ABSTRACTS

Low temperature-investigations (200 ° to 560 °C) on vapour pressures (vapour transference, Knudsen-effusion-deposition and Knudsen-effusion mass-spectrometry, double oven mass-spectrometry) and vapour composition reveal relatively complicated vapour-phase equilibria of the complex-salts LiAlCl₄, NaAlCl₄ and KA1C1₄. Over alkali chloride saturated melts starting from KA1C1₄ passing to NaAlCl₄ and to LiAlCl₄ the vapour pressures (or dissociation pressure) of AlCl³ strongly increases. Therefore AlCl⁻³-partial pressure is comparable to the AlCl³ pressure above LiAlCl₄-melts at 300 °C whereas AlCl⁻³- and AlCl³-partial pressures are negligible above KA1C1₄-melts. Partial pressures of Alkalitetrachloroalanates (AlkAlCl₄) increase strongly from KA1C1₄ to LiAlCl₄ (7.5·10⁻¹ torr and 90 torr at 560 °C). The mass-spectrometric investigations show that evaporated Alkalitetrachloro-alanates form dimers (Alk₂Al₂Cl₈) in the vapour-phase but only to an appreciable extent in the vapour of LiAlCl₄. Because the apparent vaporization enthalpy of the dimers equals nearly that of the monomer, the dimer content of saturated vapours does not depend on temperature. In vapours of LiAlCl₄ additionally Li₂AlCl₅ may be presumed.

INTRODUCTION

As fundamental basic data for process-development and engineering of aluminium electrowinning from melts of alkali-tetrachloro-alanates especially for the process of aluminiumchloride-preparation and purification and for the electrolysis proper the volatility of solid and molten alkali-chloro-alanates must be available. Different authors (e.g. L.A. King and collaborators /1/ and Øye and the Trondheim school /2/3/) have worked on this field. From the data of these authors it was already known that the volatility of the alkali-chloro-alanates increases from KA1C1₄ via NaAlCl₄ to LiAlCl₄ and that dissociation pressure of AlCl³ increases likewise above alkali-chloro-alanates from potassium via sodium towards lithium. None of these investigations, however, tried to identify different species in the vapour-phase and to solve the question whether - for instance - increased AlCl³-volatility
was due to formation of complex species with Al to alkali ratio of higher than one (e.g. AlkAl₂Cl₇).

EXPERIMENTAL

Investigation into vaporization equilibria and mass-spectra of salt vapours confined to temperature range 200° to 560 °C as the maximal temperature in order to be still close to the Knudsen-effusion condition for Knudsen-effusion mass-spectrometry and effusion-deposition-experiments. (For pressures being less than one and half an order of magnitude above the upper limit for Knudsen-effusion, experimental corrections and calibrations of MS-signal/partial pressure correlation were applied to take into account of non-Knudsen-behaviour). Within this temperature-range Knudsen-effusion and vapour-transference were used to determined formal vapour-pressures and chemical composition of the vapours and parallel to these measurements Knudsen-effusion mass-spectrometry was applied in order to get some insight into the stoichiometry of different molecular species in the vapour-phase. However, only a limited number of species could be observed and identified as (relatively unstable) radical cations of the mother-molecules whereas especially the more massive mother-molecules were missing as cationic peaks mostly and could only be supposed to exist because of some unexpected ions (so Alk₂Cl⁺ and Alk₃AlCl⁺ were indicative of the existence of Alk₂Al₂Cl₆ or Alk₃AlCl₅ resp.). Only by application of the double-furnace-technique which used constant temperature in the upper furnace and variable temperature in the lower furnace and vice versa) clear identification of decomposition-paths and of the original molecule could be made and estimates of the relative amounts of different species could be given. (Below this method will be examplified for vapours above NaAlCl₄ and LiAlCl₄).

RESULTS

a) Vapour transference and Knudsen-effusion-deposition
Apparent vapour pressures and their temperature dependence and vapour composition (e.g. Alk/Al/Cl-ratio) were investigated in temperature range 300 ° to 560 °C for KCl-saturated KAlCl₄, 400 ° to 560 °C for NaCl-saturated NaAlCl₄ and 150 ° to 250 °C for LiCl-saturated LiAlCl₄. The K/Al/Cl-ratio for KAlCl₄-vapours equals very closely /1/1/1/ over the total temperature range investigated; therefore KAlCl₄ (or its polymers) seems to be the only species of significance in the vapour-phase above KAlCl₄. In fig. 1a the apparent KAlCl₄-vapour-pressures (calculated
with the assumption that only monomeric species are present in the vapour-phase) is plotted vs $1/T$ together with data which were extrapolated to lower temperatures from Linga’s and Motzfeldt’s /3/ paper. The vaporization enthalpy is determined to be $114 \pm 14$ kJ/mole from our data. Extrapolated pressures and vaporization enthalpy ($113 \pm 11$ kJ/mole) of Linga’s and Motzfeldt’s agree with our data to a satisfactory extent. Total vapour pressure at 500 °C above KA1Cl comes close to 1 torr. The stoichiometry of NaCl-saturated NaAlCl$_4$-vapours and of LiCl-LiAlCl$_4$-vapours deviates remarkably from the Alk/Al/Cl-ratio of 1/1/4 as always more AlCl$_3$ is found in the respective vapours: The AlkCl/AlCl$_4$-ratio in NaAlCl$_4$-vapours comes close to 0.5 (but is slightly decreasing from 400 ° to 500 °C) whereas the AlkCl/AlCl$_3$-ratio above LiAlCl$_4$ is around 1/3 for the temperature range 150 ° to 250°C and is nearly independent of the temperature.

In fig. 1b the "apparent vapour pressures of sodium" and of aluminium calculated on the assumption that all sodium is present in form of one species only, namely NaAlCl$_4$, and aluminium-containing species are NaAlCl$_4$ and AlCl$_3$ only) are plotted vs $1/T$. An apparent vaporization enthalpy for sodium of 103 kJ/mole and of aluminium of 109 ± 10 kJ/mole is determined. Again the value for Na agrees quite well with the value estimated by Linga and Motzfeldt (117 ± 10 kJ/mole). It must be stressed that the observed AlkCl/AlCl$_4$-ratio of close to 0.5 is by no means significant for the stoichiometry of some majority species in the vapour (e.g. NaAlCl$_7$). The same holds for LiAlCl$_4$-vapours.

Qualitative comparison of KA1Cl$_4$-vapours generates signals of the ions K$^+$, KCl$, K_2Cl^+$, KAICl$_3^+$, K$_2$AlCl$_4^+$, AlCl$_2^+}$ and AlCl$_3^+}$. Appearance potentials of K$_2$Cl$^+$ (and the effective very low vapour pressure of KCl above KA1Cl$_4$) show very clearly, that K$_2$Cl$^+$ cannot be generated from K$_2$Cl$_2$. Likewise the generation of AlCl$_2^+$ and AlCl$_3^+$ from AlCl$_4^-$ can be excluded. K$_2$Cl$^+$ and $K_2AlCl_4^+$ can be traced back to be generated from the dimer K$_2$AlCl$_4$, which is present in KA1Cl$_4$-vapours in much lower quantities than is guessed from the signal intensities and AlCl$_2^+$ and AlCl$_3^+$ can be shown to be generated mainly from KA1Cl$_4$-molecules and their dimers. From NaAlCl$_4$-vapours the respective cations as given for KA1Cl$_4$ are generated by mass-spectrometry but...
additionally NaAlCl*, Al+, AlCl+ and AlCl3+ are detected, whereas in mass-spectra of LiAlCl4-vapours additionally the cations LiAl2Cl6 and Li2Al2Cl are observed. Table 1 summarizes the relative peak intensities of different ions in order to show that presumed mother-cations (e.g. AlkAlCl4+, Al3Cl+ and even AlCl3+) are by far the relative least intensive (AlCl3+ is always weaker than AlCl4+) and that the cation of the assumed dimer is only observed in mass-spectra of LiAlCl4-vapours.

c) Temperature dependence and double-furnace-technique.

Determination of apparent vaporization enthalpies (fig.2: plot of lg I vs 1/T for cations of the mass-spectrum of NaAlCl4) demonstrates that Alk2AlCl4+ and Alk3Cl+ certainly are generated from the same mother-molecule whereas AlCl4-, AlkAlCl3+ and Alk+ seem to originate from another common mother-molecule. Appearance-potentials for the different cations reveal that AlkCl and AlkAlCl3 as well as AlkAlCl4+, Alk2AlCl3+ and Alk2Al2Cl8+ certainly stem from the dimer 4Alk2Al2Cl8.

Fig. 3a shows for the m.s. of NaAlCl4-vapours the results of a double-furnace experiment (lower furnace, containing NaAlCl4 is kept at constant temperature, T1 = 250 °C; upper temperature T2 is variable: 250 °C to 400 °C). The steep decrease of the signals of Na,AlCl4+ and NaCl with increasing upper temperature occurs without a corresponding increase in the signal-intensity of NaAlCl4+. This different and independent temperature dependence of fragment-cation intensities for monomer- and dimer-fragments reveals the relative low degree of dimerization of NaAlCl4 in equilibria-vapours (T2 = T1). Very similar are the results of the double-furnace-measurements for KAlCl4-vapours.

Quite different, however, are the observation made with double-furnace-spectrometry for LiAlCl4 as shown in fig. 3b. A pronounced decrease of the signal intensities of the cations LiAlCl4+ and Li2Cl+ which stem from dimeric Li2Al2Cl8 is accompanied by an initial increase (with increasing temperature) of the fragment cations LiAlCl4+ and LiAlCl3+ which originate from the monomer-species. By semi-quantitative evaluation a degree of dimerization of more than 60 % is obtained for LiAlCl4-equilibrium-vapours whereas for NaAlCl4-vapours the degree of dimerization is less than 10 % and dimerization in KAlCl4-equilibrium-vapours is much lower than 10 %.

Since effective vaporization enthalpies for alkali-tetrachloroalananate-monomers and dimers are nearly equal
because the dimerization enthalpy in the gas phase per mole of dimer nearly equals the molar vaporization enthalpy for the monomers) the degree of dimerization in AlkAl\textsubscript{1-4} equilibrium-vapours changes but little with temperature. Table 2 collects partial pressure data for LiAl\textsubscript{1-4} vapours.

**FINAL REMARK**

This investigation clearly shows that the relative intensities of different fragment-ions of comparable composition (e.g. NaAlCl\textsubscript{3} and Na\textsubscript{2}AlCl\textsubscript{3} or NaCl\textsuperscript{-} and Na\textsubscript{2}Cl\textsuperscript{-}) is by no means an immediate indication for the relative concentrations of the respective mother-molecules (e.g. NaAlCl\textsubscript{4} and Na\textsubscript{2}AlCl\textsubscript{4}). It is certainly the possibility to redistribute the energy of the ionizing electron (40 eV) over a larger number of vibration modes which gives rise for a higher yield in more massive fragment-ions originating from the dimer, whereas the surplus in ionization-energy is consumed to produce numerous smaller fragments which escape detection in case of the monomeric complex molecules because they either carry negative charge or are not charged.

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Table 1:
Mass-spectra of alkalichloride-saturated melts of
LiAlCl₄ (at 460 K), NaAlCl₄ (at 560 K) and KAlCl₄ (at 560 K)
Relative intensities of different fragment-ions are corrected
for SEM-gain and mass-dependence of quadrupole transmission
The most intensive peak in each mass-spectrum is used as internal
reference (set to 1 000)

|          | Alk⁺  | AlkJ⁺ | AlkJCl⁺ | AlkJCl₂⁺ | AlkJCl₃⁺ | AlkJCl₄⁺ | AlkJ₂₂Cl₂⁺ | AlkJ₂₂Cl₆⁺ |
|----------|-------|-------|---------|----------|----------|----------|------------|------------|
| LiAlCl₄  | 183   | 7.4   | 244     | 113      | 10       | 977      | 15.5       |            |
| NaAlCl₄  | 420   | 77    | 168     | 70       | 0.7      | 107      | -          |            |
| KAlCl₄   | 1000  | 29    | 4.1     | 35       | ---      | 8.5      | -          |            |

|          | Al⁺   | AlkJ⁺ | AlkJCl⁺ | AlkJCl₂⁺ | AlkJCl₃⁺ | AlkJCl₄⁺ | AlkJ₂₂Cl₂⁺ | AlkJ₂₂Cl₆⁺ |
|----------|-------|-------|---------|----------|----------|----------|------------|------------|
| LiAlCl₄  | ---   | ---   | 652     | 333      | 1000     | 15.3     |            |            |
| NaAlCl₄  | 5     | 83    | 1000    | 418      | 1.9      | -        |            |            |
| KAlCl₄   | ---   | ---   | 65      | 10.7     | ---      | -        |            |            |

The total pressures above the melts amount to ca. 3·10⁻³ torr (Li),
1.2·10⁻³ torr (Ma) and 7.4·10⁻³ torr (K).

Table 2:
Partial pressures of different species in equilibrium-vapours and total
vapour-pressures of LiCl-saturated LiAlCl₄ (160-200 °C)

| t / °C | p(LiAlCl₄) mbar | p(Li₂₂Cl₂₈) mbar | p(AlCl₃) mbar | p(Al₂₂Cl₆) mbar | p(total) mbar |
|--------|-----------------|------------------|---------------|-----------------|---------------|
| 205    | 3.6·10⁻⁴        | 4.2·10⁻⁴        | 8.4·10⁻⁴      | 5.7·10⁻⁴        | 2.19·10⁻³     |
| 190    | 1.3·10⁻⁴        | 1.6·10⁻⁴        | 3.5·10⁻⁴      | 2.8·10⁻⁴        | 9.2·10⁻⁴     |
| 175    | 4.9·10⁻⁵        | 5.8·10⁻⁵        | 1.4·10⁻⁴      | 1.2·10⁻⁴        | 3.6·10⁻⁴     |
| 160    | 1.7·10⁻⁵        | 1.9·10⁻⁵        | 4.9·10⁻⁵      | 5.0·10⁻⁵        | 1.4·10⁻⁴     |
Fig. 1a

Fig. 1b
Fig. 2

Double Furnace Experiment
NaAlCl₄ / NaCl sat.
(t upper furnace) = 308°C

308°C

Fig. 3a

Double Furnace Experiment
NaAlCl₄ / NaCl sat.
(t lower furnace) = 255°C

Fig. 3b

Double Furnace Experiment
LiAlCl₄ / LiCl sat.
(t lower furnace) = 335°C