THE CHEMISTRY OF GALLIUM

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I. Introduction

Gallium has several unique properties which have stimulated interest in its chemistry ever since 1875 when its discovery by Lecoq de Boisbaudran (*17*) confirmed so eloquently his own predictions and those of Mendeleef for eka-aluminium. The chemistry of gallium was reviewed by Gmelin (*96*) in 1936 and in the following year by Einecke (*63*) but since that time only one extensive review has appeared (*22*), though the number of papers being published annually on this element now exceeds the total number of papers included in Gmelin's volume. Several general articles have appeared dealing with certain aspects of the history, occurrence, extraction, purification, analysis, physical and chemical properties, toxicology, or uses of the element (*10*, *18*, *23*, *32*, *65*, *233*, *276*, *285*).

During the last decade there have been five main areas of interest in the chemistry of gallium:

(a) the existence of lower valency states in which the oxidation number of the metal is +1 or +2,

(b) the structure and semiconducting properties of binary compounds of gallium with phosphorus, arsenic, and antimony, in group V and sulfur, selenium, and tellurium in group VI,

(c) the crystal chemistry of the oxides, hydroxides, and related compounds,
(d) the structure and catalytic activity of the trihalides and their molecular addition compounds,
(e) the preparation and reactions of hydrides and organometallic compounds of gallium.

These topics will be dealt with in successive sections of this review which also refers to recent work on the salts and coordination complexes of gallium.

The physical constants of gallium which are of interest to chemists are summarized in Table I. The atomic radius and first ionization potential of gallium are almost identical with those of aluminium and the two elements frequently resemble each other in chemical properties. Both are amphoteric, but gallium is less electropositive as indicated by its lower electrode potential. Differences in the chemistry of the two elements can be related to the presence of a filled set of 3*d* orbitals in gallium.

TABLE I
PHYSICAL PROPERTIES OF GALLIUM (*264, 276*)

Atomic number	31	Melting point (°C)	29.75°
Atomic weight	69.72	Boiling point (°C)	~2227°[a]
Atomic radius (Å)	1.245	d_4^{20} (solid)(gm/ml)	5.907
Ionic radius (Å)	0.62	$d_4^{29.8}$ (liquid)(gm/ml)	6.0948
Ionization potential (ev)	6.00	Atomic volume (29°)(ml)	11.81
Std. electrode potential, (volts)	0.52	Atomic volume (30°)(ml)	11.44

[a] This figure is obtained by an extrapolation of 1000° from vapor pressures below 1 mm!

The unusual physical properties of metallic gallium arise from its unique crystal structure which consists of Ga_2 units arranged in deformed sets of hexagonal rings (*20, 188*). Each gallium atom has one nearest neighbor at 2.442 Å. The orthorhombic unit cell has $4Ga_2$ units lying symmetrically in the *a-c* plane at angles of 17° to the *c*-axis, the spacing of these molecular planes being *b*/2. This rather open structure collapses to a more nearly close-packed arrangement in the liquid state, and melting is accompanied by a contraction of 3.1% in atomic volume and by a considerable increase in electrical conductivity (*222, 223, 228*). Here gallium resembles its neighbor germanium and also antimony and bismuth. The element has a very low m.p. and an extraordinary low vapor pressure (less than 1 mm at 1300°). These factors combine to give gallium the longest liquid range of any known substance and form the basis of its (very limited) use in high temperature thermometers (*285*). An alloy of gallium, indium, and tin, melting at 5° and having excellent wetting properties and a vapor pressure of $<10^{-7}$ mm at 500° has been suggested as a high-vacuum seal (*198*).

II. Lower Valencies (Oxidation States I and II)

Compounds in which the valency of gallium is less than +3 have been known since the earliest experiments of de Boisbaudran (*96*), but it is only in the last decade that structural studies have elucidated the variety of ways in which gallium achieves these lower oxidation states. It is now recognized that gallium forms a range of stable univalent compounds, many of which also contain an equal number of gallium atoms in the +3 oxidation state, thus leading to a formal over-all oxidation state equivalent to $Ga^{(II)}$. The +2 state can also be achieved by the presence of Ga—Ga bonds in the structure and unstable gaseous compounds are known in which gallium is in a lower valency state.

A. UNSTABLE GASEOUS MOLECULES

Gallium monochloride is formed at 1100° either by the dissociation of the trichloride or by the reaction of gallium metal with chlorine (*191*).

$$GaCl_3 = GaCl + Cl_2 \tag{1}$$

$$2Ga + Cl_2 = 2GaCl \tag{2}$$

Other diatomic halides are formed similarly. Faint absorption bands were also observed (*209*) when the arc spectrum of gallium was studied in the presence of hydrogen and these have been assigned to the compound GaH. The interatomic distances and energies of dissociation of these molecules into atoms are recorded in Table II.

TABLE II
DIATOMIC MOLECULES CONTAINING $Ga^{(I)}$

Molecule	GaH	GaF	GaCl	GaBr	GaI
r (Å)	~1.66	1.775	2.202	2.353	2.575
$\Delta H_{\text{dissoc.}}$ (kcal/mole)	~78	143	115	—	—
Reference	*196*	*8*	*6, 191*	*6*	*6*

It has been suggested (*196*) that these diatomic molecules are essentially ionic, like those of the gaseous alkali metal halides, but the binding energies calculated from thermochemical cycles do not agree well with those calculated on the basis of pure ionic attraction using the latest experimental values for the internuclear distances. Moreover, the radius of the Ga^+ ion calculated from the observed internuclear distances and the radii of the gaseous halides ions (*231*) decreases from 0.74 Å, to 0.56 Å, the mean value of 0.63 Å being almost identical with the accepted value for Ga^{3+}. The univalent ion would be expected to be considerably larger than this and a value of 1.17 Å has been suggested on the basis of a semiempirical theory

(*308*). On a covalent model, however, the calculated radius for gallium increases with increasing atomic number of the halogen atom from 1.06 Å to 1.241 Å, which is close to the accepted value of 1.245 Å for the covalent radius of gallium. A covalent model is also consistent with the quadrupole coupling constants of these molecules which have been interpreted in terms of partial *sp* hybridization (*6*).

Flame reactions provide another source of unstable species containing univalent gallium. Typical reactions are the following (*33*):

$$\mathrm{Ga} + \mathrm{H_2O} = \mathrm{GaOH} + \mathrm{H} \tag{3}$$

$$\mathrm{GaOH} = \mathrm{Ga} + \mathrm{OH} \tag{4}$$

The value for the heat of dissociation of GaOH according to Eq. (4) is 102 ± 5 kcal/mole (*33*). Similarly, from the partial pressure of gallium in oxyacetylene or oxyhydrogen flames of known temperature, the dissociation energy of the molecule GaO was found to be 115.6 ± 3 kcal/mole (*127*).

B. CHALCOGENIDES

Compounds of univalent gallium have been reported for all elements of group VI except polonium, but little is known of their structure. Gallium(I) oxide can be prepared by reduction of the sesquioxide with gallium at 700° and is purified by vacuum sublimation at 500° (*96*):

$$\mathrm{Ga_2O_3} + 4\mathrm{Ga} = 3\mathrm{Ga_2O} \tag{5}$$

The dark brown, diamagnetic powder is stable in dry air, but undergoes surface oxidation at higher temperatures. Above 800° it disproportionates according to the reverse of Eq. (5). More recently (*84*) Ga_2O has been made by the reaction of gallium with carbon dioxide at 10 mm pressure and 850°:

$$2\mathrm{Ga} + \mathrm{CO_2} = \mathrm{Ga_2O} + \mathrm{CO} \tag{6}$$

Gallium(I) sulfide, like the oxide, cannot be prepared directly from the elements but is obtained by thermal decomposition of higher sulfides (*96*). Thus, when gallium(II) sulfide is heated at 1100° for several hours in a stream of nitrogen, gallium(I) sulfide sublimes quantitatively as green hexagonal prisms or yellow-green plates (*263*) [see Eq. (9) below]. The compound is a phase of variable composition $Ga_2S_{0.8-1.1}$ and has a hexagonal lattice similar to that of gallium(II) sulfide (see below). Above 950° pure gallium(I) sulfide decomposes to a liquid mixture of gallium(II) sulfide and metallic gallium which becomes homogeneous above 1150°:

$$\mathrm{Ga_2S}\ (\text{solid}) \rightarrow \mathrm{GaS}\ (\text{liquid}) + \mathrm{Ga}\ (\text{liquid}) \rightleftharpoons \mathrm{Ga_2S}\ (\text{gas}) \tag{7}$$

In this temperature range the gas above the mixture is monomeric Ga_2S

and the vapor pressure of the system is given by the relation $\log p_{mm} = 7.93 - 9098/T$. From this the "b.p." is 1530°, the heat of vaporization 39.6 kcal/mole and the entropy change 21.8 e.u. (*263*).

Gallium(I) selenide and the previously unknown gallium(I) telluride can apparently be made by melting the elements together in evacuated quartz tubes for prolonged periods; their X-ray powder diagrams have been recorded and indexed (*177*).

The divalent compounds GaS, GaSe, and GaTe, can all be prepared by direct reaction of the elements at high temperatures. They have recently been investigated as semiconductor materials, their intrinsic energy gaps being about three times that of germanium. By contrast, gallium(II) oxide has not yet been prepared as a stable solid though bands have been ascribed to the gaseous, diatomic species GaO (*141*). Some physical properties are summarized in Table III. Crystal structure determinations (*128, 248, 249*) have shown that the +2 oxidation state in these compounds results from a layer lattice arrangement in which the characteristic feature is the occurrence of Ga_2^{4+} units, i.e., —SGaGaS, SGaGaS—. This immediately explains the diamagnetism of the compounds. Within each layer each gallium is tetrahedrally surrounded by three sulfur atoms and one gallium atom to which it is covalently bound, and the neighboring multiple layers are held by van der Waals attraction. Interatomic distances are Ga—Ga 2.46 Å, Ga—S 2.34 Å. The selenide and telluride have similar structures. It is interesting to note that none of the chalcogenides of gallium(II) crystallize in the TlS-type structure in which half the thallium atoms are univalent and half tervalent, i.e., $Tl^+[Tl^{III}S_2]^-$. The Tl^{III} are tetrahedrally surrounded by sulfur and the tetrahedra are linked into infinite chains by sharing edges (*69*).

TABLE III

Physical Properties of GaS, GaSe, and GaTe

					ΔE (kcal/mole)		
	m.p.	color	d_4^{25}	unit cell size (Å)	elec.	optic.	Reference
GaS	970 ± 3°	yellow	3.75	*a* 3.578, *c* 15.47	—	—	(*128, 263*)
GaSe	960 ± 10°	red brown	5.03	*a* 3.735, *c* 15.887	46.3	47.1	(*69, 241, 248, 274*)
GaTe	824 ± 2°	grey	—	*a* 23.76, *b* 4.068 *c* 10.46, *β* 45.4°	41.5	38.2	(*69, 241, 249*)

Gallium monosulfide and sesquisulfide both disproportionate at high temperatures to give a solid phase of variable composition between $Ga_4S_{4.8}$ and $Ga_4S_{5.2}$:

$$2Ga_2S_3 \rightleftharpoons Ga_4S_5 + \tfrac{1}{2}S_2 \qquad \text{above } 950° \qquad (8)$$

$$6GaS \rightleftharpoons Ga_4S_5 + Ga_2S \qquad \text{above } 970° \qquad (9)$$

The compound Ga_4S_5, which is stable up to 1200° and has a density of 3.82 ± 0.01 gm/ml, can also be formed directly from the elements (*263*).

C. HALIDES

Evidence for univalent halides in the solid state is fragmentary. The monochloride disproportionates readily into a higher halide and gallium; e.g., at 820° gallium metal rapidly volatilizes in a stream of hydrogen chloride gas to give a brown-black sublimate analyzing as $GaCl_{0.94}$ in which small drops of gallium metal can be seen (*83*). The gallium–iodine phase diagram (*44*) shows that the limiting composition of the halide phase in contact with molten gallium is $GaI_{1.19}$. When this is repeatedly extracted with dry benzene a residue of composition $GaI_{1.06}$ is obtained; the X-ray powder diagram shows this to be a distinct phase rather than a mixture and the extrapolated m.p. of the mono-iodide was found to be 271°. Other indications of unstable oxidation states below +2 come from anodic oxidation of gallium in glacial acetic acid (*52*) or anhydrous ammonia (*51*) and from the solubility of gallium in molten dihalides (*43*, *46*, *47*, *78*, *275*).

Very recently, complexes of gallium(I) chloride and bromide have been reported (*24*). They were prepared by allowing volatile ligands (L) such as dioxane, morpholine, or acetylacetone, to diffuse into a benzene solution of gallium dihalide in a closed system; disproportionation occurred into gallium trihalide, which remained in solution, and insoluble complexes of formula L_2GaX. The X-ray crystal structure of $[Ga(diox)_2]Cl$ shows it to contain discrete chloride ions and a disposition of the four oxygen atoms around the gallous ion which is in the form of a distorted trigonal pyramid (*24*).

Gallium forms stable dihalides with chlorine, bromine, and iodine and it has now been established conclusively that this oxidation number arises from the existence of equal numbers of gallium atoms in the +1 and +3 oxidation states. Pure gallium dichloride is best prepared (*120*) by heating the trichloride with slightly less than the stoichiometric amount of gallium and then volatilizing the excess of trichloride from the molten mixture. The last traces of impurity can be removed by fractional freezing to a constant m.p. of 172.4°. A variation of this method (*78*, *187*), which employs a slight excess of gallium, is less satisfactory. The dichloride has also been prepared by heating gallium in a stream of dry hydrogen chloride (*153*) or by reacting it with the stoichiometric amount of mercurous chloride in a sealed tube (*34*). The X-ray crystal structure of the dichloride (*82*), the Raman spectrum (*303*), electrical conductivity of the fused compound (*120*), and its chemical reactions in benzene solution (*3, 34*) all indicate that it is correctly formulated as gallous tetrachlorogallate, $Ga^+[GaCl_4]^-$. The compound is thus an unusual example of the stabilization of an unfamiliar oxidation state by coordination since the ion which is stabilized (Ga^+) is not the one which is coordinated, $[Cl{\rightarrow}GaCl_3]^-$. There are four $Ga^+[GaCl_4]^-$ units in the orthorhombic cell, space group *Pnna*, $a = 7.29$, $b = 9.72$, $c = 9.50$ Å. Each gallous ion is surrounded by an irregular dodecahedron of 8 chlorine atoms from six different $GaCl_4^-$ tetrahedra (*82*). The Ga—Cl distance within each tetrahedron is 2.19 Å and the crystal radius of the Ga^+ ion is 1.33 Å (*82*). This is somewhat larger than expected (cf. p. 93) and is possibly due to anion-anion contact. The Raman spectrum of the fused compound (*303*) showed four fundamentals, as expected for a regular tetrahedral species, and these corresponded closely with the known spectrum of the tetrachlorogallate ion (*305*): 115 cm^{-1} (ν_2, strong, sharp, depolarized); 153 cm^{-1} (ν_4, weak, diffuse, depolarized); 346 cm^{-1} (ν_1, very strong, sharp, polarized); 380 cm^{-1} (ν_3, very weak, diffuse, depolarized).

Fused gallium dichloride is a typical molten salt and the variation of its electrical conductivity (κ $ohm^{-1}cm^{-1}$) and dynamic viscosity (η cp) with temperature and the corresponding activation energies E_κ, E_η are characteristic of a compound in which the cation is smaller than the anion (*120*).

$$\log \kappa = 1.180 - 784/T; \qquad E_\kappa = 3.59 \text{ kcal/mole}$$
$$\log \eta = 1.768 + 1022/T; \qquad E_\eta = 4.68 \text{ kcal/mole}$$

The temperature variation of the density and surface tension have also been determined (*120*): $d_4^t = 2.4206 - 1.36 \times 10^{-3}(t - 170)$ gm/ml; $\gamma = 56.6 - 0.18(t - 170)$ dyne/cm. Above about 200° gallium dichloride disproportionates reversibly to gallium and the trichloride and above 400° the vapor density indicates considerable quantities of monomeric $GaCl_2$ molecules (*187*).

Gallium dichloride is readily soluble in benzene (*187*), a saturated solution at room temperature containing 4.60 gm/100 gm solvent (*153*). The Raman spectrum of the solution confirms the ionic nature of the solute (*195*) and a crystalline phase $[Ga{\cdot}C_6H_6]^+[GaCl_4]^-$ can be separated from the solution (*238*). Gallous tetrachloroaluminate $GaAlCl_4$ (*45*), forms a similar complex (*238*). Further proof of the two oxidation states of gallium in the dichloride comes from the reaction of a benzene solution with hydrogen sulfide: Ga^I was precipitated as the sulfide and gallium trichloride remained in solution (*34*).

The strongly reducing nature of the dichloride, which was observed by the earliest workers (*231*) has been repeatedly confirmed and it has been shown that carbon tetrachloride is reduced to carbon (*187*). Limited stabilization of the gallous ion has been achieved by coordination, and a wide variety of complexes of the form $[GaL_4]^+[GaCl_4]^-$ have been prepared with oxygen, sulfur, selenium, nitrogen, and arsenic donors where L_4 represents four monodentate ligands, two bidentate ligands, or one quadridentate ligand (*3*, *24*). Such complexes are usually white or pale cream though the adducts with 2,2′-dipyridyl and dithizone were red. Molecular-weight determinations, electrical conductivity, and diamagnetism confirm the general ionic formulation but the problem of the detailed stereochemistry of the $[GaL_4]^+$ cations has not yet been settled. The gallous ion in such complexes has five pairs of electrons and is therefore isoelectronic with phosphorus, sulfur, and chlorine in their compounds PF_5, SF_4, and ClF_3, all of which are based on trigonal bipyramidal symmetry. If, however, the $4s^2$ electrons are stereochemically inert, then presumably either planar or tetrahedral symmetries are possible though these would involve the use of unusual hybrids. The stereochemistry of the complex $[Ga(diox)_2]Cl$ has already been mentioned on p. 96.

Gallium dibromide is very similar in its structure and properties to the dichloride. It is best prepared pure by heating the tribromide in a sealed, evacuated tube at 180° with slightly less than the theoretical weight of gallium, after which excess of the tribromide is volatilized away and the compound fractionally crystallized from the melt to a constant melting point of 166.7° (*124*, *304*). Reaction of gallium with mercuric bromide also affords gallium dibromide and when this reaction is carried out in the presence of benzene, the solvate $Ga_2Br_4{\cdot}C_6H_6$ is obtained (*34*).

Crystalline gallium dibromide (*304*) like the dichloride (*171*) is diamagnetic, and the Raman spectrum of the fused compound showed only the four fundamental modes expected for the tetrahedral $GaBr_4^-$ ion (*304*): 79 cm^{-1} (ν_2, strong, sharp, depolarized); 107 cm^{-1} (ν_4, strong, sharp, depolarized); 209 cm^{-1} (ν_1, very strong, sharp, strongly polarized); 288 cm^{-1} (ν_3, weak, diffuse, depolarized). The electrical conductivity (κ $ohm^{-1}cm^{-1}$) viscosity, (η cp) and density are given by the equations:

$$\log \kappa = 1.142 - (865/T)$$
$$\log \eta = 1.793 + (1158/T)$$
$$d = 3.4656 - 1.69 \times 10^{-3} (t - 170).$$

These data, together with the activation energies ($E_\kappa = 3.96$, $E_\eta = 5.30$ kcal/mole) show that the compound is a completely dissociated molten salt in which the cation is small compared with the anion (*120*, *304*).

Gallium dibromide apparently has two crystalline modifications, α and β, melting at 153° and 165° (*43*). As mentioned on p. 96 the fused compound dissolves metallic gallium to some extent but complete reduction to the monobromide could not be effected, the limiting composition being 31.4 mole % GaBr at 170°. In the presence of aluminium tribromide, however, complete reduction to monovalent gallium occurred and the compound $Ga^+[AlBr_4]^-$ (m.p. 159°) was found to be dimorphic, each modification being isomorphous with the corresponding form of $Ga^+[GaBr_4]^-$ (*43*). A variety of complexes $[GaL_4]^+[GaBr_4]^-$ analogous to the chlorogallates has also been described (*3*, *24*).

Gallium di-iodide (m.p. 211°) can be prepared by direct reaction of the correct amounts of gallium and iodine (*44*) or by the reaction of gallium with mercuric iodide in a sealed tube (*34*). It is diamagnetic (*44*), and in the absence of further data can be presumed to have the structure $Ga^+GaI_4^-$. When heated at 250° the di-iodide loses gallium tri-iodide by disproportionation, leaving a residue of limiting composition close to the monoiodide (see p. 96).

III. Binary Compounds of Gallium(III) with Group V Elements

The compounds which gallium forms with nitrogen, phosphorus, arsenic, and antimony are isoelectronic with the Group IV elements and there has been considerable interest, particularly in the physical properties of these compounds, since 1952 when Welker first showed that they had semiconducting properties analogous to those of silicon and germanium (*287*).

Gallium nitride is the only member of the group which cannot be prepared by direct reaction of the elements. It was first made (*155*) by the reaction of gallium with ammonia at 900°–1000° and has also been prepared by the decomposition of $(NH_4)_3GaF_6$ at 600° (*131*). Crystalline gallium nitride is formed when the adduct $GaCl_3 \cdot NH_3$ is pyrolyzed at 1000° (*219*). The compound is grey or yellow (*131*, *155*, *192*, *229*), diamagnetic (*131*), and crystallizes in the Würtzite (ZnS) structure (*156*). Its physical properties are summarized in Table IV and the heat of formation $-\Delta H_f°$ is 24.9 ± 0.9 kcal/mole (*131*).

Gallium nitride is not hydrolyzed by hot water or by acids such as dilute or concentrated hydrofluoric, hydrochloric, or nitric (*155*, *229*). Aquaregia is also without effect but the compound dissolves slowly in hot concentrated sulfuric acid (*155*). With hot concentrated aqueous alkali, ammonia is evolved (*229*). There is no reaction with hydrogen at 800° but oxygen slowly reacts with gallium nitride at 900° over a period of days to give nitrogen and the sesquioxide Ga_2O_3 (*155*). The reaction proceeds with ignition in the presence of paraffin (*131*).

Although gallium nitride cannot be formed directly from gallium and nitrogen, the compound Li_3Ga reacts with nitrogen at 600° to give the ternary nitride, Li_3GaN_2 (*158*). This light-grey powder, *d* 3.35, can also be prepared by heating lithium nitride and gallium in nitrogen at 730° or by heating a mixture of lithium nitride and gallium nitride. Lithium gallium nitride is very similar to lithium aluminium nitride, Li_3AlN_2: both crystal-

TABLE IV
PHYSICAL PROPERTIES OF III-V COMPOUNDS

Property	GaN	GaP	GaAs	GaSb
m.p.	$d > 1250°$ (*156, 229*)	1350° (*258*)	1238°[a] (*19, 176*)	712°[b] (*9, 95*)
Crystal structure	Würtzite (*156, 157*)	zinc blende	zinc blende	zinc blende
	$a = 3.180$, $c = 5.166$ Å	$a_0 = 5.4505$ Å (*90*)	$a_0 = 5.6534$ Å (*90, 210*)	$a_0 = 6.0954$ Å (*90, 175*)
	$c/a = 1.625$[c]	5.436 Å (*74*)	5.6560 Å (*175*)	6.1342 Å (*15*)
Refractive index	—	3.37 (*75*), 2.9 (*258*)	3.4 (*212*), 3.2 (*258*)	3.9 (*213*), 3.7 (*258*)
κ ohm^{-1}cm^{-1}	10^{-9}–10^{-7} (*229*)	10^{-2}–10^{+2} (*75*)	10^{-6}–10^{+3} (*134*)	12 (*56*), 6–13 (*257*)
	2.5×10^{-9} (*159*)		$(0.17\text{–}1.0) \times 10^{3}$ (*175*)	10–12 (*190*)
ΔE ev (optical)	3.25 (*163*)	2.24[d] (*74*)	1.25 (*50*), 1.35[e] (*212*)	0.68 (*212*), 0.71[f] (*50*)
ΔE ev (electrical)	—	—	1.320 (*175*)	0.7–0.8[g]

[a] Also 1280° (*50*).

[b] Also 702° (*288*), 703° (*176*), 705.9° (*101*), 725° (*161*).

[c] Also $a = 3.160$ Å, $c = 5.125$ Å, $c/a = 1.622$ (*192*).

[d] $\Delta E = 2.4 - 5.4 \times 10^{-4}T$ (*211*).

[e] $\Delta E = 1.53 - 5.0 \times 10^{-4}T$ (*211*).

[f] $\Delta E = (0.695\text{–}0.704) - 2.9 \times 10^{-4}T$ (*232*).

[g] 0.71 (*175, 190*), 0.775 (*15*), 0.78 (*55*), 0.80 (*190*), 0.82 (*212, 288*).

lize in the antifluorite structure and are readily hydrolyzed by water or dilute acids (*158*). Ternary phosphides and arsenides can also be prepared by heating mixtures of the binary compounds at 450–650°. Lithium gallium phosphide, Li_3GaP_2, resembles the nitride in having the antifluorite structure but the arsenide, Li_3GaAs_2, has a tetragonal unit cell with the axial ratio $c/a = 1.016$ (*160*).

Gallium phosphide, arsenide, and antimonide can all be prepared by direct reaction of the elements; this is normally done in sealed silica tubes (*19*, *210*) or in a graphite crucible under hydrogen (*9*, *190*, *257*). Phase diagrams indicate the stoichiometry GaAs and GaSb (*176*). Similar data are hard to obtain in the gallium–phosphorus system because gallium phosphide has a vapor pressure of more than 13.5 atm at its melting point (*73*)—cf. 0.89 atm for gallium arsenide (*73*).

The physical properties of these three compounds are compared with those of the nitride in Table IV. All three adopt the zinc blende crystal structure and are more highly conducting than gallium nitride. Whereas the group IV semiconductors silicon and germanium are purely covalent, the III-V compounds have some ionic character and provide a wider range of basic semiconductor parameters such as energy gaps and mobilities. Estimates of the precise extent of heteropolarity vary widely as is to be expected, but, independently of the method used to determine ionic character (*221*, *301*), there is general agreement that this diminishes in the sequence GaP > GaAs > GaSb. The energy gap ΔE decreases in the same order (see Table IV). In general, the m.p. and energy gap of III-V compounds are higher than those of the isoelectronic Group IV elements, despite the similarity in bond distances.

Gallium phosphide forms orange, transparent crystals and is potentially useful for very high temperature work particularly where high frequency performance is not required. Gallium arsenide forms good *pn*-junctions and has been used to study photovoltaic effects. It is one of the most promising semiconductors for high frequency and high temperature work. Gallium antimonide is the most studied compound of the group because of its low melting point. It is normally a *p*-type semiconductor but *n*-type samples have been prepared by doping with tellurium.

Further flexibility is introduced by the possibility of alloying these various compounds. There is normally a complete range of solid solutions with other III-V compounds (*306*, *307*), and properties tend to vary approximately linearly with composition (*14*, *175*). By contrast, germanium ($a_0 = 5.658$ Å) is less than 2% soluble in gallium arsenide ($a_0 = 5.656$ Å) despite the near identity of their lattice parameters (*151*).

The chemical properties of this group of compounds have been less studied. There is no reaction with water or dilute alkali but dilute hydrochloric acid yields small quantities of arsine or stibine (*161*). Ternary compounds such as Li_3GaP_2 and Li_3GaAs_2 can be formed by direct reaction of lithium phosphide or arsenide with gallium phosphide or arsenide (*160*).

IV. Binary and Ternary Oxides and Hydroxides

The precipitation of the hydrous oxide of gallium from aqueous solutions and its dissolution in excess of alkali has been a subject of continuing interest (*144*, *150*, *270*, *284*). For example precipitation from an 0.007*M* solution of gallium trichloride begins at pH 3.15 and is complete at pH 6, after which redissolution begins and is complete at pH 9.5 (*183*). The solubility product $[Ga^{3+}]\cdot[OH^-]^3$ is $10^{-36.5}$ and may be compared with those of aluminium and indium hydroxides which are $10^{-33.8}$ and $10^{-33.9}$ (*183*). In the presence of sulfate ions the hydrous oxide begins to precipitate after approximately one OH^- per mole of gallium has been added, but aqueous solutions of the chloride, bromide, or nitrate can be treated with up to three OH^- per mole of gallium without precipitation though addition of more hydroxyl ions causes the solutions to flocculate sharply. Diffusion current data show that this unusual behavior is due to the formation of Ga^{3+}—OH^- aggregates rather than to peptization (*203*) and detailed isopiestic studies on perchlorate solutions suggest that the degree of polarization of the oxygen-bridged cationic gallium aggregates increases from 1.3 at a mole ratio OH^-/Ga^{3+} of 0.5, to 84 at a mole ratio of 2.0 (*215*). Further work using Rayleigh turbidities and refractive index increments indicates that Sillen's core-link hypothesis applies to these aggregates (*239*).

When freshly precipitated gallium hydroxide is dissolved in saturated aqueous lithium hydroxide and the solution evaporated, the compound $[Li(H_2O)_4][Ga(OH)_4]$ crystallizes. This readily loses water over sulfuric acid at room temperature, and again at 100° to give compounds which can be formulated as $[Li(H_2O)_2][Ga(OH)_4]$ and $Li[GaO(OH)_2]$. Further heating results in irreversible dehydration to $LiGaO_2$ (*145*). Sodium hydroxide yields $Na[Ga(OH)_4]$ and $NaGaO_2$ and potassium hydroxide yields $K[Ga(OH)_4]$, $KGaO_2\cdot1\frac{1}{2}H_2O$, and $KGaO_2\cdot H_2O$. By contrast, calcium and strontium hydroxides tend to give six-coordinate complexes of the form $M_3\,Ga(OH)_6]_2$ (*145*). The phase diagram of the system Ga_2O_3-Na_2O-H_2O has also been studied and various hydrated gallates established (*89*). (See also ref. *79*).

Gallia, like alumina, exists in a variety of structural forms and these have been extensively investigated by electron diffraction and X-ray crystallographic methods. Forms designated α, β, γ, δ, and ϵ have been distinguished, the stable form between room temperature and the m.p. being β-Ga_2O_3 which is isomorphous with θ-Al_2O_3 (*79*, *174*, *235*). The low-temperature thermodynamic properties of β-Ga_2O_3 have been tabulated (*1*, *167*) and its m.p. is 1725° (*139*). The hydrous oxide, GaO·OH, has the same structure as diaspore, β-AlO·OH (*16*), and undergoes dehydration to β-Ga_2O_3 at 300° (*185, 235*). A metastable phase $Ga(OH)_3$ and possibly also $Ga_2O(OH)_4$ have also been recognized (*185*). Treatment of the first of these compounds with calcium hydride removes only one mole of water and this has been taken to indicate that its structure is $GaO{\cdot}OH{\cdot}H_2O$ rather than $Ga(OH)_3$ (*5*).

The close similarity in ionic radii between gallium and aluminium which leads to the similarity in oxide and hydrous oxide phases just mentioned, also ensures that the two series of compounds exhibit extensive solid solution. Thus, below 810°, the compound $GaAlO_3$ and a series of solid solutions extending almost to pure alumina and gallia are stable. When water is added, these phases are stable only above a transition temperature in the region of 300–400° (depending on composition). Below this temperature a complete series of diaspore-type structures extends from AlO·OH to GaO·OH and below about 275° a series of boehmite-type structures extends from AlO·OH to a composition in which 30% of the aluminium ions have been replaced by gallium (*139, 236*). Similarly gallium analogs of the aluminosilicates and aluminogermanates have been prepared (*7*). For example, fully substituted or partly substituted counterparts have been prepared of sodium feldspar, ($NaAlSi_3O_8$), calcium feldspar, orthoclase ($KAlSi_3O_8$), leucite ($KAlSi_2O_6$), anorthite ($CaAl_2Si_2O_8$), and mullite ($3Al_2O_3{\cdot}2SiO_2$) (*86, 97, 189*). Both silicon and aluminium can be completely removed without change in structure from gehlenite ($Ca_2Al_2SiO_7$) by replacing aluminium by gallium and (Si + Ca) by (Ga + Ln) to give $CaLnGa_2O_7$ where Ln is a lanthanide element (*59*).

Similar isomorphous substitutions in the sesquioxide (Ga_2O_3) itself lead to perovskite lattices such as $LaGaO_3$, $CeGaO_3$, $NdGaO_3$ (*165, 234*) and, as expected, substitution can also occur in spinel-type lattices, e.g., half the aluminium ions in chrysoberyl can be replaced to give $BeAlGaO_4$ (*93*).

A variation on the III-V theme discussed in the preceding section concerns the replacement of pairs of silicon atoms in silica by gallium and a group V element. Thus $GaPO_4$ exists in forms corresponding to a low-temperature quartz, a metastable, low-temperature crystobalite and a high-crystobalite with transition temperatures at 933° and 616° respectively (*205, 217, 251*). The compound $GaAsO_4$ exists only in the low-temperature quartz form and with the compound $GaSbO_4$, where the increased cation radius requires 6:3 rather than 4:2 coordination, a disordered rutile (TiO_2-type) structure is adopted (*21, 251*).

V. Compounds with Sulfur, Selenium, and Tellurium

The sesqui-sulfide, -selenide, and -telluride of gallium can all be prepared by direct reaction of the elements at high temperature. The compounds are isomorphous with zinc sulfide (*132*) and this, rather than isomorphism of zinc sulfide with gallium arsenide, is now thought to be the reason for specific enrichment of gallium in sphalerite minerals (*99*).

Gallium sulfide has three crystal modifications (*128*, *132*):

γGa_2S_3 (zinc blende) $a_0 = 5.171 \pm 0.004$ Å, stable at low temperatures; the gallium atoms randomly occupy 2/3 of the tetrahedral sites in the sulfide cubic close-packed lattice.

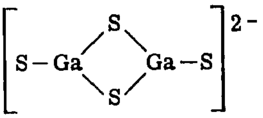
βGa_2S_3 (Würtzite) $a = 3.678 \pm 0.005$, $c = 6.016$, $c/a = 1.636$; the gallium atoms randomly occupy 2/3 of the tetrahedral sites in the sulphide hexagonal close-packed lattice; $\gamma \rightleftharpoons \beta$ transition 550°–600°.

αGa_2S_3 (Würtzite superlattice with unit cell containing $6Ga_2S_3$); $a = 6.370$; $c = 18.05$ Å, $c/a = 2.833$.

Gallium selenide and telluride exist only in the zinc blende structure with two-thirds of the cation sites occupied by gallium atoms. Unit cell dimensions are: Ga_2Se_3 $a_0 = 5.430 \pm 0.005$ Å (*99*) [or 5.418 Å (*132*)]; Ga_2Te_3 $a_0 = 5.887 \pm 0.003$ Å (*99*) [or 5.874 Å (*132*)]. In all cases bond distances are close to those expected.

All three compounds are semiconductors, though their use is somewhat restricted by their ready hydrolysis. Activation energies are intermediate between those of the isoelectronic II-VI and III-V compounds (*98*), typical values for the energy gap ΔE between bonds being: Ga_2S_3 2.85 ev (*164*); Ga_2Se_3 1.9 ev (*164*); Ga_2Te_3 1.0–1.55 ev (*136*, *137*, *138*, *164*). The energy gap decreases with decreasing ionic character (cf. Ga_2O_3 4.4 ev) and the above values are thus less than those of the corresponding aluminium chalcogenides but greater than those of the indium analogs (*164*). Ternary compounds such as $CuGaS_2$, $AgGaS_2$, and the corresponding selenium and tellurium compounds which all adopt the chalcopyrite structure (*130*) have also been investigated as semiconductors (*4*, *71*, *94*). The compounds $CdGa_2S_4$, $HgGa_2S_4$, $CdGa_2Se_4$, $HgGa_2Se_4$, and $CdGa_2Te_4$ have been prepared by direct reaction of the component binary chalcogenides and all adopt a chalcopyrite structure in which the appropriate number of cation sites is left vacant (*129*). The corresponding reaction between cuprous oxide and gallium oxide leads to the compound $CuGaO_2$, but this, being more ionic than the chalcogenides, crystallizes in the $NaHF_2$-type structure with octahedral, rather than tetrahedral coordination (*133*).

An interesting series of alkali metal thiogallates $M_2Ga_2S_4$ has been prepared (*146*) in which the anion is considered to have the structure:



The lithium and sodium compounds are prepared by heating an equimolar mixture of alkali metal carbonates and gallium sesquioxide to 900° in a stream of hydrogen sulfide whereas the potassium, rubidium, and cesium salts are prepared by heating the carbonate and oxide in molten sulfur and then leaching with water to leave the insoluble thiogallate. The five compounds are yellow or light brown, have m.p.'s in the range 952–1020°, are stable in air or water, but are decomposed by strong acids with liberation of hydrogen sulfide (*146*).

VI. Gallium Trihalides and Their Adducts

Current interest in the trihalides of gallium centers on their structure and catalytic activity, and on the stoichiometry, structure and stability of their coordination complexes. Gallium fluoride differs markedly from the other halides and in this it resembles the fluorides of aluminium and indium. For example, the m.p.'s of the fluorides are several hundred degrees above those of the chlorides, though this difference decreases from 1097° for aluminium and 872° for gallium to 584° for indium.

A. GALLIUM(III) FLUORIDE

Gallium trifluoride can be prepared by dissolving gallium hydroxide in 40% hydrofluoric acid and adding this to a saturated solution of ammonium fluoride. The complex $(NH_4)_3GaF_6$ so obtained is heated to 630° in a current of fluorine to yield the trifluoride (*135*). More recently it has been made by direct reaction of hydrogen fluoride and gallium at 440° (*25*). This method is to be preferred since samples prepared from the hexafluorogallate are invariably contaminated with nitride derivatives. When the hexafluorogallate is heated at 220° in a stream of nitrogen the compound NH_4GaF_4 is obtained. This has tetragonal crystal symmetry with $a = 3.71$ Å, $b = 6.39$ Å and is isostructural with several tetrafluoroaluminates (*25*). Gallium trifluoride is isostructural with ferric fluoride and the rhombohedral unit cell has $a = 5.20$ Å, $\beta = 57.5°$ (*25*). The density is 4.47 and the compound is said to have a m.p. greater than 1000° and to sublime readily at 950° (*135*). An electron diffraction study of the gas at high temperature indicates the presence of GaF_3 molecules in which the Ga–F distance is 1.88 Å and the F–F distance 3.25 Å; dimeric molecules, Ga_2F_6, if present, have a concentration of less than 1% (*2*).

The hexafluorogallate mentioned in the preceding paragraph presumably contains 6-coordinate gallium and there is strong presumptive evidence for sixfold coordination in the following complexes: Li_3GaF_6, Na_3GaF_6, $K_2GaF_5{\cdot}H_2O$, $RbGaF_4{\cdot}2H_2O$, $CsGaF_4{\cdot}2H_2O$, (*224*), as well as in $GaF_3{\cdot}3H_2O$ and $GaF_3{\cdot}3NH_3$ (*169*). A series of complexes $[M(H_2O)_6]$-$[GaF_5{\cdot}H_2O]$ (M = Mn, Co, Ni, Cu, Zn, Cd) has also been described and also $Ba_3[GaF_6]_2 \cdot H_2O$, $3SrF_2 \cdot GaF_3 \cdot 3H_2O$, $Ag_3GaF_6 \cdot 10H_2O$, and $Tl_2[GaF_5 \cdot H_2O]$ (*225*).

The trihydrate of gallium trifluoride is formed by dissolving gallium or its nitrate or oxide in 40% hydrofluoric acid and evaporating the solution (*169*, *271*). The triammine cannot be formed from the trifluoride directly but is prepared via the trihydrate (*169*). The affinity of the gallium ion for fluoride ions has been measured spectrophotometrically and has been found to be greater than that of chromium for fluoride. At 25° and an ionic strength of 0.5 the quotient $[GaF^{2+}][H^+]/([Ga^{3+}][HF])$ is 120 compared with 26 for the corresponding Cr^{3+} system (*300*).

B. GALLIUM(III) CHLORIDE, BROMIDE, AND IODIDE

Gallium trichloride is readily prepared in quantitative yield by the reaction of either chlorine or hydrogen chloride gas on heated gallium metal (*96*, *113*, *154*). Chlorination may also be effected by heavy metal chlorides such as AgCl, $HgCl_2$, or $PbCl_2$; in these reactions, which have potential use for preparing chlorine-36 labeled gallium trichloride, an equilibrium is established and reasonable yields can only be obtained by volatilizing the chloride from the reaction zone (*37*). Gallium trichloride is normally purified by vacuum sublimation, though zone refining has also been suggested (*218*, *230*).

The Raman spectrum of gallium trichloride has been interpreted in terms of bridged dimeric molecules Ga_2Cl_6 (*87*) and this is also consistent with the very low electrical conductivity of the melt (*119*). When the compound solidifies, however, the conductivity increases ninefold to a value comparable with that of a fully ionized salt near its m.p. It is concluded that the m.p. of gallium trichloride is the transition temperature between an ionic solid and a covalent liquid (*119*). A similar phenomenon has been observed for gallium tribromide (*119*) aluminium trichloride (*13*), and phosphorus pentachloride (*256*).

Some physical properties of gallium trichloride are given in Table V. The low m.p. is particularly noteworthy. The vapor density of the gas shows it to be dimeric with a degree of dissociation of 0.4% at the m.p. and 2% at the b.p. (*72*). The complexes of gallium trichloride are discussed in Sections VI C, D, and E.

Gallium tribromide is readily prepared by the reaction of heated gallium with a bromine-nitrogen gas mixture (*72*, *170*) and detailed experimental procedures have been described (*123*). The compound can also be prepared from gallium and hydrogen bromide (*26*).

Like the trichloride, solid gallium tribromide has an appreciable electrical conductivity which decreases by a factor of 23 when the compound is fused (*119*). Other properties of the tribromide are summarized in Table

TABLE V

PHYSICAL PROPERTIES OF GALLIUM TRIHALIDES

Property	$GaCl_3$		$GaBr_3$		GaI_3	
m.p.	77.75 ± 0.05°	(*115*)	122.3 ± 0.05°	(*119*)	211.5 ± 0.1°, 214°	(*44, 119*)
b.p.	201.2°	(*72*)	279°	(*72*)	346°	(*72*)
p(mm)	10.4 (at 78°)	(*72, 187*)	4.7 (at 125°)	(*72*)	19.2 (at 215°)	(*72*)
d_4^{25} (solid)	2.47	(*170*)	3.69	(*170*)	4.15	(*170*)
d_4^t (liquid)	$2.0531 - 0.00209(t - 78)$	(*115*)	$3.1076 - 0.00247(t - 125)$	(*121*)	$3.591 - 0.00224(t - 215)$	(*170*)
η(cp)	1.816 (at 78°)	(*115*)	2.780 (at 125°)	(*121*)	—	
E_η(kcal/mole)	3.64	(*115*)	3.94	(*121*)	—	
γ(dyne/cm)	$27.3 - 0.105(t - 78)$	(*115*)	$34.8 - 0.15(t - 125)$	(*121*)	—	
κ(ohm^{-1}cm^{-1})	1.86×10^{-6} (at 78°)	(*119*)	7.2×10^{-7} (at 125°)	(*119*)	1.18×10^{-4} (at 212°)	(*119*)
ΔH_{vap}(kcal/mole)	11.8, 12.3	(*72, 187*)	14.3	(*72*)	18.1	(*72*)
ΔH_{fus}(kcal/mole)	5.2	(*187*)	—		ΔH_{subl} 23.0	(*259*)
ΔH_{dimer}(kcal/mole)	21.0 (per Ga_2Cl_6)	(*72*)	18.5 (per Ga_2Br_6)	(*72*)	11.0 (per Ga_2I_6)	(*72*)
$\Delta H°_f$(kcal/mole)	125 ± 1	(*168*)	92.4 ± 0.3	(*168*)	(~61)	(*168*)

V from which it is seen that there are trends to increasing m.p., density, and viscosity and to decreasing volatility, heat of dimerization, and heat of formation with increasing atomic weight of the halogen.

Gallium tri-iodide is prepared by direct reaction of the elements in a sealed tube (*96*, *119*). It is important to avoid excess of iodine since this cannot easily be removed by vacuum sublimation of the compound (*44*). The trends noted in Table V for the chloride and bromide continue for the iodide. In addition the degree of dissociation of the saturated vapor into monomeric GaX_3 units at the m.p. is 0.4% for the chloride, 14% for the bromide and 96% for the iodide. The corresponding figures at the respective b.p. are 2%, 30%, and 87% (*73*). The virtually complete dissociation of the tri-iodide into monomeric molecules is confirmed by electron diffraction on the gas which indicates the predominance of planar GaI_3 units (*26*) as in GaF_3 (*2*). Structural deductions have also been made from nuclear quadrupole measurements on crystals of the trihalides of gallium (*35*).

C. ADDITION COMPOUNDS OF THE TRIHALIDES

A discussion of the molecular addition compounds of the gallium trihalides must include reference to their stoichiometry, structure, and stability. All these aspects have been studied extensively during the last decade, and a fairly complete picture is now beginning to emerge. The known complexes of gallium trichloride are listed in Table VI from which it is seen that 1:1 complexes predominate though some compounds are well established in which there are two moles of ligand, and alkyl chlorides, in addition to forming 1:1 complexes, apparently form complexes in which one more of ligand is associated with two $GaCl_3$ units. Intercalation compounds of gallium trichloride in graphite have also been described (*237*) but these nonstoichiometric adducts are of a different type and will not be considered further. Fewer complexes of gallium tribromide have been described (see Table VII) and the coordination chemistry of the tri-iodide is almost completely unexplored.

The general properties of complexes with organic ligands will be mentioned first, and this will be followed by a discussion of the complexes with inorganic ligands. Aspects which relate specifically to the electrochemistry or thermochemistry of these systems will be deferred until Sections D and E.

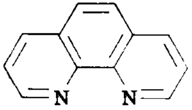
Gallium trichloride resembles aluminium chloride in forming no compound with anhydrous hydrogen chloride. However, in the presence of an aromatic hydrocarbon such as toluene a compound is formed having the structure $[PhMeH^+][GaCl_4^-]$ (*28*). Ethers can also be used to solvate the proton (*299*).

Organic nitrogen-containing ligands, as expected, form strong com-

TABLE VI
COMPLEXES OF GALLIUM TRICHLORIDE

Complex	m.p.	Reference	Complex	m.p.	Reference
$GaCl_3 \cdot MePhHCl$	—	(*28*)	$GaCl_3 \cdot MeCl$	48°	(*27, 261*)
$GaCl_3 \cdot Me_3N$	>200°	(*283*)	$2GaCl_3 \cdot MeCl$	—	(*27*)
$GaCl_3 \cdot 2Me_3N$	$d > -48°$	(*283*)	$GaCl_3 \cdot EtCl$	—	(*302*)
$GaCl_3 \cdot C_5H_5N$	126°	(*108, 116, 148*)	$2GaCl_3 \cdot EtCl$	(−29° calc)	(*302*)
$GaCl_3 \cdot 2C_5H_5N$	113°	(*108, 116, 148*)	$GaCl_3 \cdot Pr^iCl$	—	(*302*)
$GaCl_3 \cdot C_5H_{10}NH$	134°	(*108, 117*)	$2GaCl_3 \cdot Pr^iCl$	—	(*302*)
$GaCl_3 \cdot 2C_5H_{10}NH$	112°	(*108, 117*)	$GaCl_3 \cdot Ph_3CCl$	—	(*102*)
$GaCl_3 \cdot 3phen^a$	—	(*147*)	$GaCl_3 \cdot NH_3^b$	124°	(*81, 172*)
$GaCl_3 \cdot PhCN$	125°	(*280*)	$GaCl_3 \cdot NOCl$	—	(*214*)
$GaCl_3 \cdot PrCN$	—	(*280*)	$GaCl_3 \cdot PCl_3$	28° incongr.	(*111*)
$GaCl_3 \cdot PhNO_2$	64°	(*68*)	$GaCl_3 \cdot PCl_5$	368–371°	(*140a*)
$GaCl_3 \cdot p\text{-}MeC_6H_4NO_2$	95°	(*280*)	$GaCl_3 \cdot POCl_3$	118.5°	(*88, 104, 114*)
$GaCl_3 \cdot Me_2O$	3.0°	(*282, 283*)	$GaCl_3 \cdot AsCl_3$	incongr.	(*110*)
$GaCl_3 \cdot Et_2O$	16.2°	(*102, 105*)	$GaCl_3 \cdot AsCl_3 \cdot Cl_2$	5°	(*173*)
$GaCl_3 \cdot 2Et_2O$	9°	(*102, 105*)	$GaCl_3 \cdot LiCl$	—	(*81*)
$GaCl_3 \cdot Et_2OHCl$	—	(*299*)	$GaCl_3 \cdot KCl$	259°	(*81*)
$GaCl_3 \cdot Me_2CO$	42.2°(*d*)	(*106*)	$GaCl_3 \cdot CsCl$	385°	(*81*)
$GaCl_3 \cdot MeCOCl$	86°(*d*)	(*42, 106, 113*)	$GaCl_3 \cdot NH_4Cl$	304°	(*81*)
$GaCl_3 \cdot PhCOCl$	46.5°	(*113, 280*)	$GaCl_3 \cdot GaCl$	172.4°	(*82, 120, 303*)

[a] phen = *o*-phenanthroline, i.e.,



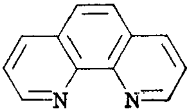
[b] Also at ratios of 3, 5, 6, 7, and 14 moles of NH_3 per mole of $GaCl_3$ (*172*).

TABLE VII

Complexes of Gallium Tribromide

Complex	m.p.	References	Complex	m.p.	References
$GaBr_3 \cdot NMe_3$	>200°	(*283*)	$GaBr_3 \cdot NH_3$[b]	—	(*172*)
$GaBr_3 \cdot 2NMe_3$	*d*> −48°	(*283*)	$GaBr_3 \cdot POCl_3$	115°	(*125*)
$GaBr_3 \cdot C_5H_5N$	126°	(*108, 122*)	$GaBr_3 \cdot POBr_3$	154°	(*121*)
$GaBr_3 \cdot 3C_5H_5N$	90–100°	(*148*)	$GaBr_3 \cdot KBr$	—	(*149*)
$GaBr_3 \cdot C_5H_{10}NH$	139°	(*122*)	$GaBr_3 \cdot CsBr$	—	(*149*)
$GaBr_3 \cdot 3phen$[a]	—	(*147*)	$GaBr_3 \cdot Et_4NBr$	—	(*149*)
$GaBr_3 \cdot Me_2O$	8.5°	(*283*)	$GaBr_3 \cdot GaBr$	166.7°	(*120, 304*)

[a] phen = *o*-phenanthroline, i.e.,



[b] Also at ratios of 5, 7, 9, and 14 moles of NH_3 per mole of $GaBr_3$ (*172*).

plexes. The 1:1 complexes of trimethylamine with gallium trichloride and tribromide are chalky powders stable in anhydrous conditions to 200° (*283*). Complexes with two moles of trimethylamine also form at low temperatures but these dissociate at temperatures above −48° to give the 1:1 compound and trimethylamine (*283*). Conductimetric behavior of these systems in nonaqueous solvents have been investigated. Thus addition of a ligand such as dimethylamine, dimethyl ether, or ammonia to a solution of gallium trichloride or tribromide in nitrobenzene rapidly increased the conductivity of the system, and this was followed by a slow increase over a period of up to two days before an equilibrium value was attained (*282*). Detailed interpretation is further complicated by the fact that gallium trichloride and nitrobenzene themselves form a complex, m.p. 64°, which can dissociate ionically, the specific conductivity of the fused compound being 5.8×10^{-3} $ohm^{-1}cm^{-1}$ at 75° (*68*).

Pyridine and piperidine also form 1:1 and 2:1 adducts with gallium trichloride, (*108, 116, 117, 148*), but only 1:1 complexes with the tribromide. The complexes with two moles of ligand are both relatively unstable and evolve 1 mole of ligand when warmed under vacuum. Evidence for the compounds $GaBr_3 \cdot 3C_5H_5N$ and $GaI_3 \cdot 3C_5H_5N$ in which the gallium is presumably six-coordinate has also been adduced (*48*). The tris(*ortho*-phenanthroline) complex appears to be of a different type and has been formulated as a six-coordinate trisbidentate complex of the Ga_3^+ cation, $[Gaphen_3^{3+}][Cl^-]_3$ (*147*).

Little is known about the complexes of gallium trichloride with benzonitrile and butyronitrile though the dipole moment of the former in benzene solution has been found to be 8.65 *D* (*280*). The corresponding value for *p*-nitrotoluene-gallium trichloride is 9.16 *D* (*280*). A cryoscopic study of the nitrobenzene-gallium trichloride system in benzene revealed an unstable incongruently melting compound $GaCl_3{\cdot}2PhNO_2$ but the stable adduct is again the 1:1 complex (*68*).

Ethers readily complex with the gallium trihalides, and there seems to be less tendency than with the aluminium analogues for thermal elimination of alkyl halides. Gallium trichloride and tribromide form 1:1 complexes with dimethyl ether which melt below room temperature (*283*). Vapor pressure-composition curves at −82° show only the 1:1 complex but in nitrobenzene solution there is some indication of the attachment of a second mole of ligand (*283*). This behavior contrasts with that of diethyl ether since the phase diagram of this ligand with gallium trichloride shows two well defined complexes melting at 16.2° and 9° (*105*). The bis(diethyl ether) complex reverts to the 1:1 complex in vacuo at room temperature. Vapor pressure data on some of these complexes are as follows (*110, 283*):

$GaCl_3{\cdot}Me_2O$: $\log p_{mm} = 6.52 - 1956/T$; $\Delta H_{vap} = 8.95$ kcal/mole; $p(43^\circ) = 2.1$ mm

$GaBr_3{\cdot}Me_2O$: $\log p_{mm} = 4.61 - 1205/T$; $\Delta H_{vap} = 5.51$ kcal/mole; $p(26^\circ) = 3.4$ mm

$GaCl_3{\cdot}Et_2O$: $\log p_{mm} = 9.56 - 2780/T$; $\Delta H_{vap} = 12.72$ kcal/mole; $p(26^\circ) = 1.8$ mm

The relatively high vapor pressure and low heat of vaporization of the bromide complex is noteworthy.

The only reported ketone complex of a gallium trihalide is gallium trichloride-acetone which has been established by phase studies; it melts with some decomposition at 42.2° (*106*). This contrasts with the many known complexes of aluminium halides with ketones and reflects the limited study which has been afforded to the gallium systems rather than their instability.

Acetyl and benzoyl chlorides form 1:1 adducts with gallium trichloride and the chemical (*113*) electrical (*113*) and infrared spectroscopic (*42*) evidence suggests that the structure is predominantly of the form $[RCO^+][GaCl_4^-]$. In benzene solution the dipole moment of the compound $GaCl_3{\cdot}PhCOCl$ is 6.85 *D* (*280*). Phase studies indicate the absence of adducts at stoichiometric ratios other than the 1:1 (*113*).

Alkyl halides form weak complexes with gallium trichloride at low temperatures (*27, 302*). In addition to the 1:1 complexes, solvates of the type $RCl{\cdot}Ga_2Cl_6$ were also observed though their structure has not been established. The heat of dissociation of the complex $EtCl{\cdot}2GaCl_3$ was found to be 0.74 kcal/mole (*302*) and dissociation pressure measurements on the corresponding system with methyl chloride led to the following heats (*261*):

$$2(\mathrm{MeCl{\cdot}GaCl_3})\ (\mathrm{c}) = \mathrm{MeCl{\cdot}2GaCl_3}\ (\mathrm{c}) + \mathrm{MeCl}\ (\mathrm{g});\quad \Delta H = 7.1\ \mathrm{kcal}$$
$$\mathrm{MeCl{\cdot}2GaCl_3}\ (\mathrm{c}) = \mathrm{2GaCl_3}\ (\mathrm{c}) + \mathrm{MeCl}\ (\mathrm{g});\quad \Delta H = 8.1\ \mathrm{kcal}$$
$$\mathrm{MeCl{\cdot}GaCl_3}\ (\mathrm{c}) = \mathrm{GaCl_3}\ (\mathrm{c}) + \mathrm{MeCl}\ (\mathrm{g});\quad \Delta H = 7.6\ \mathrm{kcal}$$

The 1:1 complex is therefore moderately stable. The slow rate of halogen exchange between gallium trichloride and methyl bromide at −80° suggests that the 1:1 complexes are not ionized as $R^+GaCl_4^-$ but should be formulated as covalent adducts $RX \rightarrow GaX_3$ (*27*). The solutions are unstable and evolve hydrogen halide below room temperature, the rate increasing with increasing chain length of the alkyl group (*302*). Isomerization of Pr^nCl to Pr^iCl has also been noted. Other compounds such as $GaBr_3{\cdot}EtBr$ have been postulated to explain kinetic results but have not been isolated (*261*). The compound $Ph_3C^+GaCl_4^-$ has been prepared as a yellow solid by mixing benzene solutions of gallium trichloride and triphenylmethyl chloride (*102*).

Ammonia forms a variety of compounds with the gallium halides of empirical formula $GaX_3{\cdot}nNH_3$ though their structure is unknown (*172*). It is not clear that all are simple adducts or solvates, and solvolysis may well have occurred at the higher mole ratios. Values of n are 1, 3, 5, 6, 7, and 14 for gallium trichloride, 1, 5, 7, 9, and 14 for the tribromide, and 1, 5, 6, 7, 9, 13, and 20 for the tri-iodide. The heat of addition per mole of ammonia as determined from vapor pressure isotherms decreases with increase in n: for gallium trichloride the decrease is from 32.9 kcal/mole NH_3 for the monoammine to 12.6 kcal/mole NH_3 for the 14-ammine; for the tribromide the decrease is from 30.3 kcal to 13.0 kcal/mole NH_3; and for the tri-iodide from 26.9 kcal to 11.4 kcal/mole NH_3 (*172*). The compound $GaCl_3{\cdot}NH_3$ has m.p. 124°; d^{25} 2.189 (*221*); b.p. 438°; ΔH_{vap} 17.7 kcal/mole and $\log p_{\mathrm{mm}}\ (\mathrm{liq}) = 7.333 - 3877/T$ (*81*).

The reaction of nitrosyl chloride with either gallium metal or gallium trichloride yields the compound $GaCl_3{\cdot}NOCl$ (*214*). Phosphorus trichloride and arsenic trichloride (*110*) form incongruently melting compounds with gallium trichloride and Raman spectra have shown in the former case that the fused compound is merely a solution of the dimeric gallium trichloride in the liquid ligand (*111*). Consistent with this the compound has negligible conductivity and a low heat of formation (*111*). By contrast, a congruently melting compound in the system $GaCl_3$—$AsCl_3$ can be prepared by adding one mole of chlorine gas; colorless, hygroscopic crystals of the 1:1:1 compound are formed m.p. 5° and it is suggested, on the basis of conductivity measurements, that the structure is $AsCl_4^+GaCl_4^-$ (*173*). The high-melting complex $GaCl_3{\cdot}PCl_5$ is apparently much more stable (*140a*).

Phase studies of the systems of phosphorus oxychloride with gallium trichloride (*114*) and tribromide (*125*) and of phosphorus oxybromide with gallium tribromide (*121*) have established well-defined congruently melting

1:1 compounds. Similarity in m.p. of $GaCl_3 \cdot POCl_3$ and $GaBr_3 \cdot POCl_3$, and of the adducts of the trihalides with pyridine and piperidine is noteworthy. A Raman investigation of the compound $GaCl_3 \cdot POCl_3$ established that oxygen is the donor atom (*88*), rather than chlorine (*121*).

Complexes with alkali metal halides and ammonium halides have the general formula $M^+GaCl_4^-$ and have been prepared by a variety of methods (*81*, *149*). These include direct reaction of the univalent halide and the gallium trihalide in a sealed tube (*81*), reaction in a nonaqueous solvent such as arsenic tribromide (*149*), or reaction in aqueous hydrochloric acid solution (*81*), though in this last procedure the product was never very pure. That the tetrachlorogallates can be regarded as typical donor-acceptor adducts is seen by the ease with which the chloride ion in the complex is displaced by a strong ligand. Thus gallium trichloride is extracted by ether from lithium tetrachlorogallate and the potassium salt reacts with gaseous ammonia at elevated temperatures to give volatile amines such as $GaCl_3 \cdot 3NH_3$ (*81*).

The particular case where gallium monohalide is the ligand is of interest since this is effectively the structure of gallium dihalides $Ga^+GaCl_4^-$ and $Ga^+GaBr_4^-$. (See Section II,C.)

D. Electrical Conductivity and Related Properties

The quantitative treatment of electrochemical data requires a knowledge of the viscosity (η cp) and density (d gm cm^{-3}) of a fused system in addition to its specific conductivity (κ ohm^{-1} cm^{-1}). The underlying theory has been developed (*103*) and indicates that the degree of ionic dissociation ($\alpha\%$) of a molten complex is given approximately by the expression

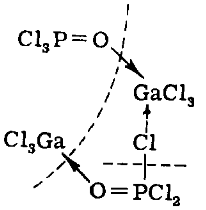
$$\alpha \simeq M\kappa\eta/d = \mu\eta$$

where M is the molecular weight and μ the molar conductivity ($M\kappa/d$). It follows that complexes which do not dissociate into kinetically free ions will have zero conductivity and those which are completely dissociated into ions will have values of conductivity, viscosity, and density which give a value of approximately 100. Some information on these properties for the complexes of gallium trihalides is assembled in Table VIII. Choice of a comparison temperature is difficult and various suggestions have been made in the literature but for the data in Table VIII the melting point of each complex has been arbitrarily chosen as the comparison temperature. (The surface tension γ dyne cm^{-1} is also included in Table VIII for convenience.)

It is clear from Table VIII that the trihalides themselves have a very low electrical conductivity and this is consistent with their structure as covalent dimeric molecules in the fused state; the degree of ionic dissociation based on these measurements is only 4–6 ppm (*115*, *119*). By contrast the dihalides are completely dissociated ionic complexes and the value of $\mu\eta$ approximates to 100%. The fact that values of $\mu\eta$ somewhat above 100 are obtained can be understood in terms of a detailed analysis of the conduction mechanism for these salts, in which the cation is much smaller than the anion (*120*). Complexes of the gallium trihalides fall between these two extremes, typical values ranging from $\frac{1}{2}$–7%. In this, the complexes resemble those of boron trifluoride and other donor-acceptor systems (*103*).

The activation energies for conduction and viscous flow fall in the range 3–12 kcal/mole, which is typical of ionizing systems and for each compound the activation energy for conduction is approximately the same as for viscous flow, the mean value for E_η/E_μ being 1.08 (*118*). This is consistent with the assumption made in developing the theory that ionic mobility in these systems is viscosity-controlled.

Little positive information is available as to the precise nature of the ionic species in these melts, except for the dihalides themselves, which have been shown to ionize as $Ga^+GaCl_4^-$ and $Ga^+GaBr_4^-$ (see Section II,C). The Raman spectrum of fused $GaCl_3 \cdot POCl_3$ has been interpreted in terms of the covalent adduct $Cl_3PO \rightarrow GaCl_3$ and this is undoubtedly the predominant species in the melt (*88*). However, the conductivity data in Table VIII suggest that in addition there is about $\frac{1}{2}$% of free ions and it is unlikely that the Raman lines from these species will be detectable in the presence of 99.5% of the undissociated complex, particularly as the positions of several of the lines from both structures will be similar. It is possible that a small equilibrium concentration of ions such as $POCl_2^+$ and $GaCl_4^-$ could be formed in this system by a ligand-switch rearrangement of the type illustrated in the figure, though there is no direct evidence for this:



The absence of gaseous products when the molten 1:1 and 2:1 adducts of gallium trichloride with pyridine and piperidine are electrolyzed eliminates the possibility that the complexes ionize as $H^+[C_5H_4N \rightarrow GaCl_3]^-$, $[C_5H_5NH]^+[C_5HN \rightarrow GaCl_3]^-$, etc. Such a formulation would also imply that the adduct with two moles of ligand would be more stable than the 1:1 complex whereas the reverse is true. This contrasts with the adducts of boron trifluoride where the 2:1 complexes are always more stable than the 1:1 and suggests that the gallium complexes have a different structure. An

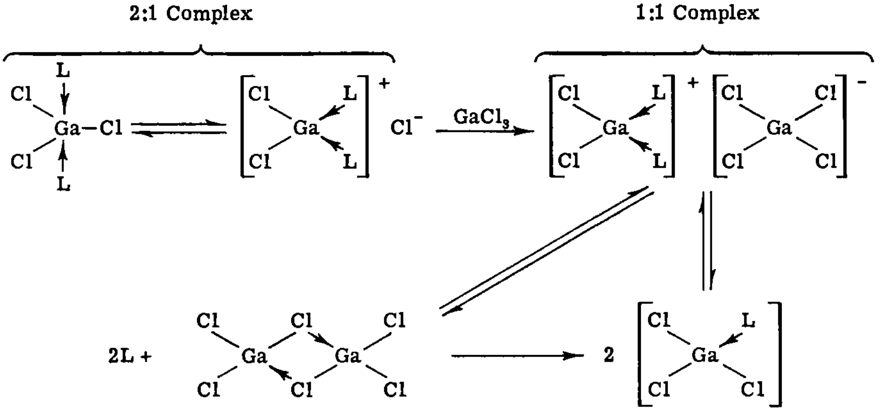
TABLE VIII
PHYSICAL PROPERTIES OF GALLIUM HALIDES AND THEIR COMPLEXES

Complex	m.p.	γ (dyne-cm^{-1})	$10^3 \cdot \kappa$ (ohm^{-1}cm^{-1})	η (cp)	d (gm-cm^{-3})	$\mu\eta$ ($\simeq\alpha\%$)	References
Ga_2Cl_6[a]	77.75°	27.3	1.86×10^{-3}	1.823	2.0536	5.8×10^{-4}	(*115*)
Ga_2Br_6[a]	122.5°	35.1	0.76×10^{-3}	2.867	3.1137	4.0×10^{-4}	(*121*)
$Ga[GaCl_4]$	172.4°	56.2	264.2	3.355	2.4173	103.3	(*120*)
$Ga[GaBr_4]$	166.7°	—	149.2	6.918	3.4712	136.3	(*120*)
$GaCl_3 \cdot POCl_3$	118.5°	32.1	1.261	1.947	1.8304	0.442	(*114*)
$GaCl_3 \cdot py$	126°	38.1	2.725	2.408	1.5552	1.077	(*116*)
$GaCl_3 \cdot 2py$	113°	50	9.67	2.911	1.368	6.88	(*116*)
$GaCl_3 \cdot pip$	134°	34.1	1.97	4.713	1.4856	1.63	(*117*)
$GaCl_3 \cdot 2pip$	112°	27.3	0.620	7.571	1.3253	1.23	(*117*)
$GaCl_3 \cdot Et_2O$	16.2°	48.5	0.810	5.77	1.8990	0.604	(*105*, *110*)
$GaBr_3 \cdot POBr_3$	154°	—	1.0[b]	4.921[b]	2.8839	1.0	(*121*)
$GaBr_3 \cdot py$	126°	42.7	1.242	7.090	2.2291	1.531	(*122*)
$GaBr_3 \cdot pip$	139°	43.8	1.503	6.844	2.1052	1.931	(*122*)

[a] The conductivities for these compounds are taken from ref. *119*.

[b] At 161.2°.

obvious possibility is that the 2:1 complexes in this case are 5-coordinate and that there is an ionization equilibrium as follows (*118*):



The 2:1 complex ionizes by rearrangement of the gallium from trigonal bipyramidal to tetrahedral configuration with elimination of a chloride ion and this ion can donate to a further $GaCl_3$ unit to give the ionic 1:1 complex. This interprets the ionization of the 2:1 complex and the greater stability of the 1:1 compound. The direct formation of the 1:1 complex from Ga_2Cl_6 and 2 moles of ligand would involve a replacement of bridged chlorine donors by either one or two moles of ligand to give the ionic and covalent form of the 1:1 complex respectively. On this basis the ionization equilibrium of the 1:1 complex itself (shown as the vertical equilibrium on the right hand side of the diagram) involves a ligand replacement reaction of precisely the same kind as that proposed for the complex $GaCl_3 \cdot POCl_3$.

E. THERMOCHEMISTRY OF GALLIUM TRIHALIDE ADDUCTS

The energy involved in donor-acceptor reactions and the heat of formation of crystalline molecular addition compounds can be measured directly in those cases where one of the compounds is a liquid and the other is a solid or a liquid. The method has so far only been applied systematically to complexes of gallium trichloride (*102*) but could be extended with advantage since data obtained in this way, in conjunction with heats of sublimation, lead directly to the gas-phase heat of interaction of donors and acceptors. The reaction sequence uses excess of the ligand as the calorimetric liquid:

$$GaCl_3\ (c) + (x + n)L\ (l) = GaCl_3{\cdot}nL\ (\text{dissolved in } x \text{ moles of L});\ -\Delta H_{\text{mix}}$$

$$GaCl_3{\cdot}nL\ (c) + xL\ (l) = GaCl_3{\cdot}nL\ (\text{dissolved in } x \text{ moles of L});\ -\Delta H_{\text{soln}}$$

hence,

$$GaCl_3\ (c) + nL\ (l) = GaCl_3{\cdot}nL\ (c);\ -\Delta H_f = -\Delta H_{mix} + \Delta H_{soln}$$

It is clearly immaterial whether the solution of the complex is ionized, dissociated, or solvated, provided only that in both reactions the same final state is achieved.

The results are summarized in Table IX and may be illustrated by the case of phosphorus oxychloride (*104*). When crystalline gallium trichloride reacts with excess of liquid phosphorus oxychloride the heat of mixing, $-\Delta H_{mix}$, is 11.01 kcal per mole of $GaCl_3$. Then the crystalline 1:1 complex $GaCl_3{\cdot}POCl_3$ is dissolved in an excess of the same liquid, the heat of solution, $-\Delta H_{soln}$, is 0.85 kcal/mole. By difference, the heat of formation of the crystalline complex from crystalline acceptor and liquid ligand, $-\Delta H_f$, is 10.17 kcal/mole. By measuring the heat of sublimation of the complex (15 kcal/mole) and using the known heat of vaporization of phosphorus oxychloride (8.4 kcal/mole), and heats of sublimation and dimerization of gallium trichloride (8.5, 10.5 kcal/mole) the heat of the gas-phase reaction, $-\Delta H_f(g)$, was found to be:

$$GaCl_3\ (g) + POCl_3\ (g) = GaCl_3{\cdot}POCl_3\ (g);\quad -\Delta H_f\ (g) = 22.6\ \text{kcal/mole}$$

Since phosphorus oxychloride is an oxygen-atom donor in this complex (*88*) this implies that the $O \rightarrow Ga$ bond in the complex is some 12 kcal stronger than the $Cl \rightarrow Ga$ bond in the bridged dimer Ga_2Cl_6 (*104*).

The ligands PCl_3 and $AsCl_3$ form incongruently melting complexes with gallium trichloride and, consistent with this, both complexes have very low heats of formation, 3.4 and 1.4 kcal/mole respectively (*109, 110, 111*). Gallium trichloride-acetyl chloride (*106*) also has a low heat of formation (4.1 kcal/mole) and the difference between this value and that for the corresponding acetone complex (15.3 kcal/mole) reflects the fact that the negative inductive effect of the chlorine atom has reduced the electron availability at the carbonyl oxygen to a point where the oxygen is no longer the donor atom, the structure of the complex being (*42*) $MeCO^+[Cl \rightarrow GaCl_3]^-$. In this case, the over-all heat of reaction not only involves the energy involved in forming the $Cl \rightarrow Ga$ bond and the reorganization energy of the gallium atom, but also the energy required to cleave acetyl chloride into $MeCO^+$ and Cl^- ions and the coulomb attraction of the resultant ionic species $MeCO^+$ and $GaCl_4^-$.

Table IX also indicates that nitrogen donors (pyridine, piperidine) evolve 2–3 times as much heat as oxygen donors (phosphorus oxychloride, acetone, ether) and this difference persists, though slightly less marked, for the gas-phase reactions. Thus the heats of formation of the gaseous complexes from gaseous ligand and monomeric gaseous $GaCl_3$ are: $GaCl_3{\cdot}POCl_3$ (g) 22.6 ± 1, $GaCl_3{\cdot}Et_2O$ (g) 22.3 ± 1, $GaCl_3{\cdot}C_5H_5N$ (g)

TABLE IX

HEAT OF FORMATION OF GALLIUM HALIDE COMPLEXES

Complex (c or l)	$-\Delta H_f$(kcal)	Reference	Complex (c or l)	$-\Delta H_f$(kcal)	Reference
$GaCl_3 \cdot POCl_3$ (c)	10.17 ± 0.01	(*104*)	$GaCl_3 \cdot Me_2CO$ (c)	15.3 ± 0.9	(*106*)
$GaCl_3 \cdot PCl_3$ (c + l)	3.40 ± 0.03	(*111*)	$GaCl_3 \cdot MeCOCl$ (c)	4.1 ± 0.1	(*106*)
$GaCl_3 \cdot C_5H_5N$ (c)	29.8 ± 0.1	(*108*)	$GaCl_3 \cdot Et_2O$ (l)	9.34 ± 0.08	(*109*)
$GaCl_3 \cdot 2C_5H_5N$ (c)	41.5 ± 0.1	(*108*)	$GaCl_3 \cdot 2Et_2O$ (l)	15.48 ± 0.09	(*109*)
$GaCl_3 \cdot C_5H_{10}NH$ (c)	33.7 ± 2.7	(*108*)	$GaCl_3 \cdot AsCl_3$ (c + l)	1.4 ± 0.2	(*110*)
$GaCl_3 \cdot 2C_5H_{10}NH$ (c)	52.1 ± 2.0	(*108*)	$GaBr_3 \cdot C_5H_5N$ (c)	34.5 ± 0.4	(*108*)

35.2 ± 2, and $GaCl_3 \cdot C_5H_{10}NH$ 38.1 ± 2 kcal/mole. As expected, piperidine is a stronger donor than pyridine in both the condensed and gas-phase reactions, and those cases where both 1:1 and 2:1 complexes are formed (pyridine, piperidine, ether) the second mole of ligand evolves much less heat on addition than the first. Equilibrium vapor-pressure measurements afford a useful check on the calorimetric data here (*108*) for the solid 2:1 pyridine complex dissociates on heating to the solid 1:1 complex and pyridine vapor:

$$GaCl_3 \cdot 2C_5H_5N \text{ (c)} = GaCl_3 \cdot C_5H_5N \text{ (c)} + C_5H_5N \text{ (g)}.$$

From the dissociation pressure equation $\log p_{mm} = 15.973 - 4670/T$, the heat of dissociation is -21.3 kcal/mole, and this, coupled with the heat of vaporization of pyridine (9.7 kcal/mole) leads to a value of $-\Delta H = -11.6$ kcal/mole for the dissociation reaction

$$GaCl_3 \cdot 2C_5H_5N \text{ (c)} = GaCl_3 \cdot C_5H_5N \text{ (c)} + C_5H_5N \text{ (l)}.$$

This compares with the calorimetric value $-\Delta H = 11.7$ kcal/mole for the reverse (formation) reaction deduced from Table IX.

The final entry in Table IX refers to the complex $GaBr_3 \cdot C_5H_5N$. The heat of formation of this crystalline complex from crystalline gallium bromide and liquid pyridine is 34.5 kcal/mole which is significantly greater than the value of 29.8 for the corresponding chloride complex. This difference appears to persist for the gas-phase reaction ($\sim$38.3 ± 2 kcal/mole) and affords an example of the sequence $I > Br > Cl > F$ for the heats of formation of boron, aluminium, and gallium halide complexes (*107*, *108*). This order is determined mainly by the extent of π bonding in the monomeric trihalides which in turn influences the energy of reorganization of the electron acceptor from planar to tetrahedral. (Key references to the rather extensive literature on this point, particularly for boron halide complexes will be found in refs. *107*, *108*, *184*.) The reorganization energies for boron and aluminium halides have been calculated by a simple molecular-orbital theory (*48*), and, on the reasonable assumption that the trends persist with the gallium halides, the reorganization energy of $GaCl_3$ can be taken to be 33 kcal/mole and that of $GaBr_3$ 30 kcal/mole (*118*). This leads to the following values for the bond dissociation energies:

Complex	$D(N \rightarrow GaX_3)$ (kcal/mole)	Complex	$D(O \rightarrow GaCl_3)$ (kcal/mole)
$GaCl_3 \cdot C_5H_5N$	68.2	$GaCl_3 \cdot POCl_3$	55.6
$GaBr_3 \cdot C_5H_5N$	68.3	$GaCl_3 \cdot Et_2O$	55.3
$GaCl_3 \cdot C_5H_{10}NH$	71.1		
mean	69.2	mean	55.5

Since the Cl→Ga bond is some 12 kcal weaker than the O→Ga bond (see above) it appears that the bond dissociation energy $D(\mathrm{Cl}\rightarrow\mathrm{GaCl_3})$ is approximately 43 kcal/mole.

F. CATALYTIC PROPERTIES

The early work of Ulich (*279*, *281*) established that gallium trichloride could be used instead of aluminium chloride in the Friedel-Crafts synthesis of ketones and hydrocarbons. Three reactions were studied:

$$\mathrm{PhH + PhCOCl \xrightarrow{GaCl_3} Ph_2CO + HCl}$$

$$\mathrm{PhH + PrCl \longrightarrow PrPh + HCl}$$

$$\mathrm{PhH + C_2H_4 \longrightarrow EtPh} + \text{higher homologs.}$$

The gallium catalyst, which formed a homogeneous reaction phase, was found to promote more rapid reaction and to be less easily deactivated than the aluminium catalyst.

In a more detailed study of the metal chloride catalyzed acetylation of aromatic hydrocarbons with benzoyl chloride, the relative rates at 25° were found to be $SbCl_5$ 1300, $FeCl_3$ 570, $GaCl_3$ 500, $AlCl_3$ 1, $SnCl_4$ 0.0029, BCl_3 0.00062 (*152*). The similarity in isomer distribution from the benzoylation of toluene argues for a common reaction intermediate, presumably $PhCO^+$. However, a carbonium ion mechanism is less likely for the alkylation of aromatic hydrocarbons with alkyl halides except in the case of readily ionizable tertiary halides (*29*).

A detailed kinetic study of the alkylation of benzene and toluene with ethyl bromide in the presence of gallium tribromide has shown that the reaction is zero order with respect both to the aromatic hydrocarbon (used as solvent) and to the ethyl bromide, and was second order with respect to gallium tribromide (*261*). Toluene reacted some $2\frac{1}{2}$ times as rapidly as benzene, suggesting that an aromatic complex is involved in the rate-determining step. It is considered that, in this reaction, gallium tribromide is a weaker catalyst than aluminium tribromide and that the second mole of trihalide is required to facilitate the transfer of the alkyl group from the bromide to the aromatic nucleus. The relative rates of reaction when ethyl bromide is replaced by a series of alkyl bromides was also studied (*262*) as were the *o*-, *m*-, and *p*-isomer distributions and partial rate factors (*30*).

Solid gallium trihalides have been used to catalyze the gas-phase addition of hydrogen chloride to olefins; e.g., the reaction with ethylene at −20°, which is particularly well adapted to the manufacture of ethyl chloride (*213*).

A continuous process for the dimerization of propylene at 200 atm and 200–350° has been developed using, among other catalysts, trimethylgallium or triphenylgallium (*310*). Similarly, ethylene is polymerized under a variety of temperature and pressure conditions in the presence of trimethyl or triethyl gallium (*49, 309*). In the analogous polymerization of vinyl ethers in inert solvents at room temperature, gallium trichloride is claimed to be a superior catalyst (*126*).

Gallium trichloride has also been found more effective than other metal halides in the Lewis acid catalyzed decomposition of benzazide to phenylisocyanate, and a kinetic investigation of the reaction indicates the initial rapid formation of the 1:1 complex which then decomposed slowly with first-order kinetics (*41*):

$$GaCl_3 + PhCON_3 \rightarrow GaCl_3{\cdot}PhCON_3 \rightarrow GaCl_3 + PhNCO + N_2.$$

The strength of catalytic activity decreased in the sequence

$$GaCl_3 > AlBr_3 > AlCl_3 > FeCl_3 \gg SbCl_5, TiCl_4, SnCl_4, TeCl_4, SbBr_3.$$

Another unusual catalytic effect which gallium trichloride has in common with many other electron-pair acceptors is the ability to enhance greatly the reducing power of sodium borohydride towards a variety of organic compounds (*31*), e.g., ethyl benzoate was rapidly reduced to benzyl alcohol in 90% yield at 75°.

VII. Other Salts and Complexes of Gallium(III)

The compounds discussed in the preceding sections have almost all been prepared and investigated either in nonaqueous solvents or in the absence of any solvent at all. Aqueous systems have also been extensively studied and the results are briefly reviewed in the present section.

Progressive dehydration of the salt $Ga_2(SO_4)_3{\cdot}18H_2O$ leads to three new hydrates, viz., 15, 14, and $7H_2O$, in contrast to aluminium sulfate which forms hydrates containing 18, 16, 10, and 6 moles of water (*278*). A large variety of other hydrated salts such as the phosphate, chlorate, bromate, iodate, and double sulfates have been described (*207, 208, 269*) as well as the hydrated perchlorate (*76, 193*). Earlier work on such compounds was reviewed in 1942 (*64*).

A series of dithiocarbamates, $(R_2MCS_2)_3Ga$, and xanthates, $(ROCS_2)_3Ga$, have been prepared (*53*). The crystal structure of the guanidinium salt $[C(NH_2)_3]Ga(SO_4)_2{\cdot}6H_2O$ (*85*) and the corresponding selenate (*216*) have been reported in connection with a study of ferroelectric domains.

The analytical chemistry of gallium ferrocyanide, $Ga_4[Fe(CN)_6]_3$ has been studied (*11, 66, 272, 273*) and the complex tetracyanonickelate, $Ga_2[Ni(CN)_4]_3{\cdot}6H_2O$, has been prepared as a bluish-grey precipitate from gallium sulfate and potassium tetracyanonickelate (*162*).

A variety of organic chelating reagents has been investigated mainly from the point of view of analytical chemistry. These include substituted quinolines (*182, 183, 199, 200, 204, 219, 226*), ethylenediaminetetra-acetic acid (*242*), 1,2-diaminocyclohexanetetra-acetic acid (*250*), acetylacetone (*36, 140, 143, 179*), pyrocatechol (*12, 240*), sodium 3,4-dihydroxyazobenzene-4′-sulfonate (*180*), trihydroxyglutaric acid (*67*) and tartaric acid (*229, 245, 277*). In addition, several tris(malonato) complexes have been prepared, e.g., $M_3Ga[CH_2(CO_2)_2]_3{\cdot}3H_2O$ (M = Na, K) (*60, 61*), and $Tl_3Ga[CH_2(CO_2)_2]_3{\cdot}H_2O$ (*265*).

It has been shown, further, that gallium has a much stronger tendency to complex with ligands such as tartrate (*245*) and oxalate (*181, 183, 244*) than has aluminium, and the species $[Ga(C_2O_4)]^+$, $[Ga(C_2O_4)_2]^-$, and $[Ga(C_2O_4)_3]^{3-}$ have been identified by emf, conductimetric, polarographic, and optical density measurements. Despite this, the tris-bidentate complexes are still too labile in aqueous solution to be resolvable into optically active diastereoisomers and an earlier claim (*206*) to have resolved the trisoxalatogallium(III) anion, $[Ga(C_2O_4)_3]^{3-}$, has been refuted (*62, 201*). Gallium acetylacetonate, m.p. 195–196° has also defied attempts to resolve it (*202*).

Preliminary experiments on the potential use of liquid gallium as an electrode in polarography have not been encouraging (*91, 100, 243*).

The use of radioactive Ga-72 in the diagnosis and treatment of bone cancer has been investigated using organic salts such as gallium citrate and lactate (*56–58*). Gallium metal itself is only mildly toxic (*197*).

VIII. Gallium Hydrides and Organogallium Compounds

It is doubtful whether uncoordinated gallium hydride has ever been prepared as a stable compound and there is no evidence for its existence as digallane Ga_2H_6. Earlier claims (*290–292*) to have prepared digallane by the disproportionation of dimethylgallium hydride in the presence of trimethylamine or triethylamine have been disputed (*254*) and a careful series of experiments designed to liberate free gallium hydride, always resulted in decomposition to gallium and hydrogen (*254*). Likewise the preparation of an ill-defined salt-like hydride by the action of atomic hydrogen on gallium metal (*220*) appears questionable (*255*). Apparently a polymeric form of gallium hydride $(GaH_3)_x$ can be prepared by the reaction of gallium trichloride with lithium gallium hydride in ether (*297*) but the compound has not been fully characterized.

By contrast, complexes of gallane (GaH_3) are well characterized and some are moderately stable. Lithium gallium hydride was first prepared in 1947 during the pioneering researches on lithium aluminium hydride (*70*); gallium chloride [or bromide (*142, 295*)] was reacted with an excess of lithium hydride in ether below room temperature and, after filtration to remove lithium chloride, the ether was removed by evaporation. The compound decomposes slowly at room temperature and more rapidly at 150° to give lithium hydride, gallium, and hydrogen (*70, 294*). It is a milder reducing agent that either lithium borohydride, or lithium aluminium hydride (*247, 294*). Silver gallium hydride (*289*) and thallium gallium hydride (*296*) have also been prepared at very low temperatures but decompose at −75° and −90° respectively.

The most stable adduct of gallane so far prepared is trimethylamine-gallane, $Me_3N{\cdot}GaH_3$, which is obtained by reaction of trimethylamine hydrochloride and lithium gallium hydride, (*112, 252*). It melts at 70.5° and its infrared (*112*) and Raman (*252*) spectra have been analyzed in some detail by comparison with the spectra of trimethylamine-trideuterogallane, m.p. 68.1° (*112*). Adducts with diethyl ether (*295*), dimethyl sulfide (*254*), and several tertiary amines (*112*) have also been prepared. The etherate reacts with hydrazoic acid below room temperature to give crystals of gallium triazide $Ga(N_3)_3$ (*293*).

Trimethylgallium (*178*), triethylgallium (*54*), and triphenylgallium (*92*), are known and their chemistry has recently been reviewed (*40*). Trimethylgallium has been prepared by the reaction of dimethyl-zinc vapor on gallium trichloride (*178*) but is most conveniently synthesized by reacting dimethylmercury with gallium metal (*38, 292*). It melts at −15.7° boils at 55.8°, has a density at 15° of 1.151 (*194*), and is monomeric in the gas phase (*178*). Vapor pressure measurements lead to the following results (*194*):

$$\log_{10} p_{\mathrm{mm}} \text{ (solid)} = 10.5664 - 2362.2/T$$

$$\log_{10} p_{\mathrm{mm}} \text{ (liquid)} = 32.9398 - 2833.4/T - 8.5201 \log T$$

$$\Delta H_{\mathrm{subl}}\ 10.81 \text{ kcal},\ \Delta H_{\mathrm{vap}} \text{ (m.p.) } 8.60 \text{ kcal},\ \Delta H_{\mathrm{fus}}\ 2.21 \text{ kcal},$$

$$\Delta H_{\mathrm{vap}} \text{ (b.p.) } 7.39 \text{ kcal, Trouton const. } 22.5 \text{ e.u.}$$

The heat of formation of liquid trimethylgallium was found to be 17.6 ± 3 kcal/mole by bomb calorimetry (*194*) and 14.5 ± 8 kcal/mole by reaction calorimetry with iodine in benzene (*80*); the former figure is probably the more accurate and leads to a mean bond dissociation energy, D(Ga—C), of 57.7 kcal. This is somewhat smaller than the value of 62.9 kcal for D(Al—C) found for trimethylaluminium and this parallels the trend found for bond dissociation energies of 4-coordinate complexes of gallium (Section VI,E) and aluminium (*118*).

Less is known about the physical properties of triethyl- and triphenylgallium though the former was the first organogallium compound to be prepared (*54*). Triethylgallium is a somewhat viscous liquid m.p. −82.3°, d_4^{30} 1.058 (*54*), and $\log_{10} p_{\mathrm{mm}} = 8.224 - 2222/T$; the extrapolated b.p.

is 142.8°, ΔH_{vap} 10.2 kcal/mole and Trouton constant 24.5 (*186*). The rather high Trouton constant may be related to the fact that, though the vapor is monomeric (*186*), the liquid is somewhat viscous and the compound is associated approximately into dimers in benzene and cyclohexane solution (*268*). Triphenylgallium, m.p. 166°, like the trialkyl compounds, is readily prepared from the corresponding organomercury compound (*92*). Its solubility in a variety of solvents has been studied at 20° and varies from 4.15 gm/liter in heptane to 289 gm/liter in chloroform (*266*). The compound is monomeric in benzene, cyclohexane, and dioxane (*268*).

Trimethyl- and triethyl-gallium are moderately good electron-pair acceptors and early work established the existence of such compounds as $Me_3Ga \cdot NH_3$ (*178*), $Me_3Ga \cdot NEt_3$ (*290*), $Me_3Ga \cdot Et_2O$ (*178*), $Et_3Ga \cdot NH_3$ (*54*), and $Et_3Ga \cdot Et_2O$ (*54*). Knowledge of such adducts has been greatly extended by the elegant work of Coates (*38, 39*) who pointed out that, because it is monomeric, trimethylgallium is a convenient acceptor with which to assess the relative donor properties of the elements of groups V and VI. Trimethylgallium is a stronger acceptor than trimethylboron but is weaker than trimethylaluminium. Despite this, weak donors which will coordinate to trimethylgallium sometimes do not form adducts with trimethylaluminium because of the 20 kcal energy required to break the dimer, Me_6Al_2, into monomeric Me_3Al. The physical properties of the gallium adducts are summarized in Table X. The compounds are all volatile liquids or low melting solids and the high values of the Trouton constants can be ascribed to the tendency for dipole association in the liquid phase and to the extensive dissociation which frequently occurs in the gas phase. The gas-phase heat of dissociation of the complexes (in kcal/mole) decreases in the sequence (*40*) NMe_3,21 > PMe_3,18 > $AsMe_3$,10 > $SbMe_3$ very small. The sequence is less regular for group VI ligands, being 9.5 kcal/mole for the dimethyl ether adduct, 10 kcal/mole for the selenium compound and about 8 kcal/mole for the sulfur and tellurium analogs; the free energies of dissociation follow the sequence $O > Se > S = Te$ (*38*).

The dipole moments of triethyl- and triphenyl-gallium have been studied in various solvents. There was zero dipole moment in heptane; the values in benzene were 0.67 and 0.4 *D*, and in dioxane 2.11 and 2.14 *D* (*267*). When compared with dipole moments of other organometallic group III acceptors the relative order was $B < Al > Ga > In > Tl$ (*267*), which agrees with conclusions drawn from dissociation-pressure measurements (*38*).

The thermal decomposition of trimethylgallium-ammonia leads to the formation of the dimeric compound $(Me_2Ga \cdot NH_2)_2$ and similar compounds can be formed from the coordination compounds with methylamine and dimethylamine (*38*). Reaction of trimethylgallium with methanol,

TABLE X
COMPLEXES OF TRIMETHYLGALLIUM

Compound	m.p.	b.p. (calc)	$\log_{10} p_{mm}$	ΔH_{vap} (kcal/mole)	Trouton constant	Reference
$Me_3Ga \cdot NH_3$	32°	179°	$7.190 - 1947/T$	8.9	19.7	(*38*)
$Me_3Ga \cdot NH_2Me$	38°	169°	$9.119 - 2760/T$	12.6	28.6	(*38*)
$Me_3Ga \cdot NHMe_2$	33.6°	170°	$8.596 - 2532/T$	11.6	26.2	(*38*)
$Me_3Ga \cdot NMe_3$	96.2°	164°	$7.974 - 2226/T$	10.19	23.3	(*292*)
$Me_3Ga \cdot PMe_3$	56.7°	173°	$8.851 - 2662/T$	12.2	27.3	(*38*)
$Me_3Ga \cdot AsMe_3$	23.7°	121°	$9.114 - 2458/T$	11.2	28.5	(*38*)
$Me_3Ga \cdot SbMe_3$	2.2°	95°	$8.591 - 2105/T$	9.6	26.1	(*38*)
$Me_3Ga \cdot OMe_2$	—	100°	$8.453 - 2078/T$	9.5	25.5	(*38*)
$Me_3Ga \cdot SMe_2$	—	116°	$9.516 - 2580/T$	11.8	30.4	(*38*)
$Me_3Ga \cdot SeMe_2$	−42°	111°	$10.118 - 2783/T$	12.7	33.0	(*38*)
$Me_3Ga \cdot TeMe_2$	−32°	122°	$9.172 - 2488/T$	11.4	28.8	(*38*)
$Me_3Ga \cdot NCMe$	25.2°	120°	$8.840 - 2342/T$	10.7	27.3	(*39*)
$Me_3Ga \cdot OCMe_2$	—	104°	$9.896 - 2648/T$	12.1	32.1	(*39*)
$Me_3Ga \cdot NEt_3$	96°	167°	$9.493 - 2909/T$	13.3	30.2	(*292*)

methanethiol, methaneselenol, and acetic acid also results in elimination of methane to give dimeric products such as $(Me_2Ga{\cdot}SMe)_2$ (*39*). These, and similar compounds, presumably contain 4-membered heterocyclic rings of alternate gallium and donor atoms and their properties have been studied in some detail. For example, in some cases the ring can be split reversibly by a ligand such as trimethylamine to give adducts of the type $MeSGaMe_2{\cdot}NMe_3$ and a wide range of analogous compounds has been prepared by this method and their properties intercompared (*38*, *39*).

Other reactions of gallium trialkyls include their conversion by halogens or hydrogen halides to gallium trihalides and mixed alkylgallium halides (*40*, *292*). Many of these form adducts with group V ligands e.g., $Me_2GaCl{\cdot}NH_3$ m.p. 54° (*178*), $Me_2GaCl{\cdot}NMe_3$ m.p. 112.5°, $Me_2GaCl{\cdot}PMe_3$ m.p. 93.5°, $Me_2GaBr{\cdot}NMe_3$ m.p. 136°, and $Me_2GaI{\cdot}NMe_3$ m.p. 128° (*40*). Dimethylgallium chloride also forms a diammoniate, m.p. 112° (*178*), which has recently been shown to have the structure $[Me_2Ga{\cdot}2NH_3]^+Cl^-$ (*253*).

Lithium aluminium hydride reacts with trimethylgallium over a period of 24 hr at room temperature to give dimethylalane, Me_2AlH, and another product presumed to be $Li^+[GaH_3Me]^-$ (*286*), which could be considered as a derivative of gallane. Diborane, on the other hand, reacts rapidly with trimethylgallium at room temperature to give methyldiborane, MeB_2H_5, together with gallium metal and hydrogen (*246*). This is a further illustration of the instability of uncoordinated gallium hydride discussed earlier in this section. When the preceding reaction is carried out at −45° a compound analyzing as dimethylgallium borohydride is formed as a liquid m.p. 1.5°, b.p. (extrap.) 92°; this is stable at −80° but decomposes slowly at room temperature (*246*). The gas-phase molecular weight corresponds to the monomer and the compound clearly merits further examination since, if it has the bridged structure $Me_2GaH_2BH_2$ it would be the first authenticated example of this structural type.

Trimethyl- and triethyl-gallium are both violently hydrolyzed by water to give compounds R_2GaOH (*54*, *178*). The reaction can be controlled by hydrolyzing the etherate in the presence of a limited amount of water (*166*). In this way, the apparently trimeric compound $(Me_2GaOH)_3$ was obtained m.p. 87°, *d* 1.75, dipole moment 1.8 *D*, molecular weight 331 (trimer requires 350) (*166*). The detailed X-ray analysis of this compound, however, showed that, at least in the crystalline state, it was a cyclic tetramer $(Me_2GaOH)_4$ (*260*). In this form the compound has a center of inversion and should therefore have zero dipole moment and it is possible that the compound is trimeric in solution and tetrameric in the solid. It will be recalled that compounds of the type $(Me_2GaOMe)_2$ were cyclic dimers (see top of this page).

In summary it can be said that organogallium compounds are highly reactive; they are violently hydrolyzed by water, and the lower trialkyls are spontaneously inflammable. However, they are less reactive than their aluminium analogs and the acceptor power of gallium alkyls towards a variety of ligands is less than that of aluminium. In this, the organogallium compounds parallel the trends in acceptor properties discussed in Section VI,E for the trihalides of gallium and aluminium (*118*).

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