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ELECTROCHEMICAL AND PHYSICOCHEMICAL PROPERTIES OF ALUMINIUM COMPOUNDS IN NON-AQUEOUS SOLUTIONS

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I. INTRODUCTION

The electrochemistry of non-aqueous solutions is mainly still in the initial stage of its development. However, the investigation of non-aqueous solutions of aluminium compounds is in a better position. Such solutions have been investigated rather widely since 60 years ago when aluminium was first separated by electrolysis of a solution of aluminium bromide in ethyl bromide[1]. Some of the solutions studied have found practical use, for example, for coating the uranium rods of nuclear reactors with aluminium[2].

The electrochemical properties of non-aqueous solutions of aluminium halides and their complexes have been considered in sufficient detail in earlier reviews and monographs[3-12], therefore here we will only look at the principal results necessary for a general statement, and also individual phenomena insufficiently stressed by the authors of previous publications.

It is established that a marked increase in electrical conductivity on mixing two weakly conducting components is due to their reaction to form more or less stable compounds[13]. On the other hand, the question as to *what* is the nature of the reaction leading to the formation of particles capable of dissociation and *how* they dissociate, is still not clear in many cases. Attention will also be directed to this below.

Not every complex formed in solution is capable of electrolytic dissociation. For example, the complexes of general composition† $AlCl_3SnEt_nCl_{4-n}$ formed during the dissolution of $AlCl_3$ in benzene solutions of ethyltin chlorides do not dissociate[14]. Similarly, not every conducting complex, even of those consistent with a stoichiometric composition, can be used for electrodeposition of the metal. One of the main questions in this connection is to seek means for *a priori* prediction of the fundamental electrochemical properties of a particular solution. The latter is obviously impossible without knowledge and generalisation of the main relations determining the properties of the solutions formed.

† The following symbols are used in the text: M metal, X halogen, R radical, Me CH_3, Et C_2H_5, Ph C_6H_5, Py pyridine, Ar aromatic hydrocarbon, Sol solution, Slv solvent.

II. HYDRIDE ELECTROLYTE (BRENNER'S ELECTROLYTE)

The electrolyte is prepared by mixing a suspension of LiH in ether or an ethereal solution of $LiAlH_4$ with an ethereal solution of $AlCl_3$.[15-17] The composition of the solution (recalculated on the initial components) can be varied within the limits: $AlCl_3$ 2–3 M, LiH 0.5–1.0 M or $LiAlH_4$ 0.13–0.4 M or above. Under these conditions and in an inert atmosphere a compact, pale silvery Al deposit is obtained at current densities $D_C \leq 5$ A dm^{-2} with current efficiencies close to 100%. The aluminium anodes dissolve with efficiencies which also approach 100%. With $D_C > 5$ A dm^{-2} the quality of the precipitates deteriorates, dendritic growth starts, and the lustre is lost.

The experiments of Brenner and coworkers led them to conclude that the ions Li^+, $AlCl_4^-$, and $(AlCl_3H.ether)^-$ exist in the solution[15]. Actually things are not so simple. The composition of the final products of the reaction of LiH (or $LiAlH_4$) with $AlCl_3$ depends strongly on many factors: an excess of one of the initial reagents, the reaction temperature, the intensity of mixing, the order of addition of the reagents, the dispersion of the LiH, etc. Different reactions which are possible between the initial substances and the products of the primary reactions can take place simultaneously, therefore the actual composition of the electrolyte can be greatly different from the simplest variants.

Finholt and coworkers found that these reactions occur[18,19]:

$$4LiH + AlCl_3 \xrightarrow{Et_2O} LiAlH_4 + 3LiCl, \quad (1)$$

$$3LiAlH_4 + AlCl_3 \xrightarrow{Et_2O} 4AlH_3 + 3LiCl, \quad (2)$$

and that $AlCl_3$ is completely converted into AlH_3. However, when there is an excess of $AlCl_3$ the formation of AlH_3 as a final product is doubtful. Since the electrolytes which are obtained when LiH and $LiAlH_4$ are used are identical as regards their principal properties, reactions of type (2) are rather limited. If the reaction leads to the formation of $LiAlCl_3H$ then it must proceed by the scheme:

$$LiAlH_4 + AlCl_3 \rightarrow LiAlCl_3H + AlH_3, \quad (3)$$

but a large excess of $AlCl_3$ is not required for this, whereas an electrolyte with the necessary properties is obtained only when it is in fivefold to tenfold excess. The course of the reaction according to Eqn.(2) requires a quaternary collision in solution, which is of low probability. A more likely supposition is that reaction (2) occurs in stages, the first being:

$$LiAlH_4 + AlCl_3 \rightarrow LiCl + 2AlH_2Cl. \quad (4)$$

The compound AlH_2Cl is unstable and disproportionates[20-22]:

$$2AlH_2Cl \rightarrow AlHCl_2 + AlH_3. \quad (5)$$

In its turn AlH_3 is able to react with $AlCl_3$ according to the schemes[20-22]:

$$AlH_3 + 2AlCl_3 \rightarrow 3AlHCl_2, \quad (6)$$

$$AlH_3 + AlCl_3 \rightarrow AlH_3 \cdot AlCl_3 \rightarrow AlH_2Cl \cdot AlHCl_2. \quad (7)$$

During this the excess of AlH_3 above that required by Eqn.(7) remains unreacted:

$$2AlH_3 + AlCl_3 \rightarrow AlH_2Cl \cdot AlHCl_2 + AlH_3. \quad (8)$$

Trichlorodialane $AlH_2Cl.AlHCl_2$ was obtained also by the overall reaction[23-44]:

$$3LiAlH_4 + 5AlCl_3 \rightarrow 4AlH_2Cl \cdot AlHCl_2 + 3LiCl. \quad (9)$$

Furthermore, certain studies[25,26] established that in the creation of an effective excess of $AlCl_3$ in the course of reaction (1), an intermediate product AlH_nCl_{3-n} is formed; this is close in composition to trichlorodialane and was separated in crystalline form.

Finally, Couch and Brenner[15] found that in the electrolysis of an ethereal solution of $LiAlH_4$ a black powder is deposited on the cathode; this powder consists of lithium and aluminium. According to their results[15] and ours during the electrolysis of an ethereal solution containing 2–3 M $AlCl_3$ and 0.5–0.75 M LiCl, aluminium is deposited on the cathode with very low current efficiencies. Gillet[27] in general did not observe deposition of aluminium from these solutions. Consequently neither $LiAlCl_4$ nor $LiAlH_4$ as such is responsible for the good properties of the hydride electrolyte.

Evans and coworkers[28] carried out a conductimetric titration of an ethereal solution of $AlCl_3$, saturated with LiCl and without it, by an ethereal solution of $LiAlH_4$ (Fig.1); the equivalent percentage was calculated by the authors[28] by reaction (2). It is evident that as the electrical conductivity of the solution increases as a result of the reaction so the course of the reaction itself is independent of the initial presence of LiCl. A very similar curve is also obtained on titrating an ethereal solution of $AlHCl_2$ by $LiAlH_4$ solution. The presence of maxima is explained by supposing the formation of strongly dissociating compounds according to the scheme:

$$LiAlH_4 + 2AlCl_3 \rightarrow LiCl + [Al_2Cl_5]^+[AlH_4]^-, \quad (10)$$

or by

$$LiAlH_4 + 2AlHCl_2 \rightarrow LiCl + [Al_2H_2Cl_3]^+[AlH_4]^-. \quad (11)$$

Both suggestions are essentially arbitrary and no additional evidence has yet been obtained. The rise in electrical conductivity (κ) after the minimum is explained by a reaction between AlH_3, formed at the completion of the reaction, and the excess of $LiAlH_4$. This agrees with the rise in κ on adding $LiAlH_4$ to an ethereal solution of AlH_3 which has been observed by the same authors[28]. On titrating $LiAlH_4$ solution with $AlCl_3$ solution a curve was obtained with a maximum at 33 equiv.% $AlCl_3$, this maximum being treated as the result of the interaction of $LiAlH_4$ and AlH_3; from 120 to 240 equiv.% the curve runs almost parallel to

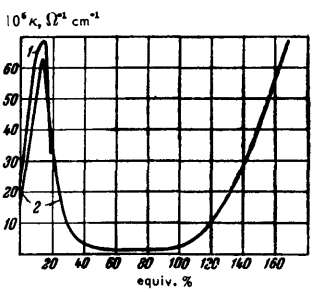


Fig.1. Curves for the conductimetric titration with $LiAlH_4$ of: 1) an ethereal solution of $AlCl_3$ (0.177 M) + LiCl (suspension); 2) ethereal solution of $AlCl_3$ (0.161 M).

the abscissa axis. It would seem that with this excess of $AlCl_3$ reaction (7) must occur. However, the electrical conductivity of trichlorodialane solutions is unknown, hence the reason for this course of the curve is not clear. Solutions of AlH_3, $AlHCl_2$, and $LiAlH_4$ have close electrical conductivities at concentrations of about 0.1–0.4 M, but κ for $AlCl_3$ is about ten times as much.

Hayashi and Ishida[29] investigated the titration of $AlCl_3$ solutions by $LiAlH_4$ solution more carefully and observed a minimum on addition of the first portions of the titrant (Fig.2). They consider the maximum to be linked with reaction (6).

It is interesting that the amount of aluminium which can be deposited from a hydride bath as a high-quality coating is equal to the quantity of aluminium taken in the form of $AlCl_3$ in making up the electrolyte. Since during the operation of the bath the solution does not become depleted in aluminium it was suggested that during its anodic dissolution the aluminium enters the bath as some compound other than that existing in the solution. There is confirmation of this in that a liquid immiscible with the remaining solution gradually accumulates in the anodic space[15,17].

Anodic and cathodic polarisation curves on aluminium electrodes taken using an aluminium wire as comparison electrode, are poorly reproducible for either an ethereal solution of $AlCl_3$ or the hydride electrolyte. These curves also suggest that polarisation is less in the hydride electrolyte, *i.e.* that electrode reactions occur with participation of ions other than those in a solution of pure $AlCl_3$.[15,34]

We consider that reactions (6) and (7) are the most probable, *i.e.* the properties of the hydride electrolyte are connected with the formation of $AlHCl_2$ or $AlH_2Cl.AlHCl_2$, but it is impossible to draw a definite conclusion. It is also not clear whether the presence of LiCl has any significance. The formation of $AlHCl_2$ is supported by Wiberg's results[20-22] [reactions (5)–(8)]; in support of the formation of $AlH_2Cl.AlHCl_2$ there is the analogy with the sesquihalides of aluminium: good aluminium deposits were obtained from solutions of $AlEt_2I$ + $AlEtI_2$ in Et_2O at D_C = 2 A dm^{-2} [30] and from a solution of $AlEt_2Cl$ + $AlEtCl_2$ in xylene at $D_C \simeq 1$ A dm^{-2} or $AlPh_2Cl$ + $AlPhCl_2$ in xylene at D_C up to 0.33 A dm^{-2}.[31] The answer to this problem may be obtained in an attempt to prepare the hydride electrolyte directly from AlH_3 and $AlCl_3$ with addition of LiCl or without it. Such an investigation has been started in our laboratories.

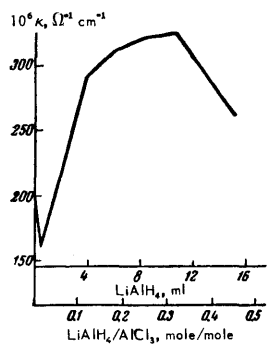


Fig.2. Conductimetric titration on curve for an ethereal solution of $AlCl_3$ (0.53 M) by an ethereal solution of $LiAlH_4$ (0.27 M).

III. ALUMINIUM HALIDES AND THEIR COMPLEXES

The electrochemical properties of solutions of aluminium chloride and bromide and their complexes, mainly with the halides of metals of Groups I, II, and V, ammonium halides, interhalogen compounds, and hydrogen halides in various solvents, have been studied.

A. Binary Systems

The halides of metals of Groups I and II and ammonium halides are almost insoluble in the solvents for which results are given in Tables 4 and 5. $MgBr_2$ is an exception, its solubility in Et_2O being 2.44 wt.% at 20°.[32] A triether compound of $MgBr_2$, stable below 12–13°, is known and its formation is accompanied by liquid immiscibility[33]. Electrolysis of the phase enriched in $MgBr_2$ (2.4 M) showed that hydrogen is liberated at the cathode with an efficiency greater than 80% and CH_4 and CO_2 at the anode; magnesium is not deposited[27].

The data in Tables 1 and 2 characterise the interaction in the MX–solvent systems. The existence of compounds and their compositions are shown from thermal analyses if there are no other indications. Equimolecular compounds are denoted by 1 : 1 and the formula composition is given for non-symmetrical compounds; "eut." denotes a eutectic, and "incongr." an incongruently melting compound.

The electrical conductivity of nitromethane itself[55] is 6×10^{-7} Ω^{-1} cm^{-1} and of the remaining solvents less than 10^{-8} Ω^{-1} cm^{-1}. Individual substances of mixtures with conductivity less than 10^{-8} Ω^{-1} cm^{-1} will subsequently be conventially termed non-conductive. The electrical conductivity of the pure liquid halides MX_3 are: $AlCl_3$ 1.1×10^{-6} (245°);[11] $AlBr_3$ 9×10^{-8} (195°); $AsCl_3$ 1.2×10^{-6} (25°); $AsBr_3$ 1.5×10^{-6} (35°); $SbCl_3$ 1.1×10^{-4} (73°); and $SbBr_3$ 2.4×10^{-4} Ω^{-1} cm^{-1} (99°).[55]

Results concerning the formation of compounds between $AlBr_3$ and benzene, toluene, or xylene are quite contradictory[59,74] and an analysis of them suggests only that there is a relatively weak interaction between the molecules of $AlBr_3$ and these solvents in the liquid phase. Judging from κ, it increases somewhat from benzene to xylene.

During the electrolysis of freshly prepared solutions of $AlBr_3$ in xylene, aluminium is deposited as individual crystallites: it is not deposited from solutions which have been kept for some time after preparation, but tarring occurs at the cathode. Aluminium is not deposited from nitrobenzene and nitromethane and tar is formed at the cathode[11]. On standing, nitromethane solutions become gelatinous[11,57,75]. Aluminium is deposited as a black powder from ether solutions[11].

The electrical conductivity of solutions in ethyl bromide and iodide with less than 10–12 wt.% $AlBr_3$ increases with time[11,77]. Aluminium is not deposited from solutions of such concentration in EtBr [77] but it is deposited from more concentrated solutions. These do not show a change in conductivity on standing and give bright deposits but dendrites are formed if the electrolysis is continued[11]: aluminium is deposited from solutions in EtI only when aluminium anodes

TABLE 1. Physicochemical characteristics of MX_3–solvent binary systems.

Salt	Solvent					
	benzene	toluene	chlorobenzene	nitrobenzene	ethyl bromide	diethyl ether
$AlCl_3$	solubility 0.02 wt. % at 19.9°[32]; does not conduct[11]	solubility 0.039 wt. % at 20.15°[32]; does not conduct[11]	sparingly soluble; does not conduct[35]	1 : 1, 1 : 2, 2 : 1[45,46]; dependence of κ on composition has maximum $1.5 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ at 14.7 wt. % $AlCl_3$[11]		1 : 1[42,43]; dependence of κ on composition has maximum $1.20 \times 10^{-3}\ \Omega^{-1} \times \times cm^{-1}$ at 33 mole % $AlCl_3$[11]**
$AlBr_3$	weak interaction (*cf.* text) $\kappa = 3 \times 10^{-9}\ \Omega^{-1}\ cm^{-1}$[11]	weak interaction (*cf.* text) $\kappa = 1 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$ at 35 wt. % $AlBr_3$[11]	eut.[39]; $\kappa = 2.4 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$[35]	1 : 1[32]; dependence of κ on composition has maximum $2.2 \times 10^{-3}\ \Omega^{-1} \times \times cm^{-1}$ at 17.2 wt. % $AlBr_3$[38]	1 : 1[50,51]* dependence of κ on composition has maximum of $3.4 \times \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ at the ratio $AlBr_3/C_2H_5Br$ = = 0.66[38]**	1 : 1[42,43]; dependence of κ on composition has maximum $1 \times 10^{-3}\ \Omega^{-1} \times \times cm^{-1}$ at 25 mole % $AlBr_3$[11]
$AsCl_3$	–	–	–	–	–	1 : 1 (κ, viscosity, at 0–50°); maximum κ = $= 2 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ corresponding to 80 mole % $AsCl_3$[48]
$AsBr_3$	eut.[37]; does not conduct[34]	–	does not conduct[35]	eut.; dependence of κ on composition has two maxima, 1.5×10^{-4} and $3 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ at 10 and 65 mole % $AsBr_3$; κ and η suggest a 1 : 1 compound[44]	–	dependence of κ on composition has maximum $4 \times \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ at 95.12 wt. % $AsBr_3$[38]
$SbCl_3$	$C_6H_6 2SbCl_3$[36]	1 : 1 incongr. $C_6H_6CH_3 2SbCl_3$[41]	1 : 1 incongr.[36]	1 : 1[36]; at 53 wt. % $SbCl_3$ $\kappa = 2.4 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$[38]	–	dependence of κ on composition has maximum $2.6 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ at 86.8 wt. % $SbCl_3$[38]
$SbBr_3$	$C_6H_6.2SbBr_3$[32]; does not conduct[40]	1 : 1 incongr., $C_6H_5CH_3.2SbBr_3$ incongr.[41]; does not conduct[35]	eut.[36]; does not conduct[35]	eut.[36]; dependence of κ on composition has maximum $1.8 \times 10^{-4} \times \times \Omega^{-1}\ cm^{-1}$ at ~33 wt. % $SbBr_3$[33]	–	dependence of κ on composition has maximum $1.25 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ at 82.3 wt. % $SbBr_3$[38]
$BiBr_3$	sparingly soluble[119]	–	–	eut.[46]; conducts[52]	–	–

* Gorenbein and Danilova's[49] assertion that when $AlBr_3$–C_2H_5Br mixtures are crystallised only the initial components separate should be noted on account of misunderstanding.

** See elsewhere[29,76,77] for electrical conductivity at low concentrations.

TABLE 2. Physicochemical characteristics of $AlBr_3$–solvent binary systems.

Solvent	Properties of binary systems
Xylene	weak interaction (*cf.* text). Freshly prepared solutions have $\kappa = 10^{-4}$–$10^{-5}\ \Omega^{-1}\ cm^{-1}$; at 18° κ increases 70 times in 18 d[11]
Ethyl iodide	dependence of κ on composition has maximum $7.2 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ at ratio $AlBr_3/C_2H_5I = 0.45$[38]
Dibromoethane	eut.[56]; does not conduct; degree of association in dimer ~50% at 6 wt. % $AlBr_3$ in the solution[11]
Nitromethane	1 : 1 (measurement of dielectric constants of mixtures)[58]; κ increases with concentration and is $1.41 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ at $c = 1.367$ M[57]

are used[78]. Probably this is due to the formation of an ethylsesquiiodide by the reaction[79]:

$$2Al + 3EtI \rightarrow AlEt_2I + AlEtI_2, \qquad (12)$$

from which Al is then deposited (*cf.* also Keyes *et al.*[30]).

Electrolysis of solutions of $AsBr_3$ and $SbCl_3$ in Et_2O gives good deposits of As and Sb,[80] and Sb is deposited when solutions of $SbCl_3$ and $SbBr_3$ in $PhNO_2$ are electrolysed[57].

The inspissation of solutions and the change in κ during electrolysis over a protracted interval are explained by association of the complexes and by solvation with introduction of molecules of the solvent into the inner sphere of the complex by the scheme[11]:

$$AlX_3 + Slv \rightarrow [AlX_2Slv]^+ + X^-. \qquad (13)$$

Processes of this type are well known for aqueous solutions. Thus the conversion of the green modification of chromium(III) into the violet takes place over a few months[81]. However, in the cases under consideration such an explanation must be used with caution, taking into account the catalytic properties of the aluminium halides, the influence of traces of moisture, etc. Actually, for example, HBr is liberated from dilute solutions of $AlBr_3$ in EtBr and alkenes are formed[50,77]. Therefore in cases not supported by special investigations, the "solvation" hypothesis must be considered as slenderly based, and its application to nitromethane solutions as simply untrue: it was found that with the reduced catalytic activity of $AlBr_3$ on complex formation with alkali metal halides thickening did not take place[75].

According to equilibrium and vapour pressure diagrams[105,106], the hydrogen halides HCl and HBr form unstable compounds with benzene, toluene, and xylene. The electrical conductivity of their solutions in moist solvents at room temperature is of the order of 10^{-4}–$10^{-5}\ \Omega^{-1}\ cm^{-1}$,[108] and in dry solvents κ is close to zero: κ for HX themselves near their boiling points is of the order of 10^{-7}–$10^{-8}\ \Omega^{-1}\ cm^{-1}$.[109]

The compounds ICl and IBr form conducting solutions with nitrobenzene; at 18° for ICl $\kappa = 7.9 \times 10^{-4}$ at ICl : $PhNO_2$ = = 1 : 9.7, and for IBr $\kappa = 3.5 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ at IBr : $PhNO_2$ = = 1 : 11.28.[110,111] Electrolysis and transport numbers results[112] suggest the formation of the ions $[PhNO_2.I]^+$ and X^-; it was also found that iodine liberated at the cathode is reduced to I^- and then transported to the anode, where it is also deposited as I_2.[113] Hence as a result of the electrolysis, both X_2 and I_2 are liberated at the anode. Values of κ for the compounds themselves at their melting points are: ICl (27.2°) 4.4×10^{-3}, IBr (42°) $4.0 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$.[114]

Table 3 gives information about interactions in the AlX_3–MX_n systems, taken mainly from a handbook[82]. The references to other sources are indicated in the table. The electrical conductivity of the melts is of the order usual for salts with the exception of mixtures with $AsBr_3$ where $\kappa \leqslant 1 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$.[11]

Complete absence of interaction between AlX_3 and HX is found; for example, on condensing HCl on $AlCl_3$ there is only weak physical absorption[105,115-118]. For 0.1 M $AlBr_3$ in HBr, $\kappa = 2 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$. Thermal analysis showed that the compounds $AlCl_3.2ICl$ and $AlBr_3.IBr$ are formed[89].

B. Ternary Systems

1. Metal (ammonium) halides–aluminium halides–solvent. Tables 4 and 5 give comparative characteristics for the solubility and electrical conductivity in ternary systems. Three characteristics are given for each system (where the data exist). The first relates to the change in κ with *increase* in the AlX_3 : Slv ratio between the limits 0.05–0.35 at $MX_n : AlX_3$ = const; inc. = increases, dec. = decreases, max.(min.) = passes through the corresponding extremum. The second similarly describes the change in the solubility of MX_n, the number denoting the order of the solubility of MX_n, expressed as a ratio $MX_n : AlX_3$, at AlX_3 : Slv = 0.1–0.3; at other AlX_3 : Slv

TABLE 3. Characteristics of AlX_3–MX_n binary systems (mole %).

MX_n	Characteristics
	$AlCl_3$
LiCl	1 : 1
NaCl	1 : 1, immiscible liquids 0–19.2% NaCl
KCl	1 : 1, immiscible liquids 0–19.1% KCl
KBr	1 : 1, immiscible liquids 0–19.8% KBr
CsCl	1 : 1[85]
NH_4Cl	1 : 1, immiscible liquids 0–20% NH_4Cl[86]
TlCl	1 : 1, $TlCl.2AlCl_3$ (?), immiscible liquids 1.2–14.7% TlCl
AgCl	1 : 1, immiscible liquids 0.7–17.6% AgCl
CuCl	1 : 1
$MgCl_2$	1 : 1 (?)
$SnCl_2$	1 : 1, $SnCl_2.2AlCl_3$, immiscible liquids 1.5–14.3% $SnCl_2$
$SbCl_3$	eut.
$SbBr_3$	eut.
	$AlBr_3$
NaCl	$NaCl.2AlBr_3$, $NaCl.4AlBr_3$, immiscible liquids 0–19% NaCl
KCl	1 : 1, $KCl.2AlBr_3$, immiscible liquids 0–20.9% KCl
LiBr	1 : 1, $LiBr.2AlBr_3$, $LiBr.7AlBr_3$
NaBr	1 : 1, $NaBr.2AlBr_3$, $2NaBr.7AlBr_3$, immiscible liquids 2.6–16.3% NaBr
KBr	1 : 1, $KBr.2AlBr_3$, immiscible liquids 0.4–22.1% KBr
NH_4Br	1 : 1, $NH_4Br.2AlBr_3$, $NH_4Br.3AlBr_3$, immiscible liquids 0.5–20.8% NH_4Br
NaI	1 : 1, immiscible liquids 2–13% NaI[83]
AgCl	1 : 1, immiscible liquids 0–19.2% AgCl
CuCl	1 : 1, $CuCl.2AlBr_3$[84]*
AgBr	1 : 1, $AgBr.2AlBr_3$, immiscible liquids 2.2–17% AgBr
CuBr	1 : 1, compound separated from benzene and ethyl bromide[11]
AgI	1 : 1[84]**
CuI	1 : 1[84]*
$SbCl_3$	exchange with anions
$AsBr_3$	eut.[11]
$SbBr_3$	1 : 1
$BiBr_3$	1 : 1
TlBr	1 : 1, $TlBr.2AlBr_3$, immiscible liquids 0.6–22.8% TlBr
$MgBr_2$	$MgBr_2.2AlBr_3$ (?)
$CdBr_2$	1 : 1
$HgBr_2$	$HgBr_2.2AlBr_3$

* Determined cryoscopically in benzene; results not completely reliable.

** Determined cryoscopically in benzene and ethyl bromide; results not completely reliable.

TABLE 4. Comparative characteristics of the $AlCl_3$–MX_n–solvent systems.

Salt	Solvent			
	chlorobenzene	nitrobenzene	diethyl ether	nitromethane
LiCl			–; 0.5; 7.4×10^{-3} | 0.2	
NaCl		inc.; const. 1.0; inc. 5.9×10^{-3} | 0.15		–; 1.0; inc. 2.9×10^{-2} | 0.135[75]
KCl		dec.; min. (?) 0.6; inc. 4.2×10^{-3} | 0.25[87]		
KBr		–; 0.77; inc. 4.5×10^{-3} | 0.23[38]		
$CdCl_2$		insoluble[53]		
$AsCl_3$			dec. | 0.37–0.71; dec. 9.0; dec. 6.9×10^{-4} | 0.37[90]	
$SbCl_3$			–; 3.0; max. 1.3×10^{-3} | 0.31[90]	
$SbBr_3$	soluble; solution does not conduct	dec.; dec. 4.0; dec. 10^{-3} | 0.137[38]		
RbCl				–; 1.0; inc. 2.7×10^{-2} | 0.05[91]
CsCl				–; 0.59; inc. 2.3×10^{-2} | 0.045[91]
NH_4Cl				–; 0.8; inc. 3.9×10^{-2} | 0.1[91]
NH_4Br				–; 0.9; inc. 2.6×10^{-2} | 0.05[91]
TlCl				–; 0.78; inc. 1.7×10^{-2} | 0.045[91]
AgCl				does not dissolve[91]

TABLE 5. Comparative characteristics of the $AlBr_3$–MX_n–solvent systems.

Salt	Solvent				
	benzene	toluene	xylene	chlorobenzene	nitrobenzene
LiCl	–; 0.8; –[92]	–; 0.8; –[92]	–; 0.6; –[12]		inc. const. 1.0; inc. 3×10^{-3} | 0.04[38]
NaCl	–; 0.5; –[92]	–; 0.5; –[92]	inc.; dec. 0.49; inc. 3.2×10^{-3} | 0.33[96]		inc.; 1.0; inc. 3.2×10^{-3} | 0.04[97]
KCl	–; 0.5; inc. 6.8×10^{-3} | 0.24[93]	–; 0.4; –[92]	–; 0.41; inc. 3×10^{-3} | 0.5[96]		~const.; 0.8; inc. 4×10^{-3} | 0.23[38]
RbCl	inc.; dec. 0.22; inc. 3.2×10^{-3} | 0.22[38,94]				–; 0.8; inc. 4×10^{-3} | 0.23[38]
NH_4Cl	inc.; dec. 0.58 | 0.15; inc. 4×10^{-3} | 0.15[38]		–; 0.44; inc. 3.5×10^{-3} | 0.5[96]		max.; 1.0; inc. 4.5×10^{-3} | 0.25[98]
LiBr	–; 0.7; max. 5.7×10^{-3} | 0.286[38]	–; 0.8; max. 4.7×10^{-3} | 0.297[38]	–; 0.5; –[12]		–; 1.0; inc. 2.8×10^{-3} | 0.23[38,92]
NaBr	–; 0.5; –[92]	–; 0.4; –[92]	inc. 0.3; inc. 1.8×10^{-3} | 0.33[12,96]	sparingly soluble; κ hardly changes[35]	–; dec. 0.7; –[12,100]
KBr	inc.; dec. 0.5; inc. 4.5×10^{-3} | 0.15[11]	inc.; 0.5; inc. 5.3×10^{-3} | 0.45[38,92]	inc.; inc. 0.3; inc. 2.1×10^{-3} | 0.33[96]	sparingly soluble; κ hardly changes[35]	–; inc. 0.86; inc. 3.7×10^{-3} | 0.23[38]
RbBr	–; 0.33; inc. 4.3×10^{-3} | 0.23[38]			sparingly soluble; κ hardly changes[35]	max.; max. 0.77; inc. 3.5×10^{-3} | 0.24[38]
NH_4Br	inc.; inc. 0.5; inc. 7×10^{-3} | 0.23[11]		inc.; inc. 0.3; inc. 3.6×10^{-3} | 0.33[96]		max. ~const. 1.0; inc. 4.8×10^{-3} | 0.25[11]
LiI	–; 0.7; –[92]	–; 0.7; –[92]	–; 0.7; –[12]		
NaI	inc.; dec. 0.7; max. 2.7×10^{-3} | 0.25[11]	–; 0.4; –[92]			max.; dec. 0.5; inc. 5×10^{-3} | 0.105[99]
KI	inc. const. 0.5; inc. 8.4×10^{-3} | 0.25[93]	–; 0.5; –[92]			
NH_4I	inc.; dec. 0.5; inc. 6.2×10^{-3} | 0.23[38]		–; 0.34; inc. 2.4×10^{-3} | 0.33[96]		max.; dec. 0.9; inc. 5×10^{-3} | 0.106[98]
AgCl	–; 0.89; inc. 6×10^{-3} | 0.23[38]				
AgBr	–; 0.61; inc. 5.5×10^{-3} | 0.23[38]	–; 0.8; inc. 4.3×10^{-3} | 0.24[38]		sparingly soluble; κ hardly changes[35]	
CuBr	–; 0.99; max. 4.5×10^{-3} | 0.23[38]	–; 1.0; max. 4.8×10^{-3} | 0.23[38]		sparingly soluble; κ hardly changes[35]	
AgI	–; 0.47; inc. 2.7×10^{-3} | 0.23[38]				
$SbCl_3$					max.; dec. 5.0; dec. 10^{-3} | 0.29[53]
$AsBr_3$	conducts, κ changes strongly with time[11]			very soluble; ternary solution does not conduct[35]	dec.; dec. 8.0; dec. 1.3×10^{-3} | 0.23[38]
$SbBr_3$	–; (1.0); max. 1.2×10^{-3} | 0.37[38]	inc.; –; max. 2×10^{-3} | 0.25[38]		inc.; dec. 2.0; inc. $\sim10^{-4}$[35]	
$BiBr_3$	inc.; max. 1.0; 0.24; max. 6×10^{-4} | 0.24[38]			sparingly soluble, κ hardly changes[35]	dec.; dec. 0.4; dec. 6.7×10^{-4} | 0.23[38]
TlBr	inc.; const. 0.5; inc. 9.5×10^{-3} | 0.24[98]				

Salt	Solvent				
	ethyl bromide	ethyl iodide	dibromoethane	nitromethane	diethyl ether
LiCl	–; 1.12 : 0.42; inc. 7.2×10^{-4} | 0.42[38]	inc.; dec. 0.5; dec. 5×10^{-3} | 0.23[102]	–; 0.9; –[104]	inc.; 1.0; inc. 2.3×10^{-2} | 0.04[38]	
NaCl	–; 1 | 0.41; max. 1.1×10^{-3} | 0.41[38]	inc.; dec. 0.21; dec. 5.6×10^{-3} | 0.24[102]	–; 0.6; –[104]	inc.; 1.0; inc. 3×10^{-2} | 0.123[78]	
KCl	–; 0.235 | 0.41; inc. 4.2×10^{-4} | 0.41[38]	inc.; const. 0.1; dec. 5×10^{-3} | 0.23[102]	–; 0.6; –[104]	inc.; 1.0; inc. 2×10^{-2} | 0.04[38]	
NH_4Cl	inc.; inc. 0.15; inc. 3.1×10^{-3} | 0.15[101]				
LiBr	–; inc. 0.9 | 0.29; inc. 9.5×10^{-4} | 0.29[38]	inc.; const. 0.26; dec. 5.5×10^{-3} | 0.24[102]	–; 0.8; –[92]	–; 1.0; –[104]	
NaBr	inc.; max. 1.0; inc. 8×10^{-3} | 0.27[11]	inc.; dec. 0.25; const. 5.7×10^{-3} | 0.24[102]	–; 0.4; –[92]	–; 1.0; –[104]	

TABLE 5. (cont'd)

Salt	Solvent				
	ethyl bromide	ethyl iodide	dibromoethane	nitromethane	diethyl ether
KBr	inc.; dec. 0.3; inc. 2.3×10^{-3} | 0.18 [38]	inc.; dec. 0.12; const. 5.7×10^{-3} | 0.24 [102]	inc.; inc. 0.5 | 0.35; inc. 2.9×10^{-3} | 0.22 [38,95]	–; 1.0; inc. 2.9×10^{-2} | 0.033 [75]	
RbBr	–; 0.04 | 0.24; inc. 2.1×10^{-3} | 0.24 [38]				
NH_4Br	inc.; const. 0.2; inc. 2.9×10^{-3} | 0.15 [101]				
LiI		inc.; dec. 0.45; dec. 4.1×10^{-3} | 0.23 [102]			
NaI	inc.; max. 1.0; max. 1.2×10^{-2} | 0.27 [11]	inc.; inc. 0.2; dec. 4.6×10^{-3} | 0.23 [102]			
KI	inc.; max. 0.13 | 0.18; inc. 5.8×10^{-3} | 0.18 [38]	inc.; inc. 0.1; dec. 5×10^{-3} | 0.24 [102]			
NH_4I	inc.; const. 0.14; inc. 5.4×10^{-3} | 0.15 [101]				
AgCl	–; 0.96 | 0.23; inc. 1.4×10^{-3} | 0.233 [38]	dec.; min. 0.68; inc. 1.2×10^{-3} | 0.24 [38]	–; 0.66 | 0.37; inc. 6×10^{-3} | 0.37 [38]		
CuCl	–; 0.88 | 0.237; inc. 1.2×10^{-3} | 0.237 [38]	dec.; dec. 0.65; max. 8.5×10^{-3} | 0.24 [38]			
AgBr	inc.; max. 1.0; inc. 1.2×10^{-2} | 0.23 [11]	dec.; min. 0.67; inc. 1.2×10^{-3} | 0.23 [38]	inc.; dec. 0.58 | 0.18; inc. 3×10^{-3} | 0.18 [38]		
CuBr	inc.; dec. 0.9; inc. 8×10^{-3} | 0.233 [38]	dec.; dec. 0.73; max. 8.4×10^{-3} | 0.23 [38]	inc.; dec. 0.45; inc. 1.5×10^{-3} | 0.25 [38]		
AgI	inc.; dec. 0.94; inc. 1.4×10^{-3} | 0.23 [38]	dec.; dec. 0.75; inc. 9.5×10^{-3} | 0.23 [11]	–; 0.56 | 0.37; inc. 5.9×10^{-3} | 0.37 [38]		
CuI	–; 0.8 | 0.23; inc. 10^{-2} | 0.23 [38]	dec.; dec. 0.72; max. 6.8×10^{-3} | 0.23 [11]			
$AsBr_3$	inc.; (dec.(?) 5.8; dec. 2.9×10^{-4} | 0.19 [38]				inc.; inc. 3.7; dec. 7×10^{-3} | 0.21 [11]
$SbBr_3$	inc.; 1.8; max. 2.2×10^{-3} | 0.23 [103]				–; 3.8; min. 5.7×10^{-4} | 0.18 [87]
$BiBr_3$	inc.; 0.5; inc. 3.3×10^{-3} | 0.23 [103]				
TlBr	inc.; dec. 0.12; inc. 3.1×10^{-3} | 0.23 [38]				
$CdBr_2$	–; 0.074; max. 1.7×10^{-3} | 0.23 [103]				
$MgBr_2$					–; 0.68; inc. 3.8×10^{-3} | 0.19 [90]

ratios this value is shown after the fraction line. The third characteristic shows how κ changes with *increase* in $MX_n : AlX_3$ at $AlX_3 : Slv = 0.1–0.3$; the number in it expresses κ in Ω^{-1} cm^{-1} at $MX_n : AlX_3 = 0.5$, when solubility permits, or at saturation in MX_n, when $AlX_n : AlX_3 < 0.5$, at the $AlX_3 : Slv$ values shown after the fraction line. Values of κ are given at 18° or 25°; in view of the difference in the compositions of the mixtures the change in κ in this temperature interval is immaterial.

Consideration of Tables 4 and 5 leads to the conclusion that in general the electrical conductivity is of the order of 5×10^{-3} Ω^{-1} cm^{-1}; only in $MeNO_2$ and in certain cases in EtBr does it reach 10^{-2} Ω^{-1} cm^{-1} but for solutions of halides of Group V elements it falls to 5×10^{-4} Ω^{-1} cm^{-1}. The maxima on the electrical conductivity curves express the the rise in viscosity and disappear on introducing the appropriate corrections, as in the AlX_3–Slv binary systems [40,121,122]. In this case the κ curve is monotonic and κ rises with increasing MX_n concentration.

A comparison of Tables 1–5 shows that despite long-standing opinion [11,12] the formation of compounds in the melt is not a condition unambiguously determining the solubility and electrical conductivity in ternary systems. For example, a series of bromides is insoluble in $PhCl–AlBr_3$, AgCl is insoluble in $MeNO_2–AlCl_3$. $AsBr_3$ gives both conducting and non-conducting solutions with $AlBr_3$, etc., *i.e.* there is no sharp correlation between the formation of compounds in the melt and the properties of the ternary mixtures.

A decrease or constancy in the solubility of MX_n on increasing the $AlX_3 : Slv$ ratio and the chosen limits of this ratio give unambiguous evidence of complex formation in the ternary systems. This conclusion follows from an elementary analysis of the nature of the liquidus surface of the ternary systems on the basis of the general principles of physicochemical analysis. Actually in such cases there will always be observed a decrease in the temperature depression on introducing the third component and this is

also an indication of complex formation. Another indication is liquid immiscibility in the system. Under conditions where it exists it is possible to speak of the formation of new particles with molecular fields different from those of the initial components. It figures often in binary systems (*cf.* Table 3), and in the ternary ones it is observed in mixtures of RbCl and TlBr with $AlBr_3 + C_6H_6$.[94,95]

The composition of the complexes existing in the solutions considered is unknown, generally speaking. Cryoscopic, ebullioscopic[11], and refractometric[123] investigations have been carried out in such a way that only complex formation and not the composition of the complexes could be shown. A series of complexes was separated (Table 6) by direct evaporation of the solvent from the mother-liquor previously saturated with MX_n. It is evident from Table 6 that the ratio $MX_n : AlBr_3 = 1$ is observed, as a rule, independently of the solvent.

Taken as a whole, Table 6 shows a quite wide generality in the properties of the ternary systems. The individual differences which exist are more quantitative than qualitative in nature.

The electrolysis results, obtained over a range of compositions to which the data of Tables 4 and 5 relate can be generalised as follows. For the halides of Ag, Cu, Tl, and the Group V metals, in all solvents these metals are deposited on the cathode. For other metals and ammonium in all solvents except $PhNO_2$ and $MeNO_2$, aluminium is deposited on the cathode at $MX_n : AlX_3 \leqslant 0.6$; with $0.6 < MX_n : AlX < 1.0$, aluminium and alkali metal are deposited on the cathode; at $1.0 \leqslant MX : AlX_3$, only alkali metal is deposited (possibly, with traces of aluminium)[11,12]. From $PhNO_2$ and $MeNO_2$ at all values of the $MX_n : AlX_3$ ratio only alkali metal is deposited; tarring occurs at the cathode with ammonium halides, as in the AlX_3–Slv binary mixtures. There are departures from this rule: in the electrolysis of solutions of RbCl and CsCl in $AlCl_3$–$MeNO_2$ cathodic deposition of metal is not observed[91]; deposition of aluminium from solutions of alkali metal or ammonium halides in $AlBr_3$ + EtBr occurs on using platinum anodes only when the $AlBr_3$ concentration in the solution is above 40 wt.%, and at lower concentrations it occurs only on aluminium anodes[102].

In general the cathode material affects only the quality of the deposits but cases are known where the material of the cathode has a more pronounced effect on the process. Thus from solutions of AgX and CuX in $AlBr_3$–EtI silver is not deposited on iron or aluminium but is deposited on copper and platinum, and copper is deposited on all the metals mentioned[78].

The anodic processes have been studied rather less fully. More or less reliable results obtained by chemical analysis of the deposits formed on silver anodes are given in Table 7. One of the difficulties here is the solubility of silver halides in the solutions studied.

An interesting comparison of the results of electrolysis of ternary solutions and melts of the composition $MX_n.2AlBr_3$ and $MX_n.AlBr_3$ was made by Gorenbein and Abramova[128] for M = Li, Na, K, Zn, Pb, Sb, and X = Cl, Br. From melts of mixtures with alkali metal halides aluminium was deposited at low current density, M plus aluminium at high; M is deposited from melts of the remaining salts. Hence the melts behave similarly to solutions in oxygen-free solvents.

It is notable that deposition of alkali metals from ternary solutions in $PhNO_2$ and $MeNO_2$ is not remarkable, since it is known that Li, for example, is deposited in the electrolysis of solutions of LiI in $PhNO_2$, $MeNO_2$, and Et_2O.[129]

Since the decomposition potentials were determined with needle-shaped platinum electrodes and since the electrolytes had random composition and as a rule the electrode

TABLE 6. Complexes separated from solutions in organic solvents.

Solvent	Complex	M.p., °C*	M.p. according to equilibrium diagram, Ref. 82, °C	Reference
Ethyl bromide	$LiBr.AlBr_3$	192	195	124
Nitrobenzene	$LiBr.2AlBr_3.2PhNO_2$	63**	–	125
Benzene	$KCl.AlBr_3.8C_6H_6$	143	171	93
Benzene	$KBr.AlBr_3.nC_6H_6$	187	191.5	93
Chlorobenzene	$KBr.AlBr_3$	173	191.5	126
Benzene	$KI.AlBr_3.nC_6H_6$	120–155***	–	93
Benzene	$TlBr.AlBr_3.2C_6H_6$	182.5	210	95
Ethyl bromide	$2AgBr.3AlBr_3$	180–185***	does not exist	124
Ethyl bromide	$AgBr.AlBr_3$	175	215	126
Ethyl bromide	$CuBr.AlBr_3$	241	does not exist	124
Benzene	$CuBr.AlBr_3$	239	does not exist	125
Toluene	$CuBr.AlBr_3.PhMe$	130–140**	–	125
Benzene	$(BiBr_3.AlBr_3)_2$	–	155	119

* The solvent contained in the complexes distils off on approaching the melting points.

** Melts without loss of solvent.

*** Decomposes in melting.

TABLE 7. Liberation of halogen at the anode.

Binary system	Third component	Halogen liberated	Reference
$AlCl_3$–$PhNO_2$	$SbBr_3$	$1Cl_2 + 5Br_2$	53
$AlBr_3$–C_6H_6	KCl	Cl_2	93
	RbCl	Br_2	127
	NaI	I_2*, $I_2 + Br_2$	11
	KI	I_2	93
$AlBr_3$–PhMe	LiI	Br_2	12
	NaI	I_2*, $I_2 + Br_2$	12
	KI	Br_2	12
$AlBr_3$–C_6H_4Me	LiI	Br_2	12
	NaI	I_2*, $I_2 + Br_2$	12
	KI	I_2*, $I_2 + Br_2$	12
$AlBr_3$–$PhNO_2$	LiCl	Br_2	97
	KCl	Br_2	97
	RbCl	Br_2	97
	NH_4Cl	Cl_2	98
	$SbCl_3$**	$Cl_2 + Br_2$	11
	NaI	$I_2 + Br_2$	99
	NH_4I	I_2	98
$AlBr_3$–EtI	AgCl	I_2	78
	CuCl	I_2	78
	AgBr	I_2	78
	CuBr	I_2	78
	AgI	I_2	78
	CuI	I_2	78

* At low current densities.

** In melts (*cf.* Table 3) and in solution in PhCl complete exchange of anions takes place between $AlBr_3$ and $SbCl_3$ with formation of $AlCl_3$ and $SbBr_3$.[35]

products were not analysed, the decomposition potentials explain little and we do not consider them here, except for two special cases: (1) the determination of decomposition potentials over a wide range of compositions showed that they are strongly dependent on composition[11,100,130]. Judging from these results the deposition of an alkali metal from solutions in EtBr (the sole case of an oxygen-free solvent studied by this method) is possible not only at high concentrations but also at great dilutions: $AlBr_3$: EtBr = = 0.006, MX : $AlBr_3$ = 0.05;[100] this conclusion was not checked by analysis of the electrode products; (2) the decomposition potential in MX–$AlBr_3$–EtI mixtures is almost independent of MX and corresponds to that calculated for AlI_3.[102]

Hence in the electrochemical properties of ternary mixtures attention is again drawn not to individual particular differences but to definite generality in the properties.

2. Hydrogen halides–aluminium halides–solvent. That compounds are formed in the AlX_3–Ar–HX systems has long been known[131], as has been the existence in them of quite high electrical conductivity[132,133], in certain instances reaching 0.01 Ω^{-1} cm^{-1}.[134] Subsequent investigations showed[71,105,135-138] that the most stable compounds of this type under normal conditions have the compositions $Ar.HX.Al_2X_6$ and $(3Ar).HX.Al_2X_6$.

In the electrolysis of C_6H_6–HBr–$AlBr_3$ and PhMe–HBr–$AlBr_3$, H_2 is liberated at the cathode and an amount of solvent equivalent to it is collected; a dark product or crystals of $AlBr_3$ (anodes of Pt or Al)[132,133] are formed on the anode. In the electrolysis of xylene solutions of HX–AlX_3 (X = Cl, Br) with platinum anodes aluminium is not deposited; when aluminium anodes are employed aluminium and hydrogen are released together, tar being formed in the electrolyte during the electrolysis process[139]. It is impossible to exclude the possibility that in this case molecules of solvent split off with side formation of aluminium sesquihalides. The introduction of metal halides into a system with liquid immiscibility somewhat reduces the electrical conductivity of the lower layer but the results of the electrolysis are what they would be if the system did not contain HX. In toluene and xylene the introduction of metal halides leads to complete or partial disappearance of liquid immiscibility[134,140,141].

In connection with systems containing HX it is interesting to note the behaviour of the complex $AlBr_3.H_2S$ in C_6H_6. It is readily soluble and a solution containing 53 wt.% of the complex has $\kappa = 3 \times 10^{-4}$ Ω^{-1} cm^{-1}. On electrolysing such a solution hydrogen is liberated at the cathode and bromine and a deposit of unknown composition appears at the anode[146].

3. Interhalogen compounds–aluminium halides–solvent. The electrolysis of solutions and the study of transport numbers showed that from mixtures of ICl–$AlCl_3$ and IBr–$AlBr_3$ with $PhNO_2$ iodine is liberated at the cathode, whereas at the anode Cl_2 (or Br_2 appropriately) appears at the start of the electrolysis, and after some time the same halogens with iodine as impurity. The presence of iodine in the anodic products is explained, as in the binary systems, by reduction of I_2 at the cathode. The anode space is enriched in aluminium and chlorine (or bromine)[111,114]. These data, together with the results of thermal analysis of the IX–AlX_3 systems allowed[89] a formula of the type I^+ $(AlX_4.nIX)^-$ to be proposed for the complexes.

4. Quaternary ammonium salts–aluminium halides–solvent. Very interesting results, especially in comparison with those described above were obtained in investigating EtPyBr–$AlCl_3$ melts and their solutions in organic solvents[143,144]. Molten ethylpyridinium bromide is a good conductor and in the electrolysis of the melt bromine separates at the anode; at the cathode the $(EtPy)^+$ ions are reduced with the formation, probably, of diethyldihydrobipyridyl. In the EtPyBr–$AlCl_3$ system a 1 : 1 compound, m.p. 88°, was observed by thermal analysis; the composition of the eutectics practically coincided with the compositions 2EtPyBr + $AlCl_3$ (45°) and EtPyBr + + 2$AlCl_3$ (-40°). On electrolysis of mixtures containing < 50 mole % $AlCl_3$, $(EtPy)^+$ is discharged at the cathode, and with 50–77 mole % $AlCl_3$ good deposits of aluminium are obtained. Electrolysis of a solution of this mixture in benzene, toluene, or xylene (the aromatic hydrocarbon was added until the appearance of a second layer) showed the same relationship but the optimal limits of the $AlCl_3$ concentration were narrowed to 50–63%. At $AlCl_3$ concentrations above 63%, at the cathode there was deposition of aluminium and simultaneously separation of $AlCl_3$ crystals. On maintaining the optimum concentration of $AlCl_3$ the quality of the deposits was better than in the melt but the permissible current density was higher (0.2 A dm^{-2} and up to 2 A dm^{-2}). Investigation of the ionic transfer in a benzene solution of a mixture with EtPyBr : $AlCl_2$ = 1 showed that the concentrations of chlorine, aluminium, and bromine in the anodic space rose in the proportions 2.85 : 0.92 : 3.10. This and the results of the electrolysis suggested that the decomposition scheme was:

$$EtPyBr \cdot AlCl_3 \rightleftarrows [EtPy]^+ + [AlCl_3Br_2]^-.$$

Good results in electrolysis were also given by solutions in PhCl, Et_2O, RX, and certain other solvents.

Very pure aluminium deposits were obtained from Et_4NBr + $AlBr_3$ melts at $D_C \simeq 7$ A dm^{-2} (the precise composition of the mixture is not given)[30,145].

IV. ELECTROLYTES BASED ON ORGANOALUMINIUM COMPOUNDS

Organoaluminium compounds in the pure liquid state have $\kappa < 10^{-7}$ Ω^{-1} cm^{-1}.[147] However, even about 40 years ago it was established that the complexes $NaAlEt_4$, $Et_4NI.AlEt_3$, and $(iso\text{-}C_5H_{11})_4NI.AlEt_3$, liquids at room temperature, have $\kappa = 10^{-3}$–10^{-4} Ω^{-1} cm^{-1}.[148] Within the last decade compounds of this type were rather widely studied by Ziegler and coworkers[150-154]. It was found preparatively that the alkali metal halides form 1 : 1 complexes with AlR_3‡, some of these complexes being able to add on a second AlR_3 molecule to form $MX.2AlR_3$. The electrical conductivity of the 1 : 2 complexes, for example, is approximately two orders greater than that of the 1 : 1 complexes and reaches 10^{-2} Ω^{-1} cm^{-1}. Investigation of the stability of the complexes in relation to the removal of AlR_3 in a vacuum, the extraction of AlR_3 by heptane (an indifferent solvent) and to the action of such complex-forming agents as Et_2O and Me_3N, showed that the stability of the 1 : 1 complexes is appreciably greater than that of the 1 : 2 complexes. The general rule of stability, established by Ziegler *et al.*[154], both for the 1 : 1 and 1 : 2 complexes can be formulated very

‡ In this section the symbol R denotes aliphatic radicals.

briefly: the stability of the complexes decreases with a decrease in the ionic radius of the alkali metal cation, with an increase in the ionic radius of the halide ion, and with an increase in the length of the chain of the radical R; first the ability to form 1 : 2 complexes is lost, and then 1 : 1 complexes. The experimental results on the existence of complexes as determined by these conditions is shown in Table 8, where the sign + denotes the formation of 1 : 1 complexes, ++ 1 : 1 and 1 : 2 complexes, and - no complexes. Table 9 shows similar results for the complexes of $AlEt_3$ with alkali metal hydrides and halides. Analogous complexes are formed with the salts of quaternary ammonium bases.

The electrically conducting 1 : 1 complexes were obtained also from MX (X = Cl, Br, I) and AlR_nX_{3-n} (X = F, Cl, n = 1, 2).[154-157] In the case of MF, exchange of halogen takes place[152]:

$$MF + AlR_2X \rightarrow MX + AlR_2F.$$

The tendency to complex formation with MX is expressed by the series $AlEt_3 < AlEt_2Cl < AlEt_2Br < AlEtCl_2$, which agrees with a series for the tendency to complex formation with oxygen- and nitrogen-containing organic Lewis bases[158]. The dependence of the stability of the complexes on the nature of MX is the same as in the preceding case.

The complexes of AlR_2H with MX and MH also conduct electricity but have certain peculiarities[155,159]. Thus $NaAlEt_4$ does not mix with $AlEt_3$, but the complex $NaAlEt_4 . AlEt_2H$ is formed, which is capable of dissolving another 2–3 moles $AlEt_2H$. Investigation of the dependence of electrical conductivity on composition in the $NaAlEt_4$–$AlEt_2H$ and $NaH.AlEt_3$–$AlEt_3$ systems showed their identity, which made it possible to ascribe to this complex the schematic formula $NaH.2AlEt_3$. The existence of a complex richer in $AlEt_2H$ has also been established, namely $NaH.2AlEt_3 . AlEt_2H$. Similarly, $NaF.2AlEt_3$, which does not dissolve $AlEt_3$, dissolves 2–3 moles $AlEt_2H$. The production of mixed complexes of the type $MX.AlR_3.AlR_3'$ and $MX.nAlR_3 . mAlR_2X$ has also been described. It should be noted that although $NaAlEt_4$ and $AlEt_3$ are immiscible when pure, they are able to give a mixed solution in a small amount of toluene.

Several of the complexes described above were electrolysed[155,160-163]. Some examples are shown in Table 10.

Analogous results on the cathodic process were obtained also for the complexes listed in Table 10 in very different solvents: ethers, tertiary amines, tetrahydrofuran, dimethylaniline, dioxan, pyridine, toluene, benzene, etc.

The general rule is that in the electrolysis of fused 1 : 1 complexes or their solutions, there is codeposition of alkali metal and aluminium, the yield of alkali metal increasing with cathodic current density, D_c, and at $D_c > 1$ A dm^{-2} almost pure alkali metal is deposited. On the other hand in the case of the 1 : 2 complexes aluminium is deposited alone at all current densities studied. The latter is not true, however, for all mixtures. Thus in the electrolysis of $NaF.2AlEt_3 + AlEt_2H$ mixtures it was found[159] that at D_c = 5 A dm^{-2} sodium is not codeposited, but at 10 A dm^{-2} the cathodic deposit contains sodium as impurity, rapidly dissolving when the current is switched off.

The anodic process depends on the anode material. When hydride hydrogen does not enter into the composition of the complex, then on using insoluble anodes there is decomposition of the radicals R accompanied by the formation of corresponding organic products (CH_4 and C_2H_6 in the case of R = C_2H_5). When soluble anodes are employed the corresponding alkylmetals are formed, which pass into solution, or if there is immiscibility, with formation of a liquid layer; for example, this occurs on using aluminium anodes in electrolytes of the $NaAlEt_4$ type, in the $NaAlEt_4$ + + $KAlEt_4$ eutectic mixture, or on using lead anodes in $NaF.2AlEt_3$ electrolyte[160,164]. If one believes a patent[165], then such a process is general for the metals of Periodic Groups IA, IIA, III, and IVB. Ziegler and coworkers[161] propose for this process the scheme:

$$AlEt_4^- - e \rightarrow AlEt_4 \rightarrow AlEt_3 + Et, \qquad (14)$$

with subsequent reactions of the free radical with the metal of the anode. The formation of $PbEt_4$ also occurs in the electrolysis of a solution of $AlEt_3$ in Et_2O with a lead anode[166].

TABLE 8.

R	F⁻				Cl⁻				Br⁻			
	Na+	K+	Rb+	Cs+	Na+	K+	Rb+	Cs+	Na+	K+	Rb+	Cs
C_2H_5	++	++	++	++	–	+	+	++	–	–	+	+
C_3H_7	++	++	++	++	–	–	+	++	–	–	–	+
iso-C_4H_9	++	++	++	++	–	–	+	+	–	–	–	+
n-C_4H_9	++	++	++	++	–	–	+	+	–	–	–	+
n-C_5H_{13}	–	++	++	++	–	–	–	+	–	–	–	–
iso-C_8H_{17}	–	++	++	++	–	–	–	+	–	–	–	–
n-C_8H_{17}	–	++	++	++	–	–	–	+	–	–	–	–

TABLE 9. Existence of complexes between MH and MX and $AlEt_3$.

Cation	H⁻	F⁻	Cl⁻	Br⁻	I⁻
Li^+	+	–	–	–	–
Na^+	+	+	–	–	–
K^+	+*	+	+	–	–
Rb^+	+*	+	+	+	
Cs^+	+*	+	+	+	
$(C_2H_5)_4N^+$	+*	+*	+	+	–

* These cases have not been verified experimentally.

TABLE 10. The cathodic process during the electrolysis of aluminium complexes of organic compounds.

System	Cathodic process during electrolysis
$Al(C_2H_5)_3.NaC_2H_5$	codeposition of Na and Al; current efficiency of Na deposition increases with D_c
$NaC_2H_5.Al(C_2H_5)_3 + Al(C_2H_5) + + n$PhMe	deposition of Al
$Al(C_2H_5)_2Cl.KCl$	codeposition of K and Al
$NaF.Al(C_2H_5)_3$	codeposition of Na and Al
$NaF.2Al(C_2H_5)_3$	deposition of Al
$NaAl(C_2H_5)_4$–$KAl(C_2H_5)_4$ eutectic	deposition of Na at the Hg cathode

TABLE 11. Dependence of the composition of the anodic gases on the material of the anode. $NaF.2AlEt_3 + AlEt_2H$, 24.6 mole %, 80°, $D_a = 10$ A dm^{-2}.

Anode material	H_2	C_2H_6	C_4H_{10}	C_2H_4
Ag	91.2	8.0	[illegible]	—
Cu	93.5	6.2	[illegible]	—
Brass	79.0	17.6	[illegible]	—
Au	44.0	40.2	[illegible]	2.2
Pd	17.3	68.7	[illegible]	[illegible]
Pt	2.8	51.9	[illegible]	[illegible]
Ni	4.7	55.2	[illegible]	[illegible]
F	3.8	39.4	[illegible]	17.3
C	18.0	55.2	[illegible]	17.8

TABLE 12. Dependence of the composition of the anodic gases at a copper anode on the temperature, anodic current density D_a [not given (Ed. of Translation)], and $AlEt_2H$ concentration.

Temperature, °C	$Al(C_2H_5)_2H$, mole %	H_2	C_2H_6	C_2H_4	C_4H_{10}	C_4H_8
80	21.0	72.6	21.7	4.1	1.4	0.2
80	24.6	93.5	6.2	—	0.3	—
80	33.0	98.0	2.0	—	—	—
80	44.1	99.6	0.4	—	—	—
100	12.0	33.8	53.4	12.2	0.3	0.3
100	19.8	61.7	32.1	5.7	0.3	0.2
100	21.0	88.9	8.9	1.0	1.2	—
100	24.6	96.2	3.2	0.4	0.9	0.3
100	28.8	98.5	1.5	—	—	—
120	12.0	74.2	18.7	5.0	1.5	0.6
120	15.6	93.8	4.5	1.5	0.1	0.1
120	20.7	98.0	1.6	0.2	0.1	0.1

When the complex contains hydride hydrogen the anodic process with insoluble anodes is considerably complicated. The composition of the anode gases appears to be strongly dependent on the anode material, the amount of hydride-containing component, the anodic current density, the temperature, and the agitation of the solution at the anode. Tables 11 and 12 give results of investigation of $NaF.2AlEt_3 + nAlEt_2H$ electrolyte[159]. The primary process must be considered to be the common discharge of H^- and Et^- (from complex anions). On considering the possible secondary reactions proposed by the authors[159], the percentage of hydrogen formed as a result of discharge can be calculated. Such calculations were made and showed that this quantity is the greater the higher the energy level of the unfilled inner orbitals of the metals. For copper, not having unfilled orbitals, the percentage of hydrogen discharged is 96.5%. There is also a symbathic relation between the amount (percentage) of hydrogen discharged and the hydrogen overpotential in aqueous solutions of these metals.

V. THE NATURE OF THE IONS IN NON-AQUEOUS SOLUTIONS OF ALUMINIUM COMPOUNDS

Various authors have expressed different opinions regarding the nature of the ions in non-aqueous solutions of aluminium compounds. These opinions are based, mainly, on electrolysis results and the study of transport numbers. Clearly, however, the use of these data alone cannot give an unambiguous answer to the question proposed, especially if there coexist in the solution several species of ions or if the nature of the ionisation changes with concentration. Only in certain relatively simple cases, namely, for the solutions IX + AlX_3 + $PhNO_2$ and EtPyBr + $AlCl_3$ + C_6H_6, is it possible, in the authors' opinion, to agree without special reservations. At the same time all the material given above relates to compounds of aluminium of the general formulae $AlRR'_{n-3}$, where R and R' are oxygen-free radicals. This makes it possible to anticipate a certain generality in the properties of all solutions, and, although also with caution, to use the method of analogies. Both for the basis of the analogy, and for judging the correctness of one or another hypothesis about the structure, thermochemical data are necessary. These are given below, collected for the systems considered above.

A. Thermochemical Data

We have used handbook data[167-170] in all the thermochemical calculations and subsequently the absence of a reference for the quoted thermochemical or thermodynamic quantity means that it has been taken from one of these sources.

Table 13 gives the heats of reaction of AlR_3 with various substances. They have been recalculated from the original data to the most comparable conditions, using handbook quantities. In addition to the assumptions mentioned in the notes to Table 13, the heats of mixing of AlR_3 with indifferent solvents have been disregarded.

It is evident from Table 13 that the strength of the bonds with one and the same ligand increases in the series:

$$AlEt_3 < AlCl_3 < AlBr_3, \quad (15)$$

and for a given AlR_3 with different ligands, in the order of listing in the table. This confirms and extends the conclusion which was drawn from various studies[40,178-181] on

TABLE 13. Heats of reaction ($-\Delta H$) for AlR_3(gas) + B(gas) = = AlR_3.B (solution in indifferent solvent), kcal per mole AlR_3.

AlR_3	Component B									References
	benzene	methyl bromide	ethyl bromide	nitro-benzene	diethyl ether	benzo-phenone	benzalde-hyde	quinoline	pyridine	
$AlEt_3$	—	—	—	—	37.7	—	—	53.1	48.4	147
$AlCl_3$	13.4*	—	—	46.4 (50.6)*	48.9	57.4	62.6	72.4**	75.0**	64,171—174
$AlBr_3$	14.8***	28.5*	32.8*	57.8*	—	61.3	67.1	—	88.4	68,172—176

* Solution in B.

** The heat of fusion of the complex was taken as 5 kcal $mole^{-1}$ by analogy with the heat of fusion of $Al_2Br_6.C_6H_6$, calculated from results[68,172], neglecting the heat of mixing of this liquid complex with benzene.

*** Solution in C_6H_6. Since $AlBr_3$ is dimeric in C_6H_6, the calculation was made for the reaction:

$$\frac{1}{2}Al_2Br_6(gas) + nC_6H_6(gas) = \frac{1}{2}Al_2Br_6.C_6H_6(solution).$$

The heat of the reaction $AlBr_3$(gas) + KBr(gas) = $AlBr_3$.KBr(liquid) is[177] 87.1 kcal per mole $AlBr_3$.

The heat of fusion of the complex was taken as 5 kcal $mole^{-1}$.

the existence of complexes between AlR_3 and Slv_1 in Slv_2 and between AlR_3 and Slv_2 in Slv_1 in respect of the stability of certain complexes of $AlBr_3$ and $AlCl_3$:

$$\text{for } AlCl_3(NH_3,\ Me_3N,\ Py) > PhNO_2 \gtrsim PhCN^{178}, \quad (16)$$

$$\text{for } AlBr_3(Py,\ MeNO_2,\ Et_2O) > PhNO_2 > SbBr_3 > (EtBr,\ C_6H_6)^{40,178-181}. \quad (17)$$

It was stated above that aluminium is not deposited from binary mixtures of its halides with nitrobenzene and nitromethane, but is deposited from mixtures with ether and KBr. It is also known that good aluminium deposits are obtained from $AlBr_3$–Py mixtures[182]. Hence it also follows from the data of Table 13 that for the possible deposition of aluminium the reduction potential of the ligand is more important than the energy of the bond with the ligand: easily reducible nitrobenzene gives rise to tar formation at the cathode but the more stable pyridine permits deposition of the metal.

Since heats of the aggregation changes enter into the thermochemical cycle, Table 13 is supplemented by Table 14, giving the heats of reaction between the same substances in other states of aggregation§. Comparison of Tables 13 and 14 shows that in the energetic relations complexes of AlR_3 with organic ligands are analogous to complexes with inorganic ligands.

For certain solvents there are no data enabling recalculations to be made analogous to those carried out in compiling Tables 13 and 14. For these, experimental results on heats of solution are given in Table 15, which also includes for comparison some solvents from the previous table. The heats of solution of $AlCl_3$ in benzene and of $AlBr_3$ in benzene, toluene, and dibromoethane are close to the heats of fusion of these salts (8.5 and 2.7 kcal × × $mole^{-1}$ respectively), which is evidence of the weak interaction in benzene and toluene, where the aluminium halides at these concentrations are dimers, and of the considerably greater interaction with dibromoethane,

TABLE 15. Heats of solution of crystalline aluminium and antimony halides, kcal $mole^{-1}$.

Substance	Solvent						Reference
	benzene	toluene	nitrobenzene	ethyl bromide	sym.-dibromoethane	ethyl iodide	
$AlCl_3$	+9.1***		−12.22*				64,172
$AlBr_3$	+1.4	+0.77	−22.3*	−0.95**	+2.15**	−1.85**	172,175,186
$SbCl_3$			−0.72*				172
$SbBr_3$			+0.85*				172

* At a concentration of 1 mole salt per 100 moles solvent, 15°. This quantity is reported[99] to be 16.01 kcal $mole^{-1}$ at a significant $AlBr_3$ concentration.

** At infinite dilution, linear extrapolation[175], ~ 6°.

*** In saturated solution, 25°. In the remaining cases the concentration was ~ 10 wt.% salt, 15°.

TABLE 16. Heats of formation of the complexes in the solid state, $MX(cryst.) + nAlX_3(cryst.) = MX.nAlX_3(cryst.)$.

Composition of complex	$-\Delta H$, kcal $mole^{-1}$	Reference	Composition of complex	$-\Delta H$, kcal × × $mole^{-1}$	Reference
$LiCl \cdot AlCl_3$	2.66	188	$KCl \cdot 2AlBr_3$	16.9	188
$NaCl \cdot AlCl_3$	6.42	188	$LiBr \cdot AlBr_3$	7.9	177
$KCl \cdot AlCl_3$	12.17	188	$LiBr \cdot 2AlBr_3$	4.9	177
$NaBr \cdot AlCl_3$	3.28	188	$NaBr \cdot AlBr_3$	10.1	177
$KBr \cdot AlCl_3$	10.39	188	$NaBr \cdot 2AlBr_3$	7.0	177
$NH_4Cl \cdot AlBr_3$	16.59	187	$KBr \cdot AlBr_3$	16.0	177
$NH_4Cl \cdot 2AlBr_3$	17.36	187	$KBr \cdot 2AlBr_3$	13.9	177
$NH_4Br \cdot AlBr_3$	13.45	187	$NaI \cdot 2AlBr_3$	7.86	99
$NH_4Br \cdot 2AlBr_3$	15.62	187	$NH_4I \cdot AlBr_3$	11.82	187
$NH_4Br \cdot 3AlBr_3$	16.15	187	$NH_4I \cdot 2AlBr_3$	12.24	187
$NaCl \cdot AlBr_3$	9.93	188	$AgBr \cdot AlBr_3$	13.9	177
$NaCl \cdot 2AlBr_3$	9.15	188	$AgBr \cdot 2AlBr_3$	6.9	177
$KCl \cdot AlBr_3$	14.6*	188			

* Results poorly reproducible (note by authors[188]).

TABLE 14. Compilation of heats of reaction of Al_2R_6 with different ligands.

Reaction	$-\Delta H$, kcal $mole^{-1}$	Reference
$\frac{1}{2}Al_2Br_6(cryst.) + \frac{1}{2}C_6H_6(liq.) = \frac{1}{2}Al_2Br_6.C_6H_6(cryst.)$	1.0	68
$\frac{1}{2}Al_2Br_6(cryst.) + KBr(liq.) = AlBr_3.KBr(cryst.)$	20	177
$\frac{1}{2}Al_2Br_6(cryst.) + (Ph)_2CO(liq.) = AlBr_3.(Ph)_2CO(cryst.)$	24.2	176
$\frac{1}{2}Al_2Cl_6(cryst.) + C_9H_7N(liq.) = AlCl_3 + C_9H_7N(cryst.)$	36.0	171
$\frac{1}{2}Al_2Cl_6(cryst.) + C_5H_5N(liq.) = AlCl_3.C_5H_5N(cryst.)$	42.6	174

where the association is ~ 50% (Table 2), and consequently, during dissolution part of the heat of dissociation of the dimer is expended¶. The interaction of antimony halides with nitrobenzene is much weaker than that of aluminium halides and this is one of the reasons making it possible to obtain deposits of antimony from nitrobenzene solutions without reduction of the solvent.

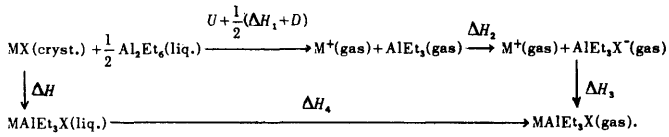
Heats of formation of complexes of MX and NH_4X with AlX_3 are collected in Table 16. The complexes for the thermochemical measurements were made by melting appropriate stoichiometric proportions of the components together. According to Table 3, not all of the complexes listed in Table 16 are observed in investigating the equilibrium diagrams, and for some systems equilibrium diagrams are not available. In these cases the authors cited

§ Direct calculation of the bond energies of AlR_3 with ligands is impossible owing to the absence of data on the heats of sublimation of the complexes. Judging from the heats of evaporation of such compounds as, for example, $AlMe_2Cl.Me_3N$ (11.0 kcal $mole^{-1}$ at 105°[167]) and $AlCl_3.NH_4Cl$ (37.5 kcal $mole^{-1}$ at 290–370°[185]), the heats of sublimation at 25° for different complexes are large in absolute value and differ considerably from one another, which excludes the possibility of their reasonable evaluation.

¶ The heats of solvation of $AlBr_3$ in bromoform, dibromoethane, MeI, EtBr, and EtI have already been calculated[175] as the sum of the heats of solution at infinite dilution and the heat of fusion of $AlBr_3$. This is incorrect, since for an unassociated substance the heat of sublimation, not the heat of fusion, should be taken and for an associated one, such as Al_2Br_6, its state in solution at infinite dilution must be considered and a corresponding fraction of the heat of dissociation of the dimer into the monomer included.

in Table 16 considered that such complexes exist by analogy with known ones, sometimes despite the objective information of the equilibrium diagram. In the absence of other data the heats of formation in such cases should be considered to belong not to individual compounds but to the corresponding mixtures. The information in Table 16 shows that the heats of formation of the 1 : 1 compound with the same component are greater for $AlBr_3$ than for $AlCl_3$, *i.e.* the same as in the case for organic ligands (*cf.* Table 13). In the case of the 1 : 1 compounds for MX the heats of formation increase with a decrease in the crystal lattice energy, and for NH_4X the reverse dependence is observed, but here the equilibrium diagrams for NH_4Cl and NH_4I are unknown. The heats of formation of the complexes (or mixtures) were used for calculations of the decomposition potentials by Thomson's formula[11,12]. Since the heats of solution of the complexes (mixtures) are comparable or exceed (*cf.* Table 19) their heats of formation, such a calculation is inadequate and the conclusions based upon it are not valid. This is one of the reasons why we say almost nothing about decomposition potentials (a second reason is the unreliability of the methods for their determination, which we have already mentioned).

Ziegler *et al.*[154] attempted to obtain a rule for the stability of the MX. $AlEt_3$ complexes by thermochemical means. Certain assumptions were made for this purpose with which it is impossible to agree. Let us consider the thermochemical cycle:



The conditions for the stability of the complex in the liquid state will be

$$\Delta H = U + \frac{1}{2}(\Delta H_1 + D) + \Delta H_2 + \Delta H_3 - \Delta H_4 < 0, \qquad (18)$$

where U is the energy of the crystal lattice MX, ΔH_1 and ΔH_4 are the heats of vaporisation of the corresponding substances, D is the heat of dissociation of Al_2Et_6, and the significance of ΔH_2 and ΔH_3 is clear from the cycle. In the work of Bonitz[147] assumptions are made that: (1) $\frac{1}{2}(\Delta H_1 + D) = 10$ kcal; (2) $\Delta H_4 = 0$; (3) $\Delta H_2 \gg \Delta H_3$; (4) ΔH_2 is inversely proportional to the radii of the anions and by virtue of assumption (3) the same dependence also applies to $\Delta H_5 = \Delta H_2 + \Delta H_3$. Hence the condition for stability is obtained in the form.

$$\Delta H = U + 10 + \Delta H_5 < 0 \qquad (19)$$

and it is possible to calculate ΔH_5 for MX with different X, knowing its value for one salt. ΔH_5 for the KCl complex is taken as this standard, since $AlEt_3$ is quite unstable and $\Delta H \simeq 0$ is assumed for it.

As ΔH is a small difference between large quantities, it is not permissible to disregard the quantities ΔH_1 and ΔH_4. At 80°, $\Delta H_1 = 26$ kcal mole^{-1}; the value of D is unknown, but it is known that for Al_2Me_6 $D = 20.2$ kcal.[189] It is also known that Al_2Me_6 is completely associated in the vapour at 70° and in solutions, whereas Al_2Et_6 is only 12% associated at 150° and is incompletely associated in indifferent solvents, in particular, in C_6H_6 at a concentration of 0.1 mole % it decomposes completely into the monomer in 5 h.[189-191] We can therefore take $D \simeq 10$ kcal. Hence $\frac{1}{2}(\Delta H_1 + D) = 18$ kcal. ΔH_4 is unknown, but it can scarcely be less than 18 kcal (*cf.* the note on p. 130). Hence Eqn. (18) must be used, not (19). Furthermore, ΔH_2 and ΔH_3 are of the same order, therefore assumption (3) is invalid and consequently a basis for calculating ΔH_5 is lost. We require the values of ΔH_2 for the reaction

$$R^- + AlR_3 \rightarrow AlR_3R^- ,$$

and subsequently we will evaluate them. For this we must assume that $\Delta H_2 \simeq \Delta H_6/3$, where ΔH_6 is the heat of the reaction

$$Al(gas) + 3R(gas) \rightarrow AlR_3(gas).$$

These values of ΔH_2 are given in Table 17. For the formation of AlH_3 from the elements we took $T\Delta S \simeq 6$ kcal, by analogy with reactions of the same type[167], and used the value for the change in free energy in this reaction, -34 kcal mole^{-1}.[192] Now, taking $\Delta H = 0$ for KCl, we obtain $\Delta H_3 \simeq \Delta H_2$, despite arbitrary assumption (3). However, the main opinion of the authors, that under the other different conditions the dominating part is play by the energy of the crystal lattice, must be considered valid, as this follows from Eqn. (19).

According to X-ray analysis[193], at the nodes of the $NaAlCl_4$ crystal there are Na^+ ions and the tetrahedral $AlCl_4^-$ ions. This conclusion was drawn on the basis of infrared spectra of $KAlCl_4$.[194] The same conclusion followed for crystalline $LiAlH_4$ and its solutions in Et_2O, from studies of Raman spectra and infrared spectra[195], and conductimetric titration in ethereal solution[196]. This suggests that the formation of the AlR_4^- ion is a general phenomenon for all reactions of AlR_3 with MR, resulting in the formation of the compound MR. AlR_3. If this is so, then the crystal lattice energies of $MAlR_4$ must decrease as the radius of M increases. Table 18 gives the crystal lattice energies calculated from the data of Tables 16 and 17. As is evident, a fall in U actually occurs, which agrees with the assumption as to the ionic structure of the compounds $M^+[AlR_4]^-$. We note that the crystal lattice energy of $KClO_4$ (calculated by us from heats of solution[167] and hydration of ions[197]), which is constructed of K^+ ions and tetrahedral ClO_4^- ions, is 147 kcal mole^{-1}, which confirms the correctness of the evaluation of the values of ΔH_2. Assumptions

TABLE 17. Heats of the reactions $R^-(gas) + MR_3(gas) = MR^-(gas)$, ΔH_2, kcal × × mole^{-1}.

	AlH_3	$AlBr_3$	$Al(CH_3)_3$	$AsBr_3$	$SbBr_3$
$-\Delta H_2$	82	85	59	46	58

TABLE 18. Crystal lattice energy of MAlBr, kcal mole^{-1}.

Salt	$U + \Delta H_4$	U
$LiAlBr_4$	225	140
$NaAlBr_4$	212	127
$KAlBr_4$	202	117

about the ionic structure of organoaluminium complexes with MX are confirmed also by the decrease in melting point in the series of KCl. AlR_2Cl complexes with an increase in the radical length[157], which can be explained by a decrease in the Coulomb interaction in the lattice as the dimensions of one of the ions are increased. It is also possible to explain from the viewpoint of ionic structure why the halides AlX_3 do not form compounds with HX without the participation of a third component. If for MX U is introduced into Eqn. (19), then in the case for the analogous cycle with HX the ionisation energy for gaseous HX will be introduced; for HCl this is 331 kcal mole^{-1}, for HBr 321 kcal × × mole^{-1}, which exceeds U for the most stable MX crystal lattices by almost 100 kcal†. The presence of a third component makes it possible to compensate this outlay to the first order, evidently on account of interaction with a proton. Benzene and alkylbenzenes release ~ 25–30 kcal × × mole^{-1} on this account[71,199]. When the third component itself reacts strongly with AlX_3, then no compound is formed between HX and AlX_3, since a further additional expenditure of energy will be required for displacing the strongly bound ligand: thus HBr does not form complexes with $AlBr_3$ in nitrobenzene[200]. On the other hand, in the reaction of gaseous HBr with crystalline Al_2Br_3 and liquid PhMe with the formation of a liquid complex of probable composition $HBr.Al_2Br_6.3PhMe$ 10–30 kcal of heat are released[201] (accurate calculation is impossible on account of the indeterminancy of the composition of the complex and of the experimental conditions).

Tables 19 and 20 give the heats of solution of the $MX.2AlBr_3$ complexes in a series of solvents and MX salts in solutions containing 2 moles $AlBr_3$ per 1 mole MX in the same solvents. The concentrations of the working solutions were not given in the original papers, in any case they were not less than 10 wt.% calculated on $AlBr_3$. The authors note that at such concentrations the heat of solution depends on the concentration comparatively weakly. A distinctive feature is the sharply exothermic nature of the processes of dissolution of the complexes, especially in nitrobenzene. During dissolution in water, only the dissolutions of H_2SO_4 and $MgSO_4$ give comparable effects, -23 and -20 kcal mole^{-1} respectively. At the same time dissolution of crystalline

TABLE 19. Heats of solution of the crystalline complexes, $-\Delta H$, kcal per mole complex.

Composition of complex	Solvent			Reference	Melting point of complex, Ref. 82
	benzene	toluene	nitro-benzene		
$LiCl.2AlBr_3$			39.14	12	equilibrium diagram unknown
$LiBr.2AlBr_3$			50.46	12	131°
$LiI.2AlBr_3$			72.13	12	equilibrium diagram unknown
$NaCl.2AlBr_3$			29.55	12	55°
$NaBr.2AlBr_3$			31.07	12	105°
$NaI.2AlBr_3$			66.70	12	1 : 1, 177° (incongruent)
$KCl.2AlBr_3$	5.6	3.2	30.16	12, 187	83.5°
$KBr.2AlBr_3$	6.85	3.40	34.16	12, 177	95.8°

† The values of U for copper(I) halides given in a handbook[198] are too low by on an average 30 kcal mole^{-1}, for example, 198 kcal is given for CuBr, whereas the correct value (calculated from published data[167]) is 231 kcal mole^{-1}.

TABLE 20. Heats of solution MX(cryst.) + + $(2AlX_3 + n$Slv)(sol.) = (MX + + $2AlX_3$ + Slv)(sol.), $-\Delta H$, kcal per mole MX.

MX(cryst.)	$(2AlX_3 + n$Slv)(sol.)	$-\Delta H$	Reference
KCl	$2AlBr_3+nC_6H_6$	25.30	202
KBr	$2AlBr_3+nC_6H_6$	23.55	186
KCl	$2AlBr_3+n$PhMe	21.64	202
KBr	$2AlBr_3+n$PhMe	18.84*	*cf.* Table in 15
LiBr	$2AlBr_3+n$PhNO$_2$	23.34*	99
NaCl	$2AlBr_3+n$PhNO$_2$	6.68*	99
NaBr	$2AlBr_3+n$PhNO$_2$	6.05*	99
NaJ	$2AlBr_3+n$PhNO$_2$	43.69	99
KCl	$2AlBr_3+n$PhNO$_2$	15.04*	99
KBr	$2AlBr_3+n$PhNO$_2$	16.04*	99

* Calculated by us from data for heats of solution of $2AlX_3 + n$Slv, heats of formation of $MX.2AlX_3$ (Table 16) and heats of solution of $MX.2AlX_3$(cryst.) + nSlv (Table 19).

$AlBr_3$ in benzene and toluene is accompanied by endothermic effects (Table 15). This and the high electrical conductivity of the resulting solutions (Table 5), together with the insolubility of MX in benzene and toluene, make it possible, in our opinion, to suggest with a high degree of probability that the structure of the 1 : 2 complexes is ionic, with a comparatively low crystal lattice energy; the latter is shown particularly by their low melting points (Table 19). A striking fact is that the exothermic effects in the dissolution of KX in benzene and toluene are appreciably greater than in the dissolution of the same salts and NaX in nitrobenzene, the dielectric constant of which is approximately 15 times greater (Table 20). Evidently this can be explained only by the replacement of $PhNO_2$ by X in the coordination sphere of aluminium; in benzene and toluene such replacement does not cause trouble, on account of the low energy of interaction of the solvent with $AlBr_3$ (Tables 13–15). Nevertheless, the heats of solution of KX in toluene are somewhat less (in absolute magnitude) than in benzene, since the energy of interaction of toluene with $AlBr_3$ is somewhat greater than that for benzene (Table 15). The complexes with LiI and NaI are somewhat peculiar; possibly this is connected with the peculiarities of the solvation of the iodide ion.

B. Dissociation Schemes

1. Binary Systems. The most varied dissociation schemes have been suggested. One of these can immediately be shown to be improbable, the others require more detailed consideration. Thus, Wohl and Wertyporoch[203] have given a scheme for a dissociating complex of the form

$$[Al\cdot(BrEt)_n]^{3+}[AlBr_4]^-_3. \qquad (20)$$

The crystal lattice energy of $AlBr_3$ is 1266 kcal mole^{-1} (calculated by us from tabulated data[167,168]). The energy of interaction of aluminium with the ligand does not exceed 100 kcal per bond (*cf.* Tables 13 and 17). The usual coordination number of aluminium is 4, but compounds are known with coordination numbers 5 and 6,[174,204] therefore

we observe that $n = 6$. In the specific case (20), the difference $1266 - [(33 \times 6) + (85 \times 3)] = 813$ kcal must be balanced by the energy of formation of the ion pair (20), multiplied by the degree of association, plus the energy of solvation of its constituent ions multiplied by the degree of dissociation. Since the radii of the ions are large, evaluation of the compensation gives a quantity not exceeding 500 kcal. Hence the minimal deficit, $813-500 \simeq 300$ kcal, is still very large and the possibility of complexes of type (20) being formed must be rejected. A criticism of scheme (20) from a chemical viewpoint has been given by Korshak and Lebedev [206].

By studying the electrical conductivity of the MEt_2–Slv and MPh_2–Slv systems and the exchange activity in these same solvents between M^*Br_2 and MEt_2 (M = Mg, Cd), Strohmeier and Seifert [210] also concluded that the ions M^{2+} are not formed.

Table 21 shows proposed schemes of dissociation based on measurements of transport numbers and electrical conductivity, and on electrolysis results. Some of the data are derived from a brief review on the composition of ions in MX–AlX–Slv systems [207]. The existence of X^- ions is doubtful. Although the energy of solvation of these ions is unknown, it is still reasonable to consider that the total energy of addition of X^- to AlX_3 and solvation of AlX_4^- is greater (in absolute magnitude) than the energy of solvation of X^-. Furthermore, if the dissolution were to proceed by the scheme:

$$AlX_3 + p\,Slv \rightleftarrows [AlX_2 \cdot n Slv]^+ + [X \cdot m Slv]^- + (p - n - m)Slv, \qquad (21)$$

then it would be difficult to explain why halides MX, which are insoluble in solvent, Slv, dissolve in AlX_3 + Slv mixtures with strong exothermic effects (Table 20). The energy of the $X-Al_2X_6$ bonds is unknown. Evidently, one can with sufficient confidence consider $\Delta H_2 < -20$ kcal [presumably $-\Delta H_2 < 20$ kcal is intended (Ed. of Translation)]. Therefore it has to be confined to the assumption that probably both AlX_4^- and $Al_2X_7^-$ ions exist.

A very successful scheme for dissociation in AlX_3–Slv systems has been proposed [175,176,206,211]:

$$[AlX_2 \cdot 2Slv]^+ + AlX_4^-. \qquad (22)$$

The energy for removal of X^- from AlX_3 is unknown. For an estimate it can be taken as equal to the crystal lattice energy of the hypothetical crystal $AlX_2^+.X^-$, 250 kcal × × mole^{-1}, which is clearly much too high. The energy of interaction of AlX_2–2Slv is taken as 70 kcal (Table 13). Then the uncompensated part of the energy of process (22) is 250 - (70 + 85) = 95 kcal. With complete dissociation the total energy of solvation of ions (22) to completion may be of the same order, which permits process (22) to be considered completely permissible.

We can now proceed to some generalisations for binary systems.

(a) *Self-dissociation of AlR_3.* The most probable scheme is:

$$Al_2Br_6 \rightleftarrows AlR_2^+ + AlR_4^- \quad \text{or} \quad \frac{3}{2}\,Al_2R_6 \rightleftarrows AlR_2^+ + Al_3R_7^-. \qquad (23)$$

In the absence of a second component this process is energetically unfavourable, which also determines the low κ of pure liquid Al_2R_6. Confirmation of dissociation with formation of AlR_2^+ and AlR_4^- is found by Bonitz [147] in the reaction:

$$NaAlR_4 + BrAlR_2 \rightarrow \underset{\downarrow}{NaBr} + AlR_3 \cdot AlR_4 \rightleftarrows \underset{\downarrow}{NaBr} + Al_2R_6.$$

In addition he considers that the cations, which contain aluminium, are disclosed by polarographic methods; details of this investigation are not given.

(b) *Dissociation of Complexes.*

$$MR - AlR_3\,(M = M^+, NR_4^+, EtPy^+, X^-; R = H^-, X^-, R^-),$$

$$MR + AlR_3 \rightleftarrows M^+ + AlR_4^- \quad \text{or} \quad MR + Al_2R_6 \rightarrow M^+ + Al_2R_7^-\ddagger. \qquad (24)$$

In a considerable number of studies (*cf.*, for example, Refs. 11, 98, 207, and 211) one of the decisive facts in support of the existence of aluminium-containing cations was considered to be the deposition of aluminium on the cathode during electrolysis. Nevertheless, it is well known that often cathodic deposition of a metal takes place from an anion, especially from a complex one (for example, in copper plating or silver plating from cyanide electrolytes; *cf.* also Ukshe [212]), so that the fact of cathodic deposition of metal is still not evidence of the existence of corresponding cations. Actually it is quite difficult to prove the existence of AlX_n^{+3-n} cations in the MX. AlX_3 complexes, and meanwhile at *low* current densities aluminium is deposited, and at *high*, M plus aluminium.

Elementary electrostatic calculations of the stability of ions of various configurations in the MX–AlX_3 systems leads to a conclusion concerning the possibility of existence of the ions M^+, AlX_4^-, and $Al_2X_7^-$. [213]

The formation of AlR_4^- ions is confirmed also by the reaction of replacement of ether in the complex $Et_2O.AlEt_3$ by the ethyl ion:

$$Et_2O \cdot AlEt_3 + NaEt \rightarrow NaAlEt_4 + Et_2O;$$

and an analogous substitution proceeds with LiEt or Py. [214]

In attempting to explain experimental facts on the deposition of metals from MX + $n AlR_3$ mixtures ($1 \leqslant n \leqslant 2$), Ziegler [161] advanced two different hypotheses with which it is impossible to agree.

According to one hypothesis the primary process is the liberation of sodium, which then reacts with $AlEt_3$:

$$Na + 4AlEt_3 \rightarrow 3NaAlEt_4 + Al.$$

TABLE 21. Results of the determination of the composition of the ions in binary systems.

System	Cation	Anion	Reference
NaCl + $AlCl_3$	$[Na.nNaCl]^+$	$AlCl_4^-$ or $AlCl_6^{3-}$	208
KBr + $AlBr_3$	$[K_2Br]^+$, K^+	$Al_2Br_7^-$, $Al_2Br_8^{2-}$	209
ICl + $AlCl_3$	I^+	$AlCl_4^-$	111
IBr + $AlBr_3$	I^+	$AlBr_4^-$	89
$PhNO_2$ + AlX_3 (X = Cl, Br)	$[Al.nPhNO_2]^{3+}$ in dilute solution, $[AlX_2.nPhNO_2]^+$ in more concentrated solution	X^- in dilute solution, AlX_4^- in more concentrated solution, $Al_2X_7^-$ in concentrated solution	207
MeBr + $AlBr_3$	$AlBr_2^+$	Br^-	67
EtBr + $AlBr_3$	$[Al.nEtBr]^{3+}$, $[AlBr.nEtBr]^{2+}$	$Al_2Br_7^-$, $AlBr_4^-$	207
EtBr + $AlBr_3$	$[AlBr_2.EtBr]^+$	Br^-	77

‡ *Note added in proof.* According to X-ray analysis, which the authors learnt about after the manuscript had gone to be typeset, crystals of $KF.2Al(C_2H_5)_3$ are made up of K^+ and $[Al_2Et_6F]^-$ ions [236].

This hypothesis is contradicted by experiment in the following respects: (*a*) the high degree of purity of cathodic aluminium at $n = 2$; (*b*) the low bath potential, 0.3–1 V at an interelectrode distance of 3 cm; (*c*) the low probability of existence of a notable quantity of free $AlEt_3$, particularly in the case $n = 1$, when deposition of aluminium at low current densities is observed.

According to the other hypothesis the deposition of aluminium proceeds during the discharge of cations Al^{3+}, AlR^{2+}, and AlR_2^+, the source of which Ziegler considers to be partially uncombined AlR_3. What was said above concerning the possibility of existence of Al^{3+} ions evidently also applies in essence to the existence of AlR^{2+}. As for the dissociation of unbound $AlEt_3$ with the formation of AlR_2^+, there is no reason which could explain why such a process should intensify in $MX.AlR_3 + AlR_3$ mixtures in comparison with pure AlR_3 to such a degree that κ for the mixture becomes two orders of magnitude higher than for $MX + AlR_3$ mixtures with $n = 1$ and six orders greater than for pure AlR_3. Furthermore this hypothesis also cannot explain the deposition of aluminium from mixtures at $n = 1$.

The regularity in the deposition of aluminium from $MR–AlR_3$ mixtures is readily explainable with the aid of a reasonable assumption about the cathodic discharge of complex anions containing aluminium. Such an assumption does not contradict any of the known experimental facts.

(c) *Dissociation in Slv–AlR_3 systems.* For such systems in the general case scheme (22) is the most probable. It is in accord with both the results of electrochemical investigations and with the thermochemical data. Obviously, this scheme remains true also for solutions of aluminium sesquihalides. In special cases when the solvent can form ions as a result of interaction with AlR_3§ here there can also be other variants. Thus interaction between RN≡NCl and $AlCl_3$ with the formation of $(RN{\equiv}N)^+.AlCl_4^-$ has been established[194]. This refers especially to solutions of AlX_3 in alkyl halides. The results of studies of isotopic exchange between EtBr* and $AlBr_3$ [215-217] and the isomerisation of hydrocarbons in the presence of RX and AlX_3 [218,219] show the formation of $R^+[AlX_4]^-$ complexes.

Good confirmation of the structure of complexes expressed by the formula $RAlX_4$ is given by the retardation or complete cessation of exchange of bromine between $AlBr_5$ and EtBr in solvents exhibiting strongly expressed donor properties. The rate of exchange changes thus: $Et_2O < PhNO_2 < MeNO_2 < MeCN$,[217] which should also be expected on the basis of series (16) and (17). It is interesting to note also that exchange of ethyl radicals is absent in mixtures of $AlEt_3$ and EtBr,[221-224] which is understandable, considering that the ethyl radical in EtBr has a positive charge and the orientation of EtBr in relation to $AlEt_3$ takes place according to the scheme $EtBr \rightarrow AlEt_3$ with formation of $Et^+.AlEt_3Br^-$. The possibility of appreciable dissociation of $RAlX_4$ into the ions R^+ and AlX_4^- was doubted[211] and it was suggested that possibly the matter is restricted by the strong polarisation of the R–X bond[218]. In support of the existence of such dissociation there is the slow decomposition of EtBr + $AlBr_3$ solutions with formation of alkenes and HBr;[50,51,77] from the measurements of the dielectric polarisation of these mixtures the conclusion was drawn that 3–4% of the EtBr molecules undergo dissociation[220]. Taking ΔH_1 for the reaction

$$EtBr(gas) \rightarrow Et^+(gas) + Br^-(gas),$$

as 183 kcal mole^{-1} after Streitwieser[225], we can evaluate ΔH for the reaction in an indifferent solvent:

$$EtBr + AlBr_3 \rightarrow Et^+ + AlBr_4^-, \qquad (25)$$

using the usual thermochemical cycle. We obtain

$$\Delta H = 117 + \Delta H_S \text{ kcal mole}^{-1}, \qquad (26)$$

where ΔH_S is the sum of the heats of solvation of the ions Et^+ and $AlBr_4^-$. Franklin[226] calculated the heat of solvation of Et^+ in H_2O and in MeOH as -54 and -59 kcal g-ion respectively. Taking into account that ΔH_S of $AlBr_4^-$ is of the same order, from Eqn. (26) it is evident that process (25) is by no means impossible. With increase in the length of the alkyl radical the quantity ΔH_1 decreases[225] and the formation of R^+ becomes more probable. Actually the decomposition of RBr + $AlBr_3$ solutions increases strongly on passing from ethyl to butyl[50,51]. However, concentrated EtBr–$AlBr_3$ solutions are completely stable and exhibit too high an electrical conductivity to suggest that they dissociate according to scheme (25). It seems that in this concentration region the bulk of ions is formed by scheme (22).

Jander and Kraffczyk[227] suggested, on the basis of the reaction between NaOEt and $AlBr_3$ in Et_2O, starting from the formation of NaBr and $Al(OEt)_3$, that in the solution there is a complex $Et^+[AlBr_3.OEt]^-$, reacting according to the scheme:

$$3NaOEt + Et^+[AlBr_3{\cdot}OEt]^- \rightarrow \underset{\downarrow}{3NaBr} + Al(OEt)_3 + Et_2O. \qquad (27)$$

Concerning the possibility of formation of this complex, all that has been said above regarding the EtBr–$AlBr_3$ system can be repeated. As for the reaction itself, it is by no means necessary to introduce any special hypotheses, as it can take place completely by the scheme:

$$3NaOEt + Et_2O{\cdot}AlBr_3 \rightarrow \underset{\downarrow}{3NaBr} + Al(OEt)_3 + Et_2O.$$

2. Ternary systems. Table 22 contains dissociation schemes proposed on the basis of the results of measurements of transport numbers and electrical conductivities, electrolysis data, and in some cases cryoscopic information. The possibility of the existence of Al^{3+} and AlX^{2+} ions was discussed above. The existence of ions of the type $(M_2AlX_4)^+$ is at least doubtful, since there are no evident reasons which might lead to their formation. On the contrary, all the remaining ionic formations are completely real and are precisely such as would be expected on the basis of the thermochemical and structural data. We note additionally that from the results of measurements of molar refraction in $MX–AlBr_3–C_6H_6$ solutions (M = Li, Na, K; X = Cl, Br), it was concluded[228] that the ions AlX_4^- and $Al_2X_7^-$ were formed.

From investigations of the spectra of solutions[71,229] and of the isotopic exchange of hydrogen between DX and aromatic hydrocarbons[120,230] it was concluded with a great deal of reliability that the complexes in the $HX–AlX_3–Ar$ systems have the structure $(ArH)^+(Al_2X_7)^-$ or $(ArH)^+AlX^-$. This conclusion agrees well with the electrolysis results (*cf.* p. 127).

§ Because of the conductivity of the pure solvents themselves it is necessary to assume that they are subject to self-dissociation. Reaction with AlR_3 can either facilitate this process, when at least one of the ions formed during self-dissociation will be present in mixtures with AlR_3, or give rise to the formation of other ions. Only the first case will be considered here.

TABLE 22. Results of investigating the composition of the ions in the ternary systems.

System	Cation	Anion	Reference
$KBr-AlBr_3-C_6H_6$	$[K_2AlBr_4]^+$	$Al_2Br_7^-$	207
$KBr-AlBr_3-PhNO_2$	K^+, $[Al.nPhNO_2]^{3+}$, $[AlBr.nPhNO_2]^{2+}$ at $KBr/AlBr_3 = 0.2-0.5$; K^+ at $KBr/AlBr_3 = 0.9$	$AlBr_4^-$	207
$NaBr-AlBr_3-EtBr$	Na^+, $[Al.nEtBr]^{3+}$, $[AlBr.nEtBr]^{2+}$ at $NaBr/AlBr_3 = 0.2-0.5$; Na^+ at $NaBr/AlBr_3 = 0.9$	$AlBr_4^-$ and $Al_2Br_7^-$	207
$IX-AlX_3-PbNO_2$ (X = Cl, Br)	I^+	AlX_4^-	111, 113
$EtPyBr-AlCl_3-C_6H_6$	$EtPy^+$	$[AlCl_3Br]^-$	143

Hence the main ionisation processes in the $MR-AlR_3-Slv$ ternary systems can be represented by the schemes:

1. For solvents which do not exhibit strong donor properties, in which AlR_3 is in the dimeric form:

$$MR + Al_2R_6 + nSlv \rightleftarrows M^+ + Al_2R_7^- + nSlv\,.$$

2. For solvents with strong donor properties:

$$2MR + [AlR_2 \cdot 2Slv]^+ + AlR_4^- + nSlv \rightleftarrows 2M^+ + 2AlR_4^- + (n+2)Slv.$$

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The generality of the properties of solutions of the aluminium compounds AlR_3 finds a natural explanation in the aluminium's having two free $3p$ levels. Such natural two-stage differences between particular solutions are linked both with the properties of R and consequently with a difference in the hybrid levels of AlR_3, and also with a difference in donor character of the solvents. The general position considered here can easily be applied both to solutions of Al homologues (for example, gallium [231]) and also to other solutions, for example, compounds of antimony [75], tin, etc.

We did not set ourselves the task of examining the influence of changes in concentration and the nature of the solvent on the properties of solutions of the complexes $MX.2AlX_3$ (*cf.*, for example, Refs. 232–235), considering that this could hardly add anything to the characteristics of the principal properties, although the investigations of such a nature are not without interest for the theory of solutions in media of low dielectric constant.

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ELECTRICALLY CONDUCTING NON-AQUEOUS SYSTEMS FORMED FROM NON-CONDUCTING COMPONENTS

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