certain salts of organic bases which are fusible without decomposition. For these substances all the atomic parachors involved are known with certainty and, from the work of Walden, Ulich, and Birr (*Z. physikal. Chem.*, 1928, **131**, 1, 21, 31), it is clear that fused salts of this type are highly dissociated into ions. The parachors of ten such salts are collected in Table I and are there compared with the parachors calculated on the assumption that the polar bond gives an increment of $-1{\cdot}6$ units. The first six substances in the table give parachors which, within the limits of experimental error, agree with the calculated values. The parachor of tetrapropylammonium picrate is of special interest, since Walden, Ulich, and Birr (*loc. cit.*) conclude that the picrates of quaternary bases are almost completely dissociated in the fused state. It is clear that the contribution of the polar bond to the parachor is very small and that the value $-1{\cdot}6$ for this constant can be regarded as satisfactory.

The six salts giving normal parachors are derived from secondary,

TABLE I.

Salts of Organic Bases.

	Substance.	Observer.*	[P] obs.	[P] calc.	Diff.	k.
(1)	Methylaniline hydrochloride	S. & W.	348·6	345·5	+ 3·1	2·11
(2)	Ethylaniline hydrochloride	,,	381·9	384·5	— 2·6	2·08
(3)	Dimethylammonium nitrate	W.	249·7	251·4	— 1·7	0·64
(4)	Diethylammonium nitrate	,,	324·8	329·4	— 4·6	0·79
(5)	Dimethylaniline bisulphate	S. & W.	469·5	472·3	— 2·8	1·28
(6)	Tetrapropylammonium picrate ...	,,	931·8	928·3	+ 3·5	2·88
(7)	Ethylammonium nitrate	,,	239·2	251·4	—12·2	0·47
	,, ,, ...	W.	234·9	,,	—16·5	0·50
(8)	Dimethylaniline hydrobromide ...	S. & W.	412·8	398·2	+14·6	1·06
	,, ,, ...	W.	406·3	,,	+ 8·1	1·64
(9)	Tri-*i*-amylammonium thiocyanate	,,	761·6	776·4	—14·8	1·48
(10)	Tetra-*i*-amylammonium iodide ...	,,	895·5	950·3	—54·8	1·77

* For full references see p. 1296.

tertiary, and quaternary bases, and the first abnormal salt, No. 7, is the only salt of a primary base so far examined. A large specimen of this substance was prepared and purified by repeated freezing until its melting point became constant at 8°. Its purity was also confirmed by analysis, yet our measurements confirm the earlier results of Walden and show a parachor anomaly of —12 units. The behaviour of this substance is in striking contrast to that of the isomeric nitrate of dimethylamine, No. 3, which gives a normal parachor. A positive anomaly of the same order of magnitude (+ 15 units) is found for dimethylaniline hydrobromide (No. 8), whereas the bisulphate of the same base (No. 5) gives a nearly normal parachor. Walden's observations give large negative anomalies for the last two substances in the table; the very large deficit for No. 10 requires confirmation and may be due, in part, to the presence of a denser impurity.

Table I includes the value of the Ramsay–Shields coefficient, $k = d\gamma(M/D)^{2/3}/dT$, where the symbols have their usual significance. The molecular weight of the undissociated salt has been used to calculate the constant, yet none of the salts examined give a value of k approaching 3·5 which, on the usual interpretation of this constant, would correspond to complete dissociation into two ions. (The value 2·88 for tetrapropylammonium picrate is paralleled by values of k greater than 2·2 for many normal liquids of high molecular weight.) No connexion can be traced between the values of k and the occurrence of parachor anomalies; both normal and abnormal salts show a wide variation in the value of this coefficient.

The first two substances in Table I give $k = 2·1$, and in this respect might be regarded as normal (non-dissociated) liquids. We have therefore determined their electrical conductivity, with the results shown in Table II. These hydrochlorides are evidently

TABLE II.

Specific (κ) and Molecular (λ) Conductivities of Fused Salts of Organic Bases.

Methylaniline hydrochloride.			Ethylaniline hydrochloride.			Tetrapropylammonium picrate.			
t.	κ.	λ.	t.	κ.	λ.	t.	κ.	λ.	$\lambda\eta$.
134°	0·0131	1·77	185°	0·0122	1·90	120°	0·0071	2·58	0·484
143·5	0·0156	2·12	197·5	0·0158	2·49	150	0·0140	5·19	0·453
155·5	0·0195	2·66	203·5	0·0176	2·77	180	0·0230	8·68	0·434
165·5	0·0259	3·55	209·5	0·0195	3·09	210	0·0327	12·57	0·411

largely ionised in the liquid state and have conductivities comparable with those of the fused picrates studied by Walden, Ulich, and Birr (*loc. cit.*). Some of the data of these workers on tetrapropylammonium picrate are included in Table II for comparison. For this substance, as for other salts of quaternary bases, the product of molecular conductivity and viscosity ($\lambda\eta$) diminishes slowly with rising temperature and has approximately the same value as is found for the same salt in dilute aqueous solution, *viz.*, 0·486. It must therefore be almost completely dissociated into ions in the fused state.

A discussion of the parachors of the salts of inorganic bases involves first of all a knowledge of the atomic constant for the metal. These constants are known with fair accuracy from measurements on covalent compounds of mercury (68·7), thallium (65·5), aluminium (38·6), tin (56·5), lead (76·2), and antimony (66·0). Table III gives the parachors of a number of salts of these elements and also those of the free metals. The latter are assumed to be monatomic and the polar bond in the salts is assigned the value $-1·6$. Some of the experimental data are open to criticism; in particular Smith's data for the surface tension of the metals are often not confirmed by later workers.

It will be seen that the parachors of these metals and salts frequently exhibit large positive anomalies. In many cases these are too large to be accounted for by association of two or more atoms or ions to give a complex linked by multiple bonds. For instance, if two thallous ions unite to give a complex ion (I), containing a double bond, the parachor increment per thallium atom is $23·2/2 = 11·6$, whereas the anomaly found in the nitrate is nearly twice this quantity. Similarly for metallic tin it is necessary to assume the

Tl=Tl	Sn≣Sn	=Sn=Sn=Sn=
$\Delta P = 11·6$	$\Delta P = 23·2$	$\Delta P = 23·2$
(I.)	(II.)	(III.)

improbable structure (II), in which two tin atoms are linked by a quadruple bond and share eight electrons, or the equally improbable

TABLE III.

Fused Metals and Inorganic Salts.

Substance.	Observer.	[*P*] obs.	[*P*] calc.	Diff.
Thallous formate	S.	150·3	145·8	+ 4·5
,, acetate	,,	183·5	184·4	— 0·9
,, nitrate	,,	177·3	158·0	+19·3
,, ,, ...	J.	180·7	,,	+22·7
Stannous chloride	,,	183·8	165·1	+18·7
Lead chloride	L. & K.	194·5	184·8	+ 9·7
Mercury	Smith	68·0	68·7	— 0·7
,, ...	H. & E.	69·0	,,	+ 0·3
,, ...	H	69·4	,,	+ 0·7
,, ...	Br.	69·4	,,	+ 0·7
Aluminium	Smith	55·0	38·6	+16·4
Tin	,,	83·4	56·5	+26·9
,, ...	Bi.	83·8	,,	+27·3
,, ...	S. & D.	86·8	,,	+30·3
Lead	Smith	114·2	76·2	+38·0
,, ...	H.	89·3	,,	+13·1
,, ...	Bi.	91·5	,,	+15·3
,, ...	D. & S.	93·5	,,	+17·3
Antimony	Smith	76·8	66·0	+10·8
,, ...	Bi.	82·0	,,	+16·0
,, ...	D. & S.	83·9	,,	+17·9

structure (III), containing chains of tin atoms linked by double bonds, in order to account approximately for the parachor anomalies. It is more probable that some other factor has to be taken into account due either to the presence of a high concentration of ions or of loosely bound electrons, or else to some special condition of the metallic atom. In this connexion it should be noted that Sidgwick ("The Electronic Theory of Valency," Clarendon Press, 1927, pp. 179—181) has directed attention to the remarkable chemical inertness of a pair of electrons in the atoms of certain elements, *e.g.*, thallium, tin, lead, and antimony, all of which exhibit positive parachor anomalies. In many compounds this pair of electrons behaves as if it were part of the core and could not be removed by ionisation.

Jaeger (*Z. anorg. Chem.*, 1917, **101**, 1) has measured the surface tensions and densities of a number of salts of the alkali metals. The parachors calculated from these observations are summarised in Table IV and are used to obtain approximate atomic parachors for the metallic elements. Jaeger's surface tensions often cover a much wider range than his density measurements; to avoid errors of extrapolation the parachors have been calculated only for the range of temperatures covered by the density observations. This range is indicated in the second column and the variation in parachor over this range is given in the third column. The fifth column gives the parachor of the anion + the constant for a polar bond; by subtracting this from the mean parachor of the salt, the constant for the metal is obtained.

TABLE IV.

Salts of the Alkali Metals.

Substance.	Temperature.	Parachor.	Mean [P].	$\Sigma[P]$.	Atomic parachor.
LiF	850—1000°	57·8— 59·3	58·5	24·1	34·4
LiCl	600— 775	97·2— 99·6	98·4	52·7	45·7
$LiNO_3$ ...	350— 500	130·0—132·9	131·5	91·5	40·0
Li_2SO_4 ...	860—1150	212·4—220·6	216·0	121·8	47·1 × 2
NaF	1010—1190	81·5— 83·9	82·7	24·1	58·6
NaCl	800— 900	123·4—126·7	124·8	52·7	72·1
NaBr ...	760— 900	142·2—145·4	143·8	66·4	77·4
NaI	700— 750	169·4—171·3	170·8	89·4	81·4
$NaNO_3$ ...	320— 600	147·9—158·4	152·9	91·5	61·4
$NaPO_3$ ...	800—1100	175·4—181·7	178·1	117·7	60·4
Na_2SO_4 ...	900—1100	257·5—265·8	261·1	121·8	69·6 × 2
KF	900—1100	106·7—111·0	109·0	24·1	84·9
KCl	800— 900	154·6—158·4	156·6	52·7	103·9
KBr	775— 825	173·6—175·1	174·3	66·4	107·9
KI	737— 812	204·3—206·8	205·2	89·4	115·8
KNO_3 ...	380— 580	184·2—193·6	189·0	91·5	97·5
KPO_3 ...	900—1200	201·4—207·0	204·4	117·7	86·7
K_2SO_4 ...	1070—1350	319·5—336·5	328·0	121·8	103·1 × 2
RbF	800—1040	121·2—125·9	123·1	24·1	99·0
RbCl	750— 880	181·0—185·0	182·8	52·7	130·1
RbBr ...	730— 830	190·5—195·0	192·7	66·4	126·3
RbI	670— 820	224·3—229·5	226·8	89·4	137·4
$RbNO_3$ ...	320— 580	192·5—203·7	197·9	91·5	106·4
Rb_2SO_4 ...	1080—1350	356·9—368·1	361·8	121·8	120·0 × 2
CsF	720— 880	135·4—138·6	136·9	24·1	112·8
CsCl	660— 770	186·6—190·7	188·7	52·7	136·0
CsBr	650— 770	205·2—209·2	207·5	66·4	141·1
CsI	650— 770	239·8—245·0	242·4	89·4	153·0
$CsNO_3$ ...	425— 575	215·7—221·2	218·0	91·5	126·5
Cs_2SO_4 ...	1030—1220	386·8—393·1	388·8	121·8	133·5 × 2

Approximate atomic parachors : Li = 50, Na = 80, K = 110, Rb = 130, Cs = 150.

From a survey of the data in Table IV it will be seen that the bromides and iodides usually give the highest values for the metallic parachors and the sulphates, nitrates, phosphates, and particularly the fluorides give much lower figures. At present the only other evidence for the parachors of these elements is furnished by the determination of the surface tension of metallic sodium by Poindexter (*Physical Rev.*, 1926, **27**, 820), from which Na = 97·4. This is much larger than the highest value deduced from the salts. It must be remembered, however, that this figure refers to a neutral sodium atom with an electron in the M level, whereas the constant deduced from the salts refers to a sodium ion in which this level is unoccupied. It is hoped shortly to obtain the parachors of co-ordinated compounds of the alkali metals, *e.g.*, with β-diketones, which should give further information as to their atomic parachors. Meanwhile the figures given at the bottom of Table IV may be taken as rough minimum values.

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EXPERIMENTAL.

Surface tensions were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27); and densities by means of the U-shaped pyknometer previously described (J., 1924, **125**, 1171), except for the more hygroscopic salts, for which calibrated floats were used in sealed tubes. The parachor is calculated by the formula $[P] = M\gamma^{1/4}/D$, where M is the molecular weight, γ the surface tension in dynes/cm., and D the density of the liquid.

Methylaniline hydrochloride, $C_7H_{10}NCl$, $M = 143{\cdot}6$, was prepared by passing dry hydrogen chloride into a ligroin solution of the base and was recrystallised from benzene–chloroform. The specimen used melted at 122·5—123° (corr.) after thorough drying in a vacuum desiccator. Densities determined (floats): $D_{4^\circ}^{126{\cdot}5^\circ}$ 1·0660, $D_{4^\circ}^{143^\circ}$ 1·0590, $D_{4^\circ}^{148{\cdot}5^\circ}$ 1·0557, $D_{4^\circ}^{167{\cdot}5^\circ}$ 1·0447; whence $D_{4^\circ}^{t^\circ} = 1{\cdot}0808 - 0{\cdot}000527\ (t - 100)$.

t	130°	140·5°	150·5°	160°	
γ	44·53	43·50	42·68	41·29	
D	1·0634	1·0564	1·0517	1·0462	
$[P]$	348·7	348·9	348·8	347·7	Mean 348·5

Ethylaniline hydrochloride, $C_8H_{12}NCl$, $M = 157{\cdot}6$, was prepared by dissolving the base (100 g.) in concentrated hydrochloric acid (70 c.c.). On cooling, the salt crystallised. The base was regenerated and again crystallised as hydrochloride. A little reddish colouring matter was removed by washing with absolute alcohol, and the product thoroughly dried; m. p. 178·5° (corr.). Densities determined (floats): $D_{4^\circ}^{182{\cdot}5^\circ}$ 1·0085, $D_{4^\circ}^{203^\circ}$ 0·9984; whence $D_{4^\circ}^{t^\circ} = 1{\cdot}0492 - 0{\cdot}000493\ (t - 100)$. Above 200° the substance decomposed with evolution of gas.

t	173·5°	180·5°	188·5°	
γ	35·82	35·41	34·50	
D	1·0098	1·0061	1·0019	
$[P]$	382·0	382·3	381·4	Mean 381·9

Tetrapropylammonium picrate, $C_{18}H_{30}O_7N_4$, $M = 414{\cdot}3$. The bromide was first prepared and recrystallised from ethyl acetate until pure, m. p. 252° (corr.) (Found : Br, 29·66. Calc. : Br, 30·03%). This was converted into the picrate, which melted at 117·5—118° (corr.). Densities determined : $D_{4^\circ}^{125\cdot5^\circ}$ 1·136, $D_{4^\circ}^{141\cdot5^\circ}$ 1·122, $D_{4^\circ}^{149^\circ}$ 1·115; whence $D_{4^\circ}^{t^\circ} = 1{\cdot}159 - 0{\cdot}00086(t - 100)$. These figures are in good agreement with the densities found by Walden, Ulich, and Birr (*loc. cit.*).

t	129°	135°	143·5°	152·5°	
γ	41·80	41·30	40·72	40·03	
D..................	1·134	1·129	1·122	1·114	
$[P]$	929·0	929·9	932·6	935·6	Mean 931·8

Ethylamine nitrate, $C_2H_8O_3N_2$, $M = 108{\cdot}1$, was prepared by dissolving a slight excess of the base in 20% nitric acid and removing the water under diminished pressure. The residual oil was frozen and the crystals were collected in a chilled funnel. This process was repeated until a constant melting point of 8° (corr.) was attained [Found : HNO_3 (by nitron), 59·1, 59·25. Calc. : HNO_3, 58·3%]. Densities determined : $D_{4^\circ}^{12^\circ}$ 1·216, $D_{4^\circ}^{32^\circ}$ 1·199, $D_{4^\circ}^{55^\circ}$ 1·182, $D_{4^\circ}^{70^\circ}$ 1·168; whence $D_{4^\circ}^{t^\circ} = 1{\cdot}225 - 0{\cdot}00080\ t$.

t	11°	30°	56·5°	82·5°	97°	
γ	48·8	47·6	46·2	45·4	44·9	
D.........	1·216	1·201	1·180	1·159	1·148	
$[P]$	235·0	236·5	238·8	242·1	243·8	Mean 239·2

Dimethylaniline hydrobromide, $C_8H_{12}NBr$, $M = 202{\cdot}0$, was prepared by dissolving the base in a slight excess of constant-boiling hydrobromic acid and removing the water under diminished pressure. The solid product was purified by precipitation from solution in dry chloroform by the addition of ethyl acetate. The specimen used melted at 84·5—85·5° (corr.) (Found : Br, 39·5. Calc. : Br, 39·6%). Densities determined : $D_{4^\circ}^{110\cdot5^\circ}$ 1·302, $D_{4^\circ}^{120^\circ}$ 1·294, $D_{4^\circ}^{130^\circ}$ 1·286, $D_{4^\circ}^{141\cdot5^\circ}$ 1·277; whence $D_{4^\circ}^{t^\circ} = 1{\cdot}398 - 0{\cdot}00864\ t$.

t	97°	112°	118·5°	129°	136·5°	
γ	50·40	49·55	49·00	48·60	48·07	
D.........	1·314	1·301	1·296	1·287	1·280	
$[P]$	409·7	412·1	412·3	414·4	415·7	Mean 412·8

Dimethylaniline bisulphate, $C_8H_{13}O_4NS$, $M = 219{\cdot}2$, was prepared by dissolving the calculated amount of the base in 50% sulphuric acid and removing the water under diminished pressure. It was purified by solution in dry chloroform and precipitation at 0° by addition of ethyl acetate; m. p. 88—89° (corr.) (Found : SO_4, 43·1. Calc. : SO_4, 43·8%). Densities determined : $D_{4^\circ}^{111\cdot5^\circ}$ 1·272, $D_{4^\circ}^{122\cdot5^\circ}$ 1·268, $D_{4^\circ}^{129\cdot5^\circ}$ 1·260, $D_{4^\circ}^{137^\circ}$ 1·256; whence $D_{4^\circ}^{\circ} = 1{\cdot}283 - 0{\cdot}00074\ (t - 100)$.

t	105·5°	114·5°	126°	133°	
γ	55·2	54·9	54·0	53·7	
D	1·279	1·272	1·264	1·259	
$[P]$	467·1	469·0	470·0	471·3	Mean 469·5

One of us (S. S.) is indebted to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of this investigation.

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[*Received, April* 24*th*, 1929.]