332. *Electrical Conduction in Fused Gallium Dichloride and Gallium Dibromide.*

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Fused gallium dichloride and dibromide are typical molten salts. The variation of their conductivity and viscosity with temperature is characteristic of compounds in which the cation is considerably smaller than the anion. These results are consistent with recent structural investigations [1,2,3] which have shown the compounds to be $Ga^+[Ga^{III}Cl_4]^-$ and $Ga^+[Ga^{III}Br_4]^-$. The effect on the conductivity of adding excess of gallium to the dichloride was also studied. In addition, the density of pure gallium dichloride and dibromide and the surface tension of the dichloride have been determined over a range of temperature.

X-Ray crystal structure analysis [2] has shown that gallium dichloride is ionic, $Ga^+[GaCl_4]^-$, and the Raman spectrum of the fused compound indicates that this structure persists in the liquid state.[1] Gallium is therefore present equally in the oxidation states +1 and +3, consistent with the diamagnetism of the solid.[4] The diamagnetism of solid gallium dibromide and the Raman spectrum of the fused compound likewise indicate an ionic formulation $Ga^+[GaBr_4]^-$,[3] and, in the absence of more specific evidence, a similar structure may be presumed for the di-iodide on the grounds of its diamagnetism and the similarity in m. p. of the three compounds.[5] The dihalides can therefore be considered as addition compounds of the trihalides in which the unstable monohalides act as ligand, $GaX \rightarrow GaX_3$. Indeed, they constitute an unusual example of stabilization of an oxidation state by co-ordination for, in this instance, the complex ion (GaX_4^-) involves the normal valency state of the gallium atom whilst the less common +1 state is left unco-ordinated. Other examples of this phenomenon occur [6] in $Ga^+[AlCl_4]^-$ and $Bi^+[AlCl_4]^-$.

The importance of the dihalides in a study of the complexes of gallium trihalides lies in their unambiguously established structure and the fact that they should behave as molten salts despite their low m. p.s. Instructive comparisons can thus be made between the dihalides and addition compounds such as $POCl_2^+GaCl_4^-$ [7] and $POBr_2^+GaBr_4^-$,[8] the differences between the two sets of compounds residing in the size and electropositivity of the cations. Similarly, the properties of the complexes which the trihalides form with pyridine and piperidine have been interpreted on the basis of the structures $[py_2GaX_2]^+GaX_4^-$ [9,10] and $[pip_2GaX_2]^+GaX_4^-$ [10,11] in which the cations are even larger.

This investigation concerns the electrical conductivity and related properties of gallium dichloride and dibromide. The less stable di-iodide was not investigated. The compounds are true molten salts; the reduced conductivity indicates that they are completely dissociated into ions, and the variation of conductivity and viscosity with temperature is characteristic of compounds in which the cation is smaller than the anion. These properties are compared with those of silver nitrate as an analogous molten salt and with those of the previously mentioned co-ordination compounds of the gallium trihalides. Some results on gallium dibromide have already been summarized.[3]

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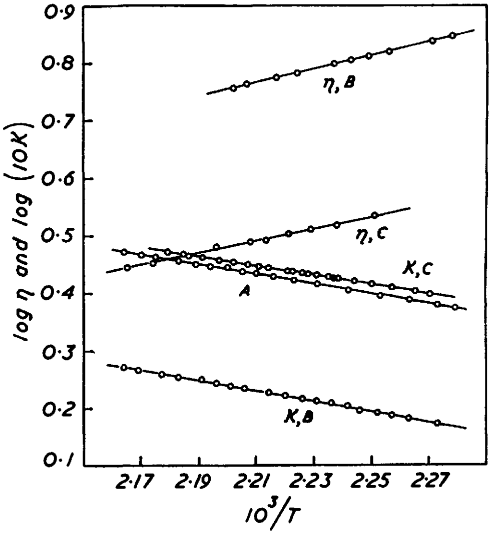
[1] Woodward, Garton, and Roberts, *J.*, 1956, 3723.
[2] Garton and Powell, *J. Inorg. Nuclear Chem.*, 1957, **4**, 84.
[3] Woodward, Greenwood, Hall, and Worrall, *J.*, 1958, 1505.
[4] Klemm and Tilk, *Z. anorg. Chem.*, 1932, **207**, 175.
[5] Corbett and McMullan, *J. Amer. Chem. Soc.*, 1955, **77**, 4217.
[6] *Idem, ibid.*, 1956, **78**, 2906.
[7] Greenwood and Wade, *J.*, 1957, 1516.
[8] Greenwood and Worrall, *J. Inorg. Nuclear Chem.*, 1958, **6**, 34.
[9] Greenwood and Wade, *J.*, 1958, 1663.
[10] Greenwood and Worrall, unpublished observations.
[11] Greenwood and Wade, preceding paper.

EXPERIMENTAL AND RESULTS

Gallium dichloride was prepared by heating the trichloride [12] with slightly less than the stoicheiometric amount of gallium and then volatilizing the excess of trichloride from the molten mixture, and was purified by fractional freezing to constant m. p. 172·4°. The solid was pure white. Preparations in which there was an excess of gallium had lower m. p.s (169—170°); they were quite colourless and transparent when fused but were grey and opaque as solids. Literature values for the m. p. of the dichloride are 164°,[13] 165°,[1] and 170° ± 0·5°; [14] descriptions of these preparations indicate that the first contained excess of gallium and that the other two were contaminated with traces of the trichloride, which cannot be completely removed by volatilization.



Conductivity and viscosity of Ga$^+$GaBr$_4^-$ (*B*) *and* Ga$^+$GaCl$^-$ (*C*), *with* (*A*), κ *for a solution of gallium in* Ga$^+$GaCl$_4^-$.

The preparation and purification of gallium dibromide (m. p. 166·7°) have been described.[3] The techniques used to measure conductivity, viscosity, density, and surface tension are as in earlier work.[9]

Gallium Dichloride, Ga$^+$[GaCl$_4$]$^-$.—The specific conductivity of fused gallium dichloride near its m. p. is given in Table 1. The results were reproducible during several hours and can be represented by the equation (see Fig.)

$$\log \kappa = 1{\cdot}180 - 784/T$$

This implies an activation energy, E_κ, of 3·59 kcal. mole^{-1}. Values of the molar conductivity, μ, calculated on the basis of the " dimeric " formula weight Ga[GaCl$_4$], are also listed in Table 1 and lead to an activation energy, E_μ, of 3·81 kcal. mole^{-1}. This, as expected,[15] is larger than E_κ by an amount $\boldsymbol{R}T^2\alpha$ where α is the coefficient of thermal expansion. At the m. p. (172·4°) the specific conductivity is 0·264$_2$ ohm^{-1} cm.$^{-1}$, the molar conductivity 30·7$_6$ cm.^{2} ohm^{-1} mole^{-1}, and the reduced conductivity (which compensates for the influence of viscosity on ionic mobility) 103·3 cm.^{2} cP ohm^{-1} mole^{-1}. The significance of these values is discussed later.

The effect of dissolved gallium metal on the conductivity of the dichloride was studied by heating pure gallium dichloride with excess of gallium at 180° for several hours and then transferring the clear solution into the same conductivity cell as was used for the preceding measurements. Under these conditions about 2 moles % of gallium is dissolved in the fused state [16] but this precipitates as an opaque grey dispersion in the solid state.[13] The process is reversible and the m. p. of the solid was 169°. Results are presented in Table 2 and the Figure

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[12] *Idem, J.*, 1956, 1527.
[13] Lecoq de Boisbaudran, *Compt. rend.*, 1881, **93**, 294.
[14] Laubengayer and Schirmer, *J. Amer. Chem. Soc.*, 1940, **62**, 1578.
[15] Martin, *J.*, 1954, 3246.
[16] Corbett and von Winbush, *J. Amer. Chem. Soc.*, 1955, **77**, 3964.

which indicates that dissolution of gallium in the dichloride lowers the conductivity by about 3·7% in the temperature range studied. The results can be expressed by the equation $\log \kappa = 1{\cdot}235 - 815/T$, which corresponds to an activation energy E_κ of 3·73 kcal. mole^{-1}.

TABLE 1. *Electrical conductivity of fused gallium dichloride.*

Sequence	Temp.	κ (ohm^{-1} cm.$^{-1}$)	μ (cm.^{2} ohm^{-1} mole^{-1})	$\mu\eta$ (cm.^{2} cP ohm^{-1} mole^{-1})	Sequence	Temp.	κ (ohm^{-1} cm.$^{-1}$)	μ (cm.^{2} ohm^{-1} mole^{-1})	$\mu\eta$ (cm.^{2} cP ohm^{-1} mole^{-1})
21	167·4°	0·2510	29·13	103·9	6	177·0°	0·2743	32·06	102·0
20	168·4	0·2540	29·50	104·1	15	177·2	0·2753	32·12	102·0
19	169·8	0·2576	29·87	103·4	7	178·4	0·2780	32·47	101·6
18	171·2	0·2610	30·36	103·4	14	179·0	0·2789	32·58	101·2
1	172·4	0·2642	30·76	103·3	8	180·0	0·2817	32·92	101·3
2	173·5	0·2667	31·05	102·7	13	181·0	0·2844	33·26	101·2
17	173·8	0·2667	31·06	102·5	9	182·0	0·2873	33·62	101·0
3	174·2	0·2684	31·26	102·8	10	183·3	0·2903	33·99	100·8
4	175·0	0·2700	31·47	102·4	11	184·5	0·2932	34·35	100·5
16	175·5	0·2709	31·59	102·1	12	185·7	0·2963	34·74	100·1
5	176·0	0·2727	31·80	102·3					

TABLE 2. *Specific conductivity of a solution of gallium in gallium dichloride.*

Temp.	165·7°	166·7°	168·7°	170·7°	172·9°	175·0°	176·5°	178·0°	179·4°
κ (ohm^{-1} cm.$^{-1}$)	0·2383	0·2410	0·2454	0·2499	0·2557	0·2607	0·2645	0·2696	0·2723
Temp.	180·4°	181·5°	182·7°	183·5°	184·9°	186·4°	187·4°	189·0°	
κ (ohm^{-1} cm.$^{-1}$)	0·2746	0·2776	0·2802	0·2821	0·2857	0·2893	0·2916	0·2955	

TABLE 3. *Viscosity of gallium dichloride.*

Temp.	171·0°	173·6°	175·4°	177·0°	178·6°	179·7°	182·2°	184·3°	186·8°	188·8°
ν (cs)	1·412	1·367	1·346	1·315	1·289	1·280	1·258	1·222	1·183	1·165
η (cP)	3·416	3·302	3·247	3·172	3·106	3·081	3·025	2·935	2·835	2·788

TABLE 4. *Density, surface tension, and parachor of gallium dichloride.*

Temp.	d_4^t (g. ml.$^{-1}$)	γ (dyne cm.$^{-1}$)	$[P] = V_M\gamma^{\frac{1}{4}}$	Temp.	d_4^t (g. ml.$^{-1}$)	γ (dyne cm.$^{-1}$)	$[P] = V_M\gamma^{\frac{1}{4}}$	Temp.	d_4^t (g. ml.$^{-1}$)	γ (dyne cm.$^{-1}$)	$[P] = V_M\gamma^{\frac{1}{4}}$
166·7°	2·4249	57·68	319·8	171·1°	2·4190	56·41	318·6	175·0°	2·4134	(57·24)	(320·7)
168·0	2·4231	57·05	319·1	172·0	2·4178	55·80	318·0	176·0	2·4124	56·02	319·0
169·1	2·4216	56·08	317·7	173·2	2·4163	(54·55)	(316·4)	177·0	2·4116	55·36	318·2
170·1	2·4201	57·20	319·2	174·1	2·4150	55·25	317·5				

The dynamic viscosity of pure gallium dichloride is given by $\log \eta = -1{\cdot}768 + 1022/T$ from which the activation energy for viscous flow, E_η, is 4·68 kcal. mole^{-1}. Individual results for the range 171—189° are in Table 3 and the Figure. As the times of outflow were of the order of 70 sec., the figures are only precise to about 1 part in 500 but four significant figures have been retained to reduce errors in the computations of activation energy and reduced conductivity. At 172·4° the kinematic viscosity is $1{\cdot}38_8$ cs and the dynamic viscosity $3{\cdot}35_5$ cP.

The density of gallium dichloride in the temperature range 166—177° is shown in Table 4 and may be reproduced with a mean deviation of 2 in the last figure by the equation

$$d_4^t = 2{\cdot}4206 - 1{\cdot}36 \times 10^{-3}(t - 170)$$

At the m. p. the density of fused gallium dichloride is 2·4173, consistent with the only reference in the literature to the density,[14] *viz.*, that it is greater than that of Pyrex glass (2·238). Table 4 also records approximate values of the surface tension measured simultaneously with the density. Except for the two values in parentheses, we can express the results with a mean deviation of 0·4 dyne cm.$^{-1}$ by the equation

$$\gamma = 56{\cdot}6 - 0{\cdot}18(t - 170)$$

The molar surface free energy ($\omega = \gamma V_M^{\frac{2}{3}}$) is then

$$\omega = 1350 - 3{\cdot}9(t - 170)$$

Values of the parachor, $[P]$ are listed in the last column of Table 4. The function is constant, within experimental error, over the temperature range investigated and has a mean value of $318{\cdot}5 \pm 0{\cdot}5$. It is not possible to compare this with a theoretical value since there is no satisfactory method of calculating the parachor of fused salts.[17]

Gallium Dibromide, $Ga^+[GaBr_4]^-$.—The corresponding data on gallium dibromide are presented in Tables 5, 6, and 7 and are compared with those on the dichloride in the Figure. At the m. p. (166·7°) the specific conductivity is $0{\cdot}149_2$ ohm^{-1} cm.$^{-1}$ which is about half the value found for the dichloride. That this is predominantly a viscosity effect is shown by the fact that, although the molar conductivity, $19{\cdot}7_3$ cm.^{2} ohm^{-1} mole^{-1}, is still only about two-thirds that of the dichloride, the reduced conductivity, 136·3 cm.^{2} cP ohm^{-1} mole^{-1}, is rather greater than the corresponding figure for the dichloride (103·3 cm.^{2} cP ohm^{-1} mole^{-1}). The conductivity equation is $\log \kappa = 1{\cdot}142 - 865/T$, and the activation energies are $E_\kappa = 3{\cdot}96$ kcal. mole^{-1} and $E_\mu = 4{\cdot}16$ kcal. mole^{-1}.

TABLE 5. *Electrical conductivity of fused gallium dibromide.*

Sequence	Temp.	κ (ohm^{-1} cm.$^{-1}$)	μ (cm.^{2} ohm^{-1} mole^{-1})	$\mu\eta$ (cm.^{2} cP ohm^{-1} mole^{-1})
19	166·7°	0·1492	19·73	136·3
1	168·8	0·1521	20·13	135·5
6	169·8	0·1543	20·44	135·3
7	170·8	0·1560	20·67	135·0
8	172·0	0·1581	20·95	134·7
9	173·0	0·1601	21·23	135·1
10	174·0	0·1616	21·45	134·3
11	175·0	0·1631	21·67	133·9
12	176·0	0·1650	21·94	133·8
13	177·2	0·1670	22·20	133·1
14	178·4°	0·1690	22·48	132·6
15	180·1	0·1717	22·85	132·1
16	181·1	0·1734	23·10	131·7
17	182·2	0·1752	23·35	131·4
18	183·3	0·1774	23·65	131·3
5	184·8	0·1793	23·92	130·0
4	186·2	0·1820	24·30	129·9
3	187·8	0·1843	24·62	129·0
2	189·0	0·1867	24·97	129·0

TABLE 6. *Viscosity of gallium dibromide.*

Temp.	165·9°	167·1°	170·0°	171·3°	172·7°	173·8°	176·5°	177·8°	179·9°	180·9°
ν (cs)	2·014	1·983	1·904	1·873	1·841	1·813	1·751	1·718	1·682	1·660
η (cP) ...	6·991	6·881	6·596	6·488	6·373	6·271	6·050	5·930	5·800	5·721

TABLE 7. *Density of molten gallium dibromide.*

Temp.	160·5°	162·5°	164·4°	166·4°	168·5°	170·5°	173·3°	175·1°
d_4^t (g. ml.$^{-1}$)	3·4820	3·4788	3·4751	3·4711	3·4682	3·4656	3·4604	3·4577
Temp.	176·6°	178·1°	179·7°	184·2°	186·8°	187·7°	189·6°	
d_4^t (g. ml.$^{-1}$)	3·4557	3·4521	3·4510	3·4408	3·4370	3·4357	3·4326	

The dynamic viscosities listed in Table 6 can be represented by $\log \eta = -1{\cdot}793 + 1158/T$. The activation energy for viscous flow, E_η, is 5·30 kcal. mole^{-1} and the viscosity at the m. p. is $6{\cdot}91_8$ cP. Outflow times were in the range 470—570 sec. and a complete temperature run lasted about 8 hr.

The densities in Table 7 lead to an equation

$$d_4^t = 3{\cdot}4656 - 1{\cdot}69 \times 10^{-3}(t - 170)$$

which reproduces the values with a mean deviation of 5 in the last decimal place. Surface tension was not measured because of a tendency to form small bubbles in the narrow capillary; this made differences in levels difficult to interpret but had little effect on the density results since it was possible to estimate the volume of the bubbles with a cathetometer.

DISCUSSION

When we started, the only information on the physical properties of gallium dichloride were its m. p. [4, 13] and vapour pressure [14] together with statements that the solid

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[17] McGowan, *Rec. Trav. chim.*, 1956, **75**, 193.

was diamagnetic[4] and that the fused compound conducted electricity.[18] Nothing was known of the properties of the dibromide. Recent investigations by means of Raman spectra[1, 3] and X-ray analysis[2] have shown that both compounds are ionic and have the structures $Ga^+[GaCl_4]^-$ and $Ga^+[GaBr_4]^-$. The present results, summarized in Table 8, considerably extend our knowledge of the physical properties of these compounds and are entirely consistent with the ionic formulation.

The magnitude of the electrical conductivity of fused gallium dichloride and dibromide indicates that these compounds are true molten salts. At the m. p. (172·4°) the reduced conductivity of gallium dichloride is 103·3 and that of the dibromide at its m. p. (166·7°) 136·3 cm.^{2} cP ohm^{-1} mole^{-1}. These values may be compared with the reduced conductivity of a typical molten salt such as silver nitrate at its m. p. (208·9°).[19] The following data, extrapolated from figures in Landolt and Börnstein's tables, lead to a value for $\mu\eta$ of 136 which is virtually identical with the reduced conductivity of gallium dibromide: $AgNO_3$, $\kappa = 0{\cdot}641$ ohm^{-1} cm.$^{-1}$, $\eta = 4{\cdot}96$ cP, $d = 3{\cdot}974$ g. ml.$^{-1}$. More recent determinations on silver nitrate[20] vary among themselves by a few per cent. but are in essential agreement with these values.

The rather large activation energies of viscous flow (E_η in Table 8) are also typical of molten salts and are greater than values normally obtained for covalent liquids.[21] Moreover, the activation energy of viscous flow for both dihalides is appreciably greater than the activation energy of ionic migration, the values of the ratio E_η/E_μ being 1·23 for the dichloride and 1·27 for the dibromide (1·26 for silver nitrate). This suggests that the small Ga^+ ion is moving comparatively independently of the larger GaX_4^- ions, an effect which is frequently encountered in molten salts when the sizes of the cation and anion are very different.[22] This interpretation is consistent with two further observations which might

TABLE 8. *Properties of the dihalides of gallium at their m. p.s.*

Property	$Ga^+GaCl_4^-$	$Ga^+GaBr_4^-$
Mol. wt.	281·27	459·10
M. p.	172·4°	166·7°
d (g. ml.$^{-1}$)	2·4173	3·471$_2$
Temp. coeff. of d	1·36 × 10^{-3}	1·69 × 10^{-3}
V_M (ml. mole^{-1})	116·36	132·26
p (mm. Hg)	0·15 or 0·30 [a]	—
ΔH_{vap} (kcal. mole^{-1})	16·3 or 19·5 [a]	—
$\Delta H_{vap}/E_\eta$	3·49 or 4·17	—
γ (dyne cm.$^{-1}$)	56·2	—
Temp. coeff. of γ	0·180	—
ω (erg mole$^{-2/3}$)	1340	—
k (Eötvös)	3·9	—
$[P]$	318·5	—
ν (cs)	1·38$_8$	1·99$_3$
η (cP)	3·35$_5$	6·91$_8$
ϕ (cP^{-1})	0·298	0·145
B (ml. cP g.$^{-1}$)	6·39 × 10^{-2} [b]	6·69 × 10^{-2} [b]
E_η (kcal. mole^{-1})	4·68	5·30
κ (ohm^{-1} cm.$^{-1}$)	0·264$_2$	0·149$_2$
μ (cm.^{2} ohm^{-1} mole^{-1})	30·7$_6$	19·7$_3$
$\mu\eta$ (cm.^{2} cP ohm^{-1} mole^{-1})	103·3	136·3
E_κ (kcal. mole^{-1})	3·59	3·96
E_μ (kcal. mole^{-1})	3·81	4·16
E_η/E_μ	1·23	1·27

[a] Calculated from data in ref. 14. [b] Batschinski's constant in the equation $v = b + B\phi$; see also ref. 8.

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[18] Hampe, *Jahresber.*, 1888 (Part I), p. 388.

[19] Doucet, Le Duc, and Pannetier, *Compt. rend.*, 1953, **236**, 1018.

[20] Bokhovkin, *J. Gen. Chem. U.S.S.R.*, 1950, **20**, 397; Byrne, Fleming, and Wetmore, *Canad. J. Chem.*, 1952, **30**, 922; Pugsley and Wetmore, *ibid.*, 1954, **32**, 839; Kaoru Sakai, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1954, **75**, 182.

[21] Ward, *Trans. Faraday Soc.*, 1937, **33**, 88.

[22] Greenwood and Martin, *J.*, 1953, 1427.

otherwise be difficult to understand: (1) dissolution of gallium in the dichloride *lowers* the conductivity and *increases* the activation energy of conduction; (2) the molar volumes of the trihalides and dihalides are in the ratio 3 : 2, *i.e.*, in the ratio of the number of halogen atoms in the compounds.

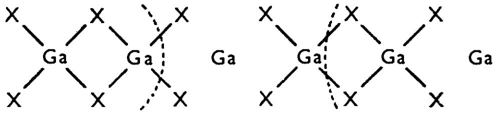
(1) The effect of dissolved gallium in lowering the conductivity of gallium dichloride provides an unusual example of the influence of disparity in size on the mobility of ions in molten salts. In the pure dichloride, most of the current will be carried by the small Ga^+ cation moving rapidly through the interstices of the relatively immobile network of $GaCl_4^-$ anions. When gallium is dissolved in this melt, chemical reduction occurs according to the equation

$$(n + 1)Ga^+GaCl_4^- + 2Ga = nGa^+GaCl_4^- + 4Ga^+Cl^-$$

The two added atoms of gallium increase the number of ions present from $(2n + 2)$ to $(2n + 8)$ so that, in effect, each added gallium atom is equivalent to three added ions. That this decreases rather than increases the conductivity is due to the fact that, in the solution, the gallium ions have to compete with the similarly sized chloride ions travelling in the opposite direction, with consequent decrease in mobility and increase in activation energy. The partial collapse of the anion network due to the replacement of the large $GaCl_4^-$ ions by the smaller Cl^- ions also contributes. A similar effect is observed in the classic case of α-silver iodide. Above the $\beta \rightarrow \alpha$ transition point (146°) the solid has an extraordinarily high unipolar electrical conductivity[23] because the relatively small silver ions can travel virtually unimpeded through the anion lattice of the crystal, there being thirty interstitial sites available for each two silver ions. However, when the crystal melts (554°) the iodide lattice collapses, reducing the number of interstices available to the silver ions and thus reducing their mobility. The mobility of the silver ions is further diminished by having to compete with the now mobile anions, so that the conductivity of the compound actually decreases on melting (from 2·64 to 2·36 ohm^{-1} $cm.^{-1}$)[23] though virtually all of the current is still carried by the cation ($E_\eta/E_\mu = 6{\cdot}4$).

An interesting rider to this description of the conduction process in the fused dihalides is that the reduced conductivity of the dibromide should be greater than that of the dichloride (as observed). It might at first be thought that the reverse would be true since the $GaBr_4^-$ ion is larger than the $GaCl_4^-$ ion and should move more slowly, thus lowering the conductivity, the cation being the same in each compound. However, if the conduction is unipolar, as postulated, the anions will be relatively immobile and the Ga^+ cation will move more freely through the interstices the greater the disparity in size between the cation and anion. This appears to be generally true of most molten salts; for example the reduced conductivity of the silver halides increases in the order $AgCl < AgBr < AgI$ and for the alkali metal chlorides the sequence is $KCl < NaCl < LiCl$.[22,24] In short, for a given series of compounds, $\mu\eta$ increases as the ratio E_η/E_μ increases.

(2) A second illustration of the ease with which Ga^+ ions can pack into the irregular interstices between the GaX_4^- ions comes from a comparison of the molar volumes of the fused dihalides and trihalides. The molar volumes of the dihalides are exactly two-thirds of the molar volumes of the corresponding trihalides. This implies that the gallium metal which is added to reduce the trihalides fits into existing " holes " in the liquid structure and causes no expansion of the melt, the factor of two-thirds arising because two moles of the trihalide furnish three moles of the dihalide:



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[23] Tubandt and Lorenz, *Z. phys. Chem.*, 1914, **87**, 513.
[24] Karpachev, *J. Phys. Chem. U.S.S.R.*, 1935, **6**, 1079.

Values at the respective m. p.s being quoted, $2V_M(\mathrm{Ga_2Cl_6}) = 343$ [25] and $3V_M(\mathrm{Ga_2Cl_4}) = 349$; $2V_M(\mathrm{Ga_2Br_6}) = 398$ [8] and $3V_M(\mathrm{Ga_2Br_4}) = 397$. It is sometimes argued that a better comparison temperature is 10% above the absolute m. p. because of residual "solid" structure in the liquid near the m. p.[26] To check that the above agreement was not fortuitous, especially in view of the drastic structural changes which occur in the trihalides during melting,[27] molar volumes were also calculated by extrapolation to temperatures 10% above the absolute m. p. For the two chlorides the values of $2V_M$ and $3V_M$ are 356 and 357 respectively and for the bromides 410 and 406 ml. mole^{-1}. It is clear that the effect persists, the 23·0 ml. of gallium metal required for reduction of two moles of trihalide being completely accommodated in the interstices between the large anions.

TABLE 9. *Reduced conductivity of addition compounds of gallium trihalides at their respective m. p.s.*

Compound	Structure	$\mu\eta$	Ref.	Compound	Structure	$\mu\eta$	Ref.
$\mathrm{GaCl_3,GaCl}$	$\mathrm{Ga^+GaCl_4^-}$	103·3	—	$\mathrm{GaBr_3,GaBr}$	$\mathrm{Ga^+GaBr_4^-}$	136·3	—
$\mathrm{GaCl_3,POCl_3}$	$\mathrm{POCl_2^+GaCl_4^-}$	0·44	7	$\mathrm{GaBr_3,POBr_3}$	$\mathrm{POBr_2^+GaBr_4^-}$	1·0	8
$\mathrm{GaCl_3,py}$	$\mathrm{[py_2GaCl_2]^+GaCl_4^-}$	2·15	9	$\mathrm{GaBr_3,py}$	$\mathrm{[py_2GaBr_2]^+GaBr_4^-}$	3·1	10
$\mathrm{GaCl_3,pip}$	$\mathrm{[pip_2GaCl_2]^+GaCl_4^-}$	3·26	11	$\mathrm{GaBr_3,pip}$	$\mathrm{[pip_2GaBr_2]^+GaBr_4^-}$	3·9	10

A comparison of the reduced conductivities of the gallium dihalides with those of complexes of the gallium trihalides suggests that the complexes are incompletely dissociated into ions. Some figures are given in Table 9. The mean value of $\mu\eta$ for the complexes of gallium trichloride with phosphorus oxychloride, pyridine, and piperidine is less than $\mu\eta$ for gallium dichloride by a factor of 53. The factor for the bromides is 51. These differences are due both to mobility effects and to differences in the number of ions present.[23] It is unlikely that the high mobility of the small $\mathrm{Ga^+}$ ion could account for a factor of more than about 5 and it is further apparent that the mobility is not the only factor operating since the reduced conductivities of the phosphorus oxyhalide complexes are not larger than those of the pyridine and piperidine complexes but are only about a quarter of these, despite the fact that their cations are smaller and therefore presumably more mobile. The remaining factor of 10—20 must presumably be ascribed to ion-pair formation though it is not yet possible to calculate the equilibrium constant from first principles in such complicated molten-salt systems. Indeed it is still difficult to explain even qualitatively why so many ionic complexes appear to be dissociated into kinetically free ions only to the extent of about 1—10%.

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[25] Greenwood and Wade, *J. Inorg. Nuclear Chem.*, 1957, **3**, 349.
[26] Bloom and Heymann, *Proc. Roy. Soc.*, 1947, *A*, **188**, 392.
[27] Greenwood and Worrall, *J. Inorg. Nuclear Chem.*, 1957, **3**, 357.