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Physicochemical Properties and Structure of Complex Compounds of Aluminium Hydride

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I. INTRODUCTION

Thanks to the diverse properties of solvents the electrochemistry of non-aqueous solutions allows processes which are inaccessible for study in aqueous solutions to be brought about and investigated. In particular, there is considerable interest in the experimental investigation of the anodic discharge of hydride hydrogen. The corresponding cathodic process in aqueous solutions—the discharge of H^+—has been studied rather fully. In the investigation of an anodic process it is sufficient to operate with discharge of anions of the type $(M^{+m}H_n)^{-n+m}$, which are precisely what exist in non-aqueous solutions. Since the binding energy of H^- in an anionic complex can depend significantly on the medium, it follows that there are at least indications about the nature of the bonding of this anion with the solvent. The behaviour of the anode during polarisation is also essential —its solubility, the nature and properties of the soluble products which are formed, and in the absence of solubility the order of the strength of the bonding of atomic or molecular hydrogen at its surface. Interest in the process of the discharge of hydride hydrogen, which was first observed by Bardwell[1] for a melt of CaH_2 in KCl–LiCl eutectic and by Ziegler and coworkers[2] for non-aqueous solutions, stimulated us to differentiate AlH_3 and its complexes of the $MAlH_4$ type from the class of compounds $MAlR'_nR''_{4-n}$, the electrochemical properties of which were considered earlier[3]. It was interesting to review the properties, a knowledge of which is needed in investigating the discharge of hydride ions. From the practical viewpoint the solutions of such substances can be used both for the electrodeposition of aluminium‡, and also for obtaining solutions of aluminium hydride[6], the chemical preparation of which is rather complicated.

In the anodic discharge of the AlH_4^- ion, AlH_3 and H_2 should be formed. The subsequent behaviour of AlH_3 and its influence on the kinetics of the anode process depends on the interaction of AlH_3 with the components of the solution, that is, on the nature of the complex formation. We will therefore begin with consideration of the properties of the complexes of AlH_3. Hydroaluminates§ must formally be considered as complexes $AlH_3.MH$. However, they exhibit a series of characteristic differences from the complexes of AlH_3 with organic ligands and are of special interest for electrochemistry. Therefore an examination of several of their properties and methods of preparation is treated under a separate heading. A separate chapter is devoted to the important problem of the structure of the complexes of AlH_3, in which those of the type $AlH_3.MH$ are considered as a special case of the complexes $AlH_3.L$. Finally, the last chapter is devoted to the natural electrochemical properties of the aluminium hydrides.

II. COMPLEXES OF ALUMINIUM HYDRIDE $AlH_3.nL$

In the pure solid state AlH_3¶ is known only as a polymer. $(AlH_3)_x$ is a white involatile substance, usually not free from diethyl ether. Aluminium hydride is insoluble in inert solvents, but soluble with the formation of complexes and depolymerisation in tetrahydrofuran, dioxan, triethylamine[9], diamines[10], and methylcellosolve[11]. The ethereal solution of AlH_3 obtained from $LiAlH_4$ and $AlCl_3$ by the method of Finholt and coworkers[12], is unstable† and on standing it deposits an ether-containing polymer $(AlH_3)_x$[9,14–16], the composition of which depends on the conditions of isolation[9,12,15,17].

† Symbols used in the text: L ligand; M metal; R alkyl, halogen, or hydrogen; NR_3 tertiary amine; Hal halogen; μ dipole moment of the molecule in Debye units; t_b boiling point; t_f melting point; C.N. coordination number; κ electrical conductivity, $\Omega^{-1}\,cm^{-1}$. The thermochemical sign convention is used for denoting the thermal effects.

‡ Kessler and coworkers have reviewed the work of Brenner and coworkers on the electrodeposition of aluminium from hydride solutions. See also Refs.4 and 5.

§ Unfortunately obsolete terminology is often used (for example, in a review[7] which appeared after the present article had been sent to the press).

¶ The monomer AlH_3 and the dimer Al_2H_6 have been obtained in the gas phase at low pressure in the vaporisation of aluminium from a tungsten wire into a vacuum system with partly dissociated hydrogen[8].

† More stable ether addition compounds are known for the aluminium hydrohalides than for AlH_3, for example, $AlHCl_2.O(C_2H_5)_2$, and $AlHBr_2.O(C_2H_5)_2$.[13]

Table 1. Complexes of aluminium hydride.

System	Complex, production or method of detection	Properties
AlH_3-tetrahydrofuran	$AlH_3.2C_4H_8O$ *, 1) C_4H_8O vac. from soln. of AlH_3 in C_4H_8O at -45°C;[18] 2) Infrared[19] and NMR[16] spectra in soln. of AlH_3 in C_4H_8O.	stable at t_{room} only in soln. in C_4H_8O.[9] P_d = 6 mmHg, -5°C; 15 mmHg, +20°C.[18]
	$AlH_3.nC_4H_8O$, $n > 2$ not observed up to -65°C (tensimetric measurements)[18].	
	$AlH_3.C_4H_8O$, 1) C_4H_8O vac. from soln. of AlH_3 in C_4H_8O at t_{room}.[9,20] 2) 1 mole C_4H_8O vac. from $AlH_3.2C_4H_8O$ at -5°C.[18].	White cryst. subst., t_f = 56–57°C[16,20], sol. in e., THF, d., b., cyclohexane, iso-octane[16].
AlH_3-dioxan	$AlH_3.2OC_4H_8O$, $AlH_3.OC_4H_8O.C_4H_8O$, NMR[19] and infrared[9,16] spectra of soln. in d, and $AlH_3.OC_4H_8O$ in THF.	
	$AlH_3.OC_4H_8O$, OC_4H_8O vac. from soln. of AlH_3 in OC_4H_8O.[9,16]	white cryst. subst., does not melt, sol. in THF, d., insol. in b.[16].
AlH_3-trimethylamine	$AlH_3.2N(CH_3)_3$, 1) Treatment with amine of products of reaction in glow discharge: $Al(CH_3)_3 + nH_2 \rightarrow Al(CH_3)_{3-n}H_n + nCH_4$,[13] 2) $N(CH_3)_3 + (C_2H_5)_2O$ vac. from soln. AlH_3** and amine in e. at comp. ratio 1 : 2 or excess of amine[9,16,23,24]. Purification of subl.[23,25] or extr. b.[16]; 3) condensation of amine on $AlH_3.N(CH_3)_3$;[26] 4) tensim. titration of $AlH_3.N(C_2H_5)_3$ with gaseous $N(CH_3)_3$.[27].	white cryst. subst., t_f = 94–95°C[16,23], sol. in e., THF, b., cyclohexane, iso-octane[16,23]. Subl. impure subst., 30–40°C/1 mmHg[23] or at t_{room}.[24] At t_{room} stable in cryst. and in soln., dissoc. in gas[9,13,26,28] $AlH_3.2N(CH_3)_3 \rightleftarrows AlH_3.N(CH_3)_3 + N(CH_3)_3$.
	$AlH_3.N(CH_3)_3$*** 1) e. vac. from soln. AlH_3 and $N(CH_3)_3$ in e. at equimol. ratio of comp. or excess AlH_3. Purif. subl.[9,16,23] or extr.[9,16]. 2) Ruff's method[25,31] $LiAlH_4 + N(CH_3)_3.HCl \xrightarrow[t_{room}]{e.} AlH_3.N(CH_3)_3 + LiCl + H_2$, e. vac., subl. complex.	white cryst. subst., t_f = 74–76°C[16,23,26,29], sol. in e., THF, b., d., cyclohexane, iso-octane[16,23], P_d = 2–3 mmHg[26], subl. impure subst. 35–40°C, in vac.[26,31], 50–60°C, 1 mmHg.[23]
	$AlD_3.N(CH_3)_3$, Ruff's method[31], see above.	t_f = 77–78°C[31]
	$AlH_3.N(CH_3)_2CH_2CH{=}CH_2$, Ruff's method[31], see above.	t_f = 12°C[31]
AlH_3-dimethylamine	$AlH_3.2(CH_3)_2NH$, mixt. in e. AlH_3 with excess amine at -50°C, e. and excess amine vac. at -40°C[32].	at $t >$ -20°C, chemical reaction: $AlH_3.2(CH_3)_2NH \rightarrow 2H_2 + AlH[N(CH_3)_2]_2$[32]
	$AlH_3.(CH_3)_2NH$, Ruff's method $LiAlH_4 + (CH_3)_2NH.HCl \xrightarrow[-40°C]{e.} H_2 + LiCl +$ $AlH_3.(CH_3)_2NH$[31]; assumed to be the same as preceding formation of $AlH_2N(CH_3)_2$.[32]	at $t >$ -10°C, chem. reaction, see above[32].
AlH_3-methylamine	$AlH_3.2CH_3NH_2$, mixt. comp. in e. at -55°C at ratio 1 : 2 or excess of amine[33].	white solid, at $t >$ -40°C, chem. reaction, $AlH_3.2CH_3NH_2 \rightarrow 2H_2 + HAl(NHCH_3)_2$.[33]
	$AlH_3.CH_3NH_2$, mixt. equimol. amount of comp. in e. at 55°C.[33].	white solid, at $t >$ -40°C, chem. reaction, see above[33].
AlH_3-ammonia	$AlH_3.2NH_3$, proposed as preceding the formation of $H_2AlNH_2.NH_3$ at liq. nitrogen temp.[34]	at -80°C, chem. reaction $AlH_3.2NH_3 \rightarrow H_2 + H_2AlNH_2.NH_3$[34] at -45°C, chem. reaction, see above.[35]
	$AlH_3.NH_3$, mixt. equimol. amount comp. in e. at -80°C.[35]	
AlH_3-pyridine	$AlH_3.2C_5H_5N$, mixt. comp. in e. at -30°C to -40°C, e. and C_5H_5N vac.[36]	white cryst. subst., at 0°C, chem. reaction $AlH_3.2C_5H_5N \rightarrow HAl(NC_5H_6)_2$[36]
	$AlH_3.C_5H_5N$, mixt. comp. in e. at -30°C at equimol. ratio[36]	white cryst. subst., at t_{room}, chem. reaction, see above[36]
AlH_3-triethylamine	$AlH_3.N(C_2H_5)_3$: 1) e. vac. from equimol. soln. comp. in e.[16,36]. 2) Ruff's method[31] $LiAlH_4 + N(C_2H_5)_3.HCl \xrightarrow{e.} LiCl + H_2 + AlH_3.N(C_2H_5)_3$.	white cryst. subst.[36], t_f = 18–19.2°C,[31,36] melts readily supercools to -60°C,[36] subl. 0°C, high vac.[36], + 30°C/4.5 mmHg[36], sol. in e., b., triethylamine[16,36].
	$AlH_3.2N(C_2H_5)_3$ is not formed even in soln. of AlH_3 in $N(C_2H_5)_3$.[16,36]	
AlH_3-tripropylamine	$AlH_3.N(C_3H_7)_3$: 1) Ruff's method[31]: $LiAlH_4 + N(C_3H_7)_3.HCl \xrightarrow{e.}$ $LiCl + H_2 + AlH_3.N(C_3H_7)_3$; 2) mixt. comp. in e.[36]	white cryst. subst., t_f = 79.6–81.0°C,[27,29] sol. in e. and b.[36], subl. 30–40°C, in high vac.[36].
AlH_3-tributylamine	$AlH_3.N(C_4H_9)_3$, mixt. comp. in e.[36], purification only by recrystn. from b.[36]	t_f = 41.5°C, does not subl., decomp. into comp. at room temp.[36]
AlH_3-*NNN'N'*-tetramethylethylenediamine (L)	$AlH_3.L$: 1) Ruff's method: $LiAlH_4 + L.2HCl \xrightarrow[excess]{L} LiCl + H_2 + AlH_3.L$[37];	white solid, P_d = 1.5 mmHg, 99.3°C, 10.6 mmHg, 119.3°C, sol. in L[37].
	2) displacement of $N(CH_3)_3$ from the complex: $AlH_3.2N(CH_3)_3 + L \xrightarrow[excess]{L}$ $2N(CH_3)_3 + AlH_3.L$[37]	
AlH_3-*NNN'N'*-tetramethylpropanediamine ****(L)	$AlH_3.L$, displacement of $N(CH_3)_3$ from complex $AlH_3.N(CH_3)_3 + L \xrightarrow[excess]{L}$ $AlH_3.L + N(CH_3)_3$, purif. by subl.[10].	white solid, t_f = +140°C, subl. impure subst. 80°C, 0.05 mmHg[10].

* It was shown[21,22] by the isomolar series method (viscosity, density, electrical conductivity) that C_4H_8O forms complexes with $AlBr_3$ and $AlCl_3$, for example, in b. and $C_6H_5NO_2$ the complex $AlBr_3.C_4H_8O$.

** AlH_3 in e. obtained by $3LiAlH_4 + AlCl_3 \rightarrow 3LiCl + 4AlH_3$;[16,23] or $LiAlH_4 + HCl \rightarrow LiCl + H_2 + AlH_3$;[24] the polymer $(AlH_3)_x$, which dissolved in a soln. of $N(CH_3)_3$ in e.[9] was also used.

*** 1 : 1 adducts are known of $N(CH_3)_3$ with H_2AlCl, $HAlCl_2$, H_2AlBr, $HAlBr_2$;[29] aluminium alkyl hydrides also form complexes, for example, $CH_3AlH_2.N(CH_3)_3$, $(CH_3)_2AlH.N(CH_3)_3$.[30]

**** Complexes of AlH_3 with other polyamines are also obtained[10]; however, in these instances a chemical conversion is possible, which hinders the interpretation of the results. The complexes $AlH_3.L$ (L = triethylenediamine), stable up to > 200°C and insoluble in the usual organic solvents, were obtained[38] in tetrahydrofuran from Al, H_2, and L at moderate temperatures and hydrogen pressures.

Table 1‡ gives the methods of preparation and proof of the existence and also certain properties of the complexes of AlH_3. An appreciable proportion of the complexes exist only at low temperatures, above which a chemical reaction starts between the AlH_3 and the ligand.

Depending on the strength of the bonding of the ligands with AlH_3, some ligands can displace others to form more stable complexes, for example, NaH, LiH, and CaH_2 displace $N(CH_3)_3$ from its complexes with AlH_3[27] by reactions of the type:

$$LiH + AlH_3 \cdot N(CH_3)_3 \xrightarrow{(C_2H_5)_2O} LiAlH_4 + N(CH_3)_3 .$$

‡ In Tables 1 and 4 the following abbreviations and conventional symbols are used: vac. removal in a vacuum, soln. solution, subst. substance, sol. soluble, e. diethyl ether, THF tetrahydrofuran, d. dioxan, b. benzene, P_d dissociation pressure, comp. components, mixt. mixture, extr. extraction. The other symbols are understandable from the text.

NNN'N'-tetramethylethylenediamine (L) taken in excess, has a similar action[37]:

$$AlH_3 \cdot 2N(CH_3)_3 \xrightarrow[\text{solvent}]{L} AlH_3 \cdot L + 2N(CH_3)_3.$$

The same reactions take place with *NNN'N'*-tetramethylpropanediamine[10] and trimethylhydrazine[39].

By tensimetric titration of the complex $AlH_3.N(C_2H_5)_3$ with trimethylamine it was found that $N(CH_3)_3$ displaces $N(C_2H_5)_3$,[27] for $AlH_3.2N(CH_3)_3$ was isolated from the reaction mixture. NMR has shown[9] that C_4H_8O does not displace the amine from the complex $AlH_3.N(CH_3)_3$, and C_4H_8O in $AlH_3.C_4H_8O$ can be partly replaced by dioxan. The existence of the mixed complexes $AlH_3.N(CH_3)_3.C_4H_8O$, $AlH_3.N(CH_3)_3.OC_4H_8O$, and $AlH_3.C_4H_8O.OC_4H_8O$, has been found[16,19] in an excess of the complex-forming agent or solvent. The infrared spectra of solutions of $AlH_3.N(CH_3)_3$ in $N(C_2H_5)_3$, C_4H_8O, and OC_4H_8O showed[9] the presence of the compounds $AlH_3.N(CH_3)_3.N(C_2H_5)_3$, $AlH_3.N(CH_3)_3.C_4H_8O$, and $AlH_3.N(CH_3)_3.OC_4H_8O$, stable only in solution in an excess of the corresponding complex-forming substance. It is interesting that C_4H_8O and OC_4H_8O taken in excess give diadducts with AlH_3, but $N(C_2H_5)_3$ does not[9].

To explain the solubility of AlH_3 in diethyl ether, many authors propose the existence of the complexes $AlH_3.n(C_2H_5)_2O$, which were not isolated owing to their instability.

The precipitation of the ether-containing polymer $(AlH_3)_x$ from ethereal solutions of AlH_3, the stability of AlH_3 solutions in tetrahydrofuran and dioxan and of ethereal solutions of AlH_3 in the presence of LiBr or NR_3, and also the depolymerising action of tetrahydrofuran, tertiary amines, LiBr [3,9,16,36] on polymeric AlH_3 suggests that tetrahydrofuran, tertiary amines, and LiBr are stronger complex-forming agents than diethyl ether.

Accordingly, a series can be drawn up with the ligands arranged according to diminishing strength of the bond with AlH_3: alkali or alkaline earth metal hydrides > diamines > $N(CH_3)_3$ > OC_4H_8O, C_4H_8O, $N(C_2H_5)_3$ > $(C_2H_5)_2O$.

The ability of complexes to dissociate

$$AlH_3.L \rightleftharpoons AlH_3 + L$$

is also interesting. For the complexes of AlH_3 with alkali metal and alkaline earth metal hydrides such dissociation seems improbable although the decomposition

$$MAlH_4 \rightarrow MH + AlH_3$$

is proposed as a stage preceding certain chemical reactions[40] or the catalytic decomposition of $MAlH_4$ in ethereal solution[41,42].

Table 2 gives some information about the possibility of the dissociation in a vacuum

$$AlH_3.L \rightleftharpoons AlH_3 + L$$

of complexes with amines§.

The sequence of ligands according to the tendency of their complexes to dissociate from AlH_3 is: diamines < $< N(CH_3)_3 < N(C_2H_5)_3 < N(C_3H_7)_3 < N(C_4H_9)_3$. It should be noted that complexes with an odd number of carbon atoms in the alkyl radical of the amine melt at a higher temperature than those with an even number.

Depending on the ligand L and steric factors the complexes $AlH_3.L$ can add a second molecule of ligand ($AlH_3.L + L \rightleftharpoons AlH_3.2L$).

Quantitative data characterising this ability exist only for complexes with tertiary amines. The cryoscopic method was used[27] to measure the mean molecular weight of mixtures of NR_3 and $AlH_3.NR_3$, in benzene and the formation constants of the complexes, K, were calculated for certain amines: $AlH_3.2N(CH_3)_2CH_2CH{=}CH_2$, $K = 2 \times 10^2$; $AlH_3.2N(C_2H_5)_2CH_3$, $K = 3$; $AlH_3.2N(C_2H_5)_3$, $K = 8 \times 10^{-2}$. For $N(CH_3)_3$ the formation of the 1 : 2 complex is thought to be complete¶.

Table 2. Dissociation temperatures and melting points of the complexes $AlH_3.NR_3$.

Ligand	t_{dis}, °C	t_f, °C	References
$N(CH_3)_3$	100	75—76	20, 23, 27, 31
$N(C_2H_5)_3$	40 slow, 80 rapid	18—19.2	31.36
$N(C_3H_7)_3$	~40 in vacuum	79.6—81	31.36
$N(C_4H_9)_3$	readily dissociates in a vacuum, - does not distil	41.5	36
$N(CH_3)_2CH_2CH{=}CH_2$	—	12	31
$(CH_3)_2N(CH_2)_2N(CH_3)_2$	does not dissociate at 133	—	37
$(CH_3)_2N(CH_2)_3N(CH_3)_2$	does not dissociate at 140	136—140	10

Similar cryoscopic measurements were also made for the mixed complexes: $AlH_3.N(CH_3)_3.N(C_3H_7)_3$, $K = 7 \times 10^{-1}$; $AlH_3.N(CH_3)_3.N(C_2H_5)_3$, $K = 9$; $AlH_3.N(CH_3)_3.N(C_2H_5)_2CH_3$, $K = 5 \times 10^2$.

According to these results the stability order of the amino-complexes is: $N(CH_3)_3 > N(CH_3)_2CH_2CH{=}CH_2 > > N(C_2H_5)_2CH_3 > N(C_2H_5)_3 > N(C_3H_7)_3$. This series is also confirmed by qualitative results.

III. ALKALI METAL TETRAHYDROALUMINATES $MAlH_4$ AND THEIR COMPLEXES $MAlH_4.nL$

1. Methods of Preparation of $MAlH_4$

Rather effective methods for making alkali metal tetrahydroaluminates are now known, including the following which are suitable for industrial preparation:

(a) The reaction of the alkali metal hydride MH with $AlHal_3$ may be carried out in various solvents, the choice of which depends on the nature of M and Hal [12,15,41,43-53]. When MH is insoluble then the reaction proceeds in the presence of aluminium alkyls, the role of which reduces to the conversion of the MH into the soluble complexes $MAlHR_3$.[51,52] $LiAlH_4$, $NaAlH_4$, and $KAlH_4$ are obtained in this way, and the reaction of LiH and $AlCl_3$ in $(C_2H_5)_2O$ serves for the industrial production of $LiAlH_4$.

It is thought[44,49,53] that the reaction of MH with $AlHal_3$ proceeds through the intermediate formation of AlH_3. The coordination unsaturated AlH_3 should, in our opinion, lead also to the formation of soluble complexes of composition

§ For other complexes the dissociation is complicated by the catalytic or thermal decomposition of AlH_3.

¶ This assumption is well based. The molecular weight of this complex in ether (ebullioscopy) and in benzene (cryoscopy) has been determined[8,16,26]. It has been shown that in both the compound is monomeric and not dissociated. The complex is completely stable in solution and in the crystalline form, whereas dissociation occurs in the gas

$$AlH_3.2N(CH_3)_3 \rightleftharpoons AlH_3.N(CH_3)_3 + N(CH_3)_3;$$

$$AlH_3.N(CH_3)_3 \rightarrow (AlH_3)_x + N(CH_3)_3.$$

as vapour pressure measurements and the infrared spectra have shown[9,26,28,37]. The polymers which are formed gradually break down into Al and H_2, that is, complete decomposition of $AlH_3.2N(CH_3)_3$ can proceed over a long time. The excess of $N(CH_3)_3$ shifts the equilibrium to the left.

$n MAlH_4.mAlH_3$. Evidently, at the start of the reaction $m \gg n$ and aluminium hydride predominates; at the end of reaction $m \ll n$ and $MAlH_4$ predominates in the solution. The decomposition of non-recrystallised $LiAlH_4$ usually observed is apparently connected above all with the decomposition of the impurity $MAlH_4.nAlH_3$. The hypothesis of the intermediate formation of the complex $LiAlH_4.AlH_3$ is made also for the reaction

$$3LiAlH_4 + AlCl_3 \rightarrow 3LiCl + 4AlH_3$$

from the results of NMR spectra [54].

(b) Direct reaction of the elements or MH, Al, and H_2 (the Al is specially activated [55-57]) on heating with hydrogen in solvating solvents [58-64], or hydrocarbons in the presence of aluminium alkyls and analogous compounds as activators [60,61,65]. In tetrahydrofuran and diglyme, Li, Na, and K tetrahydroaluminates have been obtained, in hydrocarbons, Na, K, and Cs.

In solvating media the direct preparation is complicated by cleavage of the solvent which at a definite temperature and concentration takes place explosively. Pyrophoric impurities are formed in the cleavage [58-61]. Solvent cleavage is intensified in the sequence Li–Cs, since $KAlH_4$ is obtained strongly contaminated and $CsAlH_4$ cannot be obtained at all in diglyme [60,61]. The explosive cleavage of diglyme by lithium tetrahydroaluminate [66] and of tetrahydrofuran by sodium tetrahydroaluminate [67] have been noted. The limiting temperatures for the coexistence of $LiAlH_4$ with diglyme, $NaAlH_4$ with C_4H_8O, and $NaAlH_4$ with diglyme are 200°, 165°, and 180°C respectively [60,61].

The vacuum distillation of the solvent after the preparation leads to contamination of the products from solutions of $MAlH_4$ in tetrahydrofuran and diglyme. On salting out the $MAlH_4$ from these solutions with ether or toluene, sufficiently pure $NaAlH_4$, $KAlH_4$, and $CsAlH_4$ are precipitated, but $LiAlH_4$ could not be isolated in this way.

In hydrocarbons, the direct preparation gives products with alkyl-substituted $MAlH_4$ as impurities, formed as a result of the reaction of aluminium alkyls with alkali metal hydrides.

The activating action of aluminium alkyls is explained by the formation of intermediate soluble complexes $MH.AlR_3$. [51,52,65] It has been suggested [56,58,65] that during the direct preparation of $MAlH_4$ there is the intermediate formation of AlH_3 from the elements, although this has been doubted [60,61], since the direct preparation of AlH_3 did not take place under conditions analogous to the direct preparation of tetrahydroaluminates [56]. Nevertheless without assuming the intermediate formation of AlH_3 or its subhydrides it is difficult to understand how the metallic aluminium is involved in the reaction.

It should be noted that the complex $AlH_3.L$ (L = triethylenediamine) has been prepared from Al, H_2, and L in tetrahydrofuran at moderate temperatures and hydrogen pressures [38].

In this reaction the formation of AlH_3 and polyhydroaluminates (or their partial alkyl derivatives) as a result of the hydrogenolysis of the compounds AlR_3 and $nMAlH_4.mAlR_3$ is quite probable [68,69]:

$$AlR_3 \xrightarrow{H_2} AlH_3 \xrightarrow{MH} MAlH_4;\ n\,MAlH_4 \cdot m\,AlR_3 \xrightarrow{H_2} n\,MAlH_4 \cdot m\,AlH_3.$$

Partly alkyl-substituted compounds give $MAlH_4$ as a result of the catalytic displacement of α-alkenes on heating [70,71].

From an analysis of the results on the direct preparation it can be concluded that the formation of $LiAlH_4$ from the elements is evidently determined ultimately by the magnitude of the solvation energy, which in tetrahydrofuran is sufficient for the formation of $LiAlH_4$. In diethyl ether and hydrocarbon solvents it is low and the change in free energy in the reaction [72]

$$LiH + Al + \tfrac{3}{2}H_2 \rightarrow LiAlH_4,\quad \Delta G = -3.9 \text{ kcal mole}^{-1}$$

is too insignificant to be the determining factor.

For sodium, potassium, and caesium tetrahydroaluminates the change in free energy is a significant quantity: for $NaAlH_4$ ΔG° = +3.0 kcal mole^{-1}, $KAlH_4$ ΔG° = +14.9 kcal mole^{-1}, $CsAlH_4$ ΔG° = +16.5 kcal mole^{-1}; [72] this also determines the possibility of their production in non-solvating media.

In the series $NaAlH_4$, $KAlH_4$, $CsAlH_4$ there is increasing solvent cleavage in their formation from the elements (125–150°C). The stability of the solvates should decrease in the same order (see below).

(c) Double decompositions of the type:

$$MAlH_4 + M'Hal \rightarrow M'AlH_4 + MHal\ [58,60,61,75]$$

and

$$M'AlH_4 + MH \rightarrow MAlH_4 + M'H\ [74],$$

the occurrence of which is determined by the ratios of the energies of formation of the reactants and final products and by solubility factors.

(d) Reactions for the replacement of an amine by a metal hydride [27]

$$AlH_3 \cdot NR_3 + MH \rightarrow MAlH_4 + NR_3.$$

Here the alkali metal hydride emerges as a stronger donor than the amine. The reaction

$$AlH_3 + MAlR_2H_2 \rightarrow MAlH_4 + R_2AlH,$$

where M = Na, K, has been proposed [65].

(e) The displacement

$$MAlH_4 + M' \rightarrow M'AlH_4 + M$$

where M = Li; M' = K, Rb, Cs [75].

2. Solubility and Complex Formation

The alkali metal tetrahydroaluminates are destroyed by water, ammonia, and other compounds with labile hydrogen. They are insoluble in non-polar solvents: benzene, toluene, aliphatic hydrocarbons. Table 3 gives the available information on solubility (m = moles per 1000 g solvent, c = moles per litre solution). In addition the solubility of $LiAlH_4$ is m = 1.1 in diethyl Carbitol [diethylene glycol diethyl ether] [12], m = 0.5 in dibutyl ether [12], m = 0.025 in dioxan [12], and $m > 1.5$ in methylal [80] (acetals are not reduced by $LiAlH_4$). A new solvent for lithium tetrahydroaluminate is "T-solvent"—tetrahydrofurfuroxytetrahydrofuran. The solubility of $LiAlH_4$ at 90°C is 22%. "T-solvent" boils at 238°C, which allows the reaction to be carried out at elevated temperatures [81].

$LiAlH_4$ is very slightly soluble in tertiary amines [12].

The great scatter in the results on the solubility of $LiAlH_4$ in diethyl ether is striking; it is due to the quality of the material dissolved [82]. Freshly prepared $LiAlH_4$ is more soluble in ether than the available commercial preparations [77]. The solubility of $MAlH_4$ is closely connected with the solvating ability of the solvents [58].

In several instances the solubility of tetrahydroaluminates can be compared with the properties of the complexes formed by $MAlH_4$ with the solvent. Table 4 gives the properties of the known complexes.

A series of complexes of the type $MAlH_4.nER_3$, where m = alkali metal and E = Al, Tl, In; R = alkyl; n = 1–4,

are also known; they were obtained by heating mixtures of the components[68]. The properties of most of these complexes have not been described, apart from $NaAlH_4.Al(C_2H_5)_3$, t_f = 60°C. It is also interesting to note the probable existence of $LiAlH_4.AlH_3$ [54] and $NaAlH_4.AlH_3$.[6]

Table 3. Comparison of the solubility of $MAlH_4$ in various solvents at room temperature.

Solvent	$MAlH_4$				
	$LiAlH_4$	$NaAlH_4$	$KAlH_4$	$CsAlH_4$	$Ca(AlH_4)_2$
Diethyl ether	m = 6.7-7.9[12] m = 6.7[17] m = 10.8[76] c = 7.9[77] c = 0.83[78]	insoluble[49,50**]			
Tetrahydrofuran	c = 3; 20°C[12]	c = 3; 20°[6,58]	poorly soluble[60,61] c = 0.03[58]		$c > 0.25$[6]
Monoglyme	c = 2.0; 20°C[58]	soluble[49]			
Diglyme	c = 1.0; 20°C[58]	c = 2,2; 20°C[58]	soluble[60,61]	soluble[60,61]	
Triglyme	c = 0.8; 20°C[58]	c = 2.8; 20°C[58]			
Tetraglyme	c = 1.8; 20°C[58]				

* The solubility was calculated by the authors[76] from the pressure-composition isotherm.

** $NaAlH_4$ is insoluble in $CH_3OC_2H_5$ and $CH_3OC_3H_7$.[49] The number of solvents for $NaAlH_4$ is limited to tetrahydrofuran and the methyl esters of mono- and poly-glycols.[79]

The instability of the complexes $MAlH_4.n(C_2H_5)_2O$ is illustrated by the solubility of only $LiAlH_4$ in $(C_2H_5)_2O$, the low heat of mixing of ether with $LiAlH_4$ (+1.95 kcal mole^{-1} [76]), and the ease of isolation of $LiAlH_4$ by simple vacuum distillation of ether from the solution.

The practical insolubility of $KAlH_4$, $RbAlH_4$, and $CsAlH_4$ in tetrahydrofuran, the relative ease of isolation of pure $NaAlH_4$ from C_4H_8O by salting-out with ether[58] or toluene[60] and the impossibility of this for $LiAlH_4$, and also the possibility of salting-out $KAlH_4$, $RbAlH_4$, and $CsAlH_4$ from their solutions in diglyme with toluene and the incompleteness of this for $LiAlH_4$ and $NaAlH_4$,[60] show the fall in stability of the solvates in the series $LiAlH_4 \rightarrow NaAlH_4 \rightarrow KAlH_4 \rightarrow RbAlH_4 \rightarrow CsAlH_4$. The essential role in solubility is evidently played not only by complex formation as such, but also the solvation of the alkali metal ions. In the series Cs, Rb, K, Na, Li the solvation of the ions by the ethers should increase. Moreover, it has been shown[93] that single complexes $[AlH_4.nL]^-$ are formed in C_4H_8O and diglyme, irrespective of M (see below). It should also be noted that although $LiAlH_4$ also forms comparatively stable complexes with dioxan and tertiary amines, it is practically insoluble in them[12]. In the strength of bonding of $LiAlH_4$ in the complex the ligands considered above can be arranged in the order:

$$(C_2H_5)_2O < C_4H_8O < OC_4H_8O \simeq NR_3.$$

From the point of view of the bond type and the possibility of existence of polyhydroaluminates, compounds with the general formula $MAlH_4.nAlR_3$, where R is an alkyl

Table 4. Complexes of the alkali metal tetrahydroaluminates.

System	Complex, production or method of observation	Properties
$LiAlH_4$–diethyl ether	$LiAlH_4.2(C_2H_5)_2O$ e. vac. from soln. of $LiAlH_4$ in e. at -60°C to constant weight[83].	$t_f \simeq$ -70°C, P_d = 38 mmHg, 0°C, readily sol. in e., loses e. even at t_{room}[83]
	$LiAlH_4.(C_2H_5)_2O$* (1) e. vac. from soln. of $LiAlH_4$ in e. at -15°C to const. weight[83]; 2) tensimetric measurements in the $LiAlH_4$–$(C_2H_5)_2O$ system[76,83].	e. light vac. (analogously at atm. pressure), being converted into $LiAlH_4$ on slight rise in t.[12,58,83] Isolation from e. on addition of b.[41,58,60] or hydrocarbons, which gives $LiAlH_4$ of higher purity than vac. e.[85]
$LiAlH_4$–tetrahydrofuran	$LiAlH_4.3C_4H_8O$, THF, vac. from soln. of $LiAlH_4$ in THF[16,83,86], for example, 17-20 mmHg, t_{room} or -20-0°C.[83]	colourless cryst. mass, t_f = 29-30°C[16,83,86], P_d = 16 mmHg, 0°C; 40 mmHg, 40°C[83]; sol. in e., THF, b.[83,86]; conc. soln. in e. forms layers, lower layer $LiAlH_4.3C_4H_8O$, upper satd. soln.[83].
	$LiAlH_4.2C_4H_8O$, tensimetric measurements during conversion of $LiAlH_4.3C_4H_8O$ into $LiAlH_4.C_4H_8O$;[83] 2) gas chromatography during addition of THF to soln. of $LiAlH_4$ in e.[87]	P_d = 15 mmHg, 34°C.[83]
	$LiAlH_4.C_4H_8O$, THF, vac. from soln. $LiAlH_4$ in THF 20-40°C[83,86], 40°C/3 mmHg.[16]	white solid, P_d = 1 mmHg, 20°C; 7 mmHg, 34°C[83]; readily sol. in e., THF, almost insol. in b.[16,83], last traces of THF difficult vac.[58,60].
$LiAlH_4$–trimethylamine	$LiAlH_4.3N(CH_3)_3$, mixt., comp. in e. at large excess of amine at -80°C.[88]	amine vac. even at -40°C, > 0°C converted into $LiAlH_4.N(CH_3)_3$.[88]
	$LiAlH_4.2N(CH_3)_3$, mixt. ethereal soln. of comp. at -50°C.[88]	white cryst. subst., in vac. at t_{room} converted into $LiAlH_4.N(CH_3)_3$.[88]
	$LiAlH_4.N(CH_3)_3$, mixt. ethereal soln. comp.[88]	white subst. sparingly sol. in e., insol. in b., decomposes in vac. at 180–200°C with separation of Al.[88]
$LiAlH_4$–triethylamine	$LiAlH_4.N(C_2H_5)_3$[89]	
$LiAlH_4$–triethylaluminium	$LiAlH_4.4Al(C_2H_5)_3$ Heating comp. at 80°C.[68,69]	liq., $\kappa = 3.72 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$, 100°C.[69]
	$LiAlH_4.3Al(C_2H_5)_3$ Heating comp. at 80°C.[68,69]	liq., $\kappa = 2.55 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$, 100°C.[69]
	$LiAlH_4.2Al(C_2H_5)_3$ Heating comp. at 80°C.[68,69]	t_f = 29°C, $\kappa = 1.46 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$, 100°C.[69]
	$LiAlH_4.Al(C_2H_5)_3$ Heating at 100°C.[69]	solid, sol. in pet. ether[69], toluene[68]
$MAlH_4$–hydrides of tervalent elements	$MAlH_4.nEH_3$, n = 0.25-16, for example, $LiAlH_4.\frac{1}{4}AlH_3$, $NaAlH_4.\frac{1}{2}GaH_3$, $LiAlH_4.\frac{1}{2}InH_3$, $NaAlH_4.AlH_3$, $LiAlH_4.GaH_3$[90], combination of $MAlH_4$ in org. solvents, conductimetric and ebullioscopic measurements[90]. Series of substances isolated [from solution] by crystn. in vac.[90].	sol. in polar solvents (THF, e.)[90]
$NaAlH_4$–sodium hydride	$NaAlH_4.2NaH$, 1) $NaAlH_4 + 2NaH \rightarrow Na_3AlH_6$ in ball mill in heptane or xylene, 20–100°C; 2) $2Na + NaAlH_4 + H_2 \rightarrow Na_3AlH_6$; 3) $3Na + Al + 3H_2 \rightarrow Na_3AlH_6$, 150–160°C, H_2 pressure 180–110 atm[65,91].	solid, insol. in org. solvents[91].
$LiAlH_4$–lithium hydride	$LiAlH_4.2LiH$, $LiAlH_4 + 2C_4H_9Li \rightarrow Li_3AlH_6 + 3C_4H_8$ mixt. soln. C_4H_9Li in hexane with soln. $LiAlH_4$ in e. t_{room}[92].	solid, insol. in org. solvents, decomp. without fusion and sublimation 210°C.[92]

* The complex $NaAl(C_2H_5)_4.(C_2H_5)_2O$.[84]

radical or hydrogen, are extremely interesting. The complexes $MAlH_4.nAlR_3$, including $RbAlH_4.4Al(C_2H_5)_3$, have already been isolated and partly characterised[68]. It remains unclear whether the compounds $MAlH_4.nAlH_3$ are actually isolated in the pure state, or whether their existence is only surmised in solutions. It is curious that recently halogen analogues of the first member of the hydroaluminate series $LiAl_2H_7$ have been obtained: $LiAl_2Br_7$ and $LiAl_2I_7$.[94]

3. Some Reactions of Tetrahydroaluminates

For the electrochemistry of $MAlH_4$ it is essential to consider firstly those reactions which characterise the thermal and catalytic stability of $MAlH_4$, the capability of hydride hydrogen to be replaced, and solvent interaction.

Behaviour on heating. The thermal stability of lithium, sodium, and potassium tetrahydroaluminates increases in the order $LiAlH_4$–$NaAlH_4$–$KAlH_4$.[95-99] This suggests that $RbAlH_4$ and $CsAlH_4$ should have even greater thermal stability.

A peculiarity of the thermal decomposition of $LiAlH_4$, $NaAlH_4$, and $KAlH_4$ is the stepwise evolution of hydrogen. Half the hydrogen is lost initially: $MAlH_4 \rightarrow MAlH_2 + H_2$. The temperature of this stage is: for $LiAlH_4$, 154–161°C[96] or 187–218°C[97]; for $NaAlH_4$, $> tf = 184$°C[97], for $KAlH_4$, 292–315°C[99]. The second stage corresponds to the decomposition $MAlH_2 \rightarrow MH + Al + \frac{1}{2}H_2$ and its temperature is: for $LiAlH_4$, 197–227°C[96], or 228–282°C[97]; for $NaAlH_4$ 290–298°C[98]; and for $KAlH_4$, 335–365°C[99]. The remaining hydrogen is lost by decomposition of the alkali metal hydride: $MH \rightarrow M + \frac{1}{2}H_2$, which corresponds to the temperatures: for $LiAlH_4$ 580–586°C[96], or 370–483°C[97], for $NaAlH_4$ 422–432°C[98], and for $KAlH_4$ 425–430°C[99]. The scatter of the results for lithium hydroaluminates is probably due to a difference in the purity of the substances tested.

Mikheeva and coworkers consider that all the stages of the decomposition of $LiAlH_4$ are endothermic[96]. However others[97] have found that the first stage of the decomposition (to $LiAlH_2$) is exothermic. The latter agrees with the thermochemical results. The decomposition of $LiAlH_4$ to LiH is exothermic, which is contrary to the behaviour of the other hydroaluminates[72]. All stages of the decomposition of $NaAlH_4$ and $KAlH_4$ are exothermic. $NaAlH_4$ melts almost without decomposition.

We note also that a reversible phase transformation of unknown nature has been found[97] for $LiAlH_4$ in the range 160–177°C.

Catalytic decomposition of $LiAlH_4$. In accordance with the decrease in free energy in the decomposition $LiAlH_4 \rightarrow LiH + Al + \frac{3}{2}H_2$,[72] $LiAlH_4$ is metastable, in contrast with sodium, potassium, and caesium tetrahydroaluminates. Solid preparations of $LiAlH_4$ darken on long storage, especially in the light, and gradually decompose, especially in the presence of catalytic additions of Ti, Si, Fe, Cu, or B[41]. When aluminium powder is dusted into an ethereal solution of $LiAlH_4$ the latter decomposes violently[58]. Highly disperse aluminium formed in the decomposition of solid $LiAlH_4$ is evidently the cause of the self-acceleration of the process. The decomposition of $LiAlH_4$ has been connected[100] with the initial homolytic splitting of $LiAlH_4$ into LiH and AlH_3. However, we think it much more probable that the initiation of the decomposition of the preparations is connected with the instability of the complexes $LiAlH_4.nAlH_3$ present as impurities (see p. 101/102).

This suggestion fits in well with the fact that the stabilisation of solid preparations of $LiAlH_4$ involves removal of the impurities as much as possible. This is done by dissolution of the preparations in $(C_2H_5)_2O$ and long boiling[100], especially in the presence of LiH[42], and also by bonding the impurities in complexes by the addition (up to 6%) of dioxan, dimethylcellosolve, and trimethylamine[101]. The complexes formed with AlH_3 are capable of regenerating $LiAlH_4$ in ethereal solution in the presence of lithium hydride[42]:

$$AlH_3 \cdot L + LiH \rightarrow LiAlH_4 + L.$$

A stabilising action on $LiAlH_4$ due to complex formation is shown by tetrahydrofuran and diglyme, which form completely stable solutions with $LiAlH_4$ at room temperature[58,60]. Here the stability of the solvates of $LiAlH_4$ is so great that it cannot be freed from solvent (see p. 102/103).

Reaction of $MAlH_4$ with solvents. Alkali metal hydroaluminates are not completely inert to solvents, especially on heating (see p. 102).

Explosive reactions of $LiAlH_4$ with dimethyl ether[102] and perfluorosuccinamide[103] have been noted, in addition to the splitting of tetrahydrofuran, dioxan, diethoxyethane, and dibutyl ether by a mixture of $LiAlH_4$ and $AlCl_3$.[104,105] Information about the splitting of $(C_2H_5)_2O$ by lithium tetrahydroaluminate is not available.

IV. STRUCTURE OF THE COMPLEXES $AlH_3.nL$ AND $MAlH_4.nL$

The complexes of AlH_3 have been better studied than the complexes of the alkali metal tetrahydroaluminates and for $n = 1$, 2 and various L they are known in all states of aggregation. The most reliable and confidently interpreted results were obtained for the gaseous complexes with $N(CH_3)_3$. At $n = 1$ the infrared spectra show the tetrahedral configuration of the molecules of the complex with symmetry C_{3v}.[9,26,106] In this sense they are similar to the anions formed in the aluminium compounds of type $MAlR_4$, where R is halogen or alkyl[3,107-109]. The anion AlH_4^- in $MAlH_4$ also exhibits an analogous structure[77,93,110] with an Al–H distance between 1.61[111] and 1.66 Å,[112] a conclusion reached on the basis of an investigation of the infrared and Raman spectra in ether[77,110] and in the solid state[77]. The valence state of the aluminium atom in such compounds corresponds to sp^3 hybridisation[20,113]. For other compounds of aluminium hydride in which the aluminium has coordination number four such definite conclusions cannot be drawn owing to the absence of corresponding experimental data: not one of them apart from $AlH_3.N(CH_3)_3$ has been studied in the gas phase and only two—$AlH_3.C_4H_8O$ and $AlH_3.N(C_2H_5)_3$ have been studied in inert solvents[9,16,20,114,115]. In the last examples the considerable similarity between these spectra and the spectra of solutions of the complex $AlH_3.N(CH_3)_3$ in the same solvent suggests that the molecules of these complexes have analogous structure[20].

For the complex $AlH_3.2N(CH_3)_3$ information is available about the infrared spectra in the gas[9,26,106] and in inert solvents[16,20,114,115], the Raman spectra of solutions[26,106], and the structure of crystals[24]. These results show definitely that the molecule of the complex is a trigonal bipyramid with three H atoms in the base [sic], an Al–N distance of 2.18 Å and an N–Al–N angle of 180°. Such a

structure corresponds to sp^2-pd hybridisation (three planar sp^2-bonds and two pd-orbitals perpendicular to their plane)[19,20,27], symmetry group D_{3h} [20,26,106] or D_3.[106] From the similarity of the spectra of solutions of AlH_3 in complex-forming solvents and by general analogy such a structure can also be suggested for complexes with $2C_4H_8O$, $2OC_4H_8O$, and the mixed compound $AlH_3.C_4H_8O.OC_4H_8O$.[16]

At the same time some uncertainties about the frequencies still exist even for the complexes with $N(CH_3)_3$. The Al–N stretching vibration in compounds of the 1 : 1 type has been assigned the frequency 533 cm^{-1} on the grounds that it is unchanged on going to $AlD_3.N(CH_3)_3$, whereas all the others show a decrease in frequency of a factor of $\sqrt{2}$.[26] However, the absorption in this region is very weak so that Roszinski and Dautel[9] could not even detect it in deuteriation. This fact is puzzling.

In the 1 : 2 complexes the N–Al–N symmetric stretching vibrations are from the same considerations assigned the frequency 461 cm^{-1} (Raman spectra, inactive in the infrared spectrum) and the asymmetric, 460 cm^{-1} (infrared spectrum, inactive in the Raman spectrum)[26], 466 cm^{-1}, and 460 cm^{-1}.[106] The proximity of these values is strange, since the light aluminium atom takes part in the asymmetric vibrations, and consequently the shift should be more pronounced. This contradiction has been explained[106] by the spectra's being obtained under different conditions—the infrared spectrum in the gas, and the Raman spectrum in $N(CH_3)_3$ as solvent. An attempt has been made[116] to calculate the frequency of the corresponding vibrations theoretically; however, by making a series of necessary assumptions the authors did not obtain values which agree well with those observable experimentally. They all concluded that the frequency of the symmetric vibrations should be found in the 150–200 cm^{-1} region. Actually, in the Raman spectrum absorption is observed[106] at 197 cm^{-1}, which the authors[106] assigned to the deformation vibrations of the Al–N bond and two absorption bands at 142 and 114 cm^{-1}, not assigned to any vibrations owing to the absence of an absorption spectrum for $N(CH_3)_3$ in this frequency range. In fact, one of them could be a deformation vibration since it is known that the N–Al–N bond is very readily deformed[24,106]. Evidently, further investigation is necessary.

In the complexes with tetrahydrofuran and dioxan the position is still more uncertain. The stretching vibration of the Al–O bond in $AlH_3.C_4H_8O$ was assigned the frequency 538 cm^{-1} in benzene solution, by analogy with the corresponding frequency in the complex with $N(CH_3)_3$.[9] However, in the spectra of solutions of AlH_3 in $AlH_3.N(CH_3)_3$ in tetrahydrofuran frequencies above 400 cm^{-1} which could be assigned to the Al–O or Al–N vibrations are not observed[9,16]. On the contrary, the frequency 455 cm^{-1}, provisionally assigned to the Al–O stretching vibrations is observed in the spectra of these substances and of $AlH_3.C_4H_8O$ in dioxan and of $AlH_3.OC_4H_8O$ in tetrahydrofuran[9]. There are, however, grounds for assuming that it is due to the deformation vibrations of the dioxan ring, inactive in the infrared spectrum in pure dioxan and which appears on destroying its symmetry by interaction with AlH_3.[16] Precise determination of the vibration frequencies of the aluminium–donor atom bond would be extremely desirable to solve problems connected with the stability of the complexes.

In this respect the dependence of the stretching frequencies of AlH_3 on the strength of the ligand–aluminium bond is interesting. Zeil and coworkers[20], having comparatively meagre data at their disposal, evaluated the force constant of this bond and found that it decreases in the series of compounds $AlH_3 > AlH_4^- > AlH_3.C_4H_8O > AlH_3.2N(CH_3)_3$. Schomburg and Hoffman[115] compared the displacement of the Al–H vibration frequency with the heat of reaction of AlH_3 with various ligands[117] and observed that they were symbathic. Later this relation was used repeatedly, was generalised, and was taken as a general rule[9,16,114]. However, the conclusions given in the literature need to be reconsidered, since they were obtained by comparing spectra for different states of aggregation and using spectra of crystalline substance, which is scarcely permissible in the absence of reliable assignment of frequencies and clear information about the character of the interaction of the molecules of the complexes in the crystalline state. Table 5 gives the stretching vibration frequencies of the Al–H bond from the spectra obtained under comparable conditions. The concentration of the test solutions is not always given in the original studies, but as far as can be judged in all the instances quoted it does not exceed 0.5 M. The observed difference between the various data are evidently explained by the experimental difficulties with such active substances.

Table 5 suggests that the ligands can be arranged according to the strength of the bond with aluminium in the 1 : 1 complexes in the series: $N(CH_3)_3 > C_4H_8O > N(C_2H_5)_3$. It is also evident that the solvents concerned are sufficiently inert in relation to these complexes, since the frequency

Table 5. Stretching vibrations of the Al–H bond in dilute solutions of the complexes AlH_3L in inert solvents at room temperature, cm^{-1}.

Complex	Solvent	Stretching vibration	Reference	Complex	Solvent	Stretching vibration	Reference
$AlH_3.N(C_2H_5)_3$	C_6H_6	1778	16	$AlH_3.N(CH_3)_3$*	C_6H_6	1778	16
	C_6H_{12}	1779	115		C_6H_{12}	1786	16
		mean 1778			C_6H_{18}	1786	16
$AlH_3.C_4H_8O$	C_6H_6	1778	16		C_6H_6	1786	114
	C_6H_{18}	1786	16		C_6H_{12}	1788	115
	C_6H_6	1786	114		C_6H_6	1803	315
	C_6H_{12}	1794	16			mean 1787	
		mean 1786					

* In the gaseous state: 1792 cm^{-1}.[26]

in the gas and in them are very close. The latter relates also to $AlH_3.2N(CH_3)_3$, the only non-mixed 1 : 2 complex, studied in inert solvents: 1706 (C_6H_{12} [115]), 1702 (C_6H_6 [16]), and 1690 (C_6H_6 [114]) (mean 1700) and 1709,[26] 1709,[9] and 1711 cm^{-1} [106] (mean 1710 cm^{-1}) in the gas. For the remaining complexes, which contain more than one ligand molecule per AlH_3 molecule, information exists only for their solutions in the same ligand (Table 6) or in another (Table 7). In all these instances the frequency relates to the Al–H asymmetric stretching vibrations, since they are obtained from the infrared spectra, in which the symmetric vibrations are inactive.

To draw the correct conclusions from Table 6 it is necessary to bear in mind two additional circumstances. Firstly, a second $N(C_2H_5)_3$ molecule is not added even in a solution of AlH_3 in this substance[9,16,26]. Secondly, $(C_2H_5)_2O$ exhibits some anomalies in comparison with other ligands, namely, in benzene solution, with AlH_3 and $(C_2H_5)_2O$ in the ratio 1 : 4, absorption is observed at 1840 cm^{-1}, and at 1800 cm^{-1} there is only a "shoulder". Evidently this must be understood as an indication that in a solution of AlH_3 in

$(C_2H_5)_2O$ a 1 : 2 complex is formed, which in benzene is largely decomposed into the 1 : 1 complex and free $(C_2H_5)_2O$. True, it has been suggested[16] that at coordination number 5 the Al–H frequency should be $\geqslant$ 1750 cm^{-1}, but probably the anomaly once again consists in a departure from this rule, which holds well for other ligands. When this observation is taken into account, then according to Table 6 we obtain the following series of strengths of the bond between the ligands and aluminium hydride in the 1 : 2 L complexes: $N(CH_3)_3 > C_4H_8O > OC_4H_8O > (C_2H_5)_2O > N(C_2H_5)_3$.

This conclusion is confirmed in the NMR spectra for AlH_3 in the 1 : 1 and 1 : 2 complexes with $N(CH_3)_3$ and C_4H_8O, the chemical shift in which is greater for $N(CH_3)_3$.[19]

Table 6. Stretching vibrations of the Al–H bond in solutions of the complexes $AlH_3.L$ in corresponding solvents L, cm^{-1}.

Complex	Stretching vibration	Reference	Complex	Stretching vibration	Reference
$AlH_3 \cdot N(CH_3)_3$	1710	26	$AlH_3 \cdot OC_4H_8O$	1754	16
$AlH_3 \cdot C_4H_8O$	1724	114	$AlH_3 \cdot N(C_2H_5)_3$	1778	16
$AlH_3 \cdot C_4H_8O$	1739	16	$AlH_3 \cdot (C_2H_5)_2O$	1801	114

Table 7. Stretching vibrations of the Al–H bond in solutions of the complexes $AlH_3.L$ in complex-forming solvents L', cm^{-1}.

Complex	Solvent	Stretching vibration	Reference	Complex	Solvent	Stretching vibration	Reference
$AlH_3 \cdot LiH$	C_4H_8H	1674	16	$AlH_3 \cdot N(CH_3)_3$	C_4H_8O	1710	114
$AlH_3 \cdot LiH$	C_4H_8O	1678	93	$AlH_3 \cdot N(CH_3)_3$	C_4H_8O	1724	16
$AlH_3 \cdot LiH$	$(C_2H_5)_2O$	1733	77			mean 1717	
$AlH_3 \cdot LiH$	$(C_2H_5)_2O$	1740	110	$AlH_3 \cdot N(CH_3)_3$	$(C_2H_5)_2O$	1724	114
$AlH_3 \cdot LiH$	$(C_2H_5)_2O$	1746	118	$AlH_3 \cdot N(CH_3)_3$	OC_4H_8O	1732	16
		mean 1740		$AlH_3 \cdot N(C_4H_8)_3$	C_4H_8O	1740	115
				$AlH_3 \cdot C_4H_8O$	OC_4H_8O	1747	16
				$AlH_3 \cdot OC_4H_8O$	C_4H_8O	1747	16

For the formation of 1 : 2 mixed complexes of type $AlH_3.L.L'$ the position is more complex. It is evident directly from Table 7 that in the addition of various ligands to $AlH_3.N(CH_3)_3$ the compounds which are formed are arranged in the following series according to stability: $C_4H_8O > (C_2H_5)_2O > OC_4H_8O$, where OC_4H_8O and $(C_2H_5)_2O$ change places in comparison with the 1 : 2L complexes. The same order for C_4H_8O and $(C_2H_5)_2O$ is kept also in their addition to $AlH_3.LiH$.

On the basis of the results collected in Tables 5–7 and those on a solution of $AlH_3.C_4H_8O.(C_2H_5)_2O$ in C_6H_6,[114] it can be shown that the shift in the Al–H frequency on the addition of L' to $AlH_3.L$ depends on the nature of L and L', despite conclusions[16] drawn from a comparison of spectra obtained under poorly comparable conditions (Table 8). For comparison, Table 8 also gives the displacement in the formation of complexes of type $AlH_3.2L$. The NMR spectra also confirm that the addition of the second C_4H_8O molecule to $AlH_3.C_4H_8O$ is less favourable than that of $N(CH_3)_3$ to $AlH_3.N(CH_3)_3$.[19] Unfortunately, on account of the absence of information under comparable conditions the shift in frequency during the formation of AlH_4^- from AlH_3 cannot be determined. However, reliable estimates using the results on solutions of $LiAlH_4$ in C_4H_8O and $(C_2H_5)_2O$ show that it lies within the limits 60–100 cm^{-1}, that is, almost equal to the shift brought about by the most strongly bound ligands. The values found for $\Delta\nu$ agree with the facts that $N(CH_3)_3$ is not displaced from the complexes by tetrahydrofuran and dioxan, whereas in an excess of OC_4H_8O the C_4H_8O is partly replaced with the formation of $AlH_3.2OC_4H_8O$.[19] At the same time it should be noted that the symbathic relation between $\Delta\nu$ and the tendency for complex formation is absent. Thus the addition of the first $N(C_2H_5)_3$ molecule brings about almost the same displacement as the addition of $N(CH_3)_3$; however, in the first instance the 1 : 2 compound is not formed completely, whereas in the second it is formed and seems completely stable. Further, the compounds with $2C_4H_8O$ and $2OC_4H_8O$ are formed only in an excess of the ligands[9], but the addition of $(C_2H_5)_2O$ to $AlH_3.N(CH_3)_3$, even in $(C_2H_5)_2O$ takes place only partially despite the high value of $\Delta\nu$. This is so because the absorption at 1724 cm^{-1}, which corresponds to the complex $AlH_3.N(CH_3)_3.(C_2H_5)_2O$, is very weak and the strong absorption corresponding to the $AlH_3.N(CH_3)_3$ molecules is retained[114]. In the literature these facts are attributed to steric hindrance[9,114], but no additional confirmation of this has yet been found. It therefore remains uncertain what aspect of the steric factors are significantly less favourable for $N(C_2H_5)_3$ than for $(C_2H_5)_2O$ or C_4H_8O and OC_4H_8O. The uncertainty is even further aggravated by the fact that the rather stable compounds $AlH_3.2NCH_3(C_2H_5)_2$ and $AlH_3.N(CH_3)_3.N(C_2H_5)_3$ are formed[27].

From the results of Tables 6 and 7, clearly in an excess of ligand the compounds $AlH_3.L$ (L $\neq$ LiH) do not give complexes with $n > 2$. From Table 8 it follows that the most favourable formation of mixed complexes occurs at L = $N(CH_3)_3$. At the same time, according to Ehrlich and coworkers[114] the vibrations of the Al–H bond for solutions of $AlH_3.2N(CH_3)_3$ in C_4H_8O—the strongest ligand after $N(CH_3)_3$—and in $(C_2H_5)_2O$ lie at 1695 cm^{-1} and the same vibrations for solutions of $AlH_3.2N(CH_3)_3$ in benzene, at 1690 cm^{-1}. Hence, clearly, complexes with a coordination number 6

Table 8. Displacement of the frequencies of the Al–H stretching vibrations on going from $AlH_3.L$ to $AlH_3.L.L'$.

L*	L'	Condition of production of spectrum of $AlH_3.L.L'$	$\Delta\nu$, cm^{-1}	L	L'	Condition of production of spectrum of $AlH_3.L$	Condition of production of spectrum of $AlH_3.L.L'$	$\Delta\nu$, cm^{-1}
$N(CH_3)_3$	C_4H_8O	soln. in C_4H_8O	70	$N(CH_3)_3$	$N(CH_3)_3$	inert solvent	soln. in C_6H_6	88
$N(C_2H_5)_3$	C_4H_8O	soln. in C_4H_8O	38	C_4H_8O	C_4H_8O	inert solvent	soln. in C_4H_8O	54
$N(CH_3)_3$	OC_4H_8O	soln. in OC_4H_8O	55					
C_4H_8O	OC_4H_8O	soln. in OC_4H_8O	39					
C_4H_8O	$(C_2H_5)_2O$	soln. in C_6H_6	76	$(C_2H_5)_2O$	$(C_2H_5)_2O$	soln. in $(C_6H_6)+(C_2H_5)_2O$	soln. in $(C_2H_5)_2O$	40
$N(CH_3)_3$	$(C_2H_5)_2O$	soln. in $(C_2H_5)_2O$	63					

* All the spectra of $AlH_3.L$ were obtained in inert solvents.

for aluminium are not formed in such mixtures. However, $\nu_{Al-H}LiAlH_4$ in C_4H_8O (Table 7) and the liquid mixture $AlH_3.LiH:C_4H_8O = 1:8$ lies at 1674 cm^{-1}, but in a solution of the mixture $AlH_3.LiH:C_4H_8O = 1:3$ in benzene, at 1724 cm^{-1}.[16] Hence the conclusion (which should be confirmed by a more thorough and detailed investigation) that instances of complex formation in the liquid phase with a coordination number of 6 for Al are clearly possible. This is suggested, in particular, by the infrared spectra of solutions of the alkali metal tetrahydroaluminates, $CsAlH_4-LiAlH_4$, in diglyme and of $LiAlH_4$ and $NaAlH_4$ in C_4H_8O.[93] It was found[92] that the spectra agree with the existence of the anion $[AlH_4.2L]^-$. However, they can be interpreted also without this assumption, which needs additional proof.

The next question, directly connected with the stability of the complexes formed, is the change in the state of ligand molecules on coordination with Al. Unfortunately, little information is available here. Of the 1:1 complexes only that with $N(CH_3)_3$, and of the 1:2 complexes those with $N(CH_3)_3$ and C_4H_8O, have been investigated. In $AlH_3.N(CH_3)_3$ a shift in the N–C stretching frequency in the $N(CH_3)_3$ molecule from 1040 cm^{-1} in pure $N(CH_3)_3$ (gas) to 1005 cm^{-1} in complexes (gas)[26] or 1000 cm^{-1} (solution in C_6H_6)[16] is observed. In the solutions of the complex in C_4H_8O and OC_4H_8O this frequency lies at 1018 and 1015 cm^{-1} respectively[16]. The 997–1002 cm^{-1} absorption band was also observed in the liquid 1:1 complexes of $N(CH_3)_3$ with $(C_2H_5)_2AlH$, $(C_2H_5)AlH_2$, $(CH_3)_2AlH$, and CH_3AlH_2.[30] For the 1:2 compounds with $N(CH_3)_3$ the results are less unequivocal: Heitsch and Kniselly[106] did not observe a change in the infrared spectrum of $N(CH_3)_3$ in the gaseous complex, and Dautel and Zeil[16] observed an absorption band at 1015 cm^{-1} in the benzene solution of the complex. They did not observe[19] a chemical shift of the NMR lines for the protons of the CH_3 groups. Evidently these results suggest a comparatively weak change in the state of the $N(CH_3)_3$ molecules. This can be explained by the free electron pair of the nitrogen in $N(CH_3)_3$ already participating in the sp^3-hybridisation of this atom (the angles of the C–N–C bonds are close to tetrahedral)[19]. On the other hand, in the $AlH_3.2C_4H_8O$ complexes a drop in the resonance frequency in the NMR spectrum of the proton in the α-CH_3 group by 10 Hz is observed, whereas in the β-CH_2 groups there is no chemical shift. This is explained by the strong change in the valence state of the O atom, the [bonding] eigenfunction of which in the free ligand is the p-function (possibly, with a small fraction of s-character)[19]. It is quite probable that the change in energy level of the molecule of the ligands plays a considerable part of the role which is ascribed to steric hindrance in the attempts to explain the observed regularities in complex formation.

Generally speaking, the structure of the complexes considered above in the condensed state can undergo definite changes owing to association if this involves a change in the coordination number of aluminium or the setting up of ligand–ligand bonds. Table 9 gives results on the degree of association of several complexes. The possibility of the formation of bonds between these ligands, already coordinated with aluminium, is almost absent. Consequently, the association can be due either to the high values of the dipole moments ($\mu \simeq 3-5$ D[26,115,118]) or the formation of hydrogen bridges, the possibility of which for solid AlH_3 was first shown by Longuet-Higgins[119]. Subsequently this idea was extended by other authors to solutions of its complexes. Let us first consider the liquid state.

The formation of hydrogen bridges should be indicated in the infrared spectra by: (1) broadening of the bands for the Al–H stretching vibration, (2) the shift to lower frequencies of this vibration, and (3) the appearance of certain new lines in the spectrum. In the NMR spectra there should be corresponding displacements. Not one of these phenomena occurs in the solutions in inert solvents, at least up to 0.5 M concentration[19,20,26,31,77,115]. Moreover, Wiberg and coworkers[25] found that at the b.p. of solutions of $LiAlH_4$ in diethyl ether the molecular weight of $LiAlH_4$ increases with concentration and corresponds to $(LiAlH_4)_2$ at 0.08 M, and to $(LiAlH_4)_3$ at 0.8 M, which they explain by the formation of hydrogen bridges, However, a change in the form and a displacement of the absorption bands of the complex up to 3.4 M was not observed in the infrared and Raman spectra[77,110] of these solutions although the degree of association is sufficiently high even in dilute solutions (cryoscopy, Table 9), and a concentration of 0.3–0.5 M is completely sufficient for obtaining clear spectral data. The association of hydrides of the type R_2AlH has been investigated by cryoscopic methods and by infrared and Raman spectroscopy[118,120]. It was found that in the liquid state, dilute solutions, inert solvents, and in the gas these compounds are trimers owing to the formation of hydrogen bridges with aluminium in coordination number 4. Very strong absorption bands for the Al–H of the trimers lie in the 1770 cm^{-1} range and have a half-width of $\sim$ 100 cm^{-1} (concentration of solutions $\sim$ 0.1 M). The addition of strong complex-forming ligands, such as $N(CH_3)_3$, C_4H_8O, and $(C_2H_5)_2O$ leads to the breakdown of the trimers and the formation of 1:1 complexes with the aluminium coordination number remaining at four, this being accompanied by a marked narrowing of the absorption bands and their displacement to lower or higher frequencies (see also Schomburg and Hoffman[115]), depending on the ligand. The latter is understandable, since here there are two effects superimposed—displacement to higher frequencies on breaking the hydrogen bridge, and to lower during coordination of the ligand. However, no narrowing of the absorption bands takes place during the formation of the complexes $AlH_3.2L$ or $AlH_3.L.L'$ from $AlH_3.L$.[9,14] Further, in the addition of L' to $AlH_3.L$ the maximum displacement of frequency to the side of lower frequencies takes place for $L = N(CH_3)_3$ (Table 8), that is, when α is

Table 9. Degree of association α of the complexes from cryoscopic results.

Complex	Solvent	Concentration, M	α	Reference
$AlH_3 \cdot N(CH_3)_3$	C_6H_6	0.13—0.61	1.40—1.44	23, 25, 31, 114
$AlH_3 \cdot C_4H_8O$	C_6H_6		1.55	114
$AlH_3 \cdot (C_2H_5)_2O$	C_6H_6		1.21	114
$AlH_3 \cdot N(CH_3)_2CH_2CH{=}CH_2$	C_6H_6		1.37	31
$AlH_3 \cdot NCH_3(C_2H_5)_2$	C_6H_6	0.48—0.78	1.33	31
			1.10	31*
$AlH_3 \cdot N(C_2H_5)_3$	C_6H_6	0.19—0.39	1.57	23,25
$AlH_3 \cdot N(C_3H_7)_3$	C_6H_6	0.30—0.57	1.05	31
$AlH_3 \cdot N(C_4H_9)_3$	C_6H_6		1.17	23,25
$CH_3AlH_2 \cdot N(CH_3)_3$	C_6H_{12}		1.95	30
$(CH_3)_2AlH \cdot N(CH_3)_3$	C_6H_{12}		1.34	30
$C_2H_5AlH_2 \cdot N(CH_3)_3$	C_6H_{12}		1.60	30
$(C_2H_5)_2AlH \cdot N(CH_3)_3$	C_6H_{12}		1.18	30
$AlD_3 \cdot N(CH_3)_3$	C_6H_6		1.43	31
$AlH_3 \cdot 2N(CH_3)_3$	C_6H_6		1	9, 16, 26

* The authors[31] found it difficult to explain this departure from Wiberg's results[23,25].

highest (Table 9) and a significant difference in sign of the contribution from the breaking of the hydrogen bridges would be expected. Hydrogen bridges are absent from a solution of AlH_3 in diethyl ether, in which AlH_3 is monomeric[12] although the bonding of AlH_3 in ether is weak. Probably the $(C_2H_5)_2O \rightarrow AlH_3$ donor–acceptor bond, in decreasing the formal positive change on Al, leads to loss by the AlH_3 molecule of the ability to give hydrogen bridges. It therefore seems improbable that bridges can be formed by AlH_3 molecules bound with such strong donors as amines.

Ruff[29], in considering the results of Ulich and Nespital[121] for solutions of complexes of aluminium halides, also considers that the association of these complexes is more similar to the dipole–dipole interaction than to polymerisation through halogen bridges.

The dipole–dipole interaction hypothesis accords with symmetric $AlH_3.2N(CH_3)_3$, the dipole moment of which is close to zero, not being associated in benzene (Table 9), although the coordination number of aluminium does not have the maximal value of 6 (see Refs. 9, 13, 119, 122).

The association of $AlH_3.NR_3$ in benzene decreases with increase in the length of the amine radical (Table 9)[23,25,31]. Such a relation contradicts the hypothesis of hydrogen bridge formation, since with decrease in the radical length the stability of the complexes of AlH_3 with NR_3 increases, corresponding to a decrease in the effective positive charge on the Al in the $Al^{\delta+}-H^{\delta-}$ bond[19], which should hinder the formation of hydrogen bridges, that is, decrease the degree of association.

The main argument supporting the existence of hydrogen bonds in benzene solutions is thought[23,25,31] to be the association of $AlH_3.NR_3$, in contrast with the monomeric nature of $AlH_3.NR_3$ in diethyl ether. This, in the opinion of the authors, is connected with the breaking of hydrogen bonds due to donor–acceptor interaction with ether. However, the monomeric nature can be explained also by inhibition of the dipole–dipole interaction of the $AlH_3.NR_3$ molecules in diethyl ether, because of the somewhat greater dielectric constant of ether in comparison with benzene, and also the weakening due to the decrease in μ of the complex, since in an excess of ether unstable mixed diadducts can be formed, $AlH_3.NR_3.(C_2H_5)_2O$ with $\mu \simeq 0$.

The absence of association (according to ebullioscopic results[88]) of $LiAlH_4$ in C_4H_8O can be explained in a similar manner.

Hence if the possibility of association due to dipole–dipole interaction is considered then it must be acknowledged that in dilute solutions there are no objective reasons for assuming the existence of hydrogen bridges, provided only that the latter do not exhibit any new properties distinguishable from those for bridges in $(R_2AlH)_x$. For compounds of the type $R_2AlH.N(CH_3)_3$ and $RAlH_2.N(C_2H_5)_3$. another method of association is possible—due to the carbon of the methyl (for R = CH_3) and methylene CH_2 group (for R = C_2H_5). Such a possibility follows from the splitting of the NMR lines[30]. We note that the dimerisation of $Al(C_2H_5)_3$, also investigated by the NMR method[123] also takes place because of the CH_2 group. Doubt about the formation of hydrogen bridges has repeatedly been expressed[16,115,123]. In particular, it is thought[16] that: (a) it is difficult to assume that tetrahedral 1 : 1 complexes lose symmetry and acquire sp^3-spd-hybridisation† with five-coordinated aluminium owing to the formation of hydrogen bridges, and (b) the assumption of dimerisation should imply the presence in the solution of an equilibrium between the monomers and dimers which should enrich the spectra with new lines, which is not observed. True, later the same authors concluded that dimers existed[9], arguing mainly from a comparison of the spectra of $AlH_3.N(CH_3)_3$ and $AlH_3.2N(CH_3)_3$ in the crystalline state, in concentrated and dilute solutions in benzene, and in the gas, and the spectra of $AlH_3.N(C_2H_5)_3$ and $AlH_3.C_4H_8O$ in the crystalline state and in concentrated solution in C_6H_6. In particular they observed the appearance of weak absorption bands in the 1550–1650 cm^{-1} range in concentrated solutions and in the crystals and a displacement of the Al–H frequency to 1762 cm^{-1} for $AlH_3.N(CH_3)_3$ and $AlH_3.C_4H_8O$ in comparison with the dilute solutions (Table 5). From what has been said above, clearly these results cannot themselves be considered as any significant argument in support of the formation of hydrogen bridges. The discussion of Roszinski and Dautel[9], leading them to conclude the formation of hydrogen bridges, also cannot be considered as substantiated. They found by comparison of the spectra in various states of aggregation that the spectrum of $AlH_3.N(CH_3)_3$ in the crystal differs considerably from its spectrum in the gas, but the spectra of $AlH_3.2N(CH_3)_3$ agree. Hence it was concluded that the first compound in the crystal is dimerised, but the second is not. On comparing further the spectra in the crystal and in the concentrated solution and establishing their similarity, the authors drew conclusions about association in the solution. There are two weak spots in this approach which lead to quite unreliable conclusions. Firstly, it is not explained why associates do not appear in the spectra of moderately concentrated solutions. Secondly and mainly, there is no basis for ascribing the difference in the spectra in the crystal and the gas to associates when there is no additional information about the crystal structure, since the appearance of new frequencies and a displacement of the known frequencies can be due to the deformations of the molecules in the crystal field (this, to a certain extent, also relates to concentrated solutions). Such deformation is observed, for example, for the tetrahedral anions $Al(CH_3)_4^-$ in the field of the cations[108] in the $LiAl(CH_3)_4$ crystals. Moreover, the solid compound $AlH_3.NR_3$ sublimes comparatively readily, which would be improbable in the presence of hydrogen bonds.

Finally, association in benzene solutions of $AlH_2N(CH_3)_2$ and $AlH_2N(C_2H_5)_2$ takes place[31] most quickly due to Al–N–Al bonds by analogy with $BH_2N(CH_3)_2$, where such a structure was found by X-ray diffraction[124].

As regards the structure of the complexes in the crystalline state, here except for $AlH_3.2N(CH_3)_3$, which has been investigated by X-ray diffraction, much is not clear. Table 10 shows the frequencies of the Al–H bonds for several compounds.

$AlH_3.2N(CH_3)_3$ crystals consist of individual molecules of the complex[24] without directed bonds between them[9,16]. The spectra of $LiH.AlH_3$ crystals accord with an ionic structure in which the nodes of the lattice are occupied by tetrahedral AlH_4^- ions with Li^+ ions distributed between them[77]. Possibly there is some distortion of the regular tetrahedral form of the anion in the field of the cation[93], like that observed in $LiAl(CH_3)_4$,[108] and responsible for some complication of the spectrum observed in later investigations[9]. On the basis of a comparison of the infrared spectra of crystalline alkali metal tetrahydroaluminates, the authors[93] consider that such distortion is maximal for $LiAlH_4$ and minimal for $CsAlH_4$, with the symmetry of the former being decreased to C_{2v} owing to the formation by the lithium of covalent bonds with two hydrogens of

† Three tetrahedral sp^3-orbitals; instead of a fourth orbital, two spd-orbitals with an included angle of 71°.

the AlH_4^-. The structure of $CsAlH_4$ is thought to be much more ionic with retention of the tetrahedral structure of the anion. For $AlH_3.OC_4H_8O$ a chain structure is proposed with

$$Al-OC_4H_8O-Al-OC_4H_8O$$

bonds on the following grounds: (1) the compound is insoluble in inert solvents; (2) it does not melt; (3) the frequencies of the vibrations are close to those of the 1 : 2 complexes; and (4) in the spectrum there is no 455 cm^{-1} band, corresponding to the deformation vibrations of the dioxan ring and inactive in the infrared spectrum under

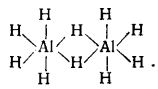
Table 10. Vibration frequencies of the M–H bond of the compounds AlH_3 in the crystalline state, cm^{-1}.

Complex	Vibration frequency	Reference	Complex	Vibration frequency	Reference
$AlH_3 \cdot OC_4H_8O$	1748	9	$AlH_3 \cdot C_4H_8O$	1802	9
$AlH_3 \cdot OC_4H_8O$	1762	16		1810	16
$AlH_3 \cdot LiH$	1778	77	$AlH_3 \cdot 2N(CH_3)_3$	1692	9
	1779	9,13		1702	16
	1782	16	$AlH_3 \cdot LiH \cdot C_4H_8O$	1724	16
$AlH_3 \cdot N(CH_3)_3$	1783	9	$AlH_3 \cdot LiH \cdot 3C_4H_8O$	1695	16
	1786	16	AlH_3*	1592	9
				1600	16

With $(C_2H_5)_2O$ as impurity.

symmetrical loading of the dioxan molecule[16]. For $AlH_3.N(CH_3)_3$ and $AlH_3.C_4H_8O$ association due to hydrogen bridges is proposed, based on the work[9,16] and their criticism given above. To the critical remarks it must be added that the breadths of the absorption bands in all the instances in Table 10 except AlH_3 are similar. On the other hand the absorption band of AlH_3 is very wide and no narrower than the corresponding bands in $(R_2AlH)_3$.[118,120]

The physicochemical properties of $(AlH_3)_x$ also show its high degree of polymerisation, which is usually connected with a high coordination number of aluminium, namely, 6,[9,13,119,122] leading to the formation of a hydrogen-bridged space lattice, which can be provisionally represented in the form of the fragment:

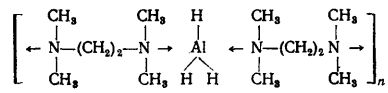


The absorption frequencies of $AlH_3.N(CH_3)_3$ and $AlH_3.C_4H_8O$ —allowing for the fact that they contain a coordinated ligand—lie too high, but for $AlH_3.N(CH_3)_3$ they are still very close to the absorption frequency in the gas (1792 cm^{-1}),[9,26] to support the formation of hydrogen bridges.

Hence it is possible to agree with certain authors[9,16] concerning the polymerisation of AlH_3 due to the formation of hydrogen bridges and to consider their existence at least non-proven in all the remaining complexes of AlH_3. The problem of the structure of the crystals of $AlH_3.LiH.C_4H_8O$ and $AlH_3.LiH.3C_4H_8O$ remains almost completely open.

This section shows rather reliably the existence of compounds of aluminium with coordination number 6, namely, for $(AlH_3)_x$; the same number exists in the complexes which have recently become well-known: Na_3AlH_6 [65,91] and Li_3AlH_6.[82] Six-coordination also may occur in solutions of $AlH_3.MH$ in tetrahydrofuran and diglyme and in a liquid mixture of composition $AlH_3.LiH + 3C_4H_8O$ where the Al–H absorption band is displaced[16] to 1674 cm^{-1}. Most probably, however, it does not exceed 5. In this connection it is interesting to note the remarkable similarity in the structure of the spectra of solutions of $AlH_3.LiH$ in THF and of gaseous $AlH_3.2N(CH_3)_3$ (see Table 11).

However, when the ligand entering the complex is bidentate polymerisation is possible for complexes of AlH_3. Polymeric structures which are well-founded are proposed[10] for complexes of AlH_3 with diamines[10,97]. Thus, a structure with a unit cell containing eight dimeric units:



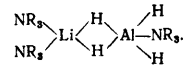
has been given[10] for the complex of AlH_3 with tetramethylethylenediamine.

The high melting points and sublimation temperatures of such complexes and their thermal stability[10,37] also confirm the presence of a polymeric structure. There is probably an analogous structure in the complex of AlH_3 with triethylenediamine[38].

Table 11. Spectrum of a solution of $AlH_3.LiH$ in tetrahydrofuran[16] and of gaseous $AlH_3.2N(CH_3)_3$.[9,26]

$AlH_3.LiH$ in tetrahydrofuran, cm^{-1}	Gaseous $AlH_3.2N(CH_3)_3$, cm^{-1}
1674	1709
895	894
763	793
426	727
416	460

Polymerisation due to ligand has also been proposed for the complex $AlH_3.OC_4H_8O$.[9,16] The complexes $AlH_3.NC_5H_5$,[36] $AlH_3.LiH.N(CH_3)_3$,[88] $AlH_3.NaH.C_4H_8O$,[108] and $AlH_3.LiH.3N(CH_3)_3$[88] are ascribed a structure based on general considerations and chemical properties. It is thought that in these compounds the aluminium has coordination number five and that in the first three complexes the ligand is coordinated by aluminium whereas the last has the structure



Further investigations are needed to establish the complete structure of these compounds.

V. ELECTROCHEMISTRY OF SYSTEMS CONTAINING ALUMINIUM HYDRIDE

1. Electrical Conductivity of Solutions of $MAlH_4$

To show the nature of solutions of hydroaluminates and to make electrochemical preparations information about the electrical conductivity of such systems is needed. The published data are very limited and contradictory.

Solutions of $LiAlH_4$ in diethyl ether have a very low electrical conductivity; κ for a 1 M solution at 15°C is $(4.43 \pm 0.02) \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$,[125] κ for ethereal solutions of $LiAlH_4$ is less by a factor of ~ 2.5 than for such solutions

of $LiClO_4$.[126] The relation between the electrical conductivity of $LiAlH_4$ solutions and their purity has also been noted[127]. The variation of the electrical conductivity with the $LiAlH_4$ concentration is shown in Fig. 1, curve *a*,[127] and agrees in order of magnitude with other results[125]; however, in another study[126] κ is approximately an order

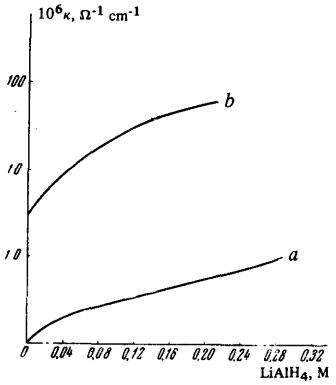


Figure 1. Variation of the electrical conductivity, κ, Ω^{-1} cm^{-1}, with the $LiAlH_4$ concentration: *a*) in pure diethyl ether; *b*) in diethyl ether containing 0.394 M AlH_3.

of magnitude less. Curve *b* shows the variation of κ with $LiAlH_4$ concentration in the presence of AlH_3. Here κ is greatly above the additive value, as with MHal–AlR_3 systems[128]. It is also interesting that the electrical conductivity of ethereal solutions of $LiAlH_4$ and AlH_3 at the same concentrations is similar[127].

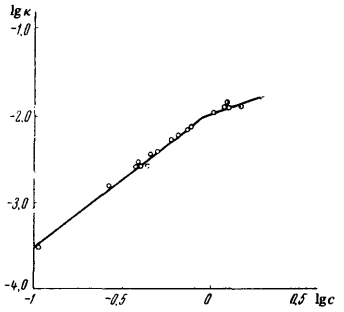


Figure 2. Variation of the electrical conductivity, κ, Ω^{-1} cm^{-1}, of a solution of $LiAlH_4$ in tetrahydrofuran with the concentration *c*, M.

The electrical conductivity of solutions of $LiAlH_4$ in tetrahydrofuran has been measured over the concentration range 0.1–1.5 M at $t = 25° \pm 0.5°C$ (Fig. 2).[129] It was found that such solutions are quite stable even in contact with platinum electrodes.

The variation of the molar conductance with concentration (Fig. 3) does not obey the Ostwald dilution law for weak electrolytes.

Solutions of $NaAlH_4$ in tetrahydrofuran also have high electrical conductivity: $\kappa = 2 \times 10^{-2}\ \Omega^{-1}$ cm^{-1} at $c = 3$ M and 40°C (for 1 mole KCl per dm^3 water $\kappa = 1.10 \times 10^{-1}\ \Omega^{-1}$ cm^{-1} at 25°C [130]).

The electrical conductivity of solutions in tetrahydrofuran greatly exceeds that of solutions in diethyl ether. This is probably because the latter is a weaker complexing agent than tetrahydrofuran in relation to $MAlH_4$, although some effect must be due to the somewhat greater dielectric constant of tetrahydrofuran (7.87) compared with that of diethyl ether (4.34). However, the degree of dissociation of $LiAlH_4$, even in tetrahydrofuran is always small and amounts to 1–10%, which can be estimated from the ebullioscopic value of the molecular weight 38 ± 1 (calculated value 38)[83] and the value of κ on making reasonable assumptions about the mobility of the ions in tetrahydrofuran.

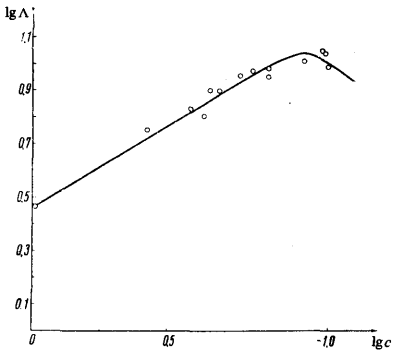


Figure 3. Variation of the molar conductance, Λ_m, Ω^{-1} cm^2 mole^{-1}, of a solution of $LiAlH_4$ in tetrahydrofuran on the concentration, *c*, M.

Most authors assume that $LiAlH_4$ in diethyl ether dissociates into Li^+ and AlH_4^-.[40,125,126,131] However, such a scheme is hardly correct for solutions in tetrahydrofuran. An anomalous dependence of molar conductance[129] of $LiAlH_4$ on concentration‡ can be explained by the complex interaction of the particles of the solute with one another[132,133] or with solvent. The hypothesis of complex formation, probably with participation of the solvent, is confirmed by the fact that the electrical conductivity of dilute solutions of $LiAlH_4$ in tetrahydrofuran has a negative temperature coefficient[129], which could be connected with the breakdown of the compounds formed on raising the temperature. At high concentrations of lithium tetrahydroaluminate in tetrahydrofuran the temperature coefficient of electrical conductivity is greater than zero[129]. Possibly here the increase in electrolytic dissociation of the complexes with rise in temperature exceeds the effect of the breakdown of the complexes into components. On the grounds that the reduction of covalent chlorides (PCl_3, BCl_3, etc.) by lithium tetrahydroaluminate takes place only in the presence of donor solvents, some authors consider that the further dissociation

$$AlH_4^- \rightleftharpoons H^- + AlH_3$$

‡ An increase in molar conductance on increasing the concentration is also observed in solutions of $NaAlR_4$ in diethyl ether (R = alkyl)[84].

is possible[82,125]. The role of the donor here consists in the shift of the equilibrium to the right owing to the bonding of AlH_3 in the complex. It has also been suggested that ethereal solutions of $LiAlH_4$ possibly contain the cations AlH_2^+,[82,134] by the further dissociation

$$2AlH_3 \rightleftharpoons AlH_2^+ + AlH_4^-.$$

The scheme for the breakdown of AlH_4^- with the formation of H^- and AlH_3 seems improbable for energetic reasons although the dissociation of AlH_3 in ether by itself evidently takes place[3]. The latter is confirmed by the conductance of ethereal solutions of AlH_3 (for ~ 0.4 M solution, $\kappa = 3 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$).[127] For reasons stated in relation to the compounds $MAlR_4$ (R = alkyl or halogen)[3] it appears that dissociation of $LiAlH_4$ to the H^- ion does not take place. Dissociation with the formation of H^- has also been rejected in another study[135], where the AlH_4^- ion is considered to be the reducing agent. An increase in the reducing ability of $LiAlH_4$ under the influence of donor solvents should evidently be connected with the formation of $LiAlH_4$ complexes which are more active reductants.

The anions AlH_4^- in an ethereal solution of $LiAlH_4$ are probably only slightly solvated in agreement with the instability of the ethereal complexes of $LiAlH_4$ (Table 4) and with the relatively large size of the AlH_4 ion[40] (r = 2.45 Å, calculated on the Al–H distance of 1.66 Å) and also with the absence of a change in breadth and position of the absorption bands of AlH_4^- in the spectra with change of concentration[77,110]. The Li^+ ions in an ethereal solution of $LiAlH_4$ are thought to be strongly solvated[53]. This accords with the weakening of the ether CO absorption bands in the Raman spectra of such solutions[77].

The greater-than-additive values of the electrical conductivity of ethereal solutions of $LiAlH_4$ mixed with AlH_3 (Fig. 1) shows the formation of alternative ions to those arising from $LiAlH_4$ and AlH_3 separately. In accordance with this[3,136] and by analogy with observations on MHal–AlR_3 systems, it is natural to suggest the formation of $MAlH_4.nAlH_3$ complexes or polyhydroaluminates, in particular, heptahydrodialuminate, $LiAl_2H_7$. The dissociation of such complexes should lead to the formation of polyhydrodialuminate ions:

$$LiAl_2H_7 \rightleftarrows Li^+ + Al_2H_7^-$$

and in view of the larger anions the degree of dissociation and consequently the electrical conductivity should exceed the corresponding values for $LiAlH_4$ and AlH_3§.

The relatively high values of the electrical conductivity for the complexes $LiAlH_4.nAl(C_2H_5)_3$ (n = 2–4) and the rise in conductivity with increase in the number of ligand molecules (Ref. 69, see Table 4) also support the hypothesis of the formation of $LiAlH_4.nAlH_3$ in mixtures of $LiAlH_4$ and AlH_3.

2. Electrode Processes

Claisen's patent deals with the electrolysis of solutions of $NaAlH_4$ and $Ca(AlH_4)_2$ in tetrahydrofuran. Mercury was used as cathode and an aluminium rod as anode. During electrolysis sodium amalgam formed on the cathode and AlH_3 accumulated in the solution but at the anode (according to the authors) hydrogen is released by the overall reaction

$$NaAlH_4 \rightarrow Na_{amal} + AlH_3 + \tfrac{1}{2}H_2.$$

It is thought[6] that the accumulation of AlH_3 in solution is accompanied by the formation of the complex $NaAl_2H_7$:

$$2\,NaAlH_4 \rightarrow Na_{amal} + NaAl_2H_7 + {}^1/_2H_2.$$

After the saturation of the electrolyte with the products the "pure" AlH_3 starts to be precipitated. By the term "pure" the author evidently understands AlH_3 free from chloride impurities, as distinct from the hydride obtainable by a chemical method[12]. For the production of unsolvated AlH_3 by this method the hydride cannot be freed completely from impurities, as is evident from the work described earlier. Therefore a similar electrochemical process has no advantages in comparison with the usual chemical preparation.

Information was recently published on the electrolysis of a solution of $NaAlH_4$ in tetrahydrofuran[137]. Several different metals and low-resistance or p-type Ge and Si have been used as anodes, platinum as cathode (Table 12).

Table 12. Behaviour of a series of anions in $NaAlH_4$ + C_4H_8O.

Anode	Current density, mA cm^{-2}	Current efficiency, %	Gas evolution
Mg	9	70	+
Ga	15	100	—
Si	15	124 (Si^{4+})	—
Ge	10—18	13	+
Na	10	not determined	—
Pt, Cu, Hg, Zn	15—22	0	+

Even from a purely qualitative examination of the anodic dissolution of metals it is clear that a sharp difference exists not only between the "noble" and strongly electropositive metals but also between the latter, for example, Mg and Zn. The existence of "free" ions of polyvalent metals in solution is improbable since they tend to form complexes. Moreover, if it is assumed that the initial electrode act is the discharge of AlH^- ions or molecules of $NaAlH_4$ [sic], the atomic hydrogen liberated could form hydrides with the electrode metal. There is therefore a definite probability that in the anodic dissolution of metals hydrides or hydroaluminates of the corresponding metals will be formed. In this connection it is interesting to compare certain properties of these compounds with the ability of the corresponding metals to dissolve during anodic polarisation in solutions of $NaAlH_4$ or $LiAlH_4$ in ethers (Table 13)[134].

By analogy with the solubility of sodium and lithium tetrahydroaluminates it can be suggested that the tetrahydroaluminates of Mg, Ga, and Be are soluble in tetrahydrofuran. Silicon and germanium hydrides are gases and if soluble in ethers the solubility is insignificant. On comparing these results with Table 12 on electrolysis, clearly anodic dissolution occurs for those metals the hydrides or tetrahydroaluminates of which are soluble in the solvent concerned. With germanium the products of

§ After writing this review we learnt that G.Schrauzer (Thesis, Munich, 1956) found an increase in the molar conductance of solutions of alkali metal tetrahydroaluminates with increase in concentration and the electrical conductivity of solutions of $LiAlH_4$ in tetrahydrofuran exceeded the value for a corresponding solution in diethyl ether. He also considers that the dissociation scheme

$$2AlH_3 \rightleftharpoons AlH_2^+ + AlH_4^-$$

is possible.

the anodic dissolution can be removed as gases. With silicon the problem remains unresolved since little gas is released during electrolysis but on the surface a red-brown film forms; this film rapidly turns white and crumbles in air, disclosing a smooth etch surface. Hence, if the proposed hypothesis about the connection of the anodic dissolution of metals with the solubility of their hydrides or hydroaluminates is true, then it could be expected that in this electrolyte not only the metals listed would be soluble, but also Be and Al. The latter was negated by Claisen's results[6], for he did not observe the anodic dissolution of aluminium. However, it should be noted that the patentee did not measure the current efficiency in respect of the metal but the gas liberated, and firstly it is easy to confuse with the boiling of the solvent at the surface of the electrode, and secondly gas liberation is usually observed at the start of electrolysis during the breakdown of the surface film of oxide on the metal.

The process for soluble anodes can then, with some reliability, be described by the equation:

$$M + n AlH_4^- - ne \rightarrow n AlH_3 + MH_n$$

where M is the metal of the anode. It should be noted that the final products of the anodic reaction may be not only the hydride but also $M(AlH_4)_n$. The probability of the formation of the latter depends on its physicochemical properties.

Table 13. Properties of the hydrides and tetrahydroaluminates of certain elements.

Element	$M(AlH_4)_n$	Decomposition temperature, °C	Solubility in $(C_2H_5)_2O$*	MH_n	Decomposition, temperature, °C	Solubility in $(C_2H_5)_2O$*
Mg	$Mg(AlH_4)_2$	~140	+	MgH_2	>200	+
Ga	$Ga(AlH_4)_3$	0	+	GaH_3	>35	+
Al				AlH_3		+
Be	$Be(AlH_4)_2$	>room	+	BeH_2 or $BeH_2 \cdot LiH$	>room	—
Si				SiH_4		
Ge				GeH_4		
Cu				CuH	>60	—
Hg				HgH_2	—125	—
Zn				ZnH_2	90	—
Ag	$AgAlH_4$	—50	—			
Cd				CdH_2	—20	—
In	$In(AlH_4)_3$	>—40	—	InH_3	80	—
Sn	$Sn(AlH_4)_4$	—40		SnH_4		

* + = soluble.
- = insoluble.

At insoluble anodes during the electrolysis considerable evolution of gas is observed, which shows the discharge of hydride ions (molecules). Therefore in this example the anodic process is simpler and can be described by the equation:

$$AlH_4^- - e^- \rightarrow AlH_3 + \tfrac{1}{2}H_2.$$

The electrolytes considered here are extremely complex. Therefore, despite the experimental difficulties further information is necessary, since the mechanism of the reaction can change sharply according to the nature of the anode material. In addition the study of kinetics at insoluble anodes can give interesting information on the hydrogen overpotential for the discharge of hydride ions.

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Progress in the Synthesis of Peptides on Polymers

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I. INTRODUCTION

The synthesis of polypeptides is not only one of the present theoretical problems but also a great scientific task and a great economic undertaking. During the last decade in several countries the synthesis of the less complex polypeptides has become attainable not only in laboratories but also on the industrial scale. These are mainly such important biologically active peptides as the hormones oxytocin and vasopressin, which are now easier to synthesise than to isolate from natural sources. The artificial peptide synthesis was developed so that a few years ago three groups of investigators: Katsoyannis and coworkers[1] (USA), Zahn and coworkers[2] (Federal Rupublic of Germany), and Tsou, Wang, and their coworkers[3] (People's Republic of China) succeeded in synthesising the first simplest protein —the hormone insulin, which consists of 51 amino-acids. The complete synthesis of this hormone was effected in 221 stages. This is indeed a great achievement, which itself characterises the modern level of development of peptide synthesis. However, every synthetic chemist knows very well that the multi-stage nature of a synthesis leads to a sharp drop in the yield of the final compound. Thus it is easy to calculate that in carrying out a twenty-stage synthesis with an 80% yield at each stage, the yield of the final product is only 1.2%. In the example of the synthesis of insulin, where the yields were not 100%, the inadequacy of the existing arsenal of methods of peptide synthesis appeared especially sharply.

The formation of the peptide bond is only part of the task. A more important obstacle is the purification of the peptide product from impurities formed during the course of the synthesis and which usually have properties very similar to those of the main product. Moreover there is a series of difficulties connected with the low solubility of the peptides in organic solvents, which decreases with increase in the number of amino-acid residues in the molecule. All this placed on the agenda the problem of the creation of more up-to-date methods of synthesising polypeptides. In recent years a way, new in principle, of overcoming the above difficulties has appeared—the construction of peptide chains on three-dimensional polymers in the solid phase and on linear polymers in solution.